DOE FG02 91ER12107---Final Report:**A Study of Potential High Band-Gap Photovoltaic Materials for a Two Step
Photon Intermediate Technique in Fission Energy Conversion**

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Summary

Diamond photovoltaic cells were obtained using p-type diamond layers grown by Dr. Prelas' group at the University of Missouri. These layers were then sent to the Russian group of Dr. Perov from the Moscow Radio Engineering Institute of Russian Academy of Sciences. Dr. Perov's group then made Schottky barriers with the diamond film using nickel. Dr. Perov's group tested the cells and found that the quantum efficiency was very high ~70%. Additionally, they found that the open circuit voltage was ~1 V. This open circuit voltage is higher than any openly published Schottky barrier results. A journal paper was written on these results and submitted to Appl. Phys. Lett.

A barrier height of about 1 V is very good for diamond Schottky cells. To obtain a larger barrier one must have a p-n junction. A larger barrier height is needed because energy conversion efficiency depends upon the barrier height as shown in equation 1.

$$(1) \eta_c = \eta_q \times BH/hv$$

where η_c is the maximum energy conversion efficiency for the cell, η_q is the quantum efficiency, BH is the barrier height energy, h is Plank's constant, and v is the photon frequency.

From equation 1, Dr. Perov's cell has an energy conversion efficiency of about 8%. So, our work has centered around raising the barrier height. An approach to increase barrier height is to build heterojunctions between p-type diamond and another wide band gap material which is n-type. In this project, we built two types of heterojunctions. In the first, Ohmic contacts were obtained using sputtered Ti for p-type diamond and Ni for n-type SiC, with a thermal treatment at 900 °C in vacuum. This work was done in the Electrotechnical Lab. Tsukuba, Ibaraki, during Dr. Popovici's visit to Japan. In the second approach aluminum nitride and diamond were used for the heterojunction material. With this goal in mind we obtained aluminum nitride from Dr. Belyanin from the Central Research Technical Institute in Moscow. With his samples, we have diffusion doped the material with an impurity which should make it n-type. We are still trying to sort out the results from this approach. The third approach for raising barrier height is the one which we believe is a major breakthrough. Up until our work, only p-type diamond has been obtained using boron doping. We believe that we have a major breakthrough in producing n-type diamond by a forced diffusion method. The n-type behavior of samples forced diffused with lithium salts were confirmed independently by two research groups: 1) Dr. Galina Sokolina from Institute of Physical Chemistry in Moscow confirmed by Hall effect measurements that the samples were n-type; 2) Dr. A. Zaitsev's group, from Bellorus State University, Belorussia measured the samples and obtained the following results; n-type conductivity, a carrier concentration of about $5 \times 10^{15} \text{ cm}^{-3}$, an activation energy level of ~ 0.09 eV, and a mobility of $50 \text{ cm}^2/\text{V-s}$.

We plan to use our n-type diamond to produce a p-n junction. This junction, should have a barrier height of about 5.4 eV. We believe that its quantum efficiency will be on the order of 90%. Thus we would predict much larger energy conversion efficiencies than possible with Schottky barriers.

We have placed diamond films in a high flux irradiation position in the University of Missouri Research Reactor. This reactor position has a total neutron flux (fast and thermal) of 2×10^{14} n/cm²-s and a hard gamma ray flux of the same order of magnitude as the neutron flux. Our diamond samples were exposed to this radiation for a period of two weeks. We examined the films after irradiation using Raman spectroscopy. The samples showed some radiation damage. We then annealed the samples and again examined them with Raman spectroscopy. We found that the samples completely recovered. In one case an annealed sample actually had better characteristics after irradiation. It is our guess that the neutrons may have had some beneficial effects by destroying large defects while leaving behind point defects. Point defects are annealable.

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This report summarizes the major achievements in sections. The first section covers n-type diamond. The second section covers forced diffusion. The third section covers radiation effects. The fourth section covers progress in Schottky barrier and heterojunctions photovoltaic cells produced by our Russian collaborators. The fifth section covers cell and reactor development. And the sixth section covers reactor development.

Section 1. Production of N-Type Diamond Films

The most significant breakthrough in this work is the development of n-type diamond.

High quality freestanding "white" CVD diamond films, 230 μm thick, polished on both sides, with resistivity 10^{14} Ohm cm, were used for diffusion of impurities to obtain n-type conductivity. Diffusion of lithium, oxygen, and chlorine was performed under bias. Auger analysis was used to determine the impurity concentration. After diffusion, the concentration of Li, O, and Cl in the diamond films were found to be about $(3-4) \times 10^{19} \text{ cm}^{-3}$. Raman scattering, cathodoluminescence, microwave photoconductivity, electron spin resonance, optical absorption, Hall effect and electrical conductivity were employed for the film characterization. The measurements showed that the initial high structural quality of the film was not deteriorated after diffusion. Hall effect measurements showed n-type conductivity. Sheet resistance of the diffused layer was 10^5 Ohm /square. Carrier mobility was estimated to be about $50 \text{ cm}^2/\text{V s}$.

Diamond is a promising material for electronic application due to its unique properties. However, the development of diamond electronic technology requires solving the problem of reproducible doping by donor and acceptor impurities to obtain p-n junction, which is a basic unit of many electronic devices and integrated circuits. It is well known that p-type conductivity can be obtained by boron doping. [19] The results reported so far on n-type doping are controversial [20]. The experiments on obtaining n-type conductivity in diamond by phosphorus doping have not been encouraging until now, despite many attempts and different methods employed (21-24).

The resistivity of the samples was high and the phosphorus level was found deep (~ 0.9 eV). Interstitial impurities which can give n-type conductivity are Li and Na. Activation energies of 0.1 and 0.3 eV below the conduction band minimum for Li and Na, respectively, have been computed [25-26]. Doping by lithium was tried in ion implantation [27-28], during growth [29], and by diffusion [30-31]. None of these methods worked. Reports on Li diffusion into diamond are inconsistent. In reference [30] it was reported that Li atoms diffused at temperatures between 400 and 900 $^{\circ}\text{C}$ as measured using secondary ion mass spectrometry (SIMS) analysis. In reference [29] opposite results were obtained: no diffusion of implanted Li was detected after annealing at 1400 $^{\circ}\text{C}$ for several hours. In reference [30] implanted Li did not redistribute during 1000 $^{\circ}\text{C}$ thermal treatment.

As the solubility of Li and Na in the diamond lattice is predicted to be low [25-26], the method of forcing the introduction of impurities into the diamond lattice should be of interest. We performed the diffusion of lithium, chlorine and oxygen under electric field in a high quality freestanding diamond films [32]. We found that a large amount of impurities diffused at relatively low temperatures.

In this work diffused samples were characterized by Raman scattering, cathodoluminescence, microwave photoconductivity, electron spin resonance, optical absorption, Hall effect and electrical conductivity. The Hall measurements showed n-type conductivity.

Experimental

Free standing transparent diamond films, supplied by Norton Diamond Film Co, 230 μm thick, polished on both sides, with resistivities of about 10^{14} Ohm cm have been used in this work. Usually the top side of the CVD grown samples has larger crystals and is of better quality, than the bottom side near the substrate. However the films having been polished on both sides, there were

no essential differences between the sides, as our measurements show. Diffusion was performed into the top side of the sample, (labeled A in the text; the bottom side is labeled B). The films were mounted on a graphite base with an imbedded tungsten heater. The base temperature was monitored by a chromel-alumel thermocouple.

The dopant source was a lithium salt. During the diffusion process a DC potential was applied to the samples. The diffusion process is described elsewhere.[32]

After the diffusion process the samples were boiled in a $\text{Cr}_2\text{O}_3 + \text{HSO}_4$ mixture for 20 min and washed in deionized water.

Cathodoluminescence was measured in the spectral range 200-900 nm at temperature of 80 K. The electron energy was 6-15 kV. Microwave photoconductivity was performed in the spectral range 200-800 nm at room temperature. Electron spin resonance (ESR) was measured at room temperature at the wavelength 3 cm. The transmission spectra were measured at room temperature in the spectral range 0.2-25 mm.

Aquadag was used for the contacts for electrical measurements.

Figure 1. Doping Profiles of Chlorine and Oxygen in the Diffused Samples Determined by Auger Measurement

Results and Discussions

Concentration profiles of the impurities in the samples were determined by Auger spectroscopy. The samples were gradually sputtered to a depth of 1600 Å. The results for oxygen and chlorine are shown in Figure 1. A chlorine concentration of about 0.1 at.% ($2 \times 10^{19} \text{ cm}^{-3}$) was achieved at 1500 Å depth. An oxygen concentration at 1500 Å of approximately 0.05 at.% was found. Hydrogen can not be detected by Auger analysis.

Lithium was not found in the samples, but the sensitivity of the Auger method to Li is very low. However, as SIMS measurements showed the amount of lithium of about $3 \times 10^{19} \text{ cm}^{-3}$ in the free-standing Norton samples diffused in the same conditions [32], we conclude that amount of Li diffused in these samples was also of this order of magnitude. The detailed investigation of one of the diffused samples was performed

Raman spectrum (Figure 2) reveals a single strong line with a maximum at 1332 cm^{-1} , that has an intensity and shape similar to that of natural diamond.

The cathodoluminescence spectrum of the diffused side A of the sample is presented in Figure (3a). The spectrum of the undiffused B-side is very similar to the diffused side. (Figure 3b). The spectrum have a strong band with a maximum at 440 nm (A-band) as a main feature, free exciton lines at 235 and 242 nm, a weak 575 nm luminescence center which result from nitrogen containing defect of interstitial type.

Figure 2. Raman Spectrum of the Diffused Film.

There are weak lines with a zero photon line at 270.5 nm (5RL system). It is difficult to explain the presence of these lines in CVD samples, as these centers usually were observed in the samples having radiation defects. [33]

The presence of excitone lines (235 and 242 nm) is a most sensitive parameter indicating the structural perfection of the film. [33] The strong intensity of the free exciton line relative to A-band points to a low concentration of the structural defects and centers of the nonradiative recombination. The A-band is related to the presence of dislocations. [33] The band is relatively narrow which is a characteristic of natural diamond with good structural quality. The full width at half maximum of 370 meV shows the relatively low concentration of dislocations ($\sim 10^2 \text{ cm}^{-2}$).

Change of exciting electron energy within a range 6-15 keV (change of the depth of an effective excitation from 0.2 to 1 mm) does not result in noticeable variations of the cathodoluminescence

spectra showing a good homogeneity of 1 mm layer near the surface.

Figure 3. Cathodoluminescence of the Diffused Film: (a) diffusion side, (b) back side.

The microwave photoconductivity spectrum is presented in Figure 4. The weak photoresponse in the range 300-600 nm is due to the presence of defects, probably dislocations. The strong line in the range of the diamond intrinsic absorption with a maximum at 222 nm indicates a long lifetime of the nonequilibrium carriers in the layer of a few micrometers thick. The slow decrease of the photoconductivity at small wavelengths (Figure 8b) where the light absorption is limited to the near-surface layer of thickness less than 1 mm is evidence for a long lifetime of non-equilibrium carriers in the near-surface layer

The comparison of the diffused diamond film with a natural diamond using microwave photoconductivity results is given in Table I. The reference sample is a piece of a high quality natural diamond used for making electronic devices. The quality of the reference sample is arbitrarily set to unity. It is seen that the surface quality of the diamond film is nearly the same as the mechanically polished surface of good quality natural IIa diamond. The quality of the bulk is about one order of magnitude lower than the reference sample, and can be compared to natural diamond of medium quality. Films of such quality can be used in semiconductor technology for active electronic devices.

Table I. The comparison of the diffused film with natural diamond.

Table 1:

Parameter	Reference	A side	B side
Quality of bulk	1	0.142	0.096
Quality of the surface	1	0.655	1.1

Table 1:

Parameter	Reference	A side	B side
Surface recombination rate	1	1.53	0.91

Figure 4. Microwave Photoconductivity Spectra of the Diffused Film

Figure 5. ESR Spectrum of the Diffused Film

ESR shows a single weak line with $g = 2.00251$ and width $\Delta H = 9.1$ G. (Figure 5) The concentration of paramagnetic centers is evaluated as $\sim 7.6 \times 10^{12} \text{ cm}^{-3}$. The large width of the line and low concentration of the centers can be attributed to interface dangling bonds. The concentration of the paramagnetic nitrogen in the crystal is below of the detection limit. The spectrum of the diffused film is similar to the spectrum for natural type IIa diamond of the high structural perfection

The transparency of the crystals was measured at room temperature in the range of 0.2 to 25 μm ($54 \times 10^3 - 0.5 \times 10^3$). The spectrum presented in Figure 6 is also similar to the spectrum of the natural IIa diamond

The above methods of investigation give information on the bulk as well as the near-surface diffused layer. The similarity of the characteristics of the film bulk and the diffused layer allows to conclude that diffusion does not introduce additional structural defects in the initial high quality CVD film.

The room temperature electrical measurements gave a surface resistivity of 1.4×10^5 Ohm/square. Hall measurements gave carrier concentration of $5 \times 10^{15} \text{ cm}^{-3}$. Assuming that the thickness of the diffused layer to be about 2 μm , one can estimate the carrier mobility to be approximately $50 \text{ cm}^2/\text{Vs}$. Due to the difficulty of obtaining good ohmic contacts to n-type diamond we should consider these data as estimates. The problem of good contacts to n-type diamond has not been solved yet and needs a supplementary research effort.

Figure 6. Transparency Spectrum of the Diffused Film

We can not say for sure to what impurity the n-type conductivity is due. Li is the most probable candidate. However, the other two impurities, oxygen and chlorine, or some combination of the diffused impurities might also be taken into account. To make a comparison with silicon, nitrogen and oxygen form relatively deep donor levels in Si ($\Delta E_N = 0.190 \text{ meV}$, $\Delta E_O = 160 \text{ meV}$), while a

nitrogen-oxygen complex does form a shallow level with activation energy $\Delta E=35-37$ meV. [20]

High quality CVD diamond films were diffused with lithium, oxygen and chlorine under bias. The diffused films demonstrate n-type conductivity. Raman scattering, cathodoluminescence, microwave photoluminescence and optical absorption measurements revealed the high quality of the diffused films. This proves that diffusion is a reliable method of diamond doping. Diffusion permits the introduction of a large amount of impurities in the sample without deteriorating its structural and recombination characteristics. It can thus be used for fabrication of electronic devices on diamond and for the formation of a p-n junction. It should be noted that this process was used with type II a diamond substrates as well. The results are consistent with those on the high quality CVD diamond films.

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Doping Diamond by forced Diffusion

I. Introduction:

Intrinsic diamond has a lot of good characteristics for industrial applications (like cutting tools, electronic devices, detectors and so on). There is also a great potential for electronic and optical application of extrinsic diamonds. To achieve the requirement of these applications, it is important to control doping diamond by optical and electrical active impurities.

There are two popular doping methods are developing for diamonds: ion implanted and addition of dopants during diamond growth. These two methods successfully dope boron into diamond and get the good characteristics that the electronic applications require. Most diamonds doped by other impurities than boron did not have good properties that can be used for the electronic applications. Other doping methods are developing to exceed this goal or to have more cheap and efficient process.

Diffusion is a natural behavior that the particles attend to move from higher concentration area to lower concentration area and is widely used for semiconductor doping. The speed of diffusion process depends on the diffusion coefficient that is described in the Fick's law. Diffusion coefficient depends on the jump frequencies, potential barrier for impurities moving inside the host lattice and the distance of the two potential barriers. If the lattice constant is large (or the impurity is small) or at high temperature environment, the impurities will diffuse into the host lattice very quickly, otherwise the diffusion process will be very slow.

Diamond is the most rigid crystal of all known material. Even at high temperature, diffusion coefficient of impurities in diamonds are very small that indicate the diffusion process is very slow for these impurities into diamonds. In order to apply diffusion method to dope diamond, the external force to enhance the diffusion process must be considered. Our group have developed the forced diffusion method to dope diamonds that apply the electric field, the impurity must be charged, that is ionized.

Optical ionization by laser can help to ionize the impurities that can not be ionized thermally. Optically enhanced forced diffusion can be considered a new hope for diamond doping.

II. Forced diffusion theory:

Diffusion process is well described by Fick's law (Equation 1). The particles move due to the gradient of concentrations.

$$J_{diffusion} = -D\nabla C \quad [1]$$

where $J_{diffusion}$ is the diffusion current; D is the diffusion coefficient and C is the concentration.

The goal of forced diffusion is to produce external driven force other than chemical potential driven force (that is the gradient of concentration). By adding this external force, the Equation 1 becomes to Equation 2.

$$J_{diffusion} + J_{drift} = -D\nabla C + \mu EC \quad [2]$$

where J_{drift} is the drift current due to the electric field; μ is the mobility and E is the electric field.

The constant dopant source will be put on the film surface and the concentration depends on the solid solubility of dopant atoms in the doped material. According to the diffusion equation, the dopant profiles will be a complementary-error-function, without any external force, as

$$C(x, t) = C_s \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad [3]$$

where x (cm), is the depth of the doped material, C_s (cm⁻³) is the surface concentration of dopants, D (cm²/sec) is the diffusion coefficient and t (sec) is the time period for diffusion. With an applied electric field E , the dopant distribution will be modified as

$$C_{pos}(x, t) = \frac{C_s}{2} \left(\left(1 - \operatorname{erf}\left(\frac{x - \mu Et}{2\sqrt{Dt}}\right) \right) + \exp\left(\frac{\mu Ex}{D}\right) \left(1 - \operatorname{erf}\left(\frac{x - \mu Et}{2\sqrt{Dt}}\right) \right) \right) \quad [4]$$

$$C_{neg}(x, t) = \frac{C_s}{2} \exp\left(\frac{-\mu E x}{D}\right) \left(\left(1 - \operatorname{erf}\left(\frac{x - \mu E t}{2\sqrt{Dt}}\right)\right) + \exp\left(\frac{\mu E x}{D}\right) \left(1 - \operatorname{erf}\left(\frac{x - \mu E t}{2\sqrt{Dt}}\right)\right) \right) \quad [5]$$

where $\mu = Dq/kT$ is the mobility of dopant atoms, and C_{pos} and C_{neg} are the dopant distribution with the electric field to enhance or suppress the diffusion of the dopant ions respectively. From these two equations mentioned above, one can find the relationship of the C_{pos} and C_{neg} .

$$\frac{C_{pos}}{C_{neg}} = \exp\left(\frac{\mu E x}{D}\right) \quad [6]$$

By using these equations, one can get some ideas how the forced diffusion works. For example, if we choose the diffusion parameters as follows:

$$D = 1 \times 10^{-14} \text{ cm}^2/\text{sec}; E = 30000 \text{ V/cm}; \mu E = 2.36 \times 10^{-9} \text{ cm/sec}; t = 8 \text{ hours}$$

Applying these parameters into Equation 6, one can find the C_{pos}/C_{neg} is about 1×10^5 at $0.5 \mu\text{m}$. The impurity concentration of the enhanced biased diffusion is about 1×10^4 times more than the impurity concentration of the thermal diffusion at $1 \mu\text{m}$ depth.

Figure 1 shows the calculation of forced diffusion based on the Equation 3,4 and 5. From the calculation, it is obviously that one can increase the electric field to get more impurities into the crystal lattices. The penetration depth of diffusion also is increased by increasing the electric field. At $0.5 \mu\text{m}$, the impurity concentration of $1 \times 10^4 \text{ V/cm}$ biased samples is about 5 times larger than the impurity concentration of non-biased sample but the impurity concentration of $5 \times 10^4 \text{ V/cm}$ biased sample is about 100 times larger than impurity concentration of non-biased sample. The increasing of impurity concentration is faster than the linear increasing of the electric bias. The assumption of these calculation is based on that the impurities are totally ionized. Because only charged impurities can be influenced by the electric field, impurities must be ionized.

Figure 1 The calculation of concentration profiles at different conditions where CO is the thermal diffusion; CP is C_{pos} and CN is C_{neg} ; C_0 is the surface concentration; C/C_0 is the relative concentration.

III. Experimental setup:

The diffusion reactor:

The diffusion reactor is shown in Figure 2. Samples were placed on the graphite support and with an embedded tungsten electric heater. Chromel-alumel thermal couple was used for temperature measurement. The DC power could supply 1kV, 40 mA electric bias. Hydrogen or argon flushed the chamber to prevent the oxidation and graphitization of diamonds.

Figure 2 The apparatus of the diffusion reactor

Forced diffusion without optically enhancement:

Three natural type IIa diamonds which are supplied by Gemspectrum were prepared for boron doping using forced diffusion. These diamonds were cleaned in $\text{CrO}_3 + \text{H}_2\text{SO}_4$ hot solution (200 C) 20 minutes and then boiled in $\text{HNO}_3 + \text{HCL} + \text{H}_2\text{O}$ solution 20 minutes. Finally, these diamonds were rinsed by de-ionized water.

These diamonds were put in the same reactor and kept the same parameters except the diffusion bias during the diffusion process. Figure 3 shows the arrangement of these diamonds. Diamond #1 was only diffused thermally. It was covered by graphite cap to prevent the electric field influence. Diamond #2 was negatively biased on the diffusion surface. Diamond #3 was positively biased on the diffusion surface.

Figure 3 The arrangement of diamonds for forced diffusion

These diamonds were kept in the diffusion reactor for 60 minutes at 1000 °C. The diffusion bias was 850 V and the bias current was from 2.4 mA to 6.45 mA. The 99.999% lump red phosphorus was used for dopant source. After diffusion, these diamond were cleaned by the same procedure which was used before diffusion process. Although the phosphorus was used for dopant source, the unintentional boron also diffused into the diamonds. Phosphorus has not been measured by secondary ion mass spectrometry (SIMS) because the standards for phosphorus have not been prepared yet. The profiles of boron concentration were measured by SIMS. The SIMS data were obtained using a CAMECA sector magnet instrument with a Cs primary ion beam and using negative BC secondary ions. Quantity analysis was done using a SIMS relative sensitivity factor for that species derived from a B-implanted standard in another piece of Ila diamond.

Forced diffusion with optical enhancement:

Four natural diamond Ia crystals were used for diffusion. The experimental setup was the similar as Figure 3 and the laser was added. P_2S_5 and $LiClO_4$ salts were used as a diffusion source. The diffusion source was placed between the samples. In this arrangement the doped surface have practically the same temperature and the same surface conditions. The only difference is the sign of the applied electrical field. Diffusion was performed in an argon atmosphere. Table I shows the conditions of the diffusion.

Table 1: The conditions of the diffusion

Sample	T (C)	Laser	V (V)	I (mA)	t (min)
5	770	off	+236	(0.3-0.4)	24
6	770	off	-236	(0.3-0.4)	24
7	730	on	+228	(0.2-0.8)	24
8	730	on	-228	(0.2-0.8)	24

A He-Ne laser was used to ionize impurities optically. Samples 5 and 6 were diffused under electric field without laser irradiating and samples 7 and 8 with laser irradiation. Before

and after diffusion, the samples were cleaned by the procedure mentioned above. The diffusion profiles were determined by SIMS.

IV Results and Discussions:

Forced diffusion without optically enhancement:

Figure 4 shows the boron concentration profile of diamond #1 and Figure 5 shows diamond #3 and #4 that are biased by electric field. Figure 4 shows that there are two steps of diffusion processes. The diffusion coefficient is $8.4 \times 10^{-15} \text{ cm}^2/\text{sec}$ near the surface and the diffusion coefficient is $4 \times 10^{-14} \text{ cm}^2/\text{sec}$ inside the bulk of diamond using Equation 1 to fit the SIMS data. Figure 5 presents the electric field has enhance and suppress effect. At $0.2 \mu\text{m}$, the concentration of diamond #3 (negatively biased) is four orders of magnitude larger than diamond #2 (positively biased). Because boron has three electrons in the outside shell, boron attends to get one more electron and becomes the negative ion. So the boron ions will be attracted by positive electric bias and pushed by negative electric bias.

Figure 4 SIMS profile for diamond #1

Figure 5 SIMS profile for diamond #2 and #3

The diffusion coefficient $4 \times 10^{-14} \text{ cm}^2/\text{sec}$ that was inside the bulk of diamond was used for the calculation of forced diffusion. The velocity (μE) $12 \times 10^{-9} \text{ cm}^2/\text{sec}$ were chosen for the calculation. The fitting curves in Figure 5 were based on the solutions of the one dimensional

model of Equation 3. It seems that the fitting curve does not fit very well for diamond #3, but it gives the idea how the electric field works. The assumption of fully ionization was used in the calculation but actually the boron was not fully ionized at 1000 °C. The diffusion behavior may be more complicate than this simple model. More research has to be done.

Forced diffusion with optical enhancement:

Figure 6 SIMS profiles of sulfur

Figure 7 SIMS profiles of chlorine

The results on diffusion of sulfur are presented in the Figure 6. The sulfur concentration of sample 6 which was biased negatively approximately two times larger than that of sample 5 which was biased positively at depth of 0.5 μm . Sample 5 had some irregularities on the diffused surface, which can explain the irregularities in the depth profile for this sample. The sulfur concentration of the positively biased sample 7 increased at least two orders of magnitude, which laser irradiation was used. The concentration of negatively biased sample 4 remained approximately the same as the biased, but non irradiated, sample 6. The results for chlorine diffusion (Figure7) are similar to that of sulfur. The concentration of Cl for sample 5, which was biased negatively, was about $1 \times 10^{18} \text{ cm}^{-3}$ at the depth of 0.5 μm , and is larger by an order of magnitude at the same depth than the concentration of the negatively biased sample 6. The concentration of the positively biased laser irradiated sample 7 is $2 \times 10^{18} \text{ cm}^{-3}$ at the depth of 0.5

μm and is larger by two orders of magnitude than the concentration of laser irradiated negatively biased sample 8.

The difference in the diffusion curves for the positively and negatively biased samples (5 and 6 respectively) in the electric field may be due to the thermal ionization of the sulfur and chlorine atoms in the diamond lattice. That means both levels are shallow enough to be partially ionized at the diffusion temperature implying that the energy of ionization of these levels is the order $2kT \approx 0.2 \text{ eV}$. The chlorine level might be shallower than the sulfur level, as the influence of the electric field is stronger for chlorine (the concentration is one order of magnitude larger in the positively biased sample for chlorine and only twice as large for the sulfur). Laser irradiation enhanced the concentration of diffused atoms of the positively biased sample 7 by two orders of magnitude for both chlorine and sulfur, compared with the negatively biased sample 8. As the ionization energy of the He-Ne laser is 1.96 eV , much larger than the thermal ionization energy, one can assume that all chlorine and sulfur atoms were ionized by the laser and their movement was influenced by the electric field. The optically enhanced forced diffusion of the impurities may have practical interest for diamond and other wide band gap semiconductors, allowing larger concentration of diffused atoms to be obtained at lower temperatures.

The enhancement of diffusion due to the positive bias infers that both sulfur and chlorine diffuses as negative ions. This means these atoms might form acceptor levels in the diamond band gap.

V. Conclusion:

The forced diffusion effect was displayed by the graphic solutions. One can increase the diffusion speed by increasing the bias. By the way, the increasing of impurity concentration is faster than the linear increasing of the electric bias.

Boron was doped into natural type IIa diamonds by forced diffusion. Diffusion coefficients of boron into diamond at 1000°C were $8.4 \times 10^{-15} \text{ cm}^2/\text{sec}$ near the surface and

4×10^{-14} cm²/sec inside the bulk of diamond was determined. The concentration of boron was four orders of magnitude larger at 0.2 μ m in positively biased sample than in negatively bias samples.

The concentration of the sulfur and chlorine was two orders of magnitude larger at the same temperature in positively biased samples compared with negatively biased samples when optical ionization was used. The optically enhanced forced diffusion of impurities may have practical interest for diffused atoms to be obtained at low temperatures.

Final Report

on Joint Research "Diamond - based Photovoltaics"

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1. INTRODUCTION

Silicon, cadmium sulphide and gallium arsenide are the traditional materials used for the manufacturing of transducers. As the boundaries for separating the minority carriers there are used p-n junction, Schottky contact or heterojunction. There is a growing interest also to the photovoltaics having the metal-insulator-semiconductor structure.

It should be mentioned however that photovoltaic devices made of traditional materials can work only at the temperatures not exceeding 300°C within a spectral range of 200-1000 nm, besides that they have low radiation resistance. The unique combination of physical properties of the diamond, such as the high thermal conductivity, the broad forbidden gap (5.47 eV), the high carrier mobility, the high mechanical strength and radiation resistance, - makes this material the most attractive for creating on its base the electronic devices which can operate in extreme conditions having the parameters superior to those obtained with the use of the traditional materials.

The aim of this work what summarized in the final report was to investigate the possibility of creating the photovoltaic devices on the base of the diamond, which could work in the spectral range of 150 - 200 nm in the conditions of ionizing radiation and high temperatures.

2. PHOTOCONDUCTIVITY

Photoconductivity is the property of semiconductor material, e.g. diamond, closely related to its development as base for photovoltaic devices.

Therefore we have studied the spectral dependencies of photoconduction of diamond films (DF) and crystals.

At present the conduction of natural and synthetic diamond has been already studied in sufficient details [2.1 - 2.4].

Some data on photoconductivity of CVD diamond films have been also published [2.5].

Because of the extremely low lifetime of carriers (even in perfect natural singlecrystals of diamond it is of the order of several nanoseconds), it is very difficult methodologically to investigate the kinetics of the first stage of photoconductivity of diamond specimens. We have carried out the work on determining the magnitude of the stationary photoconductivity I_{ph} , for diamond films (DF), free standing polycrystalline diamond plates (DP), and diamond single crystals, in order to obtain the information on energy bands and electron transitions in the different kinds of diamond materials.

2.1 Stationary photoconductivity

When a photon flux with the photon energy $h\nu > E_g$ (E_g is the width of forbidden gap) falls onto the sample of intrinsic semiconductor the photons transmit their energy to the electrons of valence band, thus exciting them into the conduction band. Nonequilibrium electrons (n) in the conductivity band and nonequilibrium holes (p) in the valence band have been created. The rate of optical generation of the charge

carriers is:

$$g = \alpha \eta (\lambda) N_{ph} \quad (1)$$

where: α - light absorption factor;

$\eta (\lambda)$ - quantum efficiency of photoionization (the number of electron - hole pairs generated by one quantum of light);

N_{ph} - photon flux passing through the semiconductor surface ($\text{cm}^{-2} \text{s}^{-1}$).

The stationary photoconductivity is expressed as:

$$G_{ph} = G_{ph,n} + G_{ph,p} = e \alpha (\lambda) \eta (\lambda) N_{ph} (\mu_n \tau_n + \mu_p \tau_p) \quad (2)$$

where: e - is the electron charge; μ_n , μ_p - mobilities of electrons and holes, correspondingly; τ_n , τ_p - life times of electrons and holes.

In some cases a monopolar photoconduction can realize due to the great differences in nonequilibrium carriers, n and p , concentrations, mobilities or lifetimes.

The intensity of radiation falls in semiconductor depth, in the dependence on distance, x , from the illuminated surface, by the law:

$$N_{ph}(x) = N_{ph,0} [1 - r(\lambda)] \exp(-\alpha x) \quad (3)$$

where: $N_{ph,0}$ - photon flux at the semiconductor surface; $r(\lambda)$ - is the spectral reflection factor.

The bulk rate of current carriers generation at plane which is at a distance x from the illumined semiconductor surface, is determined by the equation:

$$g(x) = \alpha \eta (\lambda) N_{ph}(x) = \alpha \eta (\lambda) [1 - r(\lambda)] N_{ph,0} [\exp(-\alpha x)] \quad (4)$$

The rate of carriers generation at the surface of semiconductor is:

$$g(0) = \alpha \eta (\lambda) N_{ph,0} [1 - r(\lambda)] \quad (5)$$

If the absorption factor α is small and / or the plate has low thickness, which gives $\alpha W \ll 1$, then the value of g is practically independent of x . Such an approximation is valid for carriers generation from the impurity levels. The radiation almost completely reaches the back surface of the semiconductor plate and reflects from it. To account this reflection one must times the expression (4) by a factor

$$\{[1 - r(\lambda)] \exp(-\alpha x)\}^{-1}$$

The rate of current carriers generation in the case of impurity absorption, if the plates are not very thick, is independent of x and equals to:

$$g = \alpha \eta (\lambda) N_{ph} \quad (6)$$

In the case of the self-absorption α is great and the inequality $\alpha W \gg 1$ is valid. The radiation is almost completely absorbed in the subsurface region of semiconductor.

The spectral dependence of photoconductivity corresponds to the dependence of α and η on the quanta energies. Photoconduction arises only in the cases of excitation by the radiation of photons, whose energies exceed some threshold value. By the self-absorption the energy threshold is defined by E_g , and by impurity - type absorption it depends on energy level of impurity or defect center.

2.2. Measurement procedure.

To determine the magnitude of photoconduction of DF, we have constructed the facility what general set-up presented at Fig. 2.1. A deuterium discharge lamp or bulb lamp used as the sources of radiation allowed to investigate the spectral dependence of photocurrent $I_{ph}(\lambda)$ in the λ range of 180 to 1200 nm.

In order to increase the sensibility of measuring the photocurrent, I_{ph} , a modulated regime of illumination was used.

The diamond samples under investigation represented 40 to 70 μm thick polycrystalline free standing films, obtained in the Laboratory of Diamond Film Crystallization (Institute of Physical Chemistry, Russian Academy of Sciences) from a methane - hydrogen gas phase activated by dc-discharge [2.6]. There were also studied the plates rendered by the Norton Company, about 500 μm in thickness. Due to the large light absorption factor in the self-absorption range, a transverse photoconduction of the samples, whose $\alpha W \gg 1$, can not be measured, because the light does not penetrate the main part of the bulk of a film owing to its strong absorption near the surface. Therefore planar contacts were made of a silver paste by application of parallel strips 4 mm in length and 1 mm remote from each other. This allowed to measure the longitudinal photoconduction of DF in the ranges of self ($h\nu > E_g$) and impurity ($h\nu < E_g$) absorption.

The magnitude of modulated photocurrent I_{ph} was measured by means of voltmeter V 6-9. A high ohmicity sample under investigation having the resistance $R = 10^{10} \div 10^{13}$ Ohm was connected seriesly to a standart resistor with the resistance 10^6 Ohm and attached to a power source UIP-2. The measuring signal was supplied to specially made high-ohmic bandwide preamplifier, whose amplification factor was 10. The using of preamplifier excluded shunting of the signal from the standard resistor by a low input resistance (10^6 Ohm) of the voltmeter, what a placed immediately close to the studied sample (in the working chamber of spectrophotometer). It allowed to decrease essentially the magnitude of a noise signal from the sample and to exclude the effect of connection wires on the amplitude-frequency characteristics in the measuring system. The equipment employed made it possible to measure currents through the high-ohmic DF, as low as 1×10^{-13} A.

2.3 . Spectral dependence of photoconductivity of diamond films.

For the DP provided by the Norton Company and for the DF obtained in the Laboratory of Diamond Films Crystallization, IPC RAS, the spectral dependencies of photoconductivity in the range of the wave lengths 190 nm - 1000 nm have been studied. Fig. 2.2 the typical graph of polycrystalline diamond sample. All the samples under investigation have a peak in the region of intrinsic conductivity $\lambda = 225$ nm (peak A in Fig. 2.2) and peak B at $\lambda \sim 420$ nm (Fig. 2.2). The DF had photoconductivity in the region of intrinsic absorption essentially lower than that of Norton's DP.

One can explain observed spectral dependencies $I_{ph}(\lambda)$ in a following manner. The width of the forbidden gap of the diamond $E_g = 5.5$ eV, than the light quantum with the wave length defined from the relation $E_g = 1.2395 / \lambda$, corresponds to the interband transition. Here E is expressed in eV; λ - in micrometers. Defined herefrom value $\lambda = 225$ nm.

The band $\lambda = 225$ nm corresponds to the fundamental absorption of light.

The photocurrent rise which is observed on decreasing λ (< 230 nm) may be caused by the rise of the number of the carriers generated by light. Because $g \sim \alpha \eta N_{ph}$, one can assume that g and, consequently, I_{ph} depend on λ . In turn, the character of $\alpha(\lambda)$ dependence is defined by the kind of dependences of the carriers energy, E , in the conduction band and in the valence band on the wave vector K . The structure of the energy bands $E(K)$ of the diamond is analogous to that of germanium and silicon. For these crystals the extremes within their valence and conduction bands do not coincide in K . Therefore there are direct carrier transitions under the action of light, when K does not change, as well as indirect ones, when K changes by carrier transitions from band to band.

In the diamond direct transitions take place at $E = 7.2$ eV. From community of the data obtained, one may conclude that the generation of the carriers in CVD films of diamond under the action of UV-radiation occurs as the result of nondirect transitions.

As the absorption factor α is large in the region of self-absorption, the generation of photocarriers takes place, as mentioned above, nearby the illuminated surface. In this case the observed dependencies $I_{ph}(\lambda)$ are explained as follows. At the photon energies that correspond to the edge of fundamental absorption the concentration of photocarriers increases with rise, according to (4) both absorption factor and the concentration of generated carriers defined by increasing the $\alpha(\lambda)$ value. However, on growth of the concentration of nonequilibrium carriers, the role of recombination processes at the surface of the film rises. The increase of the surface recombination should lead to the fall of I_{ph} with growing of the photon energy, which is observed experimentally.

Photoconductivity ratios of C - 1 type of DP and DF at different λ , Fig. 2.3

can be caused by the presence of the impurity levels of different energy level and different concentration in the both kind of specimens

Fig. 2. 4. presents the dependencies $\lg I_{ph}(\lambda)$ for DP of C-1 type, DF of No 897 and I a type single crystal natural diamond. The logarithmic scale was chosen with the aim to represent data for three kinds of samples at one graph. It is seen from the graph that the DP have the photocurrent in the 210 - 240 nm range by one order of magnitude greater than single crystal diamond. One can assume that more perfect crystalline structure in the CVD - films, causes the higher mobility of the carriers generated in 250 - 290 nm range originates of higher perfection of the surface of CVD - crystallites results in lowering the rate of surface recombination. This causes the higher I_{ph} .

Along with the $I_{ph}(\lambda)$ dependency there was investigated the action of the radiation intensity upon photocurrent in DF. For most of the studied diamond samples:

$$I_{ph} = AF^n \quad (7)$$

where: F - light flux; A - proportionality factor; n - index of a power, which characterizes the nonlinearity of the energy characteristic of a film.

At different illuminances I_{ph} in (7) can have three ranges: superlinear $n > 1$, linear $n = 1$ and sublinear $n < 1$.

The effect of the UV - radiation intensity on the photocurrent (at $\lambda = 225$ nm) is shown in Fig. 2.5, where in a double logarithmic scale is presented a graph of the I_{ph} dependence upon the light flux measured in the arbitrary units, C-1 type DP and DF.

The intensity of light flux was varied in experiments by changing the diaphragm opening of the spectrophotometer; the value F_0 corresponds to the completely open diaphragm. It can be seen from the Fig. 2.5 that in the self-absorption region the photocurrent depends linearly on the radiation intensity throughout the investigated range of the light flux changing. There was not found any photocurrent saturation so typical for many photoconductors at high intensities. Perhaps, this is due to the low radiation intensity of the deuterium lamp, used in the spectrophotometer.

Fig. 2. 6 illustrates the dependence of the photocurrent on the voltage (U) applied to the sample. There are presented in a double logarithmic scale the dependencies $I_{ph} = f(U)$ for the DP of C-1 type.

After the initial linear region of voltage - current characteristics extending up to $U = 10$ V follows a region with the dependence $I_{ph} = U^n$, where: $n = 3/2$. The obtained dependencies I_{ph} on U are typical for polycrystalline photoconductors [2.5].

2. 4 . Conclusions.

The experimental data obtained enable to conclude that the gas - phase grown diamond films and plates possess photoconductivity in the UV range which is comparable

(and for the samples provided by Norton Company even exceeding) that for the natural Ia type single crystals of diamond .

To the advantages of photoconductive diamond structures one should refer the relative simplicity of producing the photoresponsive elements of complex configuration , the cheapness of manufacturing , the high range of the resistance nominal values.

The deficiencies of photoresistors are the considerable lag , temperature and time instability of characteristics .

However obtained in this section results indicate prospectiveness of different kinds of diamond materials for producing photoresponsive and photoconverting devices .

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Fig. 2.1

Fig. 2.2

Fig. 2.3

Fig. 2.4

Fig. 2.5

Fig. 2.6

3. THE P - I - M CONCEPT OF CREATING OF DIAMOND BASED PHOTOVOLTAICS

To produce the effective photovoltaic devices it is necessary for the junction which separates the minority carriers to possess good rectifying characteristics, sufficiently long lifetime of the carriers, and separate it near the junction before the recombination takes place. At present the manufacturing of the diamond based rectifying structures goes in the direction of creating of heterojunction (semiconducting diamond - Si), Schottky junctions (metal - semiconducting diamond), p-n junction, and the structures such as semiconducting diamond - dielectrical diamond - metal (p-i-m).

The use of the heterojunction for the sake of separating the minority carriers, extends the range of the types of the solid state devices suitable for the production of the photovoltaic devices, however it has an essential deficiency consisting in the necessity to engage the semiconductor other than the diamond. This will lead to the restrictions of the extreme conditions of such a junction operation in the region of high temperatures and also will lower the radiation resistance.

The Schottky junction (semiconducting diamond - metal) has a low rectifying coefficient and also a low reproducibility if the surface of a junction is large. This restricts its utilization in the photovoltaic structures.

The creation of p-n junction at present is still embarrassed due to the difficulties of the obtaining the n-type diamond. The n - type diamond obtained by means of the ion implantation, as well as by the synthesis is characterized by the nonreproducibility of its electron parameters and has a large amount of defects, which leads to the short lifetimes of the minority carriers.

The diamond materials of various kinds were used on search the ways to produce photovoltaic structures.

According to the data of the Belorussian group [3 . 1] based on ion-implanted natural diamond single crystals p-i-m structures are one of the most suitable ones to be used as photovoltaic converters. They possess good rectifying characteristics, the rectification coefficient being more than 10^6 at 20 V. The using of a dielectric diamond as a working body allows to reach the extreme electrophysical parameters of the diamond.

Thus the rectifying structures of p-i-m look like the most optimal for producing the diamond based photovoltaic devices.

3.1. Experimental part.

There were used in the work natural diamonds of Ia type with nitrogen concentration $< 5 \times 10^{17} \text{ cm}^{-3}$. The samples were polished mechanically and cleaned by boiling in a saturated CrO_3 solution in H_2SO_4 and then washed in deionized water and acetone. The quality of the initial samples was examined by

means of the cathode luminescence and microwave - photoconductivity techniques.

After making a preliminary analysis of a defect - impurity composition and of a structure perfection the test p-i-m structures by means of photolithography and ion implantation methods, have been produced. The schematic representation of the test structures is given in the Fig. 3. 1. Heavily doped semiconducting regions were produced by the boron ions implantation (see the parameters in Table 1) followed by annealing in vacuum at 1450 °C for 30 min.

Table 1.

Energy, keV	25	36	52	71	93	118	150
Dose, 10 ¹⁵ x cm ⁻²	4.60	1.96	2.36	2.62	2.75	1.07	4.60

To achieve a homogeneous distribution of the boron concentration throughout the doping layer, the TRIM - 90 program was used for the calculation of energies and doses. Metalization of the contact areas in the doped regions and the obtaining of Schottky junction were carried out by means of Al thermal evaporation and photo - lithography.

To study the spectral dependences of photo EMF of p-i-m structures a monochromator MDR-2 was employed; the light source was a high pressure Xenon lamp of DKSSh -1000 type.

Examination of the quality of the initial samples was carried out by means of the cathode-luminescence (CL) and microwave - photoconductivity techniques. The selection of the crystals for photovoltaic devices was based on the data obtained. The typical CL spectra for the natural diamond are presented in Fig. 3. 2.

The CL spectra are characterized by the presence of a wide band with a maximum at 440 nm (A band), caused by the recombination of donor - acceptor pairs associated with dislocations and by the recombinational radiation of a free exciton (a band having maximum at 235 nm). The presence of the latter is an evidence of a high structural perfection of the crystal and of an actual absence of recombination levels in the forbidden band.

A microwave photoconductivity spectrum is shown in Fig 3. 3. It contained only photoconductivity band which is caused by generation of nonequilibrium carriers from the valence band to conductivity band. Its high intensity as compared to that for a standart sample indicates relative high lifetime of the charge carriers in the crystal and also the weak surface recombination.

3.2. Investigation of rectifying p-i-m structures.

Study of the heavy doped, by boron ions implantation (Table 1), semiconducting regions has shown that 1450 °C is the optimal temperature of annealing in order to activate the implanted boron and to anneal the radiation defects. The energy of activation of conductivity of such a layer was found to be about 0.01 eV. This indicates that the generation of an impurity band due to the heavy doping takes place. The conductivity of such a layer reaches the value of $4 \text{ Ohm}^{-1} \text{ cm}^{-1}$.

On applying a voltage to p-i-m structure (+ at p-region), at the voltages 1 to 4 V a current starts to pass across the structures, due to the holes injected into the dielectric diamond. The Volt-Ampere characteristic of such p-i-m structure is presented in Fig 3.4. The investigations of the Volt-Ampere characteristics revealed square-law character dependence of current on voltage.

This indicates that the current is limited by the space charge. It was established that p-i-m structures possess good rectifying characteristics; the rectifying coefficient at 20 V being about 10^6 at 20 °C. The rectifying characteristics of such structures retain up to the temperature 400 °C (see Fig. 3.4).

3.3. Photoelectron convertors based on p-i-m structures in diamond.

The illumination of p-i-m type structures by focused radiation of a Xenon lamp gives rise to a photo-EMF the value 0.4 V at non-load conditions for some structures; the short circuit current comes to 6 nA. Photo-EMF in such structures is caused by the separation of generated by light minority carriers at p-i-m junction. The zone diagram of such a junction is presented in Fig. 3.5.

The spectral sensibility studies of photo-EMF observed in 370 - 700 nm range is connected with the excitation of the free carriers from the defect levels in the forbidden band (apparently at dislocations).

It should be mentioned that no normalization of the spectral brightness of the Xenon lamp has been made. Taking into account that only less than 0.1% of the total power of radiation of the Xenon lamp belongs to the range 200 - 250 nm, one can neglect the contribution of the long wave radiation to photo-EMF.

The evaluation of the efficiency of a photovoltaic device based on p-i-m structure gives the value about 0.5%.

The working characteristics of photovoltaic structures can be improved significantly and the efficiency increased on illuminating by the light of high intensity with the wave length less than 225 nm, by the selection of the diamonds or on the synthesis of the diamond CVD films of appropriate defect-admixture composition and of electrophysical parameters, and by optimizing the geometry of the metallization regimes.

3 . 4 . Conclusion.

It has been shown that there is a possibility to produce photovoltaic converters of short wave radiation with the wave length less than 225 nm, based on p-i-m diamond structures. In such a structure photo-EMF is caused by the generation of free charge carriers across the forbidden band of the diamond and by their subsequent separation at p-i-m junction. The p-i-m type structures can provide the approach for the production of high-efficient photovoltaic devices based on the diamond and the diamond films [3 .1]

Reference.

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Captions to Figures

- Fig. 3 .1 Diagram of test p-i-m structure in diamond. The width of the i-i nterval is $2 \mu m$.
- Fig. 3 .2 C L spectrum of Ia natural diamond : a - at 80 K , b - at 298 K .
- Fig. 3 .3 Microwave photoconductivity spectrum of Ia natural diamond at $300^{\circ}C$. No normalization of spectral brightness of Xenon lamp and of spectral sensibility of monochromator has been done.
- Fig. 3 .4 Volt-Ampere charateristic of p-i-m structure in diamond at 300 K and 700 K. .
- Fig. 3 .5 Diagram of energy bands for p-i-m structure.
- Fig. 3 .6 Spectral sensibility of photo-EMF for photovoltaic p- i -m structure. Illumination by Xenon lamp . No normalization of spectral brightness of Xenon lamp and of spectral sensibility of monochromator has been done. .

Fig. 3.1

Fig. 3.2...

Fig. 3.3.

Fig. 3.4

Fig. 3.5

Fig. 3.6.

4. CHARACTERIZATION AND TESTING OF POLYCRYSTALLINE DIAMOND FILMS

PDF for the investigations was produced by high - current discharge (electrical activation of $\text{CH}_4 - \text{H}_2$ vapor phase and by hot - filament technique thermal activation of the vapor phase [4 . 1] .

4 . 1 . Electron spin resonance

Point defects, even of low concentration, drastically affect the physical properties of diamond films. Electron spin resonance (ESR) is a powerful technique in obtaining information related to paramagnetic point defects.

We have been searching ESR - centers in free standing polycrystalline diamond films, grown by chemical vapor deposition (CVD) in hot filament reactor [4 . 1] at crystallization temperature T in the range of 640 to 1000°C . The ESR spectra were recorded using a RE-1306 7 ESR spectrometer at a frequency of 9.5 GHz usually at room temperature.

Two types of paramagnetic defects (I and II) were being observed. We decomposed the ESR signal into two kinds of overlapping singlet lines: 1 - narrow with $H = 2.5 \text{ G}$ and II - wide with $H = 12.8 \text{ G}$ (peak-to-peak line width).

Both of lines have the same g -factor of 2.002. The line I which usually observed in diamond is attributed to the broken carbon bonds in synthetic diamond films. With our ESR - technique sensitivity ($10^{12} \text{ spin} \cdot \text{Oe}$) we have not reveal paramagnetic nitrogen defects in the diamond films.

The integral intensities spectra depend on the measurement temperature , T . When the T is lowered the contribution of broad component II increases as compared to the component I.

Similar spectra were obtained for Norton polycrystalline diamond plates, (DP) and the number of paramagnetic centers correlated well with electrical conductivity of DP .

4 . 2 . Positron annihilation spectroscopy

Positron annihilation spectroscopy (PAS) is known as a powerful nondestructive technique for research the vacancy-type defects in solids. The sensitivity of the PAS technique to open-volume defects is excellent: in semiconductors defect concentrations of the order of 0.1 ppm or less can be detected.

We have studied vacancy type defects in CVD diamond films on silicon substrate using angular correlation of annihilation radiation (ACAR) technique (long-slit geometry).

Fig.4.1. Normalized ACAR curves for natural single crystal diamond (1) and for 35 μm diamond film (2)

ACAR curves have been measured in diamond films of various thickness (12-25 micrometers) deposited under temperature from 875 to 1085 °C by thermal activated CVD of diamond [4 . 1] Diamond is known to present the record annihilation characteristics: the shortest positron lifetime (155 ps) and the broadest ACAR curves (FWHM=14 mrad) in the comparison with all the substances studied before.

The experimental ACAR curves for [100] orientation 11a natural single crystal diamond, for silicon substrate and for system "diamond film of 35 micrometers thickness on silicon substrate" represented in Fig .4.1. ACAR curve for system "film on substrate" much narrower both for crystal diamond and silicon substrate. It means that CVD film contains more defects than diamond crystal.

The contribution of silicon substrate in experimental ACAR curve can be subtracted to obtain the ACAR curve only for diamond film. It was found that ACAR curves for diamond films (FWHM=4 mrad) are extremely narrow as compared with ACAR curve for crystal diamond. This dramatic difference may be explained in terms of positrons capture and annihilation in microvoids (vacancy clusters). The mean radius of such microvoids is about 0.3 nm and its concentration is of the order 1 ppm. The size and number of defects depends on the CVD preparation conditions.

4 . 3 . UV damage threshold fluence

One of the factors limiting the power of Photon Intermediate Direct Energy Conversion System is an existence of upper level of UV light flux from excimer molecules above which a degradation (damage) of the diamond photovoltaic cell occurs. To determine damage threshold fluence the diamond films grown in General Physics Institute by electrical activated CVD technique [4. 2] were irradiated by a KrF excimer laser pulses (wavelength 248 nm, pulse duration 15 ns). The diamond films with different structure and quality, polycrystalline with grain size 3-8 microns (# 2 Table) and nanocrystalline with grain size < 100 nm, (# 1 , Table) were deposited on Si substrates in a DC arc plasma reactor using methane/hydrogen gas mixtures. A natural diamond single crystal of Ia type was also tested for laser damage as a reference high quality material. The measured threshold fluences, E (J/cm²) are shown in the Table.

Table

Sample	Structure	E (J / cm ²)
#1	Nanocrystalline	1
#2	Polycrystalline	2
# 3	Single crystal	7

Enhanced optical absorption and reduced thermal conductivity are believed to result to lower damage threshold for fine-grain diamond films. Thus depending on diamond quality the limiting intensities of UV light pulses from KrF excimer fluorecscers are in the range $(0.7 + 5) \times 10^8$ W/cm². Lower threshold intensities are expected for continuous UV irradiation.

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5 . INTERNAL FIELD CONCEPT OF DIAMOND PHOTOVOLTAICS

5.1. The peculiarity of diamond

For many years, diamond was considered to be very perspective for development of devices for radiation detection. Having such excellent parameters as mechanical hardness, radiation, chemical, and wear resistance, wide transparency window from ultraviolet to middle infrared, this material nevertheless has not found a broad application field until diamond film technology has been introduced in practice. This was connected with limited sizes of natural and synthetic diamond crystals, low reproducibility of their parameters, and lack of the possibility to control the parameters to get the optimal ones for given application.

With new technique developed for deposition diamond films using chemical vapor deposition on different substrates [5.1 -5 .2], wide perspectives have been opened for wide scope of applications of diamond including electronics and photovoltaics. However, during the first period main attention was paid to diamond film growth processes to get the possibility for deposition of high quality films with desired and controlled parameters such as crystal structure, grain size, dopant type and concentration, optical absorbance, reflectance, and scattering, etc. Recently, radiation detectors have been developed successfully using CVD diamond films [5.3 - 5.5]. These detectors were just photoresistors and consisted from photoconductive diamond film placed between metal electrodes. In such a case the mechanism of action of the detector is controlling the current through the diamond film from some external voltage supply by means of generating the photocarriers by the irradiation flux.

5 . 2 . Diamond as structures with internal field

Another type of phototransformers deals with the structures having internal electric fields which lead to separation of photogenerated carriers and to generation of photovoltage in such structures : - p-n-junction, heterojunction, Schottky barrier are some examples. Such devices unlike the photoresistors can be used not only for radiation detection but for radiation energy transformation into electrical one as well. This direction is under especially intense development in respect to solar energy conversion problem, mainly on the base of silicon and gallium arsenide type materials.

Another very important field in the energy conversion is transforming nuclear reaction energy into electricity. Prelas et al. described [5. 6] a possible process of nuclear energy conversion with a wide band gap material based photovoltaic element which was called as Photovoltaic Energy conversion of Nuclear energy System (PENS). In this system, nuclear energy is transported to a fluorescer like

Krypton-85 or some other which emits ultraviolet radiation after several intermediate steps. Using a proper phototransformer, this radiation can be converted into electricity. Therefore a very essential element of PENS is a photovoltaic structure which converts this ultraviolet radiation into electrical power.

Diamond film photovoltaic structures are among few under consideration for such application. At present, undoped and p-doped diamond film technology is mostly available, and n-doping diamond films is much more difficult to produce. Therefore, main attention was paid in this work to unipolar barrier structures, like Schottky barrier junctions, and to heterojunctions between diamond film and another n- or p-type semiconductor. In particular, it was shown that rather good rectifying contacts to CVD diamond films can be fabricate using different metals (see the review paper by Gildenblat et al. [5.7] and referencies in it). High temperature resistant, rectifying contacts to boron-doped polycrystalline diamond films were obtained by deposition of TiC film [5.8]. To fabricate photovoltaic structures with adoptable parameters, one needs to choose properly the transparent rectifying contacts to diamond film, its doping level, thickness of the film, growth and post-growth treatment regimes.

In this work, polycrystalline diamond films were grown by CVD method on different substrates; photovoltaic structures were prepared on the base of these films; the electrical, optical and photoelectric measurements were used for characterization of diamond films and diamond film photovoltaic structures.

5. 3. Preparation of polycrystalline boron-doped diamond films

The methods and techniques of Chemical Vapor Deposition (CVD) allows to produce diamond materials [5.1, 5.2] in the form of thin films, thick coatings and free-standing plates and open a way to the wide applications of CVD diamond. However there are several problems to be solved connected with grain structure, defects and non-diamond inclusions giving rise to light scattering losses and additional absorption, and to electrical parameter changes as well. Surface roughness at the growth surface depends on the growth conditions and, first of all for thin films, on the density of the growth centers. The growth of a film starts from appearing separate nucleis, and continuous covering of the substrate surface is reached at the thickness of the order of the average distance between the nucleis. As a rule, the surface roughness increases with the thickness. For photovoltaic applications, thin diamond films with the thickness up to several microns are the most appropriate. To obtain thin films with a smooth upper surface and reduced light scattering the substrates were preseeded with ultra-fine diamond powder. The diamond nucleation density up to $10^9 - 10^{10} \text{ cm}^{-2}$ was obtained.

Diamond films were grown by HF CVD from a mixture of 0.5-1.5 % methane or acetone in hydrogen on Mo or single crystal silicon substrate. For boron doping the film, the trimethylborate was added to the mixture. the boron/carbon ratio was varied in given experiments from 30 to 2000 ppm. The substrate temperature as measured by optical pyrometer was varied from 870° to 920° C , the temperature deviations during experiments as long as 18 h were less than 10° .

5.4 Samples

To be used as light to electricity converters, photosensitive elements of different kind containing internal electric field regions were prepared and investigated. The structures and their schematic band diagrams are shown in Fig. 5.1, a and 5.1, b. For better efficiency, antireflection coatings might be useful. However, at this stage the samples without such coatings were studied. Silicon/diamond/metal heterostructures contained two internal field regions - at the silicon/diamond and the metal/diamond interfaces. Therefore the photocarriers generated by the light absorbed in both diamond and silicon could be separated in these regions giving rise to photovoltage appearance between the metal electrode on diamond and the ohmic contact to silicon. For the simple model of an interface between two materials (without interface built-in charge), band bending values were obtained using known work function and electron affinity values, as shown in Fig. 5.1. For the metal/p-diamond/metal structures, band bendings are possible at each interface depending on the contact type, rectifying or ohmic one.

For part of the samples, the silicon substrate was removed by etching in the mixtures of acids to form diamond windows with area ranging from about 0.2 to 1.0 cm². The surface of the window facing the substrate was as smooth as the starting surface of the silicon wafer. The morphology of the upper surface gets more rough as the film thickness increases.

The band diagram of the photovoltaic element with undoped diamond film is shown in Fig. 5.1, c. Using metals with different work functions on opposite sides of the insulating film, it is possible to obtain different barrier heights ϕ_1 and ϕ_2 and hence the built-in electric field $(\phi_1 - \phi_2)/ed$, where d is the film thickness. Of course, real structures are more complicated than such a simple model: in particular, the barrier heights are defined not only by the work functions of the materials but also (and often mostly) by the interface states and by interface phases which may result from the interface chemistry. Interface layer formation and their strong influence on the diamond-Ti and diamond-Al barrier characteristics were demonstrated in [5, 8].

Semitransparent Ni or Ti electrodes with area about 2 mm² were deposited on the polycrystalline CVD diamond films by evaporation of Ni in vacuum and dc-magnetron sputtering of Ti, the metal substrate was used as the second electrode to the film. Current-voltage and capacitance-voltage characteristics were measured for all the samples. To decrease the leakage currents, all the samples were annealed in air at 530 °C during 30 min. Photoelectric response was measured in open circuit conditions at different bias voltages.

5. 5 . Electrical characteristics

Current- and capacitance-voltage characteristics and deep level transient spectroscopy for different conditions (bias voltage, temperature, parameters of the testing signal) were studied. Current-voltage characteristics for the most of the as-grown samples were linear or slightly non-linear. Depending on the boron concentration and on the annealing regimes, it was possible to get nonlinear rectifying I-V curves, Fig. 5.2, a. Capacitance-voltage characteristics (Fig. 5. 2, b) showed very weak capacitance dependence on the bias applied, so the depletion region was spread almost through all the thickness of the diamond film - the case the most useful for phototransducer mode of operation of the barrier structure under study.

Investigating the annealing effects on deep levels in diamond films, the isothermal Q-DLTS technique [5.9] seems to be the most appropriate. In the Q-DLTS measurements, one uses cyclic bias pulses to change the charge state of the centers just as in the case of the capacitance DLTS [5.10], but unlike the last method, the measured value is not the capacitance but the charge emitted from the traps. During the first part of the cycle, the centers are filled with charge carriers by applying a forward bias pulse to the sample. In the next part of the cycle, the traps emit the charge carriers after changing the bias on the sample to zero.

The charge emitted during the emission process is collected on a capacitor by using an integrator circuit shown in Fig. 5.3. The integrator circuit combines a high-speed operational amplifier M1 with a current amplifier in the feedback loop. Output of the integrator is a voltage signal $V(t) = Q(t)/GC$ where $Q(t)$ is the charge on the integrating capacitor C and G is a gain of the current amplifier. The charging time constant of integration is $<10^{-7}$ s. In order to obtain the Q-DLTS signal, the output of the integrator is applied to a follow-and-hold circuit through switches $Ke3$ and $Ke4$ as shown in Fig. 5 .3. The measured value of the Q-DLTS signal can be written as

$$DQ = Q(t_2) - Q(t_1) = GC[V(t_2) - V(t_1)] \quad (1)$$

where t_1 and t_2 are the time intervals from the discharge beginning.

Assuming that the charge emission from the deep level varies exponentially with time and the integration time constant is much smaller than the trap emission time constant $(\tau_n(p))^{-1}$, the signal at the integrator output represents the trapped charge emission $Q(t)=Q_0[1-\exp(-\tau_n(p)t)]$. The Q-DLTS signal is given by

$$DQ = Q_0 [\exp (-\tau_n(p) t_1) - \exp (-\tau_n(p) t_2)], \quad (2)$$

where Q_0 is the whole charge emitted from the traps of given type.

The cyclic DLTS algorithm used in this work is different from that of Lang [5.1]. In Lang's algorithm, the rate window $\tau_m = (t_2 - t_1) / \ln(t_2 / t_1)$ is kept

fixed while the sample temperature is scanned to obtain the DLTS spectrum. The alternative algorithm used in the present work obtains the spectrum by scanning the rate window t_m while keeping the temperature of the sample fixed. If we keep the ratio $t_2/t_1 = a$ constant and vary t_m , then a maximum in DQ occurs at the rate window equal to the emission rate of the trap at temperature T , i.e. $\ln a/(a-1) t_1 = \ln(p)$. The maximum value of the DLTS signal

$$DQ_{\max} = Q_0 (a_1/(1-a) - a_2/(1-a)) \quad (3)$$

In these measurements, a_2 value was selected such that $\ln(p) = \ln 2/t_1$ and $DQ_{\max} = Q_0/4$.

In comparison with widely used capacitance based C-DLTS [5,10], our methodics give one a possibility to investigate the structures which tend to be depleted at room or low temperatures and high frequency capacitance to be not dependent on the charge state of the interface and bulk traps.

For the most of the structures investigated, the high frequency capacitance dependence on the applied voltage and annealing was rather weak. On the contrast, the polycrystalline diamond film resistivity was increased by about 1-2 orders of magnitude due to the annealing even at rather low temperatures, about 200 °C. Therefore, using the isothermal charge transient spectroscopy technique was very essential in obtaining the interface and bulk deep level spectra as dependent on the annealing regimes.

The Q-DLTS spectra of the boron-doped CVD diamond films taken at room temperature are shown in Fig. 4, a,b as dependent on the charging time and annealing temperature. It is clearly seen from Fig.4,a that the peak designated as EA2 was increased in amplitude with increasing the charging time but its position was unchanged. On the contrary, the EA1 peak was shifting to higher window rate values. The same behaviour was observed for the constant charging time case but with increasing the charging voltage pulse amplitude. From such a different behaviour one can conclude that EA2 peak is related to the bulk traps and EA1 originates from the interface deep levels [5,11]. Measuring Q-DLTS spectra at several fixed temperatures and at fixed values of applied voltage pulse duration and amplitude, two activation energies, 0.2 eV and 0.4 eV were obtained for these boron-doped diamond films (Fig. 5, 5). The 0.4 eV activation energy obtained was very close to the 0.37 eV activation energy known for hole emission from boron acceptors in diamond [5,7]. As to 0.2 eV activation energy, it depended on the applied charging pulse parameters and could be related to some mean energy for the continuous distribution of interface states which are recharged by given pulse.

It was observed for the first time that annealing the samples resulted in redistribution of the Q-DLTS spectral density in favor of deeper levels as it is shown in Fig. 5.4. However, the activation energy value for the EA2 peak remained practically the same, see Fig.5.5 This activation energy could be connected with boron acceptors; in this case the increase of the DQ peak as the

result of annealing could be caused by the thickness increase of that part of the depletion layer which contain recharging acceptors for given applied biasing pulse. However, the capacitance of the sample and hence the depletion layer thickness did not change so much.

Another possible reason for such redistribution of the deep level densities with annealing could be the hydrogen removal from the diamond polycrystalline film which leads to higher concentration of dangling bonds and hence higher concentration of more deep levels. In such a case, the boron acceptor peak is superimposed on the tail of the peak (or peaks) not seen separately at room temperature and connected with these dangling bonds. The increase of the dangling bond concentration with annealing should lead to higher amplitude of this peak and hence to higher DQ values in the region of EA2 peak.

5.6 Optical characteristics of diamond films

Optical absorption measurements were performed with undoped and boron doped CVD diamond films in the 0.19-50 μm range using Specord M400 UV-VIS and Specord M80 IR spectrophotometers. The threshold for electronic interband absorption was observed for all the samples as a steep changing in the absorption (optical density) near 230 nm (Fig. 5.6).

Bonded hydrogen in polycrystalline vapor grown diamond was studied by IR spectroscopy in the first time in [5.15] and now hydrogen in diamond is a subject of a great current interest since it plays an important role in the growth of diamond films by vapor deposition and in passivation of dangling bonds in diamond films. Information on the content and the state of hydrogen in different parts of the diamond films was obtained from the IR absorption features at 2800-3000 cm^{-1} . A typical absorption band shape in this spectral region is shown in Fig. 5.7 for undoped diamond film grown with methane as active gas. Hydrogen content was obtained from the overall area under this CH-stretching band envelope. Deconvolution of this band showed the presence of CH_2 , CH_3 , CH

sp^3 -groups, and the band at 2836 cm^{-1} with half width near 10 cm^{-1} . The close similarity of 2836 cm^{-1} band to one observed on a fully relaxed diamond (111)(1x1) surface by infrared-visible sum frequency generation [5.12] and also the character of changes of the ratio between amplitudes of this band and the bands connected with sp^3 groups when the growth conditions change testify this absorption band to originate from the hydrogen located at (111) diamond grain surfaces. The real shapes of the CH-stretching envelopes differ from sample to sample, however the spectral positions of absorption bands remain constant.

Post-deposition annealing the CVD diamond films in the oxygen atmosphere is a valuable tool for obtaining information about the location of non-diamond carbon phases [5.13]. At the first stage (400° - 550°C) the concentration of C-H bonds lowered by few % due to changing near-surface layers. At higher temperatures, annealing in the oxygen containing atmosphere leads to selective, non-uniform removal of the non-diamond carbon and defect diamond from the volume of the CVD diamond films. Fig 5.8 shows the diamond film IR spectra transformation as

resulted from annealing at different temperatures. It is clearly seen that interference maxima are well observed in the spectra after annealing at the temperatures as high as 620 °-660 ° C indicating that the surface of the film is sufficiently smooth to allow interference between beams reflected internally. The average transmittance in the far IR grew from 69% up to 85-90% and even higher.

The optical constants of such annealed diamond film were simulated using an effective medium approximation [5.14], in which we assume that the film is a composite heterogeneous medium consisting of diamond and void components. A calculation of the dielectric functions based on this model showed that the volume fraction of the diamond in such porous films was decreased down to 40%. This value corresponds to the effective refractive index of the film equal to 1.5. The same results we obtained from the interference fringes analysis:

The same changes in hydrogen concentration in diamond films were observed for boron-doped diamond films grown with acetone as a carbon supplying gas. The difference was in much lower hydrogen concentrations for such films, however the integral change of the hydrogen contents due to annealing could be detected. In as grown boron-doped films, the hydrogen content was found to be about 10^{20} - 10^{21} cm⁻³. The annealing resulted in hydrogen content decreasing, like for undoped diamond films. For boron doped films the same changes in volume fractions of diamond and voids should occur as in undoped films. In such a case, the conductivity over intergrain barriers will prevail over the conductivity along the interface nondiamond phase. This could be the reason for changing the shape of current-voltage characteristics from linear to symmetrical nonlinear, which is usual for the bicrystals, see Fig. 5 . 2,a.

The concentration of noncompensated boron acceptors was determined from the one-phonon absorption band intensity centered at 1290 cm⁻¹(Fig. 5 .6,b) which is characteristic for IIb diamond.

5 . 7 . Photoelectric characteristics

The photoresponse measurements were made for open and short circuit conditions. Illuminating one of two semitransparent metal electrodes deposited onto the diamond film (see Fig. 5 .1) with a light pulse and measuring the photovoltage between the two electrodes, the unipolar photoresponse with the shape similar to the light pulse was obtained, the polarity of the response to be dependent on which of the electrodes was illuminated (Fig. 5 .9) the middle and bottom curves). The photoresponse for the structures with one contact to the diamond film and another to the silicon substrate had complicated shape with changing the polarity of the signal (upper curve). Such a shape of the photovoltaic signal might result from the nonequilibrium photogenerated charge carrier separation in two regions in the heterostructure - near the metal/diamond and diamond/silicon interfaces (Fig. 5 .1).

At high intensity pulsed illumination, the photoresponse increased in time sharply following the beginning the light pulse and reached the maximum value, Fig. 5 .10,a. After ending the light pulse, the photoresponse decreased with

a time constants which vary from sample to sample and to be dependent on the light pulse intensity, see Fig. 5 . 10,b. This time dependence was defined by the photogenerated carrier trapping, recombination, diffusion, and drift processes. One can see from Fig. 5 .10,b that the photovoltage pulse was longer in a time scale for higher intensities.

The amplitude of the photoresponse in an open circuit drastically depends on the growth conditions and the post-growth annealing procedures, (see Fig 5 .10,a.) For some heterostructures it reached 0 .48 V. It is interesting to note that even for diamond/metal junctions with linear current-voltage characteristics, photogenerated carrier separation was observed resulting in photovoltage appearing between the electrodes. In our opinion, this fact might be understood as the result of a potential barrier existence at the metal/diamond grain interface. The non-diamond carbon layers between the grains may have much higher conductivity which masks the barrier behaviour in current-voltage characteristics, but in photoresponse measurements the conductivity along the interfaces bypasses the barrier and just leads to decreasing the photoresponse. The annealings result in decreasing the conductivity of this phase and allow photovoltage to reach higher values depending on the regimes.

In the case the resistivity of the intergrain phase become too high, the serial resistance might result in decreasing the photovoltage observed. This model is supported by the existance of optimal conditions of annealing to obtain high photoresponce amplitudes, depending on the diamond film doping level. It was observed also that in the case of heavily doped films, the photovoltage could be drastically increased by deposition of a thin undoped diamond layer between the doped film and metal electrodes.

Photoelectrical measurements in open circuit conditions present a very useful technique for investigating the barrier characteristics at the interfaces in different structures including Schottky barriers, semiconductor heterostructures, metal-insulator-metal diodes, etc. It was shown [5 .10] that it is possible to measure the barrier hights at different interfaces in the structure under study when illuminating the sample with a high intensity light pulse. In this work, we used the flash lamp light pulses of about 0.2 ms duration to illuminate upper semitransparent electrodes of the samples. The light intensity was high enough to get the photovoltage about the saturation value for given conditions, so these data can be used for estimation of th barrier hights difference on opposite sides of the diamond film, see Fig. 5 .1c.

Fig. 5 .10,c and 5 .10,d show the experimental results obtained with this technique for the sample consisting of 1 micrometer thick diamond film grown on W substrate, with two different metal electrodes on top of the film. Maximum photovoltage values were near to the saturation, as was confirmed taking data with lower light pulse intensities when the neutral filters were placed between the sample and the flash lamp. One cane see that large saturation photovoltage values of 0.7 V for Ni electrode and in excess of 1 V for Ti electrode were obtained for the case of zero bias voltages. This results demonstrate the possibility to fabricate the phototransformers with the highest known till now photovoltages. The kinetics of decreasing the photovoltage after the light pulse

ending is presented in Fig. 5.10, d.

When applying the bias voltage to the sample, the built-in electric field can be increased or decreased, and even its sign can be changed. In Fig. 5.10, c and 5.10, d, the dependence of the kinetics of the photovoltage on the bias applied is presented for diodes with Ni (Fig. 5.10,c) and Ti (Fig. 5.10,d) upper electrodes. From the diminishing the photovoltage at 0.7 V bias for the Ni electrode and at 1 V for the Ti one, one can come to conclusion that the barrier differences at the interfaces diamond-W and diamond-Ni or diamond-Ti are equal to 0.7 and 1 eV, correspondingly. These data are consistent with the maximum photovoltages obtained at zero biases from the diodes with these two metals as semitransparent electrodes.

Comparing the metal - insulating diamond film - metal photovoltaic elements with other elements made with doped diamond films, like Schottky diodes or p-n junctions, the former look preferable in applications when high photovoltages are necessary. For example, for the case of Schottky diode the photovoltage is restricted by the strong increase of the photocarrier flow over the barrier with increasing the photovoltage because of the barrier height lowering by the photovoltage applied in the forward direction. On the contrary, for the structures with insulating films the photocarrier leakage from one electrode to another is defined mainly the leakage currents through the insulator, which rather weakly depend on photovoltage and for better samples not exceeded 10^{-10} A.

5.8. Conclusion

Diamond film photovoltaic elements were prepared and their electrical, optical, and photoelectric characteristics were investigated. Boron-doped CVD polycrystalline diamond films were deposited onto silicon and metal substrates. It was shown that even for non-rectifying junctions, photoresponse for open circuit conditions still exists. The effect of annealings on photoelectric, optical, and electrical characteristics was studied also. Interface and bulk deep levels were studied as influenced by the annealing at different temperatures. It was shown that deep level spectra undergo to the strong changes depending on the annealing regimes. The photovoltage of metal / polycrystalline diamond film junctions in the open circuit was assumed to be depended on the conductivity and hydrogen content of the intergrain non-diamond phase. In such an assumption, the dependencies of the photovoltage, current-voltage characteristics; and deep level concentrations on the annealing regimes were discussed. The photovoltaic parameters of the diamond/metal barrier structures were shown to be adjustable by the proper annealing treatments.

Thin (about 1 micrometer thick) undoped diamond films were grown on W substrates with hot filament CVD technique. It was demonstrated that photovoltaic elements with open circuit photovoltage as high as 1 V can be successfully fabricated using thin undoped polycrystalline diamond films grown on metal substrates.

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Legends for Figures

- Figure 5 .1. Sample structures and band diagrams. a - diamond/silicon heterostructure; b - Schottky barrier structure, c - metal/undoped diamond/metal structure.
- Figure 5. 2. Current-voltage (a) and capacitance-voltage (b) characteristics of Ni / diamond film / Mo structure. 1 - Ni electrode was deposited onto as grown polycrystalline diamond film; 2 - before the electrode deposition, the film was annealed in an air atmosphere at 470°C .
- Figure 5 . 3. Electronic circuit for Q-DLTS measurements.
- Figure 5. 4. a - Q-DLTS spectra of the HF CVD boron doped diamond films taken by the rate window scan method. The charging voltage pulse amplitude equal 2V; duration, ms: 1 - 2; 2 - 1; 3 - .5. b - Q-DLTS spectra of the HF CVD diamond film before (3) and after annealing at 200°C (2) and 350°C (1) measured at 2 V pulse and charging duration 1 ms.
- Figure 5. 5. Arrhenius plot of the deep levels detected.
- Figure 5 .6. UV-VIS (a) and IR (b) transmission spectra of $1.6\text{ }\mu\text{m}$ boron-doped diamond film.
- Figure 5 . 7. C-H stretching band of the undoped $1.8\text{ }\mu\text{m}$ thick CVD diamond film (1 - as deposited, 2 - annealed at 350°C , 3 - at 470°C , 4 - at 580°C)
- Figure 5 . 8. IR transmission spectra of undoped $10\text{ }\mu\text{m}$ thick CVD diamond film (solid line - before annealing, dash line -after annealing at 590°C , dash-dot line - at 615°C , dotted - at 640°C)
- Figure 5 .9. Photovoltage time dependencies for the diamond-silicon heterostructure when illuminating different electrodes by the flash lamp light pulse.
- Figure 5 . 10. a - photovoltage kinetics of the Ni/diamond film barrier structure before (2) and after (1) annealing at 470°C ; b - photovoltage time dependencies at different flash lamp pulse intensities : $I_1 < I_2 < I_3 < I_4$ t - is the flash lamp pulse duration; c - photovoltage kinetics

of the Ni/undoped diamond film / W substrate barrier structure; d
- photovoltage kinetics of the Ti/undoped diamond film/ W
substrate barrier structure.

6. FINAL CONCLUSION.

The research summarized in the final report have been performed with participation of:
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(a)

(b)

Fig. 5.1

Experimental phototransformer.

Sample structure

1-semitransparent electrode Ti (Ni). 2-poly-diamond, 3-W-substrate.

Energy-band diagram

CVD

Fig. 5.1.c

Fig. 5.2

Fig. 5.4

Fig. 5.3

Fig. 5.5

Fig 5.6

Fig. 5.7

Fig. 5.8

Schematic measuring diagram

Fig. 5.9

Fig. 5.10

Fig. 5.10, c

EFFECT OF RADIATION ON CVD DIAMOND AS DETERMINED BY RAMAN SPECTROSCOPY

Introduction

A technique that is widely used to characterize diamond samples is Raman scattering [Etz 1991]. It can detect the structure as well as composition of diamond. A beam of monochromatic light is passed through the sample and scattering occurs. The scattered light differs from the incident light by a quantum of energy equal to certain vibrational frequencies specific to the material. This difference in energy is called the Raman shift. For diamond there is only one peak at 1332 cm^{-1} [Sibilia 1988]. The full width at half maximum (FWHM) and height relative to background are methods whereby one can access the quality of a diamond film [Etz 1991]. Diamond like carbon will result in a broad peak around 1500 cm^{-1} . Graphite will result in peaks at 1347 and 1580 cm^{-1} . It should be indicated that the Raman effect is approximately fifty times more sensitive to graphite than it is to diamond. In this light, a sample with only a small peak at 1333 cm^{-1} can be considered to be predominately diamond [Knight 1989].

In a previous study, Khasawinah et al [Khasawinah 1995] studied the effect of irradiation on polycrystalline CVD diamond as determined by Raman spectroscopy as a function of different neutron fluencies. The same sample was subjected to the following fluencies: 1) thermal fluence of $6.5 \times 10^{19}\text{ n/cm}^2$ and a fast neutron ($E > 0.1\text{ MeV}$) fluence of $8.0 \times 10^{18}\text{ n/cm}^2$ 2) thermal fluence of $1.3 \times 10^{20}\text{ n/cm}^2$ and a fast neutron ($E > 0.1\text{ MeV}$) fluence of $1.6 \times 10^{19}\text{ n/cm}^2$ 3) thermal fluence of $2.6 \times 10^{20}\text{ n/cm}^2$ and a fast neutron ($E > 0.1\text{ MeV}$) fluence of $3.2 \times 10^{19}\text{ n/cm}^2$.

In this study five diamond samples (two undoped samples and three doped with 95% isotopically enriched ^{10}B) and three diamond-like samples were divided into two pieces. The first piece was left unirradiated and the other piece

was subjected to a thermal fluence of $1.3 \times 10^{20} \text{ n/cm}^2$ and a fast neutron ($E > 0.1 \text{ MeV}$) fluence of 1.6×10^{19} in the Missouri University Research Reactor in Columbia, Missouri. The irradiated, unirradiated, and unirradiated-annealed samples were analyzed using Raman spectroscopy. Next, the samples were annealed and analyzed by Raman spectroscopy.

Experimental

The following samples were grown as described elsewhere [Khasawinah 1995] : undoped #1, undoped #2, doped #1, doped #2, and doped #3.

Each sample was then divided into two pieces. One piece of each sample was left unirradiated and one piece of each sample was subjected to the same moderately high neutron fluence (thermal neutron fluence of $1.3 \times 10^{20} \text{ n/cm}^2$ and a fast neutron ($E > 0.1 \text{ MeV}$) fluence of $1.6 \times 10^{20} \text{ n/cm}^2$) at the Missouri University Research Reactor (MURR) in Columbia, MO.

The samples were analyzed using Raman spectroscopy. Prior to each set of measurements the system was calibrated using the same natural type IIa diamond ($3 \times 3 \times 1 \text{ mm}^3$ and polished on both sides). In every run, the Raman shift of this reference sample was observed at 1332.87 cm^{-1} . Before measurements, the samples were cleaned according to the guidelines discussed in a previous publication [Khasawinah 1995]. The spectra of the unirradiated, irradiated and irradiated-annealed samples were collected.

Results and Discussion

The Raman spectra of the unirradiated diamond samples was collected in the fashion described above and can be seen in figures 1-5. Sample undoped #1 has a peak at 1334.97 cm^{-1} and no other peaks that would indicate either the presence of graphite or diamond-like carbon. Sample undoped #2 had a much different Raman spectra. There is a small diamond peak at 1334.97 cm^{-1} and

broad bands indicative of diamond like carbon. The Raman spectra of sample doped #1 has a sharp line at 1334.97 cm^{-1} and no other features indicative of other allotropes of carbon. The Raman spectra of sample doped #2 has a small diamond peak at 1334.97 cm^{-1} and broad band at 1560 cm^{-1} indicative of diamond-like carbon. This is consistent with the poor crystallinity of this sample. The Raman spectra of sample doped #3 has a small diamond peak at 1334.97 cm^{-1} no features indicative of either diamond-like carbon or graphite.

The Raman spectra of the cleaned irradiated samples can be found in figures 1-5. The spectra of sample undoped #1 indicates a diamond peak at 1330.78 cm^{-1} and the formation the of bands at wave numbers smaller than that. Additionally, a peak at 1627 cm^{-1} was observed. The spectra of sample undoped #2 indicated a diamond peak at 1330.78 cm^{-1} and the presence of bands at wavenumbers smaller than the diamond peak as well as peaks at 1627 cm^{-1} and 1420 cm^{-1} .

The spectra of sample doped #1 indicates a diamond peak at 1328.68 cm^{-1} and the presence of the bands the right of the peak as well as the appearance of a peak at 1627 cm^{-1} . The spectra of sample doped #2 indicates a diamond peak at 1311.91 cm^{-1} (the peak is estimated to be at more than this number, the actual magnitude could be less) and the presence of the bands to the right of the peak as well as the appearance of a peak at 1627 cm^{-1} . The spectra of sample doped #3 indicates a diamond peak at 1324.49 cm^{-1} and the presence of the bands the right of the peak as well as the appearance of a peak at 1627 cm^{-1} .

The diamond samples were annealed and cleaned according to the procedure described above. The spectra of the irradiated and annealed samples were collected (see figures 1-5). The spectra of samples undoped #1, undoped #2, doped #1, doped #2 show the diamond peak at 1332.87 cm^{-1} with no other notable features. The spectrum of sample doped #2 indicates the diamond peak at 1332.87 cm^{-1} in addition to a broad band at 1560 cm^{-1} .

Due to macro stresses, Raman peaks may exhibit negative (tensile) or

positive (compressive) shifts . Thus the shifts in the diamond lines after the irradiation can be correlated with tensile stress within the films. According to Bopart et al. [Bopart] the Raman shift for diamond crystals is linear in pressure in the range 0-30 GPa and equal to approximately $3 \text{ cm}^{-1}/1 \text{ GPa}$. By assuming the entire shift of the first-order diamond line is due to stress, one can estimate stresses induced by the radiation (Table 3). It can be observed from Table 3 that after annealing all the diamond lines are at 1333 cm^{-1} . 1333 cm^{-1} was also measured for the diamond standard. In every other way the spectra of the films indicate complete recovery. Thus, it is contended that the unirradiated films are actually under compressive stress due to the large mismatch between silicon and diamond. After irradiation and annealing the stress is removed since the layers are freestanding and are no longer bound by the silicon and are free to relax.

The radiation induced stress (shift that is observed in the Raman diamond line) of the irradiated samples was observed by the authors [Khasawinah]. The magnitude of the stress was found to be directly proportional to the neutron fluence [Khasawinah]. Both undoped samples (sample UD1 and UD2) had radiation induced stresses of .67 GPa . This indicates that radiation induced stress is small in the undoped samples at a constant neutron fluence. Sample D1 (lightly doped) and sample D2 (moderately doped) had larger radiation induced stresses of 1.33 GPa and 5.67 GPa , respectively. The original boron concentration in the moderately doped sample was estimated to be several orders of magnitude higher than the lightly doped sample, as determined by electrical characterization of the unirradiated samples [Khasawinah]. Thus, the magnitude of the radiation induced stress increases for larger doping concentration of ^{10}B .

The diamond lines for the films after irradiation were seen to be significantly broadened. There can be two probable causes for broadening of the Raman lines: small crystalline size and macro and micro stresses [Gheeraert 1992, Grimsch 1991]. Morelli et al observed the same phenomena in neutron irradiated natural diamond and attributed the broadening to growing disorder in the

diamond lattice [Morelli 1993].

The broad bands observed in the spectra of the irradiated samples were also observed by Khasawinah et al. in a previous study [Khasawinah 1995]. In an ideal diamond lattice, only the triple degenerated LO phonon with a wave number at about 1332 cm^{-1} is Raman active. The breakdown of the momentum conservation laws in the presence of defects allows transitions with phonons not permitted with the ideal lattice. There are 16 critical point phonons with energies between 918 cm^{-1} and 1256 cm^{-1} , which are not active optically in an ideal diamond lattice [Klein 1991].

All the Raman spectra of the irradiated samples exhibited a peak at 1620 cm^{-1} . This was attributed by Khasawinah et al [Khasawinah] to be regions of disorder. They calculated that the size of the disordered clusters was on the order of 20 Angstroms in diameter. They deduced that such a peak should also be seen in materials that are formed highly non equilibrium conditions, such as nanocrystalline diamond formed by explosion. They compared the Raman spectra of irradiated diamond and nanocrystalline diamond powder and observed a peak at 1620 cm^{-1} in both spectra. Furthermore, they concluded that such regions were not graphite since graphite is more stable than diamond, and would not disappear upon annealing (Khasawinah 1995). Morelli et al. [Morelli 1993] also observed a peak at 1620 cm^{-1} upon irradiating natural diamond. They explained this as regions of disorder. They point out that this line is characteristic of "glassy" carbons.

Conclusions

The appearance of broad bands to the left of the diamond line as well as a peak at 1620 cm^{-1} which were also found in irradiated natural diamonds [Morelli 1993] were observed by the author for the first time in CVD diamond. It was observed that in addition to a correlation between total neutron fluence and damage induced in polycrystalline CVD diamond films there is also a correlation between the concentration of ^{10}B and the damage induced. Furthermore, it was

seen that the after annealing all the additional Raman features that were present in the irradiated samples were removed and the Raman spectra of the film was similar to that of the unirradiated film.

FIGURES

Raman spectrum of sample 347

Figure 1: Raman Spectra of Sample undoped #1

Raman Spectrum of sampled 346

Figure 2: Raman Spectra of Sample Undoped #2

Raman spectrum of sample 133

Figure 3: Raman Spectra of Sample doped #1

Raman Spectrum of Sample 120

Figure 4: Raman Spectra of Sample doped #2

Raman spectrum of sample 127

Figure 5: Raman Spectra of Sample doped #3

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March 2, 1992

Dr. Walter M. Polansky
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Dear Walt:

Since the last letter of December 26, 1991, we have made several major breakthroughs. First, we have produced the finest quality p-type diamond ever reported. The purity, crystal quality, and the film resistance are better than any on record. Our trick was to use a new liquid boron dopant source (trimethyl borate -- $(\text{CH}_3\text{O})_3\text{B}$). This source is non-toxic and much simpler to use than boron oxide. The interesting property of the p-type diamond film created from this technique is that Schottky barrier diodes produced from these special p-type films were as good as Schottky diodes produced with a single crystal diamond base.

We are now working on a liquid phosphorous dopant source to produce n-type diamond. At this point in time, no one has been able to make high quality n-type films. We are hopeful that the technique we developed can be used successfully to produce high quality n-type films.

Work on the platinum-silicide has been extended into the vacuum ultra violet (VUV). The platinum silicide has excellent properties in the VUV. We believe that the quantum efficiency of the cell increases from 10% at 300 nm to nearly 100% at 180 nm. We are very excited about this development since it not only has implications as a photovoltaic cell but also because it has implications for a new type of VUV detector. Since this technology relies on the same techniques used to develop silicon detectors, it is possible to develop sensor arrays based on platinum silicide. This would open up a large number of opportunities in spectroscopy instrumentation.

We have made the highest quality AlN film ever reported. The film can be grown rapidly and cheaply. We are beginning to look at methods to dope the film. It is our hope that trimethyl borate can serve as the dopant source for p-type films and that a liquid phosphorus source can serve as the dopant source for n-type films.

Finally, we have demonstrated operation of high pressure xenon and argon microwave driven lamps and have demonstrated excimer emission. These lamps represent an efficient, high power single line vacuum ultraviolet source. We are in the process of completely characterizing these sources.

In summary, our work has progressed rapidly and has shown promise in being able to solve our most troublesome technical problems.

Sincerely,

A handwritten signature in dark ink, appearing to read 'Mark', with a stylized flourish extending from the end.

Mark A. Prelas
H. O. Croft Professor

INTRODUCTION

Semiconducting diamond is considered to be an attractive solid state material due to its unique electrical and physical properties, such as wide bandgap (5.5 eV), high breakdown voltage (10^6 - 10^7 V·cm⁻¹), high electron and hole mobilities (2000 cm²·V⁻¹·s⁻¹ and 1800 cm²·V⁻¹·s⁻¹, respectively), high thermal conductivity (20 W·cm⁻¹·K⁻¹), etc. These properties makes diamond an ideal candidate for high power, high frequency, high working temperature electronic device applications. However, so far, most diamond devices reported were fabricated using either semiconducting nature diamond or ultrahigh pressure synthesized diamond. With the rapid progress of various diamond chemical vapor deposition processes, some CVD diamond semiconductor devices have been reported since 1988, but a good understanding of the electrical properties of CVD diamond is necessary for future CVD diamond device applications

The development of chemical vapor deposition (CVD) techniques make it possible to grow diamond thin film on non-diamond substrates (e.g. silicon, molybdenum) by the deposition of carbon from a carbonaceous gas or vaporized liquid at low pressure (less than one atmosphere). Various methods for growing diamond thin film from the vapor phase have been reported in these few years. Hot filament chemical vapor deposition (HFCVD) is considered to be one of the most useful and easily controlled diamond CVD technique, because it is low cost and can conduct large area deposition with an acceptable growth rate. Extensive studies of this technique are being carried out to improve diamond film quality, deposition rate as well as ease and efficiency of doping.

In this study, diamond thin films were deposited on p-type silicon substrate by hot-filament CVD method using hydrogen and methane as reaction gases and acetone vapor as

boron dopant source carrier. By considering the chemical's toxicity and corrosiveness as well as the ease in obtaining a workable vapor pressure, a new liquid boron dopant source, trimethyl borate ($(\text{CH}_3\text{O})_3\text{B}$), which has the vapor pressure of 40 torr at 0 °C, was used for in-situ p-type doping. High quality boron doped diamond thin films were obtained and confirmed by x-ray diffraction, scanning electron microscopy. Silver on diamond schottky diodes were subsequently fabricated using these boron doped diamond film bases. Good rectifying characteristics of these diodes were obtained with I_F/I_R ratio over 10^3 , and capacitance-voltage-frequency (C-V-F) characteristics were very similar to those diodes with single-crystal diamond base.

DIAMOND THIN FILM GROWTH AND CHARACTERIZATION

Study of polycrystalline diamond thin film growth by hot-filament CVD and in-situ doping technique was undertaken using p-type <100> silicon substrates which have the resistivity of 0.5-1 ohm-cm. Prior to introduction into the reaction chamber, typical chemical cleaned silicon substrates were subjected to polishing with 1/4 micron diamond paste to promote unclean. The samples were located on a graphite base just beneath the tungsten filament. During the deposition, a mixture of acetone vapor and hydrogen was passed into a heated reaction chamber. A new dopant source, trimethyl borate was diluted into acetone for in-situ doping. The typical HFCVD diamond growth condition for this study are listed in table 1. The cross-sectional view of the stay-free diamond film is shown in Fig.1 by etching off the silicon substrate. The thickness of diamond film is about 6-7 micron.

In order to determine the quality of the deposited diamond thin films, X-ray diffraction (XRD), scanning electron microscope (SEM) were used. The X-ray diffraction pattern which is shown in figure 2 exhibits pure diamond characteristics. The lattice parameter of $3.566 \pm 0.002 \text{ \AA}$ calculated from the d-spacing of the diffraction pattern, is in the excellent agreement with the report value of cubic single crystal diamond. Figure 3 shows the typical SEM surface micrograph of the deposited film. Clearly, the deposited diamond film consists of well-faceted polycrystals with the average grain size of 5-6 micron.

SILVER ON DIAMOND SCHOTTKY DIODES

First, the diamond thin films were preannealed at 550 °C in air for 20 min to get rid

of the hydrogen effect and make films stabilized. Then, in order to remove any nondiamond surface layer, the deposited polycrystal diamond thin films were cleaned by dipping in the mixture of $\text{HF} + \text{HNO}_3 + \text{H}_2\text{O}$ and then in a saturated solution of $\text{CrO}_3 + \text{H}_2\text{SO}_4$ at 145°C for 20 min, followed by a rinse in the boiling $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ solution for 10 min. The Schottky diodes were formed by sputter depositing silver ($300\text{-}500\text{ \AA}$) on the diamond films through a shadow mask. A non-oxidizing platinum layer ($300\text{-}500\text{ \AA}$) was sputter deposited on the top of the silver contacts to increase device working temperature. A thermal annealing process was performed following metallization. Two different contact areas, 3.2 mm^2 and 0.38 mm^2 , produced similar current-voltage characteristics. The typical current-voltage curve is shown in Fig.4. A large forward current density was achieved by comparing to the data Gildenblat and Jeng reported. Fig.5 shows a natural $\log(I)$ vs. V curve. Obviously, the forward-to-reverse current ratio at 10 volts is about 1000. The forward current is limited by the large bulk diamond resistance as shown at the linear end on the forward region. A linear part greater than three decades in the small forward bias region has been obtained, from which the ideality factor of approximately 2.0 was determined. The capacitance-voltage characteristics exhibited frequency dependence as shown in Fig.6. At low frequency, the total capacitance is dominated by d.c. capacitance C_0 of silver on diamond Schottky diodes which is bias dependent and frequency independent. As the frequency is increased, the total capacitance is affected by the larger bulk diamond resistance R_b and the dispersion capacitance C_f which is frequency dependent and associated with the deep boron impurity level. Fig.7 gives the initial I-V temperature dependent measurement of silver on diamond Schottky diodes. The diodes keep rectifying characteristics up to 250°C where the temperature is limited by the test condition, not device itself.

CONCLUSION

Boron doped diamond thin films were obtained using HFCVD method and in-situ doping technique where trimethyl borate was used as a new dopant source. High quality polycrystal diamond films were confirmed by XRD and SEM studies. Silver on diamond Schottky diodes with high rectifying ratio were fabricated. Electrical characteristics studies of these diodes showed they are very similar to those of Schottky diodes fabricated using single crystal diamond base.

TABLE 1 HFCVD DIAMOND THIN FILM GROWTH CONDITIONS

GAS FLOW (SCCM)	H ₂	98
	CH ₄	1
	1000PPM B/C SOURCE*	1
CHAMBER PRESSURE (TORR)		30 - 35
FILAMENT TEMPERATURE (° C)		~ 2000
SUBSTRATE TEMPERATURE (° C)		800 - 850
PROCESS TIME (HOURS)		7

* 1000 PPM B/C OF TRIMETHYL BORATE IN ACETONE

Fig. 1 Cross-sectional view of stay-free diamond

Fig. 2 X-RAY DIFFRACTION PATTERNS OF POLYCRYSTALLINE DIAMOND

Fig. 3 SCANNING ELECTRON MICROGRAPH OF DIAMOND SURFACE

Fig. 4 SILVER-DIAMOND SCHOTTKY DIODE I-V CURVE

Fig. 5 SILVER-DIAMOND SCHOTTKY DIODE LOG(I)-V CURVE

Fig. 6 SILVER-DIAMOND SCHOTTKY DIODE C-V-F CURVES

Fig. 7 SILVER-DIAMOND SCHOTTKY DIODE I-V-T CURVES

Progress Report on Diamond Films Synthesis

Polycrystalline doped diamond thin films are known to be able to be synthesized as semiconductor devices which can operating at temperature up to 500°C. Until now, we have grown many diamond thin films for both characterization and properties measurements. We have being applied a methanol solution of boron oxide to specific amounts of acetone for three orders of magnitude doping level. Methane and acetone have been used as the carbon source for our Hot Filament Chemical Vapor Deposition method. Filament temperature typically at 1800-2000°C has been used. Substrate temperatures are normally between 750 to 900°C. Pressures are at 30-45 torrs. Substrates have been prepared by both manually and ultrasonically scratched by 15 and 0.25 micron diamond pastes following by organic cleaning to wash out the polish residues. Diamond thin films with grain sizes from 0.1 to several microns have been synthesized by the control of number of nucleation sites. Our result shows that diamond thin film tend to grow favorably at [220] direction on n-type (111) silicon substrates and at [111] on p-type (100) silicon substrates. Ohmic contacts have obtained by Pt sputtering on boron-doped and undoped diamond films. Measurements of resistivities, temperature dependencies of electrical conduction of the diamond film are now in proceeding.

Figure 1 and 2 shows the x-ray diffraction patterns of pure diamond films with and without boron doping respectively. **Figure 3 and 4** shows the SEM micrographies of diamond films with preferred orientations: [111] on p-type (100) silicon substrate; [220] on n-type (110) silicon substrate. **Figure 5** shows the photograph by light microscope (1,000X) with diamond crystal size about several microns. **Figure 6** shows the I-V characteristic curve of the Pt-diamond contact. The flat parts of curve below -7V and above +7V are due the current limitation of HP4140B at 0.01A. The diamond film was doped at B/C 600ppm.

Figure 1 shows the x-ray diffraction patterns of pure diamond films with boron doping.

Figure 2 shows the x-ray diffraction patterns of pure diamond films without boron doping respectively.

Figure 3 shows the SEM micrograph of diamond film with preferred orientations: [111] on p-type (100) silicon substrate.

Figure 4 shows the SEM micrograph of diamond film with preferred orientations: [220] on n-type (110) silicon substrate.

Figure 5 shows the photograph by light microscope (1,000X) with diamond crystal size about several microns.

Pt-Diamond OHMIC CONTACT
E4A, B203-doped 600 ppm

Figure 6 shows the I-V characteristic curve of the Pt-diamond contact.

Progress report on AlN growth

Experimental:

The setup for the mass flow controllers were (1) H_2 through the AlCl_3 container $120 \text{ cm}^3/\text{min}$, (2) NH_3 $80 \text{ cm}^3/\text{min}$ and (3) H_2 as a carrier $280 \text{ cm}^3/\text{min}$. The aluminum chloride container was maintained at 150°C to provide sufficient vapor pressure of aluminum chloride. Prior to growth, p-type Si substrate of orientation (100) and resistivity 1-3 ohm-cm was organically cleaned. The substrate was briefly annealed in flowing H_2 near 500°C prior to the growth and the substrate temperature was maintained at 700°C during the growth process.

Two samples were prepared. Sample#1 was grown for 20 min. with reactor chamber pressure of 650 torr and the thickness of the AlN film was $2 \mu\text{m}$. Sample#2 was grown for 50 min. with chamber pressure of 200 torr and the thickness of the film was $8 \mu\text{m}$ thick.

SEM micrograph, Xray diffraction and Raman spectrum were done on the samples.

Observations:

Cracked and curled up parts were observed in both samples. Curvature of the Si substrate was observed on sample#2 indicating significant amount of strain present in the sample. This is due to large mismatch in the lattice constants and thermal expansion coefficients between AlN and Si. This problem could be reduced by using substrate having lattice constant and thermal expansion coefficient closer to AlN and also slowly cooling down the samples after the growth process. Figure 1(a),(b) shows the SEM micrograph of sample#1 and 2 respectively, 2(a),(b) shows the Xray diffraction pattern of sample#1 and 2 respectively, 3 shows the Xray rocking curve of sample#1 and 4 shows the Raman spectra of sample#2.

Both the samples have a preferential orientation with the c-axis normal to the surface. However the degree of orientation is different. The Xray diffraction pattern of sample#1 shows that it is strongly oriented giving only one (002) reflection peak at $2\theta=36.26^\circ$. The other peak at $2\theta=69.1^\circ$ is due to (400) reflection of Si substrate. The degree of preferential orientation was checked for sample#1 by measuring rocking curve for the (002) line at fixed detector angle. The curve shows that c-axis

orientation distribution around the normal to the surface has a FWHM of 15° .

The Xray diffraction pattern for sample#2 shows strong reflection peaks(002) at $2\theta=36.26^\circ$, (102) at $2\theta=49.97^\circ$ and (103) at $2\theta=66.95^\circ$ indicating growth with c-axis preferentially normal to the surface. For all the peaks the calculated values for $d(hkl)$ had a little difference from the standard $d(hkl)$ values for powder AlN. This differences can be caused by the stress and stacking faults of the samples.

The Raman spectrum for both s and p polarized light gave no qualitative difference in the spectra which is expected for the polycrystalline sample . The spectra has two peaks at 607 cm^{-1} of large intensity and 653 cm^{-1} and two large bands around 750 cm^{-1} and 900 cm^{-1} of relatively smaller intensity. The largest peak at 653 cm^{-1} (665 cm^{-1} (1) and 649 cm^{-1} (2)) was attributed to the TO phonon, observed also in infrared reflectivity measurements at 666 cm^{-1} (3,4). The large weak band at 910 cm^{-1} is also observed in (1) and was attributed to LO phonon also observed in infrared reflectivity spectra at 917 cm^{-1} (3) and 902 cm^{-1} (4).

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Figure 4(a)

Figure 4(b)

Figure 2(a)

SCINTAG/USA
WL: 1.54059

Figure 2 (b)

FN:ALN345.RD ID: TIME:16:22 PT: 1.0 STEP:0.03 SCINTAG/USA
 DATE: 2/19/92 WL:1.54059

PK-POS 36.26
 NET PK-TOP 1621
 BG-INT 21

PK-POS 19.93
 DEVIATION 1.80
 PK-TOP 100680
 FWHM 15.00

EXIT=(CR)

Figure #3

Figure #4..

MacroRaman ALNS

Microwave Driven Excimer Lamps

a.0 Abstract

The goals and milestones of this project have been met or exceeded to date. The key to this project is to develop the capability to sustain a high pressure rare gas discharge. This has been done through the use of a microwave discharge. A microwave cavity has been built and has achieved high pressure plasmas and has produced excimer fluorescence.

Low Microwave Frequency (e.g., 2.45 GHz) Design

FIGURE 1

Low frequency microwave driven laser design.

b.0 Microwave Discharge

Using a model developed by CRI (Roberts, et. al.), designs of a microwave driven lamp have been developed for operation at the very economical 2.45 GHz frequency. The model which was developed was compared to the results of Offermanns experimental work using a 2.45 GHz source and agrees very well with his results. Resonance conditions for the lossy-plasma microwave resonance chamber are shown in Figure 2 for the cell with vacuum and the cell with a plasma. The results indicate that in vacuum, the resonance length is 20.1 cm and with plasma the resonance length is 21.7 cm.

FIGURE 2

Resonance frequency for lossy plasma cavity as a function of length.

In our low frequency design, we use a 2500 W microwave source. Using the TE₁₁₁ propagation mode, we used the following cavity parameters,

$$L = 0.22 \text{ m}$$

$$R_c = 0.0376 \text{ m}$$

$$R_p = 0.005 \text{ m}$$

$$\text{Re}\{f_{\text{res}}\} = 2.45 \text{ GHz}$$

$$\text{Im}\{f_{\text{res}}\} = 0.195464 \text{ GHz}$$

$$Q = 12.52$$

$$\Delta t = 8 \text{ ms}$$

$$P_{\text{microwave}} = 2.5 \text{ kW}$$

The microwave coupling is achieved by the circuit shown in Figure 3.

FIGURE 3

Microwave Circuit for the microwave driven lamp.

Two types of microwave driven lamps have been examined which have produced high pressure rare gas discharges. These lamps can be classified as aperture coupled and antenna coupled. The difference between the two lamps is that in the aperture coupled lamp, the microwaves are coupled to the resonance cavity through an adjustable aperture. In the antenna coupled lamp, microwaves are coupled to the plasma through a probe antenna. Two types of antenna can be used in the aperture coupled lamp: First a probe antenna which propagates the TE mode; Second a loop antenna which propagates the TM mode. The microwave energy can be fed into the antenna by using coaxial cable or by an antenna directly coupled to the waveguide. All of these methods have been used to couple microwave energy to the microwave driven lamp.

As shown in Figure 4, the aperture coupled lamp is referred to as a type I microwave lamp and the antenna coupled lamp is referred to as a type II microwave lamp.

FIGURE 4

The wave model for type I and type II lamps.

Plasmas have been generated in both type I and type II lamps. The type I lamp is relatively easy to make plasmas in while the type II lamp requires a great deal of adjustment. The microwave energy coupling in a type I lamp is about 60 to 70% while in the type II lamp is 90 to 100%. However, both types generate high pressure plasmas.

Using a type II lamp, the cavity length was adjusted and the transmitted and reflected power were measured as a function cavity length (Figure 5). A plasma was formed at all of the lengths because the resonance structure included the rectangular waveguide and thus many types of modes could be present. Another interesting phenomena is the increase in power readings as the length of the cavity is changed despite the fact that the microwave source current remains constant. This effect is due to the fact that the power meter detectors are calibrated for a certain mode in the rectangular waveguide. Since the waveguide is part of the resonance structure, modes other than the one which the detectors are calibrated for can propagate. Thus the readings are not calibrated. The relative readings between transmitted and reflected power are however accurate. As the cavity length is changed, the resonating modes change. At a length of 21.7 cm, the transmitted and reflected power drops to a minimum value. This is due to the fact that the TE_{111} mode within the cylindrical part of the structure becomes resonant. The length of 21.7 cm is exactly the length which the CRI model predicts for resonance (See Figure 2). This result is particularly exciting since it demonstrates the accuracy of the CRI model.

FIGURE 5

Power transmission and reflection as a function of the cylindrical cavity length.

Both type I and type II lamps have operated with both Argon and Xenon gases at pressures ranging from a few milli Torr to 760 Torr. As can be seen in Figure 6, results for Xenon gas demonstrate relatively good coupling. the transmitted power was about 200 watts and the reflected power was about 60 watts for these experiments with a type II lamp.

Xenon plasmas with gas at pressures above 50 Torr emit a high amount of excimer radiation at a characteristic wavelength of 172 nm with efficiencies of 50%. Spectroscopically, we have observed the 172 nm line in the Xenon plasma but have not characterized its intensity. Our inability to characterize the VUV intensity is basically due to a fear of burning out the expensive NIST VUV detector used for VUV studies. It is planned to find a cheaper substitute detector, calibrate it against the NIST detector and then use the cheaper detector to characterize the lamp's intensity.

Figure 7 shows the power transmitted versus the power reflected for argon gas. As can be seen from the figure, the power transmitted is 100 Watts and the power reflected is about 40 Watts. Spectra has been taken in the visible but not in the VUV.

FIGURE 6 Power transmitted versus reflected in xenon plasma as a function of pressure.

FIGURE 7 Power transmitted versus reflected in argon plasma as a function of pressure.

The plasmas in the two types of lamps look different as shown in Figure 8. These differences are a result of the different types of mode structures which result from the different cavities.

FIGURE 8

Comparison of the plasma column structure in the type I and type II lamps.

c.0 Conclusions

Two types of microwave lamps have been constructed and tested for use as rare gas excimer sources. The first type is an aperture coupled microwave resonance cavity and the second type is an antenna coupled microwave resonance cavity. Both lamps have proven to be capable of exciting high pressure rare gas discharges. A high pressure xenon gas discharge has been achieved and spectroscopically, the excimer line emission at 172 nm has been verified. The lamps behave very well but additional work is needed in order to characterize the lamps.

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Table I

	Group	Resistivity ohm-cm	Platinum Thickness Å	Number Tested	Percent Diff
SET NO. 1	1a	30-70	56	3	<31.5%
	2a	30-70	112	3	<24%
	3a	30-70	168	2	<3.5%
SET NO. 2	21	0.5-1	38	3	<9.7%
	22	0.5-1	56	3	<10%
	23	0.5-1	112	3	<9.1%

2θ

Fig. 2

electron hole pairs to incident photons will be higher due to this surface reflection. To our knowledge, the reflection coefficient of Pt₂Si has not been measured for this wavelength range. The formula used to calculate the quantum efficiency is

$$\eta = \frac{I_{\text{meas}}(\text{nA})(1.24)}{P_{\text{in}}(\mu\text{W}/\text{cm}^2)A_d(\text{cm}^2)\lambda(\text{nm})}(100\%)$$

where I_{meas} is the short circuit photocurrent,
 P_{in} is the input power density,
 A_d is the active area of the cell = 0.2 cm²,
 λ is the wavelength of the radiation.

The NIST detector's effective area is 0.66 cm².

The quantum efficiency results for the two sets of Pt₂Si photodiodes are shown in Figures ³2 and ⁴3. The best cell from each group of cells is presented in these figures; however, the differences in results within the same group did not exceed 31.5%. The percentage differences in results within each group are presented in Table 1.

Looking at the results of Figures ³2 and ⁴3, one can see that both substrate materials show the same general trend with regard to variation with wavelength. This trend is unexplained theoretically but is very repeatable. The general trend of the quantum efficiency to increase with increasing photon energy is due to the fact that the photon energy in this wavelength region is higher than the Schottky-barrier height. Thus collisions of the primary photogenerated carriers with lattice atoms may yield secondary carriers with enough energy to be emitted over the barrier [1]. The increase in quantum efficiency with decreased substrate doping is most likely due to the greater width of the space charge region. In this case the photons have a wider absorption region which is capable of separating and collecting the electron-hole pairs created.

The variation of quantum efficiency with Pt thickness is also consistent for both groups. In each case as the thickness of the Pt and the corresponding thickness of the Pt₂Si increases, the quantum efficiency first increases and then decreases. The first increase is probably due to the barrier height increasing with increasing Pt₂Si thickness, which is characteristic of very thin Schottky barriers. However, since most photons absorbed in the Pt₂Si, create electron-hole pairs which are subsequently recombined due to the high carrier concentration in the

Fig 3

Fig 4

region, there is a tendency for the quantum efficiency to decrease with increasing Pt₂Si thickness. With these two processes competing, theoretically there would be an optimum Pt₂Si thickness for maximum quantum efficiency.

As mentioned in the introduction to this section, it is our intention to use Pt₂Si diodes as the energy converters in the initial tests of the excimer laser at high light levels. The fact that these cells can convert 148 nm radiation is shown in Figure 5~~4~~⁵, which is a the fourth quadrant I-V curve for a Pt₂Si cell illuminated with 1.32×10^{-6} watts/cm² intensity. The open circuit voltage is approximately 0.6 mV with a short circuit current of 37 nA. To predict the efficiency of this cell at 100 mW/cm², one is required to know the open circuit voltage at a corresponding short circuit current of 2.8×10^{-3} A. (This assumes that the short circuit current is linear with power level.) Figure 5~~6~~⁶ shows a log₁₀ I versus V for a typical diode out of this same group. This curve was altered to subtract out the effect of the finite series resistance (1300 ohms) of the silicide at higher current values. This curve predicts an open circuit voltage of 0.353 V, using a measured saturation current value of 4.29×10^{-7} A. The ideality factor is 1.559. Assuming a fill factor of 0.25, which is worst case conditions, the conversion efficiency would be 1.238% at 100 mW/cm². We should be able to raise this to >3% with the use of a low resistance surface grid. While this is a modest conversion efficiency, it does provide us with an actual direct energy converter in the VUV with which to test the excimer lamps, which should be available by the end of this report period.

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Fig 5

Fig 6

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IV Combustion Flame Synthesis

R. Roychoudhury, E. J. Charlson and G. Popovici

Introduction

Diamond surpasses currently used materials in performance because of its remarkable combination of physical, electrical, chemical and optical properties. Diamond synthesis from carbon containing gases at lower pressures and temperatures than earlier considered, has moved use of diamond closer to the marketplace.

Several chemical vapor deposition (CVD) techniques (such as hot filament, microwave plasma, radio frequency plasma, hollow cathode plasma, laser-assisted, electron-assisted, UV-assisted and arc discharge) used for diamond growth require sub-atmospheric pressure during deposition. But the combination flame process has several advantages over the processes mentioned above, including deposition in open atmosphere, thus not requiring vacuum pumps or vacuum-tight enclosures.

This report discusses the experimental setup, the controlling parameters and ingredients, and the results of the production of diamond from a combustion flame.

Experimental Set-up

Figure 1 shows a schematic diagram of the experimental apparatus. The acetylene torch is held so that the direction of the oxy-acetylene flame is normal to a molybdenum substrate. The substrate is placed on a water-cooled copper block. The substrate temperature is measured by a thermocouple. The temperature of the substrate is controlled by the thickness of the copper block and by the rate of water flow through the copper block. Welder's grade acetylene and oxygen gases were used as the reactants. The gas flows were controlled by separate gas flowmeters to adjust the proper O_2/C_2H_2 . The gases were premixed just before the flame torch. The flow of oxygen used was 1.9 liters/minute and the flow of acetylene used was 1.8 liters/minute, giving a resultant O_2/C_2H_2 of 1.03. The substrate temperature was around 900 C. The distance between

the substrate and the flame inner core was 3-4 mm. The growing time was in the vicinity of 3 hours. The substrate turned slightly red during deposition.

Researchers have used other hydrocarbon sources, namely, ethylene, propane, ethane and methane to deposit diamond from combustion flames, but at lower growth rates than acetylene. Other materials such as Si, SiC, BN, Nb, TiC, TiN, Cu, Ta, Al, Al₂O₃, W and WC have acted as substrates for combustion flame deposited diamond with Mo and Si being most common [4].

The oxy-acetylene flame-its different parts

Figure 2 shows the configuration of the oxy-acetylene flame used. The flame usually consists of three sections-(a) the inner core (b) the acetylene feather and (c) the outer flame.

The inner core of the flame is the hottest part (temperature around 3000 C) and in this part most of the oxygen and acetylene burn. The acetylene feather is where the remaining fuel burns as it mixes with the oxygen that diffuses in from the surrounding air. Any remaining unoxidized components of fuel are burned in the outer flame, because oxygen is present in ample quantity in the surrounding air. The substrate must be placed inside the acetylene feather for growth of diamond to occur.

Controlling factors

a) Substrate temperature and the ratio of oxygen to acetylene

The growth rate, quality and crystal morphology of deposited diamond are controlled by these two parameters. The growth of diamond at substrate temperatures ranging from 370 C to 1200 C and O₂/C₂H₂ ranging from 0.7 to 1.0 was reported by Hirose [1,2]. His research argued that transparent high quality diamonds were deposited at substrate temperatures between 500 C and 750 C and O₂/C₂H₂ between 0.85 and 0.98, while opaque and more non-diamond phase containing diamonds were grown outside this range. Figure 3 shows Hirose's findings of dependence of the deposit type on substrate temperature and the ratio O₂/C₂H₂.

A similar study was conducted by Hanssen [3], and his findings are shown in Figure 4. It shows that diamond can be deposited at an O₂/C₂H₂

Fig.1 Schematic diagram of experimental apparatus.

Fig.2 Parts of the oxy-acetylene flame used.

Fig.3 Results of study conducted by Hirose-carbon deposit type as function of temp.& O_2/C_2H_2 .

Fig.4 Results of study conducted by Hanssen-carbon deposit type as a function of temp.& O_2/C_2H_2 .

of up to 1.07. After 1.07 ratio, the acetylene feather disappears. Thus, this work contradicts Hirose's findings to the fact that the flame becomes neutral at around O_2/C_2H_2 of 1.07 and not 1.0. Hanssen's work as shown in Figure 4 was not extended below 660 C and thus does not violate the 370 C lower temperature limit for diamond growth reported by Hirose.

The crystals grown are mostly dependent on substrate temperature. Diamonds grown in the high end of the temperature range are mostly (100) oriented while those grown at the lower end of the range are mostly (111). The experiment performed by us has a temperature of around 900 C, giving prominence of (111) orientation [5-7].

b) Substrate position

The uniformity of diamond growth depends on the distance between the substrate and the inner core of the oxy-acetylene flame. Growth occurs only in the region where the acetylene feather intersects the substrate. For relatively short distances low density growth occurs directly beneath the inner core with an annular high density growth present around the center of the growth region. The optimum distance is around 6 mm. If the substrate is moved farther away, the substrate area exposed to the acetylene feather is less, which results in smaller growth region. An angular flame hitting the substrate at an angle of 70 with respect to the direction normal to the substrate, has also been used to deposit diamond [9].

Role of the gases

a) Precursor radicals

There has been lot of controversy and discussion centering around the precursor radicals for growth of diamond. Researchers have seen that acetylene (C_2H_2), methane (CH_4) and the methyl radical (CH_3) are the only potential precursors present in high enough concentration to give observed growth rates. When non-activated methane was used, it gave low growth rates, suggesting that CH_3 is the more likely precursor [10]. Again, when mixture of CH_4 and C_2H_2 was used in a hot filament reactor, roughly 80% of the carbon used in diamond formation came from CH_4 . This proved that the methyl radical was the primary precursor.

To account for the tremendous increase in growth rates found in combustion flames, Matsui tried to find other precursor radicals, namely,

gas species such as C, C₂ and CH along with C₂H₂. These species have larger equilibrium concentrations than CH₃ in gases with temperature above 3000 K. His results indicated presence of CO and H₂ as main gaseous species in the post-primary flame zone with a ratio close to that used in synthesis of diamond. CH and C₂ concentrations in the acetylene feather depended on O₂/C₂H₂, similar to that of growth rate, whereas C₂H₂ and C₂H species disagreed with growth rate dependence on O₂/C₂H₂.

Matsui later found, using numerous calculations of gaseous reactions in the substrate's surface boundary layer and surface reactions on the growing diamond crystal, that the above mentioned carbon-containing radicals did not affect overall gaseous concentration and their net sticking probability was about 10⁻³. This suggested that growth rate depended on substrate temperature and O₂/C₂H₂ as already explained via CH₃-precursor model [11,12].

b) Oxygen and Hydrogen role

Several important diamond formation mechanisms are attributed to atomic hydrogen. This role of atomic hydrogen is widely accepted after Angus reported its presence at around 1000 C [10]. Hydrogen reacts with gaseous intermediates to form precursor radicals, namely, CH₃, allowing them time to reach the substrate. Models suggest that H atoms form C-H bonds terminating diamond's non-reconstructed surface. Then the H atoms are abstracted by the gas-phase species to form C-C bonds which in turn allows continued growth of diamond.

It has been seen that O and OH plays an important role in growth of diamond. They etch graphite faster than atomic hydrogen (two or three orders of magnitude) at lower temperature. This suggests that addition of oxygen to CVD systems will enhance growth of diamond at lower temperatures. Also, addition of oxygen to hot-filament and plasma assisted systems significantly increases growth of diamond. The main effect of adding oxygen is that it removes non-diamond carbon phases by oxidizing and forms a more reactive growth surface. It also forms radicals involved indirectly in diamond growth. The OH radical concentration in the oxy-acetylene flame is relatively low, but it may be high enough to account for increased growth rates of the combustion flame process [14].

Experimental Results

X-ray diffraction and scanning electron microscopy were done on the grown samples. The results are shown in Figure 5, Figure 6, ~~(a) and (b)~~, respectively. X-ray diffraction study for deposits on molybdenum showed diamond (111), (220), (311) and (400) peaks. A comparison with natural diamond peaks showed that the result was satisfactory. The SEM revealed well-faceted features and showed growth of diamond crystals up to 100 μm .

The table below shows standard relation between crystal orientation (hkl), X-ray diffraction angle (2θ) and atomic distance (d) of a powdered sample. Our sample's d shows slightly different value due to the fact that our sample was crystalline and thermal stresses might have had different effect on crystals.

hkl	2θ	d	hkl	2θ	d
111	43.916	2.06	311	91.541	1.0754
220	75.303	1.261	400	119.658	0.8916

Recent and future research

Diamond synthesis by the combustion process has several advantages over other CVD processes - higher growth rates, low running cost, open air deposition and deposition on uneven surfaces without the use of a vacuum chamber. To improve the quality of diamond synthesized by the combustion flame process, we should be able to deposit over large areas. We should also take into account that some applications need deposition at lower substrate temperatures. Moreover, efficiency of gas consumption must be increased to make this process economically feasible. Much of the recent works have been to overcome these constraints.

a) Deposition over large areas

Several researchers have done various modifications on torch design and operating conditions to improve the area of deposition. Tzeng used a multiple flame burner consisting of nine equally spaced linear holes, each having its own flame [8]. Films of up to 20 mm diameter were deposited. The uniformity of the film may be improved by controlling the gas flow in each hole.

Torch tips with larger diameters have also been used for wider

Fig.5 X-ray diffraction pattern of experimental sample.

Fig 6

acetylene feathers, thus increasing the area covered during deposition.

b) Increased growth rates

Although combustion flame synthesis of diamond show increased growth rates over other CVD processes, the usage efficiency of carbon is low. For economic reasons, this carbon usage efficiency would be increased, resulting in higher growth rates. Higher growth rates of diamond occur at lower O_2/C_2H_2 (within the earlier mentioned parameters), but the quality is lower. Thus, to increase growth of high quality diamond, a low O_2/C_2H_2 flame for deposition and an oxygen rich flame for etching away non-diamond carbon phases, can be alternated. Tzeng used this sequence to deposit high quality diamond. The deposit quality was notable higher in the sequential process using the same deposit flame. Researchers are continuing experiments to determine the difference in growth rates between the two processes.

Conclusions

The ratio of O_2/C_2H_2 , the substrate temperature and the flow rates of oxygen and acetylene used in our experiment, gave satisfactory results of diamond growth as illustrated by X-ray diffraction pattern and scanning electron microscopic photographs. The (111) diamond orientation was most prominent as the conditions used (lower range of temperature scale - 900 C) were ideal for this orientation. Future work on this experiment with purer gases and improved parameters may result in improved growth rates and better quality of diamond.

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FIGURE CAPTIONS

FIG. 3.1. A typical X-ray diffraction pattern of hot-filament CVD grown diamond film on (100) p-type silicon substrate. Inset is a typical scanning electron micrograph of a surface of diamond film.

FIG. 3.2. Two superimposed current density-voltage characteristics of silver on diamond Schottky diode (sample KU3-6 with contact area of 3.2 mm^2) at 25°C and 250°C (solid lines). Dashed line shows the current density-voltage characteristics of the indium-diamond-silicon-aluminum (ohmic) structure at 25°C .

VI Growth of oriented Aluminum Nitride Films on Si By Chemical Vapor Deposition

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Introduction

Aluminum Nitride (AlN) crystallizes in the wurtzite structure with lattice constants $a_0 = 3.1114 \text{ \AA}$ and $c_0 = 4.9792 \text{ \AA}$ [1]. AlN is a direct band gap material with energy gap of 6.2 eV [2]. It has a high acoustic velocity [3], a high melting point, high electric resistivity, excellent thermal conductivity and high chemical and nuclear stability. With all these properties, AlN has a potential use in optical devices operating in UV region, in surface acoustic wave devices, and also as a material for electrically insulating and passivating layers for semiconductors. Progress regarding these applications is slow due to a lack of good single crystals, or at least large area highly oriented, dense, defect free polycrystalline films.

Various techniques such as reactive sputtering [4], reactive molecular beam epitaxy [5], and chemical vapor deposition [1, 6, 7] have been used to grow AlN. CVD is the most promising and the most widely employed [8] method. It permits the AlN deposition at low substrate temperatures and high deposition rates [2, 8, 9]. It is easy to control and also high purity AlN can be obtained by this method [10].

A variety of substrates, including sapphire [11], a-SiC [12], Si [6,9], quartz [13] and others have been used for the growth of AlN films. Monocrystalline films has been obtained on basal planes of sapphire [2,11], and a-SiC[12]. However, these substrates can be used mainly for growth of AlN films for research purposes. Single crystalline a-SiC is an ideal substrate for the epitaxial growth of AlN films, having the same lattice structure, nearly the same lattice constant (1% mismatch for basal plane), and the same thermal expansion coefficient (TEC) [14]. However large area single crystalline SiC substrates are not available. Sapphire has been used as a substrate to grow AlN films, but the TEC of sapphire is nearly twice as large as that for AlN and the films usually crack on cooling [2].

Si has nearly the same TEC as AlN and is also suitable for industrial

applications due to its wide use and well known technology. Si has been used as the substrate for AlN film growth [6,9]. Epitaxial AlN has been grown by CVD on a limited area of a (111) Si substrate having an orientation of (0001). The growth took place in a temperature range of 1100^o-1300^oC using AlCl₃ and NH₃ as the constituent gases [6]. AlN growth on Si as thick as 0.5 mm has been reported [8].

In this paper we report on the growth of AlN films on Si substrates at moderate temperatures (700^o- 800^oC) in the pressure range of 100 - 650 torr by CVD processing using AlCl₃ and NH₃ as the source material. The layers obtained were highly oriented and uniform. The results include scanning electron micrographs, X-ray diffraction spectrum and Raman spectra. For the first time we are reporting Atomic Force Microscope (AFM) measurements and micro-Raman studies on epitaxial AlN films grown on Si.

Experimental

AlN films were grown on Si substrates using linear tube CVD method. AlN was formed by the chemical reaction of AlCl₃ with NH₃ in the presence of hydrogen. The overall reaction consists of the formation of a range of aluminum chloride-ammonia complexes [15] , and then the ammonolysis conversion of the complex into AlN and HCl.

A schematic diagram of the CVD apparatus is shown in Fig.1. The aluminum chloride container was maintained at 150^o C to provide sufficient vapor pressure of aluminum chloride, which was carried into the reaction tube by hydrogen at a flow rate of 120 sccm. The flow rate of ammonia was 80 sccm with 280 sccm of hydrogen used as a carrier. A part of the reaction tube was maintained at 350^o C by using resistance heating to avoid the condensation of ammonium chloride and aluminum chloride-complexes.

Prior to growth, the p-type (100) Si substrate with 1-3 ohm-cm resistivity was organically cleaned with TCE, acetone, methanol and DI water in an ultrasonic bath and then briefly annealed in flowing H₂ at approximately 500^o C prior to growth. About 40 samples at three different experimental conditions were prepared:

Type 1. Samples of ~2 mm thickness grown in 15 min. with the reactor chamber pressure of 650 Torr and substrate temperature of 700^oC.

Figure 1 A.H.Khan and *et.al*

Type 2. Samples of ~9mm thickness grown in 45 min. with a chamber pressure of 200 Torr and substrate temperature of 700°C

Type 3. Samples of ~3mm thickness grown in 20 min. with a chamber pressure of 100 Torr and substrate temperature of 800°C.

Both type 1 and type 3 samples were cooled down in 30 min. whereas type 2 sample was cooled down in 5 minutes.

The AFM images were recorded in air using the Digital Instruments NanoScope II Atomic Force Microscope.

The Raman spectra were excited by an Argon-ion laser operated at 514.5 nm. For the macro-Raman about 230 mW were incident on the sample. The laser was focused to a spot size of approximately 0.3 mm² at about 65° from the surface normal. The scattered light was gathered by an off-axis ellipsoid with an f/1.4 collection cone centered on the surface normal. For the micro-Raman about 2 mW were incident on the sample with the laser focused to a spot size of approximately 1mm². In the spectrograph a 600 groove/mm grating disperses the signal onto a liquid nitrogen cooled CCD detector. The entrance slits were set 100 mm wide, corresponding to an instrumental linewidth of about 9 cm⁻¹. For the macro-Raman the signal was integrated for 45 seconds for the s-polarized and 60 seconds for p-polarized data. The data were not corrected for detector nonuniformities and spectral sensitivity.

Results and Discussion

The scanning electron micrographs of type 1 and type 2 samples are shown on Fig. 2 (a) and Fig. 2 (b) respectively. Figure 3 shows the AFM images of type 2 and type 3 sample. The top view and the surface plot of the same scan area of the type 2 sample are shown on Fig.3 (a) and Fig.3 (b) respectively. To find the roughness of the type 2 sample, the z-range was calculated to be 0-215.47 nm with a standard deviation of 31.43 nm. Figure 3 (c) and 3 (d) respectively shows the top view and surface plot of a type 3 sample. For this sample the z-range was 0-147.97 nm with a standard deviation of 21.97. It shows that the type 2 samples are rougher than the type 3 samples. For both type 2 and type 3 samples, the grains at the surface have a conical configuration and the layers grew with the c-axis normal to the surface (Fig.3(b) and Fig.3(d)).

Figure 2 A.H.Khan and *et.al*

Figure 4 presents the X-ray diffraction patterns for all the three types of samples. All the samples have a preferential orientation with the c-axis normal to the surface. However, the degree of orientation is different. Type 1 sample (Fig.4-a) is strongly oriented giving only the reflection peak (002) at $2\theta=36.205^\circ$ (the peak at $2\theta=69.1^\circ$ is due to the (400) reflection of the Si substrate). The degree of preferential orientation was checked for this sample by measuring the rocking curve for the (002) line at fixed detector angle (Fig.5b). The rocking curve shows that the c-axis orientation distribution around the normal to the surface has a full width half height (FWHM) of 15° . The lattice constant determined from the (002) peak, $c=2.479\text{\AA}$, is smaller than the ASTM tables value of $c=2.490\text{\AA}$. This shows that the layer is stretched. The FWHM of (002) peak (Fig.5a) is large ($\sim 1^\circ$). The broadening can be due to either the presence of microstresses and/or to the small crystallite size. For the (002) direction the crystallite size is seen along the film depth, so it is expected to be approximately the film thickness (2 mm). This would give no grain size broadening. Microstresses remain therefore the most plausible cause of the observed broadening.

The X-ray diffraction pattern for the type 2 sample (Fig.4-b) has no (100) reflection. The three strong peaks obtained, (002) at $2\theta=36.205^\circ$, (102) at $2\theta=49.972^\circ$, and (103) at $2\theta=66.955^\circ$ indicate growth with c-axis preferentially normal to the surface. The differences between measured and tabulated d_{hkl} values ($d_{hkl} \text{ M} - d_{hkl} \text{ ASTM}$) for (002), (102) and (103) are -0.011, -0.005 and -0.0169 $\text{\AA}$ respectively. These differences are caused by stress.

Figure 4 (c) shows the X-ray diffraction pattern for a type 3 sample. The 33.037° , 36.096° , 81.529° and 116.612° peaks are for (100), (002), (202) and (204) AlN. The peak at $2\theta=43.759^\circ$ is due to (301) α -Si₃N₄. With type 3 samples the diffraction pattern showed (100) peaks indicating the growth with the c-axis parallel to the surface. This type of growth were observed at certain points of the type 3 sample while doing the AFM measurements.

Macro-Raman spectra of type 2 samples are presented in Fig.6 for s and p polarized light. There is no qualitative difference in the spectra for two polarizations which was expected for the polycrystalline sample. The spectra have two peaks at 607 cm^{-1} and 653 cm^{-1} , and two large bands around 750 cm^{-1} and 900 cm^{-1} , much smaller in intensity. The largest peak at 653 cm^{-1} (665 cm^{-1} [16] and 649 cm^{-1} [17]) was attributed to TO

Figure 4 A.H.Khan and *et.al*

Figure 4 A.H.Khan and *et.al*

Figure 4 A.H.Khan and *et.al*

Figure 5 A.H.Khan and *et.al*

Figure 6 A.H.Khan and *et.al*

phonons, observed also in infrared reflectivity measurements at 666 cm^{-1} [18,19]. The large weak band at 910 cm^{-1} was observed in ref. [16] and was attributed to LO phonons. It was observed also in infrared reflectivity spectra at 911 cm^{-1} [18] and 902 cm^{-1} [19]. Figure 7. shows the micro-Raman spectrum of the same sample. It showed the same peaks as the macro-Raman. Raman spectra at different points of the sample were recorded for both cases and the same peaks were observed.

Current-Voltage Measurements

I-V measurements were done on two different types of sample. Sample# AIN7A has (100) Si as substrate and sample# AIN7B has (111) Si substrate. The growth conditions were same for both the samples.

Al contacts were made on ALN7B by evaporating Al and the spot size had a diameter of 1mm. The I-V measurements were made at different spots at two different conditions. The I-V characteristics showed rectifying behaviour at first but after having 100 v jump the sample showed ohmic behaviour. Same results were observed in all the spots of the sample.

For sample# AIN7A temporary Hg-In contacts of unknown area were used for the I-V measurements. The measurements were done with and without implanting methane, also 100 v jumps were made for the sample. Spot 1 and 3 are the points where implantations were done. Ohmic behaviour were also observed for this sample.

Conclusions

The following conclusions can be drawn from this study.

1. AlN layers were grown on Si by CVD using AlCl_3 and NH_3 as source materials.
2. The films grown were uniform and of good quality as observed by the Raman spectra.
3. The layers grown had a preferential orientation with c-axis normal to the surface.
4. The d_{hkl} values calculated from the X-ray diffraction pattern were smaller than the ASTM values due to the stress in the grown layers.
5. The peak at 653 cm^{-1} of the Raman spectra is due to TO phonons

Figure 7 A.H.Khan and *et.al*

whereas the large weak band is due to LO phonons.

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FIGURE CAPTIONS

Fig. 3.1. A typical X-ray diffraction pattern of hot-filament CVD grown diamond film on (100) p-type silicon substrate. Inset is a typical scanning electron micrograph of a surface of diamond film.

Fig. 3.2. Two superimposed current density-voltage characteristics of silver on diamond Schottky diode (sample KU3-6 with contact area of 3.2 mm^2) at 25°C and, 250°C (solid lines). Dashed line shows the current density-voltage characteristics of the indium-diamond-silicon-aluminum (ohmic) structure at 25°C .

Fig. 3.3. $\log(J)$ - V characteristics of three silver on diamond Schottky diodes at room temperature. Sample KU3-1 has a contact area of 0.38 mm^2 , sample KU3-5 and KU3-6 have the same contact area, 3.2 mm^2 .

Fig. 3.4. Capacitance-voltage-frequency characteristics of silver on diamond Schottky diode KU3-6 with contact area of 3.2 mm^2

Fig. 6.1 Schematic diagram of chemical vapor deposition apparatus.

Fig. 6.2 SEM micrograph of the samples. (a) type 1, (b) type 2.

Fig. 6.3 AFM images. (a) top view of type 1, (b) surface plot of type 1, (c) top view of type (d) surface plot of type 2.

Fig. 6.4 X-ray diffraction patterns of the samples. (a) type 1, (b) type 2, (c) type 3.

Fig. 6.5 X-ray rocking curve of type 2 sample.

Fig. 6.6 Macro-Raman spectrum of type 2 sample.

Fig. 6.7 Micro-Raman spectrum of type 2 sample.

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April 19, 1995

To: Edward P. Sheridan
From: Mark Prelas
Subject: Niche Planning for Interdisciplinary groups

This document represents the strategy for niche planning in the area of wide band gap materials. This area of emphasis includes diamond films, and III-V materials (GaN, AlN, and BN).

Diamond film technology of today has been compared to silicon technology in 1960. The current market for diamond films is \$100,000,000/year primarily based on diamond's coating aspects. By the turn of the century this market is projected to grow to multibillion dollars per year. This market will be made up of diamond coatings (for cutting tools, heat sinks for the semiconductor industry, surgical blades, knives, abrasives, eye glasses, and medical implants) and diamond semiconductors (high power transistors, ultra fast & chemical, heat, and radiation resistant integrated circuits, lasers, ultra sensitive detectors, and photovoltaics).

Diamond is the most unique material in the universe. It is able to transfer heat five times better than copper, it is the hardest material known, it is resistant to chemicals, it is resistant to heat, and it is resistant to radiation.

As a coating, diamond would be virtually indestructible. As a semiconductor material diamond has the potential to compliment silicon technology in the near term, and to compete with it in the long term. Diamond films will become the world's next major high tech industrial revolution.

The III-V materials also have unique properties. Due to the recent success of making a GaN light emitting diode, this material is receiving a great deal of world wide attention. However, the promise of AlN and BN is bright making these materials of the future.

It is important that a University community take the lead in researching technologies of the future. It is the goal of this niche area to position the University of Missouri to enhance its leadership role in the development of these materials that will impact society in the next century.

This plan describes the current status of this niche area and future prospects. A major strategy in this plan is a projection of how to finance future research. In the foreseeable future, federal dollars going into basic research will undergo a major decline. The only research area which will experience a budget increase is in research that impacts upon the national economy. This area will require the partnership of industry, university, and government. As this plan shows, partnerships have already been formed with industry, university, and government and these types of partnerships will be enhanced.

In addition, it is important to have a vision for the financing of future research in an environment of federal budget cutting. As this plan shows, this niche will take advantage of new federal funds in the area of industrial/university/government cooperation (with projected revenues of over \$1,000,000/yr), will take advantage of the intellectual property that such research will develop (with projected revenues of over \$1,500,000./yr), and will take advantage of direct partnerships with industry (with projected revenues of over \$1,000,000/yr).

2.0 Interdisciplinary Interactions

2.1 Nuclear Engineering Department

Mark Prelas (Professor NE),
Sudarshan Loyalka (Professor NE, ChE, MAE, and Director PSRC),
Robert Tompson (Assistant Professor NE and PSRC),
Tushar Gosh (Assistant Professor NE and PSRC),
William Miller (Professor and Chairman NE),
Galina Popovici (Solid State Physicist, Research Manager Rockford Diamond Technology and Adjunct Professor NE)
Boris Spitsyn (Physical Chemist Director of Diamond Crystallization Laboratory Institute of Physical Chemistry, Russian Academy of Science and Adjunct Professor NE),
Dr. Steven Lin (Part time Post Doc. NE, and part time Research Scientist, Rockford Diamond Technology),
Dr. Ziming He (Post Doc, NE)

2.2 Electrical Engineering

Jon Meese (Professor ECE)
(Discussions with other faculty to join this niche plan are in progress)

In addition there are a number of international, national, and local interdisciplinary collaborators who work with this group:

2.3 Interdisciplinary Collaborations

2.3.1 National

Rockford Diamond Technology- Dr. Galina Popovici (Solid State Physicist, Research Manager Rockford Diamond Technology and Adjunct Professor NE), John Tompkins (Physics), et. al. Rockford has licenced technology from the University of Missouri which was developed on a DOE project. Rockford has provided funding, and has teamed with the University to obtain Science and Technology Transfer Research Grants from the Ballistic Missile Defense Organization and the Navy. Rockford has been an active participant in the planning of the International Diamond Research Institute for which White House funding was received.

Norton Diamond Film- Dr. K. Bigelow (Chemist), Dr. Richard Sioui (Materials Science), Dr. Ron Grieger (Materials Science), and Dr. Robert Hay (Materials Science)-. Dr. Bigelow provides us with high quality diamond film samples which we dope and send to collaborators. In addition, Dr. Bigelow and Dr. Hay are working with us on the wear resistance of diamond tools. Dr. Sioui is working with us on the wear resistance of diamond abrasives. Our group has developed a process which has successfully increased the wear resistance of diamond. Samples of tools and abrasives were provided to us by our collaborators at Norton, we post processed the samples, and Norton tested the samples. The results were stunning. Our process increased the wear resistance of all the samples by a substantial margin. The commercialization of our process appears to be achievable in a reasonable time. Norton has begun discussions with the University to begin the development phase. Additionally Dr. Bigelow is a co-editor on the Handbook for Industrial Diamond and Diamond Films.

CORDA Technologies, Kansas City- Brooks Herdon (Electrical Engineering), et. al. -. Corda helped in the planning of the NATO ARW. CORDA is interested in pursuing uses of diamond in active electronic devices and has been developing plans with our group for this activity. CORDA has been an active participant in the planning of the International Diamond Research Institute for which White House funding was received.

Huges Aircraft, California- Dr. R. Wilson (Physics), etc. -. Dr. Wilson makes SIMS measurements on forced diffusion doped diamond samples. He has co-authored many papers with the group.

SI Diamond, Texas- Dr. K. Jaminson (Electrical Engineering), etc. -. Dr. Jaminson sends us doped samples to be analyzed using our biased probe method.

Florida State University- Dr. P. Gielisse (Materials and Mechanical Engineering), Dr. E. Niculescu (Materials Science), etc. This group is collaborating on developing wide band gap electronics with AlN and BN. Prof. Gielisse provides high purity AlN and BN, and we dope the crystals. Additionally, we are collaborating on methods to press and sinter nanophase diamond powders.

BDM Corp., New Mexico- Dr. C. Wallace (Nuclear Engineering), etc. -. We provide Dr. Wallace with doped diamond films for microwave window tests.

Teledyne - Gary Tracy (Materials Science), Jim Oaks (Materials Science), Mr. Ken Burkett (Industrial Engineering). Mr. Burkett has a program to develop advanced mining tools. We are working with Mr. Burkett by diamond coating his samples.

University of Arkansas, HIDE Center- Professor Ajay Malshe (Electrical Engineering),. We provide Professor Malshe with nanophase diamond seeded samples to grow in his microwave system. We are beginning collaborating on a program for defining mechanical properties of doped diamond films.

Vanderbilt University- Prof. J. Davidson (Electrical Engineering)-. Prof. Davidson works with us on the analysis of doped material.

Nuclear Engineering Dept., Univ. of Illinois- Prof. G. H. Miley (Nuclear and Electrical Engineering), et. al. -. Professor Miley has collaborated with us on the development of diamond coated grids for the Inertial Electrostatic Confinement device which his group developed.

Straus Chemical Corp. Chicago, USA- Dr. Eric Kochman (Physical Chemistry). We are collaborating with Dr. Kochman on the development of a program on Nanodiamonds in High Technologies under the Chernomirdin-Gore Agreement of June 22, 1994. Additionally, we are collaborating on testing Straus Chemical colloids as seeding materials.

2.3.2 International

British Nuclear Fuel Ltd.- Howard Jennings (Mechanical Engineer), Allister Damm (Physics), Andy Mountford (Physics), etc.--We are working towards the development of advanced photovoltaics and low noise high resolution gamma ray cameras.

Daimler Benz-- John Sved (Mechanical Engineer), Rienhard Zachai (Electrical Engineer), etc.--We are working on the development of advanced electronic devices on wide band gap materials.

Institute of Physical Chemistry, Russian Academy of Sciences- B. V. Spitsyn (Physical Chemist), G. Sakolina (Physical Chemist), V. Builov (Physical Chemist), A. Alexsenko (Physical Chemist), V. Varnin (Physical Chemist), etc.-. We provide doped material to this group and they make measurements. This group also provides us with SiC samples for making heterojunctions with diamond. We have Supported this group as part of the White House grant.

Belarus State University- V. Varichenko (Electrical Engineering)-. We provide doped samples for analysis. This group is using our doped samples in a collaborative effort to make integrated circuits. We have Supported this group as part of the White House grant.

Chelyabinsk-70 and Krysnyarsk, Russia- Dr. P. Belabrov (Electrical Engineering) et. al. -. Dr. Belabrov is collaborating with us on the development of nanophase diamond.

Institute of Superhard Materials, Kiev, Ukraine- Dr. A. Padalko (Materials Science), et. al. Dr. Padalko produces nanophase diamond powder. We work with him on testing of properties and applications.

Microelectronics Research Laboratory, Russian Academy of Science- P. Perov (Electrical Engineering), S. Polyakov (Electrical Engineering), etc. We provide doped samples to this group and they make measurements on the material plus make electronic devices with the material. We have Supported this group as part of the White House grant.

Central Research Technical Institute, Moscow Russia- Prof. A. Belyanin (Physics),. This group provides us with AlN samples for doping and for making heterojunctions with diamond. We have Supported this group as part of the White House grant.

Kurchatov Inst., Russia- Academician A. Baranov, Troitsk Institute,. This group is working on Kr excimer spectroscopy in support of advanced nuclear battery research. In addition, we have jointly proposed a NATO Linkage grant with the Kurchatov Institute.

Ukrainian Academy of Science- Prof. A. Gontar (Electrical Engineering) et. al... Dr. Gontar is collaborating on the Handbook for Industrial Diamond and Diamond Films. We have Supported this group as part of the White House grant.

General Physics Institute, Russia- Prof. V. Vavilov (Electrical Engineering), etc. -. Dr. Vavilov is working with us on the Handbook for Industrial Diamond and Diamond Films. Additionally, Dr. Vavilov will work with us on the development of electric devices from wide band-gap materials.

Donbass Inst. of Construction, Donetsk, Ukraine- Prof. V. Timchenko (Electrical Engineering). Professor Timchenko works with us on building wide band gap electronic devices.

General Physics Institute, Moscow Russia- Prof. V. Ralchencho (Physics), Prof. Pimenov (Physics), Prof. G. Konov (Physics), etc. -. Professor Ralchencho is working with us on the Handbook for Industrial Diamond and Diamond Films and is collaborating on the fabrication of electronic devices.

University of Hagen and Belarus State University- Prof. A. Zaitsev (Electrical Engineering), Dr. V. Varechenko (Electrical Engineering) and Dr. A. Melnikov (Electrical Engineering)-. We provide doped samples for analysis. This group is using our doped diamond samples in a collaborative effort to make integrated circuits.

University of Regensburg, Germany- Professor Hopfl (Electrical Engineering) and Professor H. Hora (Electrical Engineering and Physics)-. Professor Hopfl and Prof. Hora are working with us on energy conversion devices using diamond photovoltaics. We have collaborated on the writing of a NATO linkage grant.

University of Melbourne, Australia- Prof. S. Praver (Physics)-. Prof. Praver is working with us on characterizing our diamond and doped diamond films.

Sumatomo Electric, Japan- Dr. Fujimori (Electrical Engineering)-. Dr. Fujimori provides us with high temperature high pressure diamond doped samples.

University of Tsukuba, Japan- Prof. H. Okushi (Electrical Engineering), etc. -. Professor Okushi is analyzing samples which we provide him plus he is testing the SiC-diamond heterojunctions.

University of Osaka, Japan- Prof. A. Hiraki (Electrical Engineering), etc. -. Professor Hiraki is

analyzing doped diamond samples which we provide him.
Drukker International, the Netherlands - Dr. Richard Colston (Materials Science)-. Drukker International is the largest producer of natural diamond tools. We are working with Dr. Colston to change type IIa diamond tools to type II b diamond tools.

2.3.3 Campus Wide

MURR, UMC-. Das Kuttikad, John Farmer, et. al. -. We are looking at depth profiling in boron and Li doped diamond films, transmutation doping of diamond films, and radiation damage of diamond films.

Physics Dept. UMC- Prof. H. White, etc. -. Dr. White works with us on characterizing our samples using Raman Spectroscopy.

Chemical Engineering Dept., UMC- Prof. H. Yasuda -. Professor Yasuda has collaborated on plasma problems, and plasma diagnostics.

3.0 History

Historically, this effort began with the presentation of the paper "A Potential UV Fusion Light Bulb for Energy Conversion," by M.A. Prelas, Bull. Am. Phys. Soc., 26(7), 1045 (1981). In this paper, a use of wide band gap photovoltaic cells in fusion energy conversion was proposed. This paper was of sufficient interest that it was chosen by APS for a press release. Subsequently the article was published by many newspapers and journals (e.g., Inside R & D, Vol. 10, Number 41, Oct. 14, 1981).

Diamond film research is one strategic research area identified by the government of Japan. Since the Japanese began their long term efforts in diamond film synthesis in 1981, the number of scientists engaged in the field have gone from a few hundred to over ten thousand. As an example of the strategic nature of diamond film research, in 1993 the total sales of product which utilized diamond film coatings was \$20,000,000 world wide. In 1994, the total sales has risen to over \$100,000,000. It is projected that by the turn of the century, the total sales of products using diamond film will be in the five billion dollar range.

There are two strategic problems in diamond film research, n-type doping of diamond and heteroepitaxy. We have made some major breakthroughs in both areas which are gaining the attention of the international diamond film community. We will provide supporting documentation for these advances and how we plan to take full advantage of them.

Members of this core group have been principal investigators on grants totaling 1.2 million dollars since 1990 funded by the Department of Energy, the White House (a grant administered by DOE), the National Academy of Science, Rockford Diamond Technology Inc., Norton Diamond Films, NATO, Research Board, BMDO, and the Naval Research Laboratory. With this funding a great deal of equipment was accumulated. A summary of these resources are:

Reactor 1: Hot Filament Chemical Vapor Deposition for Diamond (HFCVD-C α), in room 127EBW. This reactor was built for insitue p-type doping. (DOE funds)

Reactor 2: Radio Frequency Assisted Chemical Vapor Deposition for Aluminum Nitride (RFCVD-

AlN) in room 235 EBW. This reactor was built for AlN growth. (DOE funds)

Reactor 3: Electron Cyclotron resonance Heating Chemical Vapor Deposition for Diamond (ECH-CVD-C α) EBE 1061. This reactor was built for large scale diamond film growth. (DOE funds)

Reactor 4: HFCVD for high purity diamond growth and thermal doping with Boron-10 in EBE 1061. (National Academy of Sciences and DOE funds)

Reactor 5: Field Enhanced Diffusion for boron doping wide band gap electronic materials with impurities in W0030 EBE. (DOE funds)

Reactor 6: Microwave Assisted Chemical Vapor Deposition for diamond (MCVD-C α) in room 128 EBW. (This reactor was built by Juan Chaing with funds from Dr. Loyalka's 1993 Undergraduate Summer Research Experience Course and RIF funds.)

Reactor 7: HFCVD for insitue n-type doping in room 127 EBW. (DOE funds)

Reactor 8: HFCVD for high purity diamond growth in EBE 1061. (Research Board Funds)

Reactor 9: Field Enhanced Diffusion for lithium doping wide band gap electronic materials with impurities in W0030 EBE. (RIF funds)

Reactor 10: Hot filament CVD for insitue doping with Li impurities in 1061 EBE. (RIF funds)

Reactor 11: Microwave Driven Photochemical CVD reactor 1061 EBE. (Navy STTR funds)

Reactor 12: Microwave Assisted CVD reactor 1061 EBE. (Navy STTR funds)

Reactor 13: Combustion Flame CVD reactor Electrical Engineering (DOE funds)

3.1 Activities

This niche area was developed based on the principles that we must demonstrate leadership in the scientific community and in research.

3.1.1 Leadership in the Scientific Community

We have taken a lead role in advocating fellowship with the scientists in the Newly Independent States (NIS). These activities began in 1991 when Dr. Prelas was invited by the USSR government to lead a delegation of western scientists into Closed Cities in the USSR (see Christian Science Monitor, February 3, 1992, page 18). The goal of this delegation was to advise how military technology could be converted to civilian uses. In the following years, this group interacted with NIS Scientists in the area of diamond film technology. The NIS scientists pioneered the field of diamond films and have been active in this research for nearly 40 years. Dr. Boris Spitsyn, acknowledged as the father of diamond films was brought to the University on a National Academy of Science Fellowship in 1992. Since then he has been an adjunct Professor of Nuclear Engineering. Dr. Spitsyn has been an active collaborator ever since spending about 4 months per year at the University. Dr. Prelas and Dr. Spitsyn worked with Congressman Volkmer to obtain the White House Grant which has supported 20 NIS scientists specializing in diamond electronics. In addition, Dr. Spitsyn has collaborated on a number of innovative research programs, on the development of the first course taught in the US on diamond films and characterization, on the organization of the first NATO workshop on Wide Band Gap Electronic Materials in the NIS, the organization of the second International Symposium on Diamond Films, and currently the third International Symposium on Diamond Films to be held in St. Petersburg in 1996. The goal of the NATO workshop and the ISDF series was and is to provide a forum in a location in the NIS where NIS scientists can afford travel, and which has appeal to western scientists. We have also taken the lead in developing a comprehensive industrial handbook on diamond and diamond films for Marcell Dekker. The goal of this project is to provide a comprehensive

resource which covers the breadth of the diamond business. Below is a summary of activities in Community Leadership.

Editing of Proceedings, Handbooks, and Books

Kluwer - NATO ASI Series Book for the Workshop on Wide Band Gap Electronic Materials, Editors, M. Prelas, P. Gielisse, G. Popovici, B. Spitsyn, and T. Stacy, Published April 1, 1995 (ISBN 0-7923-3405-1).

J. Diamond and Related Materials- Proceedings of the International Symposium on Diamond Films 2. Editors, P. Gielisse, H. Nicalescu, G. Popovici, and M. Prelas. Due to be published in August, 1995

Marcell Dekker- Handbook for Industrial Diamond and Diamond Films. Editors, M. Prelas, G. Popovici, and L. K. Bigelow. Due to be published in September, 1995.

Development of Courses and Textbooks

Dr. Boris Spitsyn, Dr. Galina Popovici and Prof. Mark Prelas have collaborated on the development of a course in Diamond Films and Characterization. This course was first offered in the winter of 1994 and in the winter of 1995. Dr. Bob Hay of Norton Diamond Film said that "this is the first diamond course he is aware of." The instructors are collaborating to produce a textbook from this effort. Marcell Dekker has already offered to become the publisher of what is hoped to be the first textbook on Diamond Film.

Organizing

The International Symposium on Diamond Films and Related Materials (ISDF) Series: ISDF2 was held in Minsk, Belarus, May 2-4, 1994. Professor Prelas and Galina Popovici were the primary organizers for that meeting. Additionally, ISDF3 is currently being organized for St. Petersburg Russia, May 1996

C-BN and Diamond Crystallization under Reduced Pressure: Jablonna, Poland, June 27-29, 1995. Dr. Prelas is one of three Conference Managers and Prof. Spitsyn and Prof. Popovici are members of the honorary committee.

International Society of Diamond and Related Materials (Mark Prelas along with A. Hiraki, B. V. Spitsyn, and G. Popovici)

International Leadership

White House Grant: With the help of Congressman Harold Volkmer, we have obtained the first federal grant to assist non-weapons scientists in the Former Soviet Union. Professor Mark Prelas was responsible for the management of the White House Grant.

3.2 Leadership in Scientific Research:

This group strives to pioneer new areas, not follow the lead of others. With these goals, we have

succeeded in pioneering new science.

Examples of Pioneering Research

We were the first group to work on the development of wide band gap photovoltaics for use in nuclear energy conversion. Since these initial efforts five wide band gap electronics groups in the NIS, Deutsche Aerospace, British Nuclear Fuels, Norton Diamond Film, ISE Corporation have also begun research efforts in this area.

We developed the method of biasing substrates during CVD growth to orient the crystals in diamond films. We have applied for and expect to receive the senior patent for this valuable method. Since this work, Kobe Steel, Phillips, Daimler Benz, Sumatomo Electronics, along with many other groups have been working in this area.

Realizing the limitations of the biasing method, we developed along with Rockford Diamond Technology a method of seeding crystals and using two dimensional electric fields to align the seeds (BMDO STTR grant). The goals of this project was to solve the problem of developing a cheap source of single crystalline films. This method has already demonstrated better orientation of films than the biasing method. Recently, Dr. Robert Hay called our method the "best idea I have heard of." Norton Diamond Films, wants to participate in the commercial development of this science.

Due to our close ties with NIS (especially Russian Scientists) we were able to obtain a unique material made in Russia--nanophase diamond powder. We have used the nanophase diamond powder as a seeding material. We have developed methods of seeding the nanophase material on substrates which has led to a high nucleation density. Because of this we have made the thinnest, most uniform diamond film ever made. Norton Diamond Film was so impressed with this work that they also wish to work with our group and the University on this project.

We developed a method of forcing impurities into diamond (both natural and films) called "forced diffusion." With this method we have solved the problem of making n-type diamond. We made the initial announcement at the European Conference on Diamond Films 1994. Since this time we have found that we can place a variety of impurities into diamond and each impurity impacts on the optical, mechanical, chemical, and electrical properties of diamond. We have ongoing projects with collaborators to examine each of these aspects of impurity addition. With Rockford Diamond Technology, the University of Hagen, the University of Melbourne, and Implant Science Corporation we are trying to make the first integrated circuit out of diamond. With Norton Diamond Film, we are enhancing the chemical and mechanical properties of their diamond products. With Gem Spectrum, we are working the enhancement of diamonds optical properties. We have applied for and expect to receive the senior patent in the area of forced diffusion.

Along with John Farmer of the University of Missouri Research Reactor, we have done pioneering studies in transmutation doping of diamond films using the University of Missouri Research Reactor. By doping diamond films isotopically enriched boron-10, we found that the n-type conductivity of lithium compensates the p-type conductivity of boron.

Along with John Farmer of the University of Missouri Research Reactor, we have made pioneering discoveries of radiation damage effects on diamond films using the University of Missouri Re-

search Reactor. We have found that a post treatment method which transforms poor quality irradiated diamond films into high quality diamond films.

4.0 Future Plans

Develop More Industrial Funding for Diamond and Related Materials (Increase levels from the 100 k/yr level to the 1,000 k/yr. level)

Active Contracts:

BMDO STTR Phase I, "Processing of Diamond Films," M. Prelas PI, and E. J Charlson, E. M. Charlson, J. Meese, S. K. Loyalka, and T. Stacy. with Rockford Diamond Technology, \$70,000, University share \$31,500, 7/94-6/95.

Navy STTR Phase I, "Photochemical Production of Diamond Films," M. Prelas PI, with Rockford Diamond Technology, \$70,000, University share \$31,500, 9/94-6/95.

Rockford Diamond Technology, "UV Testing of Diamond Films," M. Prelas PI, \$10,000, 10/94-7/95.

Rockford Diamond Technology, "Impurity Additions into Diamond Substrates," M. Prelas PI, \$12,000, 2/1/95 to 1/31/96.

Contracts in Negotiation

Norton Diamond Film, "Treatment of Diamond by Forced Diffusion and Radiation to Enhance its Properties," M. Prelas PI, \$100,000/yr, 6/95-to be negotiated

Rockford Diamond Technology, "Electrical and Optical Enhancement of Diamond," M. Prelas PI, about \$100,000/yr, 6/95-to be negotiated.

Pending Proposals

BMDO STTR Phase II, "Processing of Diamond Films," with Rockford Diamond Technology, M. Prelas PI, \$750,000, University share \$325,000, 9/95-9/97.

Navy STTR Phase II, "Photochemical Production of Diamond Films," with Rockford Diamond Technology, M. Prelas PI, \$750,000, University share \$325,000, 9/95-9/97.

BMDO STTR Phase I, "Diamond UV Laser/Luminescence Devices," M. Prelas PI, with Rockford Diamond Technology, \$70,000, University share \$31,500, 10/1/95-6/30/96

Air Force SBIR Phase I, "Aluminum Nitride Doping by Forced Diffusion," M. Prelas PI, with Rockford Diamond Technology, \$70,000, University share \$31,500, 10/1/95-6/30/96.

BMDO STTR Phase I, "Diffusion of Prospective n-type Impurities in Diamond," M Prelas PI and S. K. Loyalka, with Rockford Diamond Technology, \$60,000, 10/1/95-6/30/96.

DOE STTR Phase I, "Diamond as a first Wall Material for Fusion Reactors," M. Prelas PI

and S. K. Loyalka, with Implant Science Corp., \$70,000, University share \$35,000, 6/95 to 3/96.

DOE STTR Phase I, "Aluminum Nitride Detector," M. Prelas PI and S. K. Loyalka, with Rockford Diamond Technology, \$70,000, University share \$35,000, 6/95-3/96.

Develop More Federal Funding in Diamond and Related Materials (Increase levels from the historical levels of 300 k/yr to 1,000 k/yr)

Active Contracts

DOE- Wide Band Gap Photovoltaic Cells For Fission Energy Conversion, M. Prelas PI, and E.J. Charlson, E. M. Charlson, and J. Meese, \$917,000, Dec. 1990 to Sept. 1995.

DOE- White House Grant, Support of Russian Scientists in Diamond Electronics, M. Prelas PI, and E. J Charlson, E. M. Charlson, J. Meese, S. K. Loyalka, G. Popovici, and T. Stacy. \$50,000, Oct 1993 to Sept. 1995.

DOE- Visible Lamps for Remote Pumping of Solid State Lasers and Other Commercial Processes, M. Prelas PI, \$89,000 July 1993 to July 1995.

Pending Proposals:

NASA- Modification by Forced Diffusion of Diamond Electronic Materials, M. Prelas PI, and S. K. Loyalka. \$501,913, 6/1/95-5/31/98

NSF- Field Enhanced Diffusion of Impurities into Diamonds, M. Prelas PI, and S. K. Loyalka. \$319,113, 10/1/95-9/30/98

Proposals In Planning Phase:

NSF- Materials Research Center, \$5,000,000 over five years

ARPA- N-Type Diamond, \$100,000 per year over three years

Navy- N-Type Diamond, \$100,000 per year over three years

ARPA- Jointly with Norton Diamond Films and the University of Missouri Research Reactor, Radiation Based Enhancement of Properties of Diamond, \$2,000,000 per year over three years.

ARPA- Jointly with Norton Diamond Films, Exiton Luminescence From High Purity Diamond Films, \$2,000,000 per year over three years.

Generate Revenues from Intellectual Property (Increase levels to 1,500 k/yr)

A significant but untapped resource which will come about due to the partnering with industry is royalties which result from intellectual property. An example of how significant this

resource can be derived from current negotiations with the Norton Company abrasives division. Prof. Prelas convinced Norton that the forced diffusion process pioneered by his group could have significant impact on the mechanical properties of abrasives. Norton provided Prof. Prelas with samples and his group developed a process. When Norton tested the samples the results were stunning. Currently the Norton Company (with over 5 billion dollars in sales) is negotiating with the University for rights to the process. The potential impact on patent royalties could be significant. The total abrasive market world wide is about 1 billion dollars. This process could impact upon 10% of that market. Suppose that the University is able to collect 1.5% royalties on the 10% market share which this technology will impact, the total yearly income could approach 1.5 million dollars.

It is important to note that without the founding principles of scientific leadership, opportunities such as that given in the above example would not present themselves. We are working on many more such opportunities based upon the pioneering research which has already been done.

We expect that the leadership philosophy of this niche will lead to other pioneering research and other opportunities in generating revenue from intellectual property.

Table 1: Revenue Projection for Niche Area

	Federal Grants	Industrial Contracts	Patent Royalties
Yr. 1	\$200,000	\$200,000	\$20,000
Yr. 2	\$400,000	\$400,000	\$300,000
Yr. 3	\$600,000	\$600,000	\$800,000
Yr. 4	\$800,000	\$800,000	\$1,200,000
Yr. 5	\$1,000,000	\$1,000,000	\$1,500,000

5.0 Goals As a Niche Area

5.1 Develop New Industrial Collaborators

Increase funding activity with existing industrial collaborators: Rockford, Norton, BDM, SI, Implant Science, Corda Technology, and Huges
Seek new collaborators such as GE, Ford, Westinghouse, Deautch Aerospace, Dailmer Benz, etc.

5.2 Develop an NSF Center

Make a case to NSF for a Center with MU and Industrial support.

5.3 Strengthen Our International Leadership in Research

We want to continue leadership in our pioneering work on field enhanced diffusion. We need to explore all possible impurities that can be diffused by this method. We need to test this method on other wide band gap materials (e.g., AlN, BN, etc.) and on standard semiconductor materials.

We want to continue leadership in our pioneering work on heteroepitaxy using biasing. We want to continue the development of new strategies for seed crystal alignment.

We want to pioneer new areas of research. Our efforts in n-type material and heteroepitaxy can be used to strengthen our international leadership. We need to focus this research in the development of integrated circuits on wide band-gap materials. Our goals should be: 1) the first p-n junction in diamond, 2) the first integrated circuit on diamond, 3) development of more sophisticated diamond based devices, and 4) development of electronic devices based on the nitrides.

We want to be a leader in the development and applications of nanophase wide band gap materials.

We want to be a leader in the studies of radiation damage in wide band gap electronic devices.

Catalyze the Development of an Industrial Base in Wide Band Gap Electronics in Missouri

We wish to use our pioneering works as a basis for technology transfer to build up industries in wide band gap electronics materials in this region. Our hope is to develop jobs in the next wave of high technology industries. Our goal is a "diamond valley" in Missouri.

5.4 Retain our Best and Brightest Students

Students have been major contributors to our pioneering developments. We would like to see these students continue their association with us. It is our hope that the industry which we attract to this area will hire our students. This will help to facilitate technology transfer. Additionally, it is our hope that some of the best of these students will eventually consider an academic career after their industrial experience, and perhaps they will consider coming back to MU.

6.0 Request of University to Enhance Niche Area

6.1 Expand Faculty in this Area

5 New Faculty Positions in this Niche Area: Our group is small, but is competitive with bigger groups in the world. We are overworked, but enthusiastic. Realistically, the only way that we can achieve the goals outlined in section 5.0 is to expand the faculty with interests in this area. The benefits of expanding the faculty can be surmised by looking at other successful groups in the country with a focus on wide band gap materials. Most of these successful groups have on the order of 20 faculty. The benefit of expanding our faculty is in the development of a "critical mass" of researchers who can compete nationally. By comparing research activity with our closest competitors, Pennsylvania State University and North Carolina State University, we can project that over a five year period five new faculty should be able to generate \$150,000 each in external research.

Table 2: Revenue Projections from New Faculty Positions

	University Investment (Faculty Packages)	Anticipated Direct Costs Generated through External Funding	Anticipated Indirect Costs Generated through External Funding
Yr. 1	\$312,500	\$137,500	\$112,500
Yr. 2	\$343,750	\$206,250	\$168,750
Yr. 3	\$378,125	\$275,000	\$225,000
Yr. 4	\$415,937	\$343,750	\$281,250
Yr. 5	\$457,531	\$412,500	\$337,500

6.2 Provide Minimal Laboratory Resources

Funds for a Materials Characterization Laboratory: Other groups in wide band-gap materials research have well equipped laboratories (e.g., University of Illinois, Pennsylvania State, North Carolina State, etc.). Items which we lack on campus that should be made available are a Secondary Ion Mass Spectrometer (750 k), Rutherford Backscattering (\$500 k), an upgrade of current X-Ray diffraction capabilities to do texturing studies (\$100 k), and an advanced Raman device (\$100 k). These characterization methods will blend well with what is available on campus: Geology- X-Ray Diffraction, Scanning Electron Microscope, and Cathode Luminescence; Physics- Atomic Force Microscopy, and Raman; Engineering- FTIR. This Materials Characterization Laboratory will service all faculty at the University and regional industry. We envision that qualified technicians will be hired initially on University funds (an initial \$140,000/year operation budget), but that over a five year period, the goal is to make the Characterization Laboratory self supporting through service fees.

Table 3: Projection of Service Fees for Materials Characterization Laboratory

	University Capital Investment	Operating Expenses	Fees Generated through grants*	Fees Generated through services to regional industries
Yr. 1	\$1,400,000	\$140,000	\$10,000	\$5,000
Yr. 2		\$147,000	\$50,000	\$35,000
Yr. 3		\$154,350	\$85,000	\$50,000
Yr. 4		\$162,070	\$100,000	\$60,000
Yr. 5		\$170,170	\$100,000	\$80,000

* Based on 5% of grant revenue direct costs

cc Dean J. Thompson, W. H. Miller, S. K. Loyalka, R. Thompson, T. Gosh, J. Meese

Recent Publications in the Area of Wide Band-Gap Materials Research

Editor

Proceedings of the International Symposium on Diamond Films, 3-5 May 1994, Minsk, Belarus, to be published 1994 Minsk, Belarus, edited by M. A. Prelas, P. Gielisse, G. Popovici, and B. V. Spitsyn, to be published 1995

NATO Workshop Proceeding on Wide-band Gap Semiconductors, 4-6 May 1994, edited by M. A. Prelas, P. Gielisse, G. Popovici, B. V. Spitsyn, and T. Stacy, to be published 1995

"Industrial Handbook for Diamond and Diamond Films" editors M. A. Prelas, G. Popovici and L. K. Bigelow, to be published by Marcel Dekker, Inc. 1995

Review Articles

1. Nucleation and selective deposition of diamond thin films
G. Popovici and M. A. Prelas, *Physica Status Solidi (a)* **132**, 233 (1992)
2. Problems of n-type diamond doping, G. Popovici and M. A. Prelas
SPIE/ v. 2151 1994, Diamond-Film Semiconductors (1994) edited by M. Tamor and M. Aslam, p. 99
3. Diamond film doping, B. Spitsyn, G. Popovici, M. A. Prelas, presented at the *4th European Conference on Diamond, Diamond-like and Related Coatings.*, Portugal, 1993
4. Problems of diamond film doping, B. Spitsyn, G. Popovici, M. A. Prelas; *Second International Conference on the Applications of Diamond Films and Related Materials*, ed. M. Yoshikawa, M. Murakawa, Y. Tzeng and W. A. Yarbrough, August 25-27, 1993, Tokyo, Japan p. 57-64
5. Problems of n-type diamond film doping, G. Popovici, to be published in the *Proceedings of the Second International Symposium on Diamond Films*, Minsk, Belarus, May 1994
6. Diamond lasers, S.. Lin, M. A. Prelas and G. Popovici, to be published in *NATO Workshop Proceeding on Wide-band Gap Semiconductors*, Minsk, Belarus, May 1994
7. Problems of n-type diamond doping. Forced methods of doping, G. Popovici and M. A. Prelas, to be published in *NATO Workshop Proceeding on Wide-band Gap Semiconductors*, Minsk, Belarus, May 1994
8. Diffusion in diamond, Galina Popovici, T. Sung and M. A. Prelas, invited paper at *International Conference on Diamond and Related Materials*, Poland, June 1995

Papers and presentations

9. Diffusion of boron, hydrogen, oxygen, nitrogen and lithium in diamond. Forced diffusion, Galina Popovici, T. Sung, M. A. Prelas, and S. Khasawinah, accepted to the Meeting of Electrochemical Society, Reno, Nevada, May 1995
10. Photoluminescence of free standing hot-filament cvd diamond films, using He-Ne laser L.-T. S. Lin, Galina Popovici, M. A. Prelas, S. Khasawinah, T. Sung, accepted to International Conference on Diamond and Related Materials, Poland, June 1995
11. Diffusion of impurities in single crystal diamond, Galina Popovici, T. Sung, M. A. Prelas and S. Khasawinah, accepted to the Spring Meeting of MRS, April 1995
12. Residual stress and adhesion of the chemical vapor deposited diamond films on molybdenum and silicon substrates, Galina Popovici, S. Khasawinah, T. Sung and M. A. Prelas, accepted to the Spring Meeting of MRS, April 1995
13. Diffusion of impurities in polycrystalline diamond films, Galina Popovici, T. Sung, M. A. Prelas and S. Khasawinah, accepted to the Spring Meeting of MRS, April 1995
14. Diffusion of boron and lithium in polycrystalline diamond films under DC bias, Galina Popovici, T. Sung, S. Khasawinah and M. A. Prelas, submitted to Diamond and Related Materials
15. Diffusion of boron, hydrogen, oxygen and lithium in single crystalline and polycrystalline diamond. A novel method for the determination of the state of an impurity: forced diffusion of boron in Ia type natural diamond, Galina Popovici, T. Sung, M. A. Prelas, R. G. Wilson, and S. Khasawinah, to be published in *NATO Workshop Proceeding on Wide-band Gap Semiconductors*, Minsk, Belarus, May 1994
16. Photovoltaic effects in metal/semiconductor barrier structures with boron doped polycrystalline diamond films, V.I. Polyakov, P.I. Perov, N.M. Rossukanyi, A.I. Rukovishnikov, A.V. Khomich, M. A. Prelas, S. Khasawinah, T. Sung, and Galina Popovici, submitted to Thin Solid Films
17. Neutron irradiation and annealing of ^{10}B doped chemical vapor deposited diamond films, S.A. Khasawinah, Galina Popovici, J. Farmer, T. Sung, M. A. Prelas, J. Chamberlain, and H. White, submitted to J. Mater. Research
18. Forced diffusion of boron in Ia type natural diamond, Galina Popovici, T. Sung, M. A. Prelas, and R. G. Wilson, accepted J. Appl. Phys.

19. Properties of diffused diamond films having n-type conductivity, Galina Popovici, M. A. Prelas, T. Sung, and S. Khasawinah, A. A. Melnikov, V. S. Varichenko, A. M. Zaitsev, W. R. Fahrner, presented at DF'94, Ciocco, Italy, 25-30 September 1994, to be published in *Diamond and Related Materials*
20. Diffusion of lithium, oxygen and boron in type IIa natural diamond. G. Popovici, T. Sung, M. A. Prelas, and S. Khasawinah, R. G. Wilson, to be published in *J. Appl. Phys.*
21. Raman scattering characterization of (100) and (111) oriented diamond films grown in the same run by hot filament chemical vapor deposition, G. Popovici, S. Khasawinah, T. Sung, M. A. Prelas, B. V. Spitsyn, S. Loyalka, R. Thompson, J. Chamberlaine, and H. White, *J. Mater. Research* 9, 2839 (1994)
22. FTIR measurements of the hydrogen content of heat-treated diamond films, T. Sung, S. Khasawinah, G. Popovici, M. A. Prelas, B. V. Spitsyn, G. Mannig, S. Loyalka, R. Thompson, *Diamond, SiC and Nitride Wide Bandgap Semiconductors*, edited by C. H. Carter, G. Gildenblatt, S. Nakamura and R. Nemanich, (MRS, 1994) p. 643
23. Diffusion of impurities under bias in CVD diamond films, Galina Popovici, T. Sung, S. Khasawinah, M. A. Prelas, and R. G. Wilson, *MRS Proc.*, MRS v. 339, *Diamond, SiC and Nitride Wide Bandgap Semiconductors*, edited by C. H. Carter, G. Gildenblatt, S. Nakamura and R. Nemanich, (MRS, 1994) p. 601
24. Nucleation and selective deposition of diamond thin films, G. Popovici, invited paper at the *Diamond and Diamond-like Films Workshop*, International Society for Hybrid Microelectronics, Breckenridge, CO, March 29-31, 1992
25. M. Prelas, and H. Hora, "Parameters for an Aluminum Nitride VUV Solid-State Laser," *Accepted to Lasers and Particle Beams*.
26. M. Prelas, and H. Hora, "Parameter for a Diamond Solid State Laser," *Accepted to Lasers and Particle Beams*.
27. L.-T. S. Lin, M.A. Prelas, UMC; and G. Popovici, RDT, "Laser Modes in Diamond," *Wide Band-Gap Electronic Materials*, Editors M. Prelas, P. Gielisse, G. Popovici, B. Spitsyn, and T. Stacy, Kluwer, p 187 (1995).
28. M. A. Prelas, UMC; G. Popovici, RDT; S. Khasawinah, and T. Sung, UMC, "Wide Band-gap Photovoltaics," *Wide Band-Gap Electronic Materials*, Editors M. Prelas, P. Gielisse, G. Popovici, B. Spitsyn, and T. Stacy, Kluwer, p 463 (1995).
29. H. Hora, UR; R. Hopfl, HT; and M. A. Prelas, UMC, "Theoretical Aspects of Aluminum Nitride and Diamond in View of Laser and Photovoltaic Action," *Wide Band-Gap Electronic Materials*, Editors M. Prelas, P. Gielisse, G. Popovici, B. Spitsyn, and T. Stacy, Kluwer, p 487 (1995).

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32. Smooth diamond films grown by hot filament chemical vapor deposition on positively biased silicon substrates, G. Popovici, C. H. Chao, M. A. Prelas, E. J. Charlson, and J. M. Meese, to be published in J. Mater. Research
33. Phase Transformation of smooth diamond Films grown by hot filament CVD on positively biased substrates. G. Popovici, C. H. Chao, M. A. Prelas, E. J. Charlson, and J. M. Meese, MRS v. 339, Diamond, SiC and Nitride Wide Bandgap Semiconductors, edited by C. H. Carter, G. Gildenblatt, S. Nakamura and R. Nemanich, (MRS, 1994) p.325
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36. Diamond photovoltaics in energy conversion, M. A. Prelas, E. J. Charlson, E. M. Charlson, J. Meese, G. Popovici, T. Stacy, *Second International Conference on the Applications of Diamond Films and Related Materials*, ed. M. Yoshikawa, M. Murakawa, Y. Tzeng and W. A. Yarbrough, August 25-27 1993, Tokyo, Japan, p. 329
37. Hydrogen content in diamond films grown by hot filament chemical vapor deposition method, S. Khasawinah, T. Sung, B. Spitsyn, W. H. Miller, G. Popovici, M. A. Prelas, E. J. Charlson, E. M. Charlson, J. Meese, and T. Stacy, *Diamond Materials*, ed. J. P. Dismukes and K. V. Ravi, Electrochemical Society Proc. v.93-17, 1993, p. 1032-1035
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1-Introduction:

From our previous results in the last reports, we suspected that the platinum silicide in the formation of Pt_2Si will exhibit better quantum efficiency than different formation types. Therefore two patches of cells are fabricated and tested.

2-Fabrication Parameters:

We followed the same procedure explained in our previous reports. However the parameters of interests are listed in Table 1.

Group#/ # cells tested	Sputtering time (sec)	Annealing time (min)	Annealing temp. (oC)	Substrate type& resistivity
pt-15/2	90	60	400	P. (0.5-1)
pt-16/2	90	20	350	P. (0.5-1)
pt-2a/2	90	20	350	P. (30-70)
pt-3a/2	135	20	350	P. (30-70)
pt-22/2 [*]	45	20	350	P. (0.5-1)
pt-23/2 [*]	90	20	350	P. (0.5-1)

Table 1 *(X-ray diffraction results are at the end).

3-Quantum Efficiency Measurements:

The equations used to calculate quantum efficiencies are included in the last report.

A-In the wavelength region of (200-550nm):

The cells are being tested and compared with the calibrated silicon detector whose spectral response characteristics is known. The results are summarized in Table 2.

Group#/ # cells	Time of fabrication	Time of testing	Figure#
pt15/2	8/20/91	1/14/92	1
		1/30/92	2
pt16/2	8/20/91	1/14/92	3
		1/30/92	4
pt2a/2	10/15/91	1/14/92	5
		1/30/92	6
pt3a/2	10/15/91	1/14/92	7
		1/14/92	8
pt22/2	12/23/91	1/14/92	9
		1/30/92	10
pt23/2	12/23/91	1/14/92	11
		1/30/92	12

Table 2

The reason that we tested the cells twice at different times because once we suspected that the cells are being degraded. However according to those figures (1 to 12), we can say that the cells from each group are exhibiting the same shape of curves; slit differences could be due to the testing setup.

The reason that we are not getting high efficiencies in the UV

region because the tests are done in air and the low efficiencies in the UV region is due to absorption in air. That why we had to change our setup to do the testing in vacuum. Due to some difficulties we tested only one cell which has been chosen randomly. This cell, denoted by PtSi2a-4, is tested and compared with the silicon detector. The result is shown in Figure 13. We can notice the quantum efficiency is picking up in the region of 200nm to 250nm.

B-In the Wavelength region of (100-200nm):

For this region we used a calibrated UV detector from NIST(United States Department of Commerce). The results is shown in Figure 14. for the one cell mentioned above.

4-Discussion:

The X-ray spectra confirmed the formation of Pt_2Si . Two x-ray spectra for pt-22 & pt-23 groups are shown at the end of this report.

We hope that the results in Figure 14 is correct. We will use smaller slits(500 μm) in the very near future to confirm our results. The reason we could not use this slit now because of some setting arrangements in our setup. Therefore, we hope that we can reproduce those results when we test more cells. Other than that the cells exhibit a big deal of reproducibility.

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 8/20/91

Fig 1

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 8/20/91

Fig 2

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 8/20/91

Fig 3

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 10/15/91

Fig 5

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 10/15/91

Fig 6

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 10/15/91

Fig 7

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 10/15/91

Fig 8

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 12/23/91

Fig 9

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 12/23/91

Fig 10

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 12/23/91

FIG 11

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 12/23/91

FIG 12

QUANTUM EFFICIENCY VS. WAVELENGTH

Fig 14

QUANTUM EFFICIENCY VS. WAVELENGTH

PROCESSING DONE 8/20/91

Fig 4

EXECUTIVE SUMMARY

This report describes progress made as of the 19th month of a 36 month contract to develop high bandgap photovoltaic materials for direct conversion to electricity of eximer radiation produced by a fission energy pumped laser. The tasks set forth in this project are shown in Figure 1. As with any research project, certain tasks thought essential at the beginning of the project have been suspended to concentrate on those that impact more directly on the ultimate goal of the project. Of the milestones projected to be completed by this time period (1 thru 7 from the bottom), only aluminum oxide synthesis has not been completed. This has been deliberate since the electron beam recrystallization techniques which were to have been employed in this effort have been found to work on diamond. Our opinion is that the diamond substrate will yield quicker results than aluminum oxide because of its rapidly expanding technology and our attention has been turned to applying the recrystallization techniques to this material. In the areas of Schottky barriers and in the use of glow discharge as a back contact scheme, we are ahead of schedule. In general, progress on projected tasks has been good and we are optimistic about obtaining the overall goals of the project. The following are a summary of our progress to date.

We have grown diamond films by hot filament chemical vapor deposition, microwave assisted chemical vapor deposition, and by the combustion flame method. There are five variables which affect the quality of diamond: 1) mass flow of methane, 2) mass flow of hydrogen, 3) filament temperature, 4) substrate temperature, and 5) substrate material. Thus far in the area of diamond technology the following have been accomplished:

- High quality polycrystalline diamond films have been fabricated.

- High quality p-type polycrystalline diamond films have been fabricated.

- Schottky barrier diodes have been fabricated on p-type polycrystalline films.

- Rectifying behavior has been observed in a p-type polycrystalline film implanted with trimethyl phosphate molecules.

- A simple process to fabricate single crystalline diamond films on non-diamond substrates using hot filament chemical vapor deposition has been developed.

Current work is focused on the production of single crystalline diamond films on non-diamond substrates, ion implantation to create n-type material, and on in situ doping of diamond films to form n-type materials. Professor Boris Spitsyn, head of the Diamond Film Laboratory of the Institute for Physical Chemistry of the Russian Academy of Science and father of diamond film technology, has told us about an in situ process for creating n-type material that his laboratory created. This process, which is too complicated for common use, demonstrates that high quality n-

type films can be developed. Through our efforts, Dr. Spitysn has been awarded a National Academy of Science Fellowship to the University of Missouri-Columbia to study impurity doping of diamond films. This work will compliment our efforts to develop in situ doping techniques with hot filament chemical vapor deposition and microwave assisted chemical vapor deposition.

We have epitaxially grown high quality aluminum nitride films (AlN). These high quality AlN films have been used in ion implantation experiments to create p-type material. Thus far the results are promising but inconclusive. This work will continue during the next year as well as work to in situ dope the films.

Platinum silicide photovoltaic cells have been developed. A diffused guard ring has been added to minimize leakage current. Using facilities in the photovoltaics laboratory, the mask set was designed, masks were made, and a prototype set of cells has been fabricated and packaged in TO5 packages. The platinum silicide cells have been optically characterized between 120 nm - 400 nm wavelength. Results of this work demonstrate that platinum silicide has a very high quantum efficiency of 125% at 150 nm.

A microwave driven excimer lamp has generated high intensity xenon excimer emission. This light source will be used to measure the energy conversion efficiency of the wide bandgap photovoltaic cells made from diamond and aluminum nitride.

I VUV EXCIMER LIGHT SOURCES

Introduction

A microwave-cavity-lossy-plasma excimer lamp was developed during the last reporting period. Stable production of xenon excimer fluorescence has been demonstrated at various power levels and pressures. This excimer light source has operated in a continuous wave mode with a total power deposition of one kilowatt.

Microwave Discharge

Details of the design of this system were covered in the year one progress report. Figure 2 shows details of the current configuration. The low frequency design uses a 2500 W microwave source and the TE₁₁₁ propagation mode. The following are the conventional cavity parameters.

Parameter	Value
L	0.22 m
R _c	0.0376 m

Rp	0.005 m
Re{fres}	2.45 GHz
Im{fres}	0.195464 GHz
Q	12.52
Dt	8 ms
Pmicrowave	2.5 kW

The resonant frequency as a function of length is shown in Figure 3.

These parameters represent one possible design which simultaneously matches the microwave specification and the laser specification. The electric field, magnetic field, and the power density profile are shown in Figures 4 to 6.

We have performed a resonance experiment with the microwave driven excimer lamp. As can be seen in Figure 7, the experimentally measured resonance length is 21.7 cm. This result matches exactly the predicted result in Figure 3.

The microwave driven excimer lamp operates in a continuous wave mode. Microwave power levels between 50 and 1500 watts have been used to create excimer emission in xenon. In addition the xenon pressure has been varied between several Torr to 1500 Torr. A silicon detector was used to take measurements of the xenon excimer emission. The silicon detector has a sensitivity cutoff at 170 nm. Xenon excimer emission is shown in Figure 8.

As can be seen in Figure 8, the xenon excimer emission peaks at 172 nm with a width between 150 to 200 nm. Using the microwave driven excimer lamp and a silicon detector, emission under a variety of conditions is shown in Figures 8 to 10. Because of the sensitivity problems of a silicon detector below 170 nm, the true lineshape of the excimer spectra was not observable.

II BIASED HFCVD GROWTH OF DIAMOND

Introduction

The production of single crystal diamond thin films of large area would be a technological breakthrough for a variety of electronic and optical applications. In terms of the objectives of this contract, single crystal films would produce high quality doped regions and thus better barriers for energy conversion in the vacuum ultraviolet.

To date, diamond single crystal films have been made homo-epitaxially on natural or synthetic diamond single crystals. As large single crystal diamond is prohibitively expensive, there

FIGURE 4 Electric field intensity in the plasma tube of the 2.45 GHz design.

FIGURE 5 Magnetic field intensity in 2.45 GHz resonance cavity.

FIGURE 6

Power density of 2.45 GHz resonance cavity.

Fig 7

"600w,1.78 Atm,xs"

"600w,2.4 Atm,xe"

is a need to find matching substrates for diamond heteroepitaxy. Cubic boron nitride has the diamond lattice structure and matches nearly perfectly the cell dimensions. However, large area cubic BN single crystal substrates are not available, as c-BN is stable, just like diamond, at high pressures and high temperatures only. The widely used Si substrates have a large lattice constant mismatch with diamond.

Single crystal films can sometimes be obtained without an epitaxial relationship with the substrate, provided a large number of nuclei and an early coalescence of a highly oriented film can be achieved on the foreign surface. For instance, gold single crystal films have been grown on mica [1].

In the commonly used HF or plasma assisted CVD methods of diamond growth, the number of diamond nuclei on mirror-polished single crystal surfaces is small (for Si substrates it is typically about 10^4 cm^{-2}) [2]. For obtaining a large number of nucleation sites for diamond growth, scratching the substrate surface with diamond or other grids is widely used. This method is unacceptable for single crystal growth, as the substrate surface is damaged and nonuniform. Another method to obtain a large number of diamond nucleation sites on mirror-polished substrates has been proposed and studied recently [3,4]. It consists in electrically biasing the substrate surface, positively or negatively. The number of nuclei obtained on positively biased mirror-polished single crystal Si surfaces was reported to be of about 10^8 cm^{-2} in the electron assisted (EA) HFCVD [3] method. Higher densities, of about 10^{11} cm^{-2} , have been reported for negatively biased Si in EA CVD [4].

It has been conjectured [2] that by optimizing the applied voltage and current, one might obtain the necessary number of nuclei for an early coalescence of the layer. On the other hand, the electric field may enhance the single crystalline film growth by influencing the reorientation and the recrystallization of nuclei. The electric field may also induce the coalescence at an early stage of film growth by supplementing energy to the lattice.

Experimental

In this work we report on the synthesis of smooth mosaic single crystal carbon films having the diamond lattice constant on single crystal mirror-polished Si wafers by the electric field assisted HFCVD method. Such films can be adequate substrates for epitaxial growth of diamond perfect single crystal films.

The films were grown by the HFCVD method with constant electric bias applied between filament and substrate. Polished Si (100) substrates of approximately 1 cm^2 area were used. The substrates were biased positively. The substrates were mounted on a graphite holder. The distance between filament and substrate was approximately 4 mm. The chamber pressure was

maintained at 30-40 Torr during deposition. Flow rates (measured by MKS flowmeters) of 1 sccm of methane and 99 sccm of hydrogen were used. A tungsten coil was used as the filament. The filament temperature was measured by a Micron digital two-wavelength optical pyrometer. The filament temperature varied for different runs between 1950° C and 2200° C. The substrate temperature was maintained at 800 +/- 20° C.

Applied bias voltage between 50 V and 150 V were used (50, 80, 100, 120 and 150 V). The bias current varied between 0.19 and 2.30 A, being dependent on the filament temperature. The growth time was 30 minutes. As the voltage was applied, a bright plasma ball was formed around the filament. The substrate area intersected by this ball is relevant to current densities. In our case it was the whole substrate area.

Scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman and Auger measurements were performed, in this order. The order of measurements proved to be important for our films, as they were found to have polymorphic changes with time.

Results

SEM pictures of three film cleavages are presented in Figure 1. The films were grown with the following conditions:

Sample	Voltage	Current
I-1	50 V	0.19-0.22 A
I-3	100 V	0.32-0.39 A
I-4	120 V	0.48 A

The films, a few microns thick, have smooth surfaces. The parallel cracks seen on the cleavage of the I-3 sample suggest a single crystal structure. At the applied voltage of 150 V, current 0.53 - 0.63 A for one sample and 1.30 - 2.30 A for another sample, a large amount of tungsten from the filament was deposited in the layer. The presence of tungsten was detected both by XRD and Auger measurements.

Figure 2 shows the X-ray patterns for the same three films. At a first glance one can see two diamond peaks, a strong (111) at $2\theta = 44^\circ$ and (220) at $2\theta = 75.3^\circ$ and some peaks which may belong to hexagon carbon.

The X-ray diffraction pattern for 2θ between 42° and 45° for sample I-3 is presented in Figure 3. The pattern has a strong line at 44.07° ($d = 2.054$ Å), a line at 43.8° ($d = 2.065$ Å) and a line at 42.9° ($d = 2.11$ Å). For all eleven samples grown in various conditions, the three peaks were present, with varying intensity from sample to sample, with the dominant peak at 44.07° . No

FIG. 1

FIG 2.

FIG. 3

graphite lines could be seen at 44.6° ($d=2.03\text{ \AA}$) and 42.4° ($d=2.13\text{ \AA}$).

The equilibrium polymorph of crystalline carbon at high pressure and high temperature is the cubic diamond (CD). CD or graphite are usually obtained in CVD. There are no graphite lines in our X-ray diffraction patterns. The line at 44.07° was therefore attributed to (111) CD.

As shown below, the lines at 42.9° and 43.9° are correlated. We attributed them to the same carbon polytype. It may be hexagonal diamond (HD) 4H or 8H [5]. HD polytypes were found in shock-compact-synthesized diamond (2H-lonsdaleite) [5] and in CVD diamond films (6H) [6]. Calculated X-ray diffraction data for diamond polytypes can be found in [5]. These polytypes arise from different stacking sequences of hexagonal carbon layers and are analogous to SiC polytypes. Their formation is supposed to be enhanced by rapid quench rates. Under conditions favorable to fast nucleation, kinetic factors, rather than thermodynamic, should control the growth process [6]. These special conditions seem to be created on fast nucleation under electric field in CVD.

The lines (111) CD and (001) HD should have had the same spacing, $d=2.059\text{ \AA}$. However, these lines are seen to be separated in a double ($d=2.054$ and $d=2.065\text{ \AA}$). The peak shifts may be due to deformation faulting [7] and/or strains on polymorphic changes [8]. The presence of the doublet suggests the existence of two different phases: cubic and hexagonal. If there were two hexagonal polytypes, they would have had the same (001) spacing.

A rocking curve of the line at 44.07° of the sample I-3 is presented in Figure 3. The line (111) is seen to be narrow (full width at half maximum of 0.8°), which is typical for monocrystals. So we believe that the layer (on silicon substrate) was mosaic single crystal diamond, which is similar to layers obtained homoepitaxially (on single crystal diamond) by CVD methods [9,10].

Lines at both $2.06\text{ \AA}$ and $2.12\text{ \AA}$ were observed by Badzian et al [9] in layers grown homoepitaxially on a natural diamond single crystal by the microwave plasma assisted CVC method. The perfection of diamond films was found to depend on the growth direction. The highest perfection was obtained in the $\langle 100 \rangle$ direction and the lowest in the $\langle 111 \rangle$ direction. Planar defects, like stacking faults and twins, of high density, were found to be present in the $\langle 111 \rangle$ growth direction. The additional line at $2.12\text{ \AA}$ could be seen only for this direction. It was attributed to the presence of stacking faults. Qualitatively similar results have been obtained C. J. Chu et al. [10] on homoepitaxial diamond layers grown by HFCVD on natural IIa diamonds.

The narrow rocking curve was obtained on the sample I-3 three times at the beginning of measurements, but could not be reproduced after a few days. Figure 4 presents the change of the ratio of the line intensities that occurred in that time. The narrow line at $2.054\text{ \AA}$ disappeared and the line at $2.11\text{ \AA}$ became stronger. This happened with all samples. A possible explanation is that the carbon phases obtained under electric field are metastable and can have polymorphic changes.

FIG. 4

Polymorphic transitions usually transform single crystalline films into polycrystalline ones [8].

We cannot say whether the phase transition happened in time at room temperature or was triggered by X-ray irradiation. For instance, a transformation of diamond into graphite was observed before by Auger measurements after sputtering a diamond film by Ar^+ beam at an accelerating voltage of 1.5 kV and a beam current of 2.5 microamperes [11].

Typical Raman spectra of the sample I-3 is presented in Figure 5. The Raman measurements were performed after all the X-ray measurements were completed. The samples were found to be uniform: the same spectra were obtained in different places. There is no graphite peaks [12] at 1360 or 1580 cm^{-1} . There is no disordered carbon peak [13-15] at 1500 or 1550 cm^{-1} usually obtained in diamond layers. Raman spectra similar to ours were obtained by Howard et. [16] on powder material synthesized in acetylene oxygen plasma, consisting of small diamond crystals and hexagonal diamond polytypes.

The Auger measurements were performed last. Differentiated Auger spectra are shown in Figure 6. The peaks in Figure 5 look more like diamond than graphite peaks [11]. To our knowledge, no Auger spectra on layers containing hexagonal diamond have so far been reported.

Discussion

To sum up the experimental results, a diamond mosaic $\langle 111 \rangle$ film with high density of planar defects (like stacking faults of $\langle 111 \rangle$ cubic diamond), with inclusions of hexagonal diamond polytypes, has been obtained on Si polished substrates by HFCVD in the presence of electric field. The film was similar to those obtained homoepitaxially on (111) diamond substrates [9]. However, it was not stable since a polymorphic change occurred within a few days, destroying the mosaic crystalline order.

The following model for the growth of single crystalline diamond films on Si substrates can be advanced. As observed by many researchers [2], at the beginning of the growth process, SiC is formed on the Si substrate. On SiC sometimes a thin amorphous carbon layer grows. On this layer diamond begins to nucleate. The electric field can play multiple roles in obtaining single crystalline films:

- 1) It is well established that electric fields enhance nucleation. The mechanism of this process has not been clarified yet. One can speculate that the causes of this enhancement are the activation of the surface by electron or ion bombardment and/or the activation of some species in the gas phase.
- 2) The large number of nuclei facilitates an early coalescence of the film. A smaller energy for the recrystallization of coalescent crystals is necessary at early coalescence.
- 3) Charged species bring to the surface much larger energies (in our case approximately

FIG. 5

100 eV), than the average thermal energy (about 0.2 eV at filament temperature of 2000°C). This energy can be used in the lattice reconstruction and ordering for getting a minimal lattice energy.

4) The electric field may create a preferential direction in recrystallization and coalescence of the film. In our case it was the direction $\langle 111 \rangle$ normal to the surface.

It seems more appropriate to call this method "electric field assisted CVD" instead of "electron assisted CVD" because the phenomenon is complex and can not be reduced to just the electron bombardment of the surface.

In conclusion, diamond thin films were grown on polished Si substrates by electric field assisted HFCVD method. An early coalescence was achieved in all the range of voltages (50 - 150 V) and currents (0.20 - 2.3 A) and continuous films of a few microns were obtained in 30 minutes.

At low (50V) and high (150V) applied voltage, polycrystalline films were obtained. Tungsten contamination from filament was found in films grown at high voltages.

In the intermediate range of voltages and current (100V) and (0.35 A), a mosaic monocrystalline diamond film was obtained. The film underwent a phase transition to a hexagonal diamond polymorph and lost its mosaic order in a few days.

This result gives hope that single crystalline diamond films can be grown on non-diamond surfaces by applying electric fields that give a large number of nuclei and an early coalescence of the film. Mosaic films could serve as substrates for epitaxial growth of diamond monocrystalline films. This could be done in the same run, before the polymorphic transformation takes place. Ways of stabilizing the mosaic film structure might also be found.

III Schottky Diodes on HFCVD Diamond

G. Zhao, T. Stacy, E.J. Charlson, E.M. Charlson, C.H. Chao, M. Hajsaid and G. Popovici

Introduction

Semiconducting diamond is considered to be an attractive solid state material due to its unique electrical and physical properties, such as wide bandgap (5.5 eV), high breakdown voltage (10^6 - 10^7 V cm⁻¹), high electron and hole mobilities (2000 cm² V⁻¹ s⁻¹ and 1800 cm² V⁻¹ s⁻¹, resp.), and high thermal conductivity (20 W cm⁻¹ K⁻¹). These properties make diamond an ideal candidate for high power, high frequency and high temperature electronic device applications. However, most diamond devices reported to date have been fabricated using either semiconducting

natural diamond¹ or ultrahigh pressure synthesized diamond^{2,3}. With the rapid progress which is taking place in the development of various diamond chemical vapor deposition (CVD) processes^{4,5}, a number of polycrystalline diamond semiconductor devices, in particular Schottky diodes using this material, have been reported since 1988⁶⁻⁸. To our knowledge, all of the Schottky diodes reported were produced on some type of CVD film other than hot-filament CVD (HFCVD) diamond thin films and involved either aluminum, gold or titanium contacts. Since HFCVD is considered to be one of the most useful of diamond CVD techniques because of its low cost, ease of control and its ability to produce large area films with an acceptable growth rate, it is apparent that a good understanding of the electrical properties of HFCVD grown diamond Schottky diodes will be necessary for significant diamond device applications in the future.

Experimental

In this study, diamond thin films used for Schottky diodes were deposited on p-type silicon substrates using the HFCVD method with hydrogen and methane as the reaction gases and with acetone vapor as the carrier gas for the boron dopant as well as providing an additional carbon source. A liquid source, trimethyl borate ($\text{B}(\text{OCH}_3)_3$), which has proved to be an excellent ion implantation dopant source for silicon⁹, was used as an in-situ p-type dopant source. X-ray diffraction, scanning electron microscopy and Raman spectroscopy studies indicate that high quality boron doped polycrystalline diamond films were obtained. Schottky diodes were fabricated by sputter deposition of silver on boron doped diamond thin films. The current density-voltage, capacitance-voltage-frequency and temperature characteristics of these diodes were investigated. The electrical properties of these Schottky diodes are very similar to those diodes formed on crystalline diamond.

The boron doped polycrystalline diamond thin films were prepared by the HFCVD method using an in-situ doping technique on p-type (100) silicon substrates which had a resistivity of 0.5-1.0 ohm-cm. Prior to introduction into the reaction chamber, chemically cleaned silicon substrates were polished with 1/4 micron diamond paste to promote nucleation. The silicon substrate, 3 x 3 cm² in size, was mounted on a graphite base 3 mm beneath a tungsten filament which was heated to ~2000 °C. The substrate temperature was controlled at approximately 800°C. During deposition, the chamber pressure was maintained at 30-35 Torr and the following flow rates were used: hydrogen (98 sccm), methane (1 sccm), and acetone vapor with trimethyl borate (1 sccm). The boron to carbon atomic ratio in the reaction gases was about 30 ppm. The diamond film obtained after 6 hours of growth using this process is 6-7 microns thick. The x-ray diffraction pattern of the deposited film shown in Figure 1 indicates pure diamond characteristics with a lattice parameter of 3.566 ± 0.002 Å for all phases. The inset in Figure 1 is a scanning electron micrograph of the

Fig. 1

diamond film which shows that the diamond surface consists of isotropically oriented and well-faceted polycrystals with an average grain size of 5-6 microns. Raman spectroscopy showed a 1332 cm^{-1} sharp peak which is characteristic of diamond sp^3 bonding.

Before metal deposition, the diamond thin films were preannealed at $550\text{ }^{\circ}\text{C}$ in air as suggested by Landstrass¹⁰ for 20 min to remove hydrogen effects and stabilize the films. Then, in order to remove any nondiamond surface layer, the films were cleaned by dipping in a mixture of $\text{HF} + \text{HNO}_3 + \text{H}_2\text{O}$ and then in a saturated solution of $\text{CrO}_3 + \text{H}_2\text{SO}_4$ at $145\text{ }^{\circ}\text{C}$ for 20 min, followed by a rinse in a boiling $\text{H}_2\text{O}_2 + \text{NH}_4\text{OH}$ solution for 10 min, as described by Grot *et al*¹¹. The Schottky diodes were formed by sputter depositing silver (300-500 Å) circular contacts on the chemically cleaned diamond film through a metal shadow mask. An aluminum evaporation was done on the back side of the silicon substrate to ensure good ohmic contact. A non-oxidizing platinum layer (300-500 Å) was sputter deposited on top of the silver contacts to increase the working temperature of the device. A thermal annealing process was done following metallization.

Results

In order to determine whether the rectifying characteristics exhibited by the sample were due to a Schottky contact at the silver-diamond interface or whether a silicon-diamond heterojunction had been formed, indium was used to make ohmic contact to the diamond film. The current-voltage characteristics of the indium-diamond-silicon-aluminum structure which is shown in Figure 2 are those of a good ohmic contact, from which the diamond film resistivity of 3×10^4 ohm-cm was determined. Thus, the rectifying junction was shown to be at the silver-diamond interface. This rectification nature of the silver-diamond interface is consistent with results reported by Gildenblat *et al.*¹². They demonstrated that the rectification observed in the gold-diamond-silicon structure was due to the gold-diamond interface by comparing the I-V characteristics of a diamond Schottky diode on a silicon substrate with a Schottky diode formed on a free-standing diamond film.

In this study, two different contact areas, 3.2 mm^2 and 0.38 mm^2 , were used to produce similar current density-voltage (J-V) characteristics. A typical silver on HFCVD diamond Schottky diode current density-voltage characteristic measured at room temperature (sample KU3-6 with contact area of 3.2 mm^2) is shown in Figure 2. Forward conduction occurs when the Pt/Ag contact is negatively biased with respect to the grounded backside aluminum contact. The current density in these diodes is large compared to other reported values on CVD diamond Schottky diodes^{6,7}. This is probably due to smaller diamond bulk resistance in our diodes. Figure 3 shows $\log(J)$ vs. V curves of three diodes (KU3-1 with contact area of 0.38 mm^2 , KU3-5 and KU3-6 with contact area of 3.2 mm^2). The forward-to-reverse current ratio at 5 volts bias for each diode is seen to be greater than 1000. Forward current in these diodes is limited by the bulk diamond resistance as is evident at the linear end in the forward region. On a logarithmic scale, a linear portion extending more than three decades in the low forward bias region (less than 0.5 volt) has been obtained for diode KU3-6, from which an ideality factor of approximately 2.0 was estimated. This ideality factor is close to the reported value of 1.85 on microwave plasma assisted CVD diamond Schottky diodes^{6,7}.

The capacitance-voltage characteristics of diode KU3-6 exhibited frequency dependence as shown in Figure 4. At low frequency ($\leq 1 \text{ kHz}$), the measured capacitance is dominated by the DC capacitance of the silver on diamond Schottky diode which is bias dependent and frequency independent. As the frequency is increased, the measured diode capacitance is affected by not only DC capacitance but also the larger bulk diamond resistance and the dispersion capacitance which is frequency dependent and associated with hole emission from slowly responding deep impurity levels^{3,6}. When the test frequency is higher than 1 MHz, there is no bias dependence of the capacitance.

Figure 2 also includes some initial results of high temperature measurements on the silver on

Fig 2

Fig 3 -

Fig 4

diamond Schottky diode KU3-6. As shown, the diodes exhibit good rectifying characteristics up to 250 °C. At the present time, the upper bound on temperature is dictated by test limitations not by the device itself. A better apparatus for high temperature testing is now being built.

In conclusion, silver on diamond Schottky diodes with high forward current density and high forward-to-reverse current ratio have been fabricated on high quality boron doped polycrystalline diamond thin films grown by a HFCVD process with an in-situ doping technique using trimethyl borate as a boron dopant source. The electrical characteristics of these diodes show that they are very similar to those of Schottky diodes fabricated using a single crystal diamond substrate.

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IV Platinum Silicide Photodetectors

Introduction

Work continued this past year on PtSi photodiodes for conversion of radiation in the vacuum ultraviolet. While we do not believe that this diode will be used as the direct energy converter in the final PIDECE system, continued development of this device is important for two reasons. First, since the fabrication involves known technology and a conventional silicon substrate, there is a high probability that this device can successfully convert a significant amount of radiation in the 100 - 200 nm wavelength range. It will then allow us to test the radiation sources sooner than the development of diamond converters will allow. Indeed, in this reporting period, PtSi converters have been fabricated that are projected to have absolute power conversion efficiencies in the 1 - 3 % range at 148 nm. Secondly, the PtSi detectors make excellent secondary standards for light intensity in the vacuum ultraviolet range. To our knowledge no other inexpensive system is currently available. The NIST traceable diode we are using is very expensive and is limited to very low light levels. High quality silicon diodes such as the PtSi Schottky diode, are known to be very linear in short circuit current versus light level. It is our intention to use the PtSi diode as a secondary standard to measure the high light levels of the excimer lasers developed for this contract.

Previous work on the PtSi/p-Si Schottky barrier diodes [1,2,3] has indicated good photoresponse for radiation in the 230-700nm range. Our application uses lower wavelength radiation and therefore extensive effort was spent on extending this measurement into the 100-200 nm (VUV) range. Typically, quantum efficiencies of 40 - 70% have been reported in the 230 - 700 nm range. Our initial devices matched these efficiencies. However we found that devices that were fabricated to form the Pt₂Si phase were always on the high end of the efficiency range. This superior performance was found to also be true in the VUV range and therefore we have concentrated on this variety of the device. Formation of the Pt₂Si morphology is primarily determined by the annealing temperature [4], as has been reported in previous quarterly reports.

Experimental

The structure of the Pt₂Si photocell is shown in Fig. 1. The fabrication procedure is as follows:

Fig 1

- 1) ultrasonic organic and then hot acid cleaning of a (100) p-type Si wafer.
- 2) steam oxidation to form a SiO₂ layer of about 5000 Å.
- 3) photolithography and phosphorus diffusion of the n guard ring.
- 4) photolithography for the active window.
- 5) aluminum evaporation for the back contact.
- 6) platinum sputtering.
- 7) annealing at 350° C for 20 minutes to form the Pt₂Si film.
- 8) aluminum evaporation and etching for the front side contact.

Two parameters were changed to optimize the performance of the photodiode, 1) sputtering time which affects the Pt thickness and 2) the resistivity of the silicon substrate. Table 1 shows the variation of these fabrication parameters for two sets of cells which we believe is representative of the diodes made with this procedure. Figure 1 is an X-Ray diffractometer trace of the silicide phase. The Pt peak at $2\theta = 117$ degrees is missing, having been replaced with the well known Pt₂Si peak at $2\theta = 32.5$ degrees. Of course, additional Si peaks are also present being contributed by the substrate.

Measurement of the illuminated current-voltage (I-V) characteristics of the photodiodes was done in a special vacuum chamber assembled for this experiment. The light source used in place of the excimer laser being developed, was a 200 watt mercury lamp optimized for photoresist exposure. The design of this lamp allows significant amount of VUV radiation to pass through the quartz envelope. The light standard was a NIST diode with spectral response characteristics supplied in the 116.4 - 221.4 nm wavelength range. I-V characteristics were taken with an HP4140 picoammeter, which has both current and voltage sensing along with voltage sourcing under IEEE 488 computer control.

Results

Quantum efficiencies were calculated using short circuit current without correction for surface reflection. This is sometimes called "effective" quantum efficiency since the actual ratio of photo-generated electron hole pairs to incident photons will be higher due to this surface reflection. To our knowledge, the reflection coefficient of Pt₂Si has not been measured for this wavelength range. The formula used to calculate the quantum efficiency is

$$\eta = \frac{I_{\text{meas}}(\text{nA})(1.24)}{P_{\text{in}}(\mu\text{W}/\text{cm}^2)A_d(\text{cm}^2)\lambda(\text{nm})}(100\%)$$

Fig. 2

where I_{meas} is the short circuit photocurrent,
 P_{in} is the input power density,
 A_d is the active area of the cell = 0.2 cm²,
 λ is the wavelength of the radiation.

The NIST detector's effective area is 0.66 cm².

The quantum efficiency results for the two sets of Pt₂Si photodiodes are shown in Figures 2 and 3. The best cell from each group of cells is presented in these figures; however, the differences in results within the same group did not exceed 31.5%. The percentage differences in results within each group are presented in Table 1.

Looking at the results of Figures 2 and 3, one can see that both substrate materials show the same general trend with regard to variation with wavelength. This trend is unexplained theoretically but is very repeatable. The general trend of the quantum efficiency to increase with increasing photon energy is due to the fact that the photon energy in this wavelength region is higher than the Schottky-barrier height. Thus collisions of the primary photogenerated carriers with lattice atoms may yield secondary carriers with enough energy to be emitted over the barrier [1]. The increase in quantum efficiency with decreased substrate doping is most likely due to the greater width of the space charge region. In this case the photons have a wider absorption region which is capable of separating and collecting the electron-hole pairs created.

The variation of quantum efficiency with Pt thickness is also consistent for both groups. In each case as the thickness of the Pt and the corresponding thickness of the Pt₂Si increases, the quantum efficiency first increases and then decreases. The first increase is probably due to the barrier height increasing with increasing Pt₂Si thickness, which is characteristic of very thin Schottky barriers. However, since most photons absorbed in the Pt₂Si, create electron-hole pairs which are subsequently recombined due to the high carrier concentration in the region, there is a tendency for the quantum efficiency to decrease with increasing Pt₂Si thickness. With these two processes competing, theoretically there would be an optimum Pt₂Si thickness for maximum quantum efficiency.

As mentioned in the introduction to this section, it is our intention to use Pt₂Si diodes as the energy converters in the initial tests of the excimer laser at high light levels. The fact that these cells can convert 148-nm radiation is shown in Figure 4, which is a the fourth quadrant I-V curve for a Pt₂Si cell illuminated with 1.32×10^{-6} watts/cm² intensity. The open circuit voltage is approximately 0.6 mV with a short circuit current of 37 nA. To predict the efficiency of this cell at 100 mW/cm², one is required to know the open circuit voltage at a corresponding short circuit current of 2.8×10^{-3} A. (This assumes that the short circuit current is linear with power level.) Figure 5 shows a log₁₀ I versus V for a typical diode out of this same group. This curve was altered to subtract out the effect of the finite series resistance (1300 ohms) of the silicide at higher

Table I

	Group	Resistivity ohm-cm	Platinum Thickness Å	Number Tested	Percent Diff
SET NO. 1	1a	30-70	56	3	<31.5%
	2a	30-70	112	3	<24%
	3a	30-70	168	2	<3.5%
SET NO. 2	21	0.5-1	38	3	<9.7%
	22	0.5-1	56	3	<10%
	23	0.5-1	112	3	<9.1%

Fig 3

Fig 4

Fig 5

Fig 6

current values. This curve predicts an open circuit voltage of 0.353 V, using a measured saturation current value of 4.29×10^{-7} A. The ideality factor is 1.559. Assuming a fill factor of 0.25, which is worst case conditions, the conversion efficiency would be 1.238% at 100 mW/cm². We should be able to raise this to >3% with the use of a low resistance surface grid. While this is a modest conversion efficiency, it does provide us with an actual direct energy converter in the VUV with which to test the excimer lamps, which should be available by the end of this report period.

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IV Combustion Flame Synthesis

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Introduction

Diamond surpasses currently used materials in performance because of its remarkable combination of physical, electrical, chemical and optical properties. Diamond synthesis from carbon containing gases at lower pressures and temperatures than earlier considered, has moved use of diamond closer to the marketplace.

Several chemical vapor deposition (CVD) techniques (such as hot filament, microwave plasma, radio frequency plasma, hollow cathode plasma, laser-assisted, electron-assisted, UV-assisted and arc discharge) used for diamond growth require sub-atmospheric pressure during deposition. But the combination flame process has several advantages over the processes

mentioned above, including deposition in open atmosphere, thus not requiring vacuum pumps or vacuum-tight enclosures.

This report discusses the experimental setup, the controlling parameters and ingredients, and the results of the production of diamond from a combustion flame.

Experimental Set-up

Figure 1 shows a schematic diagram of the experimental apparatus. The acetylene torch is held so that the direction of the oxy-acetylene flame is normal to a molybdenum substrate. The substrate is placed on a water-cooled copper block. The substrate temperature is measured by a thermocouple. The temperature of the substrate is controlled by the thickness of the copper block and by the rate of water flow through the copper block. Welder's grade acetylene and oxygen gases were used as the reactants. The gas flows were controlled by separate gas flowmeters to adjust the proper O_2/C_2H_2 . The gases were premixed just before the flame torch. The flow of oxygen used was 1.9 liters/minute and the flow of acetylene used was 1.8 liters/minute, giving a resultant O_2/C_2H_2 of 1.03. The substrate temperature was around 900 C. The distance between the substrate and the flame inner core was 3-4 mm. The growing time was in the vicinity of 3 hours. The substrate turned slightly red during deposition.

Researchers have used other hydrocarbon sources, namely, ethylene, propane, ethane and methane to deposit diamond from combustion flames, but at lower growth rates than acetylene. Other materials such as Si, SiC, BN, Nb, TiC, TiN, Cu, Ta, Al, Al_2O_3 , W and WC have acted as substrates for combustion flame deposited diamond with Mo and Si being most common [4].

The oxy-acetylene flame-its different parts

Figure 2 shows the configuration of the oxy-acetylene flame used. The flame usually consists of three sections-(a) the inner core (b) the acetylene feather and (c) the outer flame.

The inner core of the flame is the hottest part (temperature around 3000 C) and in this part most of the oxygen and acetylene burn. The acetylene feather is where the remaining fuel burns as it mixes with the oxygen that diffuses in from the surrounding air. Any remaining unoxidized components of fuel are burned in the outer flame, because oxygen is present in ample quantity in the surrounding air. The substrate must be placed inside the acetylene feather for growth of diamond to occur.

Controlling factors

Fig.1 Schematic diagram of experimental apparatus.

Fig.2 Parts of the oxy-acetylene flame used.

a) Substrate temperature and the ratio of oxygen to acetylene

The growth rate, quality and crystal morphology of deposited diamond are controlled by these two parameters. The growth of diamond at substrate temperatures ranging from 370 C to 1200 C and O_2/C_2H_2 ranging from 0.7 to 1.0 was reported by Hirose [1,2]. His research argued that transparent high quality diamonds were deposited at substrate temperatures between 500 C and 750 C and O_2/C_2H_2 between 0.85 and 0.98, while opaque and more non-diamond phase containing diamonds were grown outside this range. Figure 3 shows Hirose's findings of dependence of the deposit type on substrate temperature and the ratio O_2/C_2H_2 .

A similar study was conducted by Hanssen [3], and his findings are shown in Figure 4. It shows that diamond can be deposited at an O_2/C_2H_2 of up to 1.07. After 1.07 ratio, the acetylene feather disappears. Thus, this work contradicts Hirose's findings to the fact that the flame becomes neutral at around O_2/C_2H_2 of 1.07 and not 1.0. Hanssen's work as shown in Figure 4 was not extended below 660 C and thus does not violate the 370 C lower temperature limit for diamond growth reported by Hirose.

The crystals grown are mostly dependent on substrate temperature. Diamonds grown in the high end of the temperature range are mostly (100) oriented while those grown at the lower end of the range are mostly (111). The experiment performed by us has a temperature of around 900 C, giving prominence of (111) orientation [5-7].

b) Substrate position

The uniformity of diamond growth depends on the distance between the substrate and the inner core of the oxy-acetylene flame. Growth occurs only in the region where the acetylene feather intersects the substrate. For relatively short distances low density growth occurs directly beneath the inner core with an annular high density growth present around the center of the growth region. The optimum distance is around 6 mm. If the substrate is moved farther away, the substrate area exposed to the acetylene feather is less, which results in smaller growth region. An angular flame hitting the substrate at an angle of 70 with respect to the direction normal to the substrate, has also been used to deposit diamond [9].

Role of the gases

a) Precursor radicals

There has been lot of controversy and discussion centering around the precursor radicals for growth of diamond. Researchers have seen that acetylene (C_2H_2), methane (CH_4) and the methyl radical (CH_3) are the only potential precursors present in high enough concentration to give observed growth rates. When non-activated methane was used, it gave low growth rates, suggesting that CH_3 is the more likely precursor [10]. Again, when mixture of CH_4 and C_2H_2

Fig.3 Results of study conducted by Hirose-carbon deposit type as function of temp. & O_2/C_2H_2 .

Fig.4 Results of study conducted by Hanssen-carbon deposit type as a function of temp. & O_2/C_2H_2

was used in a hot filament reactor, roughly 80% of the carbon used in diamond formation came from CH_4 . This proved that the methyl radical was the primary precursor.

To account for the tremendous increase in growth rates found in combustion flames, Matsui tried to find other precursor radicals, namely, gas species such as C, C_2 and CH along with C_2H_2 . These species have larger equilibrium concentrations than CH_3 in gases with temperature above 3000 K. His results indicated presence of CO and H_2 as main gaseous species in the post-primary flame zone with a ratio close to that used in synthesis of diamond. CH and C_2 concentrations in the acetylene feather depended on $\text{O}_2/\text{C}_2\text{H}_2$, similar to that of growth rate, whereas C_2H_2 and C_2H species disagreed with growth rate dependence on $\text{O}_2/\text{C}_2\text{H}_2$.

Matsui later found, using numerous calculations of gaseous reactions in the substrate's surface boundary layer and surface reactions on the growing diamond crystal, that the above mentioned carbon-containing radicals did not affect overall gaseous concentration and their net sticking probability was about 10^{-3} . This suggested that growth rate depended on substrate temperature and $\text{O}_2/\text{C}_2\text{H}_2$ as already explained via CH_3 -precursor model [11,12].

b) Oxygen and Hydrogen role

Several important diamond formation mechanisms are attributed to atomic hydrogen. This role of atomic hydrogen is widely accepted after Angus reported its presence at around 1000 C [10]. Hydrogen reacts with gaseous intermediates to form precursor radicals, namely, CH_3 , allowing them time to reach the substrate. Models suggest that H atoms form C-H bonds terminating diamond's non-reconstructed surface. Then the H atoms are abstracted by the gas-phase species to form C-C bonds which in turn allows continued growth of diamond.

It has been seen that O and OH plays an important role in growth of diamond. They etch graphite faster than atomic hydrogen (two or three orders of magnitude) at lower temperature. This suggests that addition of oxygen to CVD systems will enhance growth of diamond at lower temperatures. Also, addition of oxygen to hot-filament and plasma assisted systems significantly increases growth of diamond. The main effect of adding oxygen is that it removes non-diamond carbon phases by oxidizing and forms a more reactive growth surface. It also forms radicals involved indirectly in diamond growth. The OH radical concentration in the oxy-acetylene flame is relatively low, but it may be high enough to account for increased growth rates of the combustion flame process [14].

Experimental Results

X-ray diffraction and scanning electron microscopy were done on the grown samples. The results are shown in Figure 5, Figure 6 (a and b), respectively. X-ray diffraction study for deposits on molybdenum showed diamond (111), (220), (311) and (400) peaks. A comparison with natural diamond peaks showed that the result was satisfactory. The SEM revealed well-faceted features and showed growth of diamond crystals up to 100 μm .

The table below shows standard relation between crystal orientation (hkl), X-ray diffraction angle (2θ) and atomic distance (d) of a powdered sample. Our sample's d shows slightly different value due to the fact that our sample was crystalline and thermal stresses might have had different effect on crystals.

hkl	2θ	d	hkl	2θ	d
111	43.916	2.06	311	91.541	1.0754
220	75.303	1.261	400	119.658	0.8916

Recent and future research

Diamond synthesis by the combustion process has several advantages over other CVD processes - higher growth rates, low running cost, open air deposition and deposition on uneven surfaces without the use of a vacuum chamber. To improve the quality of diamond synthesized by the combustion flame process, we should be able to deposit over large areas. We should also take into account that some applications need deposition at lower substrate temperatures. Moreover, efficiency of gas consumption must be increased to make this process economically feasible. Much of the recent works have been to overcome these constraints.

a) Deposition over large areas

Several researchers have done various modifications on torch design and operating conditions to improve the area of deposition. Tzeng used a multiple flame burner consisting of nine equally spaced linear holes, each having its own flame [8]. Films of up to 20 mm diameter were deposited. The uniformity of the film may be improved by controlling the gas flow in each hole.

Torch tips with larger diameters have also been used for wider acetylene feathers, thus increasing the area covered during deposition.

b) Increased growth rates

Although combustion flame synthesis of diamond show increased growth rates over other CVD processes, the usage efficiency of carbon is low. For economic reasons, this carbon usage

Fig.5 X-ray diffraction pattern of experimental sample.

Fig 6

efficiency would be increased, resulting in higher growth rates. Higher growth rates of diamond occur at lower O_2/C_2H_2 (within the earlier mentioned parameters), but the quality is lower. Thus, to increase growth of high quality diamond, a low O_2/C_2H_2 flame for deposition and an oxygen rich flame for etching away non-diamond carbon phases, can be alternated. Tzeng used this sequence to deposit high quality diamond. The deposit quality was notable higher in the sequential process using the same deposit flame. Researchers are continuing experiments to determine the difference in growth rates between the two processes.

Conclusions

The ratio of O_2/C_2H_2 , the substrate temperature and the flow rates of oxygen and acetylene used in our experiment, gave satisfactory results of diamond growth as illustrated by X-ray diffraction pattern and scanning electron microscopic photographs. The (111) diamond orientation was most prominent as the conditions used (lower range of temperature scale - $900^\circ C$) were ideal for this orientation. Future work on this experiment with purer gases and improved parameters may result in improved growth rates and better quality of diamond.

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VI P-N JUNCTION FORMATION USING ION IMPLANTATION

The difficulty in doping of diamond with n-type conductivity is a well acknowledged problem that still requires study for predictable and consistent p-n junction formation. Early work in synthesis of n-type natural diamond occurred utilizing ionimplantation [1]. Subsequent research showed, and it is generally accepted, that the conductivity changes noted were dominated by implantation damage [2]. The present approach for formation of "n-type" conducting layers in diamond is to take advantage of this "damage effect". However, it is ultimately desirable to achieve true substitutional n-type doping because of the difficulty in controlling defect formation. Additionally, the instability of defects with temperature can be problematic for high temperature device operation, thus offsetting one of the advantages of large bandgap materials such as diamond. The deleterious effect that defects have on carrier lifetime will ultimately limit the types and quality of devices synthesized. Although one group has reported formation of a diamond p-n junction on hot-filament chemical vapor deposited (HFCVD) films, that work has not, to our knowledge, been repeated [3]. Additionally, because the p-n junction was formed by in-situ doping during diamond growth, the technique is not easily scaled to multiple device applications where selective p-n junction formation is required.

We have undertaken several aspects of diamond doping that have not been previously studied which have potential for p-n junction formation in HFCVD films. This includes utilization of HFCVD diamond instead of natural diamond for implantation studies. Secondly, we are investigating the use of implanted molecules to accomplish conductivity changes in diamond, with the goal of achieving n-type doping. Additionally, several different dopant sources will be considered for both p-type and n-type doping utilizing molecular implantation and in-situ growth.

Some studies on molecular implantation of silicon were completed in the late 1970's and 1980's. Simple plasma glow discharges of unanalyzed molecular ions were accelerated into silicon samples and devices were fabricated. Molecular ions containing boron or arsenic species from halide containing sources were studied, with the results indicating that p-n junctions were formed. One study of boron halides showed that BF_3 sources produced junctions with superior electrical activation of dopants at annealing temperatures lower than those required in boron ion implantation

[4]. A comprehensive study of several molecular sources for silicon p-n junction formation performed in our laboratory identified potential dopants for silicon solar cell applications [5]. We intend to study several of these sources for in-situ diamond doping, as well as for ion implantation. One of these, trimethylborate, has been utilized by our group to produce the first Schottky diodes made from HFCVD diamond [6].

The first potential n-type source studied is trimethyl phosphite, $(\text{CH}_3\text{O})_3\text{P}$. Others have shown that for boron ion implantation into diamond, a critical dose of $2 \times 10^{14} - 10^{15}$ ions/cm² exists, beyond which the damage cannot be annealed out and the layer turns into graphite when annealed [7]. Our attempts to remain below this dose, however, resulted in no perceptible conductivity changes in samples. Implantation (without annealing) of undoped diamond to a dose just greater than the graphitization dose showed conductivity increased by three orders of magnitude. A series of implants were performed on high quality HFCVD diamond, as judged by the Raman spectrum. Whenever possible, we have compared samples from within a single diamond processing run to eliminate the ambiguity in both in-situ dopant incorporation variations and variable film hydrogen content. Several studies have noted the effect that hydrogen concentration has on diamond conductivity [8-10].

The Raman spectrum of diamond utilized in several implantation studies is shown in Figure 1. The characteristic peak of diamond at approximately 1333 cm^{-1} indicates sp³ bonding and therefore high quality diamond. The broad peak at slightly higher wavenumbers is indicative of a graphitic component. However, the relative strengths of diamond and graphite Raman signals can be utilized to conclude that the graphite peak shown represents only a minor graphitic component in the film. Samples were implanted with trimethyl phosphite at low energies (5keV) and dose of 3×10^{18} ions cm⁻², if singly charged species are assumed. The projected range for this low energy is estimated to be approximately 30.0 nm. Backside aluminum was thermally evaporated onto the silicon substrate and indium evaporation of 1mm diameter dots onto diamond followed. Indium is known to be an ohmic contact on diamond. Therefore, rectifying behavior with indium contacts will be due to the implantation and not from the metal-diamond junction. To eliminate ambiguity in diamond film composition and thickness differences, adjacent areas on some samples were utilized to compare implanted and non-implanted regions. On these samples, a silicon piece placed over a portion of the diamond served as an implantation mask. Current-voltage results, shown in Figure 2, have indicated largely high resistance films on non-implanted areas and rectifying behavior in implanted regions. Several indium contacts ("spots") made on the sample showed consistent behavior with respect to the rectifying or ohmic nature of implanted and non-implanted samples, respectively. Note that apparent forward bias current saturation at 10mA simply reflects an internal current limit of the meter utilized. Some variation in reverse bias leakage current was observed, as shown in Figure 3.

Figure 1. Typical diamond Raman spectrum for dopant implantation studies at three sample locations.

Figure 2. Current-voltage characteristics of $(\text{CH}_3\text{O})_3\text{P}$ implanted and non-implanted diamond on several locations.

Figure 3. Current-voltage characteristics of $(\text{CH}_3\text{O})_3\text{P}$ implanted samples at six sample positions.

Figure 4. Junction capacitance, measured at 50kHz and displayed as $1/C^2$, as a function of applied voltage for six positions on $(\text{CH}_3\text{O})_3\text{P}$ implanted diamond.

Capacitance-voltage data, presented as $1/C^2$ vs. V , on the same sample is shown in Figures 4 and 5 for frequencies of 50kHz and 500kHz, respectively. This data indicates a built-in potential of approximately 2.5 eV, in the range of expected values for diamond rectifying contacts. The data is surprisingly well behaved considering no film annealing was performed. Additionally, even diamond Schottky diodes exhibit complicated capacitance-voltage-frequency characteristics, and only follow Schottky theory for frequencies less than approximately 10kHz [11]. The prominent feature at approximately 0.5 volts in the 50kHz curve, appears similar to deep level capacitance effects that have been observed in silicon Schottky diodes [12].

Nitrogen implantation was performed in order to make comparisons to samples implanted with trimethyl phosphite. These samples similarly exhibited rectifying behavior, shown in Figure 6. However, voltage stressing of samples (3×10^5 v/cm) converted junctions to ohmic contacts, shown in Figure 7. Diamond samples from the same diamond deposition run were implanted with trimethyl phosphite and similarly stressed with high voltage. These maintained their rectifying behavior at the same field, shown in Figure 8. An increase to four times that field caused an increased reverse leakage current, shown in Figure 9.

The next phase of work on these samples includes annealing studies, which have begun. Additionally, dose variation and its relationship to the starting material resistivity will be studied. Preliminary studies indicate that control of the doping level of the grown diamond is very important in utilizing the previous implantation technique to achieve rectifying behavior. Work on the other potential doping sources will follow the trimethyl borate studies.

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Figure 9. Rectifying characteristic of $(\text{CH}_3\text{O})_3\text{P}$ implanted diamond following high field stressing.

I-V (ku6#5) no AL on back May 23 1992
Nitrogen Implanted jump 100volts spot1

Figure 7. Nitrogen implanted diamond ohmic characteristics following voltage stressing.

Ku6#3 Implanted jump 100v
measured June 3 1992 spot1

Figure 8. Rectifying behavior of $(\text{CH}_3\text{O})_3\text{P}$ implanted diamond stressed at the same field as the sample in Figure 7.

Figure 5. Junction capacitance, measured at 500kHz and displayed as $1/C^2$, as a function of applied voltage for six positions on $(CH_3O)_3P$ implanted diamond.

Figure 6. Nitrogen implanted diamond rectifying current-voltage characteristics.

VII Growth of oriented Aluminum Nitride Films on Si By Chemical Vapor Deposition

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Introduction

Aluminum Nitride (AlN) crystallizes in the wurtzite structure with lattice constants $a_0 = 3.1114 \text{ \AA}$ and $c_0 = 4.9792 \text{ \AA}$ [1]. AlN is a direct band gap material with energy gap of 6.2 eV [2]. It has a high acoustic velocity [3], a high melting point, high electric resistivity, excellent thermal conductivity and high chemical and nuclear stability. With all these properties, AlN has a potential use in optical devices operating in UV region, in surface acoustic wave devices, and also as a material for electrically insulating and passivating layers for semiconductors. Progress regarding these applications is slow due to a lack of good single crystals, or at least large area highly oriented, dense, defect free polycrystalline films.

Various techniques such as reactive sputtering [4], reactive molecular beam epitaxy [5], and chemical vapor deposition [1, 6, 7] have been used to grow AlN. CVD is the most promising and the most widely employed [8] method. It permits the AlN deposition at low substrate temperatures and high deposition rates [2, 8, 9]. It is easy to control and also high purity AlN can be obtained by this method [10].

A variety of substrates, including sapphire [11], a-SiC [12], Si [6,9], quartz [13] and others have been used for the growth of AlN films. Monocrystalline films has been obtained on basal planes of sapphire [2,11], and a-SiC[12]. However, these substrates can be used mainly for growth of AlN films for research purposes. Single crystalline a-SiC is an ideal substrate for the epitaxial growth of AlN films, having the same lattice structure, nearly the same lattice constant (1% mismatch for basal plane), and the same thermal expansion coefficient (TEC) [14]. However large area single crystalline SiC substrates are not available. Sapphire has been used as a substrate to grow AlN films, but the TEC of sapphire is nearly twice as large as that for AlN and the films usually crack on cooling [2].

Si has nearly the same TEC as AlN and is also suitable for industrial applications due to its wide use and well known technology. Si has been used as the substrate for AlN film growth [6,9]. Epitaxial AlN has been grown by CVD on a limited area of a (111) Si substrate having an

orientation of (0001). The growth took place in a temperature range of 1100^o-1300^oC using AlCl₃ and NH₃ as the constituent gases [6]. AlN growth on Si as thick as 0.5 mm has been reported [8].

In this paper we report on the growth of AlN films on Si substrates at moderate temperatures (700^o- 800^oC) in the pressure range of 100 - 650 torr by CVD processing using AlCl₃ and NH₃ as the source material. The layers obtained were highly oriented and uniform. The results include scanning electron micrographs, X-ray diffraction spectrum and Raman spectra. For the first time we are reporting Atomic Force Microscope (AFM) measurements and micro-Raman studies on epitaxial AlN films grown on Si.

Experimental

AlN films were grown on Si substrates using linear tube CVD method. AlN was formed by the chemical reaction of AlCl₃ with NH₃ in the presence of hydrogen. The overall reaction consists of the formation of a range of aluminum chloride-ammonia complexes [15] , and then the ammonolysis conversion of the complex into AlN and HCl.

A schematic diagram of the CVD apparatus is shown in Fig.1. The aluminum chloride container was maintained at 150^o C to provide sufficient vapor pressure of aluminum chloride, which was carried into the reaction tube by hydrogen at a flow rate of 120 sccm. The flow rate of ammonia was 80 sccm with 280 sccm of hydrogen used as a carrier. A part of the reaction tube was maintained at 350^o C by using resistance heating to avoid the condensation of ammonium chloride and aluminum chloride-complexes.

Prior to growth, the p-type (100) Si substrate with 1-3 ohm-cm resistivity was organically cleaned with TCE, acetone, methanol and DI water in an ultrasonic bath and then briefly annealed in flowing H₂ at approximately 500^o C prior to growth. About 40 samples at three different experimental conditions were prepared:

Type 1. Samples of ~2 mm thickness grown in 15 min. with the reactor chamber pressure of 650 Torr and substrate temperature of 700^oC.

Type 2. Samples of ~9mm thickness grown in 45 min. with a chamber pressure of 200 Torr and substrate temperature of 700^oC

Type 3. Samples of ~3mm thickness grown in 20 min. with a chamber pressure of 100 Torr and substrate temperature of 800^oC.

Both type 1 and type 3 samples were cooled down in 30 min. whereas type 2 sample was cooled down in 5 minutes.

Figure 1 A.H.Khan and *et.al*

The AFM images were recorded in air using the Digital Instruments NanoScope II Atomic Force Microscope.

The Raman spectra were excited by an Argon-ion laser operated at 514.5 nm. For the macro-Raman about 230 mW were incident on the sample. The laser was focused to a spot size of approximately 0.3 mm^2 at about 65° from the surface normal. The scattered light was gathered by an off-axis ellipsoid with an $f/1.4$ collection cone centered on the surface normal. For the micro-Raman about 2 mW were incident on the sample with the laser focused to a spot size of approximately 1 mm^2 . In the spectrograph a 600 groove/mm grating disperses the signal onto a liquid nitrogen cooled CCD detector. The entrance slits were set 100 mm wide, corresponding to an instrumental linewidth of about 9 cm^{-1} . For the macro-Raman the signal was integrated for 45 seconds for the s-polarized and 60 seconds for p-polarized data. The data were not corrected for detector nonuniformities and spectral sensitivity.

Results and Discussion

The scanning electron micrographs of type 1 and type 2 samples are shown on Fig. 2 (a) and Fig. 2 (b) respectively. Figure 3 shows the AFM images of type 2 and type 3 sample. The top view and the surface plot of the same scan area of the type 2 sample are shown on Fig.3 (a) and Fig.3 (b) respectively. To find the roughness of the type 2 sample, the z-range was calculated to be 0-215.47 nm with a standard deviation of 31.43 nm. Figure 3 (c) and 3 (d) respectively shows the top view and surface plot of a type 3 sample. For this sample the z-range was 0-147.97 nm with a standard deviation of 21.97. It shows that the type 2 samples are rougher than the type 3 samples. For both type 2 and type 3 samples, the grains at the surface have a conical configuration and the layers grew with the c-axis normal to the surface (Fig.3(b) and Fig.3(d)).

Figure 4 presents the X-ray diffraction patterns for all the three types of samples. All the samples have a preferential orientation with the c-axis normal to the surface. However, the degree of orientation is different. Type 1 sample (Fig.4-a) is strongly oriented giving only the reflection peak (002) at $2\theta=36.205^\circ$ (the peak at $2\theta=69.1^\circ$ is due to the (400) reflection of the Si substrate). The degree of preferential orientation was checked for this sample by measuring the rocking curve for the (002) line at fixed detector angle (Fig.5b). The rocking curve shows that the c-axis orientation distribution around the normal to the surface has a full width half height (FWHM) of 15° . The lattice constant determined from the (002) peak, $c=2.479 \text{ \AA}$, is smaller than the ASTM tables value of $c=2.490 \text{ \AA}$. This shows that the layer is stretched. The FWHM of (002) peak (Fig.5a) is large ($\sim 1^\circ$). The broadening can be due to either the presence of microstresses and/or to the small crystallite size. For the (002) direction the crystallite size is seen along the film depth, so it is expected to be approximately the film thickness (2 mm). This would give no grain size

Figure 2 A.H.Khan and *et.al*

Figure 4 A.H.Khan and *et.al*

broadening. Microstresses remain therefore the most plausible cause of the observed broadening.

The X-ray diffraction pattern for the type 2 sample (Fig.4-b) has no (100) reflection. The three strong peaks obtained, (002) at $2\theta=36.205^\circ$, (102) at $2\theta=49.972^\circ$, and (103) at $2\theta=66.955^\circ$ indicate growth with c-axis preferentially normal to the surface. The differences between measured and tabulated d_{hkl} values (d_{hkl} M- $d(hkl)$ ASTM) for (002),(102) and (103) are -0.011, -0.005 and -0.0169 Å respectively. These differences are caused by stress.

Figure 4 (c) shows the X-ray diffraction pattern for a type 3 sample. The 33.037° , 36.096° , 81.529° and 116.612° peaks are for (100), (002), (202) and (204) AlN. The peak at $2\theta=43.759^\circ$ is due to (301) a-Si₃N₄. With type 3 samples the diffraction pattern showed (100) peaks indicating the growth with the c-axis parallel to the surface. This type of growth were observed at certain points of the type 3 sample while doing the AFM measurements.

Macro-Raman spectra of type 2 samples are presented in Fig.6 for s and p polarized light. There is no qualitative difference in the spectra for two polarizations which was expected for the polycrystalline sample. The spectra have two peaks at 607 cm^{-1} and 653 cm^{-1} , and two large bands around 750 cm^{-1} and 900 cm^{-1} , much smaller in intensity. The largest peak at 653 cm^{-1} (665 cm^{-1} [16] and 649 cm^{-1} [17]) was attributed to TO phonons, observed also in infrared reflectivity measurements at 666 cm^{-1} [18,19]. The large weak band at 910 cm^{-1} was observed in ref. [16] and was attributed to LO phonons. It was observed also in infrared reflectivity spectra at 911 cm^{-1} [18] and 902 cm^{-1} [19]. Figure 7. shows the micro-Raman spectrum of the same sample. It showed the same peaks as the macro-Raman. Raman spectra at different points of the sample were recorded for both cases and the same peaks were observed.

Current-Voltage Measurements

I-V measurements were performed on two different types of samples. Sample "ALN7A" is aluminum nitride grown on (100) oriented silicon, and sample "ALN7B" is an identically processed run of aluminum nitride on (111) oriented silicon.

Aluminum contacts were evaporated on both the backside silicon substrate and on the deposited aluminum nitride film of sample "ALN7B". The aluminum nitride contact ("spots") areas are circular dots with 1 mm diameters. Current-voltage measurements were made on different positions, with some high field stressing performed to test junction integrity and electrical behavior. Current-voltage measurements on different position indicated behavior ranging from ohmic to nonlinear (somewhat rectifying). High voltage stressing (100 volt "jumps") converted rectifying junctions to ohmic junctions. The variability of electrical characteristics needs to be studied and quantified. There may be an optimum surface treatment following aluminum nitride growth (as in the case for diamond where removal of graphitic phases is required) that will make

Figure 6 A.H.Khan and *et.al*

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Figure 2 A.H.Khan and *et.al*

FIG. 1

Figure 4 A.H.Khan and *et.al*

Figure 4 A.H.Khan and *et.al*

Figure 5 A.H.Khan and *et.al*

I-V Measurements

I-V measurements were performed on two different types of samples. Sample "AlN7A" is aluminum nitride grown on (100) oriented silicon, and sample "AlN7B" is an identically processed run of aluminum nitride on (111) oriented silicon.

Aluminum contacts were evaporated on both the backside silicon substrate and on the deposited aluminum nitride film of sample "AlN7B". The aluminum nitride contact ("spots") areas are circular dots with 1mm diameters. Current-voltage measurements were made on different positions, with some high field stressing performed to test junction integrity and electrical behavior. Current-voltage measurements on different position indicated behavior ranging from ohmic to nonlinear (somewhat rectifying). High voltage stressing (100 volt "jumps") converted rectifying junctions to ohmic junctions. The variability of electrical characteristics needs to be studied and quantified. There may be an optimum surface treatment following aluminum nitride growth (as is the case for diamond where removal of graphitic phases is required) that will make the electrical characteristics more consistent.

Sample "AlN7A" was utilized to study the possibility of carbon doping utilizing methane gas as a source in molecular ion implantation. Methane was ionized and accelerated into samples (4.5kV) to a dose of approximately 10^{18} ions/cm². Temporary contacts were made to the sample utilizing Hg-In paste. Current-voltage measurements were made on implanted on non-implanted regions of the sample, where unimplanted areas were masked by placing silicon over a portion of the sample. Again, variability in behavior (in both regions) was observed. Both ohmic trends and rectifying trends were observed in the regions. At this time, a combination of surface pretreatments and implantation conditions will be studied to help explain these results.

new version

ALN7B I-V CURVE BEFORE JUMP $p=1.3$
measured June 4 1992 spot1

ALN7A stamping 11.5" In interface - noise under own
ALN7B - removed 1.5 resistors - noise known

ALN7B-I-V CURVE JUMP 100V

measured June 4 1992 spot 1

no other
limit

ALN7B I-V CURVE BEFORE JUMP

measured June 4 1992 spot2.

ALN7B I-V CURVE BEFORE JUMP

measured June 4 1992 spots

ALN7B I-V CURVE BEFORE JUMP

measured June 4 1992 spot4

ALN7B I-V CURVE BEFORE JUMP

measured June 4 1992 spots

ALN7B I-V CURVE BEFORE JUMP

measured June 4 1992 spot6

ALN7B I-V CURVE BEFORE JUMP

measured June 4 1992 spot7

ALN7A - temporary 4.9 I in and vol - 1.5 mV
ALN7A I-V CURVE BEFORE JUMP
measured June 4 1992 spot1
p 3

ALN7A I-V CURVE JUMP 100V

measured June 4 1992 spot1

ALN7A I-V CURVE BEFORE JUMP

measured June 4 1992 spot2.

ALN7A I-V CURVE JUMP 100V

measured June 4 1992 spot2

ALN7A I-V CURVE BEFORE JUMP

measured June 4 1992 spot3

ALN7A I-V CURVE JUMP 100V

measured June 4 1992 spot3

ALN7A I-V CURVE BEFORE JUMP

measured June 4 1992 spot4

ALN7A I-V CURVE JUMP 100V

measured June 4 1992 spot4

III Schottky Diodes on HFCVD Diamond

G. Zhao, T. Stacy, E.J. Charlson, E.M. Charlson, C.H. Chao, M. Hajsaid and G. Popovici

Introduction

Semiconducting diamond is considered to be an attractive solid state material due to its unique electrical and physical properties, such as wide bandgap (5.5 eV), high breakdown voltage (10^6 - 10^7 V cm⁻¹), high electron and hole mobilities (2000 cm² V⁻¹ s⁻¹ and 1800 cm² V⁻¹ s⁻¹, resp.), and high thermal conductivity (20 W cm⁻¹ K⁻¹). These properties make diamond an ideal candidate for high power, high frequency and high temperature electronic device applications. However, most diamond devices reported to date have been fabricated using either semiconducting natural diamond¹ or ultrahigh pressure synthesized diamond^{2,3}. With the rapid progress which is taking place in the development of various diamond chemical vapor deposition (CVD) processes^{4,5}, a number of polycrystalline diamond semiconductor devices, in particular Schottky diodes using this material, have been reported since 1988⁶⁻⁸. To our knowledge, all of the Schottky diodes reported were produced on some type of CVD film other than hot-filament CVD (HFCVD) diamond thin films and involved either aluminum, gold or titanium contacts. Since HFCVD is considered to be one of the most useful of diamond CVD techniques because of its low cost, ease of control and its ability to produce large area films with an acceptable growth rate, it is apparent that a good understanding of the electrical properties of HFCVD grown diamond Schottky diodes will be necessary for significant diamond device applications in the future.

Experimental

In this study, diamond thin films used for Schottky diodes were deposited on p-type silicon substrates using the HFCVD method with hydrogen and methane as the reaction gases and with acetone vapor as the carrier gas for the boron dopant as well as providing an additional carbon source. A liquid source, trimethyl borate (B(OCH₃)₃), which has proved to be an excellent ion implantation dopant source for silicon⁹, was used as an in-situ p-type dopant source. X-ray diffraction, scanning electron microscopy and Raman spectroscopy studies indicate that high quality boron doped polycrystalline diamond films were obtained. Schottky diodes were fabricated by sputter deposition of silver on boron doped diamond thin films. The current density-voltage, capacitance-voltage-frequency and

temperature characteristics of these diodes were investigated. The electrical properties of these Schottky diodes are very similar to those diodes formed on crystalline diamond.

The boron doped polycrystalline diamond thin films were prepared by the HFCVD method using an in-situ doping technique on p-type (100) silicon substrates which had a resistivity of 0.5-1.0 ohm-cm. Prior to introduction into the reaction chamber, chemically cleaned silicon substrates were polished with 1/4 micron diamond paste to promote nucleation. The silicon substrate, 3 x 3 cm² in size, was mounted on a graphite base 3 mm beneath a tungsten filament which was heated to ~2000 °C. The substrate temperature was controlled at approximately 800°C. During deposition, the chamber pressure was maintained at 30-35 Torr and the following flow rates were used: hydrogen (98 sccm), methane (1 sccm), and acetone vapor with trimethyl borate (1 sccm). The boron to carbon atomic ratio in the reaction gases was about 30 ppm. The diamond film obtained after 6 hours of growth using this process is 6-7 microns thick. The x-ray diffraction pattern of the deposited film shown in Figure 1 indicates pure diamond characteristics with a lattice parameter of 3.566 ± 0.002 Å for all phases. The inset in Figure 1 is a scanning electron micrograph of the diamond film which shows that the diamond surface consists of isotropically oriented and well-faceted polycrystals with an average grain size of 5-6 microns. Raman spectroscopy showed a 1332 cm⁻¹ sharp peak which is characteristic of diamond *sp*³ bonding.

Before metal deposition, the diamond thin films were preannealed at 550 °C in air as suggested by Landstrass¹⁰ for 20 min to remove hydrogen effects and stabilize the films. Then, in order to remove any nondiamond surface layer, the films were cleaned by dipping in a mixture of HF + HNO₃ + H₂O and then in a saturated solution of CrO₃ + H₂SO₄ at 145 °C for 20 min, followed by a rinse in a boiling H₂O₂ + NH₄OH solution for 10 min, as described by Grot *et al*¹¹. The Schottky diodes were formed by sputter depositing silver (300-500 Å) circular contacts on the chemically cleaned diamond film through a metal shadow mask. An aluminum evaporation was done on the back side of the silicon substrate to ensure good ohmic contact. A non-oxidizing platinum layer (300-500 Å) was sputter deposited on top of the silver contacts to increase the working temperature of the device. A thermal annealing process was done following metallization.

Fig 1

Results

In order to determine whether the rectifying characteristics exhibited by the sample were due to a Schottky contact at the silver-diamond interface or whether a silicon-diamond heterojunction had been formed, indium was used to make ohmic contact to the diamond film. The current-voltage characteristics of the indium-diamond-silicon-aluminum structure which is shown in Figure 2 are those of a good ohmic contact, from which the diamond film resistivity of 3×10^4 ohm-cm was determined. Thus, the rectifying junction was shown to be at the silver-diamond interface. This rectification nature of the silver-diamond interface is consistent with results reported by Gildenblat *et al.*¹². They demonstrated that the rectification observed in the gold-diamond-silicon structure was due to the gold-diamond interface by comparing the I-V characteristics of a diamond Schottky diode on a silicon substrate with a Schottky diode formed on a free-standing diamond film.

In this study, two different contact areas, 3.2 mm^2 and 0.38 mm^2 , were used to produce similar current density-voltage (J-V) characteristics. A typical silver-on HFCVD diamond Schottky diode current density-voltage characteristic measured at room temperature (sample KU3-6 with contact area of 3.2 mm^2) is shown in Figure 2. Forward conduction occurs when the Pt/Ag contact is negatively biased with respect to the grounded backside aluminum contact. The current density in these diodes is large compared to other reported values on CVD diamond Schottky diodes^{6,7}. This is probably due to smaller diamond bulk resistance in our diodes. Figure 3 shows $\log(J)$ vs. V curves of three diodes (KU3-1 with contact area of 0.38 mm^2 , KU3-5 and KU3-6 with contact area of 3.2 mm^2). The forward-to-reverse current ratio at 5 volts bias for each diode is seen to be greater than 1000. Forward current in these diodes is limited by the bulk diamond resistance as is evident at the linear end in the forward region. On a logarithmic scale, a linear portion extending more than three decades in the low forward bias region (less than 0.5 volt) has been obtained for diode KU3-6, from which an ideality factor of approximately 2.0 was estimated. This ideality factor is close to the reported value of 1.85 on microwave plasma assisted CVD diamond Schottky diodes^{6,7}.

The capacitance-voltage characteristics of diode KU3-6 exhibited frequency dependence as shown in Figure 4. At low frequency ($\leq 1 \text{ kHz}$), the measured capacitance is dominated by the DC capacitance of the silver on diamond Schottky diode which is bias dependent and frequency independent.

Fig 2

Fig 3 -

Fig 4

As the frequency is increased, the measured diode capacitance is affected by not only DC capacitance but also the larger bulk diamond resistance and the dispersion capacitance which is frequency dependent and associated with hole emission from slowly responding deep impurity levels^{3,6}. When the test frequency is higher than 1 MHz, there is no bias dependence of the capacitance.

Figure 2 also includes some initial results of high temperature measurements on the silver on diamond Schottky diode KU3-6. As shown, the diodes exhibit good rectifying characteristics up to 250 °C. At the present time, the upper bound on temperature is dictated by test limitations not by the device itself. A better apparatus for high temperature testing is now being built.

In conclusion, silver on diamond Schottky diodes with high forward current density and high forward-to-reverse current ratio have been fabricated on high quality boron doped polycrystalline diamond thin films grown by a HFCVD process with an in-situ doping technique using trimethyl borate as a boron dopant source. The electrical characteristics of these diodes show that they are very similar to those of Schottky diodes fabricated using a single crystal diamond substrate.

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IV Platinum Silicide Photodetectors

Introduction

Work continued this past year on PtSi photodiodes for conversion of radiation in the vacuum ultraviolet. While we do not believe that this diode will be used as the direct energy converter in the final PIDECE system, continued development of this device is important for two reasons. First, since the fabrication involves known technology and a conventional silicon substrate, there is a high probability that this device can successfully convert a significant amount of radiation in the 100 - 200 nm wavelength range. It will then allow us to test the radiation sources sooner than the development of diamond converters will allow. Indeed, in this reporting period, PtSi converters have been fabricated that are projected to have absolute power conversion efficiencies in the 1 - 3 % range at 148 nm. Secondly, the PtSi detectors make excellent secondary standards for light intensity in the vacuum ultraviolet range. To our knowledge no other inexpensive system is currently available. The NIST traceable diode we are using is very expensive and is limited to very low light levels. High quality silicon diodes such as the PtSi Schottky diode, are known to be very linear in short circuit current versus light level. It is our intention to use the PtSi diode as a secondary standard to measure the high light levels of the excimer lasers developed for this contract.

Previous work on the PtSi/p-Si Schottky barrier diodes [1,2,3] has indicated good photoresponse for radiation in the 230-700nm range. Our application uses lower wavelength radiation and therefore extensive effort was spent on extending this measurement into the 100-200 nm (VUV) range. Typically, quantum efficiencies of 40 - 70% have been reported in the 230 - 700 nm range. Our initial devices matched these efficiencies. However we found that devices that were fabricated to form the Pt₂Si phase were always on the high end of the efficiency range. This superior performance was found to also be true in the VUV range and therefore we have concentrated on this variety of the device. Formation of the Pt₂Si morphology is primarily determined by the annealing temperature [4], as has been reported in previous quarterly reports.

Experimental

The structure of the Pt₂Si photocell is shown in Fig. 1. The fabrication procedure is as follows:

Fig1

- 1) ultrasonic organic and then hot acid cleaning of a (100) p-type Si wafer.
- 2) steam oxidation to form a SiO₂ layer of about 5000 Å.
- 3) photolithography and phosphorus diffusion of the n guard ring.
- 4) photolithography for the active window.
- 5) aluminum evaporation for the back contact.
- 6) platinum sputtering.
- 7) annealing at 350 °C for 20 minutes to form the Pt₂Si film.
- 8) aluminum evaporation and etching for the front side contact.

Two parameters were changed to optimize the performance of the photodiode, 1) sputtering time which affects the Pt thickness and 2) the resistivity of the silicon substrate. Table 1 shows the variation of these fabrication parameters for two sets of cells which we believe is representative of the diodes made with this procedure. Figure 1 is an X-Ray diffractometer trace of the silicide phase. The Pt peak at 2 theta = 117 degrees is missing, having been replaced with the well known Pt₂Si peak at 2 theta = 32.5 degrees. Of course, additional Si peaks are also present being contributed by the substrate.

Measurement of the illuminated current-voltage (I-V) characteristics of the photodiodes was done in a special vacuum chamber assembled for this experiment. The light source used in place of the excimer laser being developed, was a 200 watt mercury lamp optimized for photoresist exposure. The design of this lamp allows significant amount of VUV radiation to pass through the quartz envelope. The light standard was a NIST xxxxx diode with spectral response characteristics supplied in the 116.4 - 221.4 nm wavelength range. I-V characteristics were taken with an HP4140 picoammeter, which has both current and voltage sensing along with voltage sourcing under IEEE 488 computer control.

Results

Quantum efficiencies were calculated using short circuit current without correction for surface reflection. This is sometimes called "effective" quantum efficiency since the actual ratio of photo-generated