8/6/92

DOE/ER/12107-T2

ER 12107

Annual 1992

UNIV. OF MISSOURI

Summary Year 2

**A Study of Potential High Band-Gap Photovoltaic Materials for a Two Step Photon Intermediate
Technique in Fission Energy Conversion**

PROCESSED FROM BEST AVAILABLE COPY
44

Mark. A. Prelas, E. J. Charlson, E. M. Charlson, J. Meese, G. Popovici, T. Stacy, C.
Chao, M. Hajsaid, Z. He, S. Kashiwana, A. Khan, M. Odeh, G. Zhao

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

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 excimer 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 to 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. Spitsyn 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.

Figure 1. Proposed tasks.

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 to be used as VUV energy converters and as secondary standards for this range of wavelengths. 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.

The following papers were published describing the past year's work on the contract.

G. Zhao, T. Stacy, E. J. Charlson, E. M. Charlson, C. H. Chao, M. Hajsaid, J. Meese, G. Popovici and M. Prelas, "Silver on diamond Schottky diodes formed on boron doped hot-filament chemical vapor deposited polycrystalline diamond films," *Appl. Phys. Lett.* 61 (10), Sept. 1992.

M. A. Prelas, E. J. Charlson, E. M. Charlson, J. Meese, G. Popovici and T. Stacy, "Diamond photovoltaic cells as a first wall material and energy conversion system for inertial confinement fusion," U.S.-Japan Seminar on Physics of High Power Laser Matter Interactions, Kyoto, Japan, March 9-13 (1992).

G. Zhao, C. H. Chao, E. J. Charlson, E. M. Charlson, J. Meese, G. Popovici, M. Prelas and T. Stacy, "Silver diamond Schottky diodes formed on boron doped HFCVD grown diamond," 3rd Annual Diamond Technology Workshop, Detroit, MI, March 17-18 (1992).

C. H. Chao, E. J. Charlson, E. M. Charlson, J. Meese, G. Popovici and M. Prelas, "Growth and characteristics of boron-doped diamond thin films by hot filament chemical vapor deposition," 3rd Annual Diamond Technology Workshop, Detroit, MI, March 17-18 (1992).

T. Stacy, G. Popovici, C. H. Chao, E. M. Charlson, E. J. Charlson, J. Meese and M. Prelas, "Effect of implanted methane on hot filament CVD diamond film growth," 3rd Annual Diamond Technology

Workshop, Detroit, MI, March 17-18 (1992).

G. Zhao, E. M. Charlson, E. J. Charlson, T. Stacy, J. Meese, G. Popovici and M. Prelas, "Effect of mechanical stress on polycrystalline diamond Schottky diode characteristics," Materials Research Society, Spring Meeting, Symposium M: Novel Forms of Carbon (1992).

I VUV EXCIMER LIGHT SOURCES

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

Figure 2. Low frequency microwave lamp design.

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
R _p	0.005 m
Re{fres}	2.45 GHz
Im{fres}	0.195464 GHz
Q	12.52
Dt	8 ms
P _{microwave}	2.5 kW

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

Figure 3. Calculated microwave resonance frequency as a function of cavity length.

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.

Electric Field Intensity in Plasma

Figure 4. Calculated electric field intensity in the microwave cavity.

Magnetic Field Intensity in Plasma

Figure 5. Calculated magnetic field intensity in the microwave cavity.

Figure 6. Calculated power density in microwave cavity.

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.

Figure 7. Measured resonance length of microwave cavity (shown to be 21.7 cm).

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.

Figure 8. Energy level diagram and emission spectra of the xenon excimer.

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.

8/6/92

Figure 9. Excimer spectra from 1.136 atmosphere of xenon and 600 watts deposited.

Figure 10. Excimer spectra from 1.78 atmospheres of xenon and 600 watts deposited.

Figure 11. Excimer spectra from 2.4 atmospheres of xenon and 600 watts deposited.

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 is a need to find matching substrates for diamond heteropolarities. 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 $800 \pm 20^\circ \text{C}$.

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 sub-

strate 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 12. 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 13 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 14. The pattern has a strong line at 44.07° ($d = 2.054 \text{ \AA}$), a line at 43.8° ($d = 2.065 \text{ \AA}$) and a line at 42.9° ($d = 2.11 \text{ \AA}$). 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 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.

8/6/92

Figure 12. Scanning electron microscope pictures of film cleavage of single crystal films.

Figure 13. X-ray diffraction patterns for the film samples of Figure 12.

Figure 14. X-ray diffraction pattern for 2θ between 42° and 45° for sample I-3.

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-compacted-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, $d=2.059$ Å. However, these lines are seen to be separated in a double ($d=2.054$ and $d=2.065$ Å). 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 14. 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 Å and 2.12 Å 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 Å 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 15 presents the change of the ratio of the line intensities that occurred in that time. The narrow line at 2.054 Å disappeared and the line at 2.11 Å 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. 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 16. 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 are 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 polymorphs.

The Auger measurements were performed last. Differentiated Auger spectra are shown in Figure 17. The peaks in Figure 17 look more like diamond than graphite peaks [11]. To our knowledge, no Auger spectra on layers containing hexagonal diamond have so far been reported.

Figure 15. Narrow rocking curve for sample I-3 presenting change of the ratio of line intensities that occurred after electron bombardment in SEM.

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 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 the 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. Mo-

saic 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 ultra-high 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 18 indicates pure diamond characteristics with a lattice parameter of 3.566 0.002 Å for all phases. The inset in Figure 18 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.

Figure 18. 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.

Results

In order to determine whether the rectifying characteristics exhibited by the sample were due to a

Figure 19. 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

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.

References

- ¹J.P.Prins, Appl. Phys. Lett. 41 950(1982)
- ²M.W.Geis, D.D.Rathman, D.J.Ehrlich, R.A.Murphy, W.T.Lindley, IEEE Electron Dev. Lett. EDL-8, 341(1987)
- ³G.H.Glover, Solid-State Electron 16 973(1973)
- ⁴W.Zhu, B.R.Stoner, B.E.Williams, J.T.Glass, Proc. of IEEE 79 621(1991)
- ⁵D.Kweon, J.Lee, D.Kim, J. Appl. Phys. 69 8329(1991)

- ⁶G.Sh.Gildenblat, S.A.Grot, C.R.Wronski, A.R.Badzian, T.Badzian, R.Messier, Appl. Phys. Lett. 53 586(1988)
- ⁷D.G.Jeng, H.S.Tuan, R.F.Salat, G.J.Fricano, J. Appl. Phys. 68 5902(1990)
- ⁸R.H.Harper, C.Johnson, P.R.Chalker, D.Totterdell, I.M.Buckley-Golder, K.Kobashi, in *Applications of Diamond Films and Related Materials*, edited by Y. Tzeng, M.Yoshikawa, M.Murakawa, and A. Feldman (Elsevier, New York, 1991), Proceedings of the First International Conference on the Applications of Diamond Films and Related Materials -ADC'91, Auburn, Alabama, U.S.A., August 17-22, 1991, p. 335
- ⁹E.J. Caine and E.J. Charlson, J. Electron Material 13 341(1984)
- ¹⁰M.I.Landstrass, K.V.Ravi, Appl. Phys. Lett 55 975(1989)
- ¹¹S.A.Grot, G.Sh.Gildenblat, C.W.Hatfield, C.R.Wronski, A.R.Badzian, T.Badzian and R.Messier, IEEE Electron Dev. Lett. 11 100(1990)
- ¹²G.S.Gildenblat, S.Grot and A.Badzian, Proc. of IEEE 79 647(1991)

Figure 20. 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

Figure 21. Capacitance-voltage-frequency characteristics of silver on diamond Schottky diode KU3-6 with contact area of 3.2 mm^2

IV PLATINUM SILICIDE PHOTODETECTORS

M. Hajsaid, G. Zhao, E. J. Charlson, E. M. Charlson, and G. Popovici

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

Figure 22. Structure of the Pt₂Si photocell.

The structure of the Pt₂Si photocell is shown in Fig. 22. The fabrication procedure is as follows:

- 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 23 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.

Table 1: Summary of Pt₂Si measurements.

	Group	Resistivity Ohm-cm	Platinum Thickness Å°	Number Tested	Percent Difference
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

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

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

Figure 23. X-ray diffractometer trace of the silicide phase.

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 24 and 25. 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.

Figure 24. Quantum efficiency of platinum silicide cells from samples 21-2, 22-3, and 23-4.

Looking at the results of Figures 24 and 25, 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 in-

creasing 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.

Figure 25. Quantum efficiency of platinum silicide cells from samples 1a-3, 2a-3, and 3a-1.

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 26, 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 27 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 cir-

cuit 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.

Figure 26. Fourth quadrant I-V curve for a Pt₂Si cell illuminated with 1.32×10^{-6} W/cm² of 148 nm light

Figure 27. $\log_{10} I$ versus V curve for a typical diode.

References

1. B. Y. Tsaur, C. K. Chen, and J. P. Mattia, "PtSi Schottky-barrier focal plane arrays for multi-spectral imaging in ultraviolet, visible, and infrared spectral bands," *IEEE Electron Device Lett.*, Vol 11, pp. 162-164, 1990.
2. W. F. Kosonocky, F. V. Shallcross, T. S. Villani, and J. V. Groppe, "160 x 244 element PtSi Schottky-barrier IR-CCD image sensor," *IEEE Trans. Electron Devices*, Vol ED-32, pp. 1564-1573, 1985.
3. Chenson K. Chen, Bettina Nechay, and Bor-Yeu Tsaur, "Ultraviolet, visible, and infrared response of PtSi Schottky-barrier detectors operated in the front-illumination mode," *IEEE Trans. Electron Devices*, Vol. ED-38, No. 5, pp.1094-1103, May 1991.
4. Electronics Microstructure Science, Vol. 6, Materials and Process Characterization. Edited by Noeman G. Einspruch and G. B. Larabee, pp. 348-349.

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 28 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 29 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.

Figure 28. Schematic diagram of experimental apparatus.

Figure 29. Parts of the oxy-acetylene flame used.

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 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 30 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 31. 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 31 was not extended below 660 C and thus does not violate the 370 C lower temperature limit for diamond growth reported by Hirose.

Figure 30. Results of study conducted by Hirose-carbon deposit type as function of temp. & O_2/C_2H_2

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].

Figure 31. Results of study conducted by Hanssen-carbon deposit type as a function of temp. & O_2/C_2H_2 .

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, 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 O_2/C_2H_2 , similar to that of growth rate, whereas C_2H_2 and C_2H species disagreed with growth rate dependence on O_2/C_2H_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 O_2/C_2H_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 32 and Figure 33, 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 100 μ m.

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.

8/6/92

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

Figure 32. X-ray diffraction pattern of experimental sample.

Figure 33. Scanning electron microscope picture of sample.

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 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.

References

1. Y. Hirose, S. Amanuma and K. Komaki, J. Appl. Phys. 68, 6401 (1990).
2. Y. Hirose, S. Amanuma and K. Komaki, Proceedings of the 1st Int. Symp. on Diamond and Diamond-like films, ECS 89, p80 (1990).
3. L. M. Hanssen, K. A. Snail, W. A. Carrington, J. E. Butler, S. Kellog and D. B. Oakes, Thin Solid Films 196, 271 (1991).
4. Y. Tzeng, C. C. Tiu, R. Phillips, T. Srivinyunon and Y. Chen, Appl. Phys. Lett. 57, 789 (1990).
5. K. V. Ravi and A. Joshi, Appl. Phys. Lett. 58, 246 (1991).
6. C. Sung Jo and S. Yae Shik, Applications of Diamond Films and Related Materials, p527 (1991).
7. K. Okada, S. Komatsu, S. Matsumoto and Y. Moriyoshi, J. Mat. Sci. 26, 3081 (1991).
8. Y. Tzeng, R. Phillips, C. Cutshaw, T. Srivinyunon, B. H. Loo and P. Wang, Appl. Phys. Lett. 58, 2645 (1990).
9. Y. Tzeng, R. Phillips, C. Cutshaw, T. Srivinyunon, B. H. Loo and A. Ibrahim, Appl. Phys. Lett. 56, 134 (1990).
10. J. C. Angus, H. A. Will and W. S. Stanko, J. Appl. Phys. 39, 2915 (1968).
11. Y. Matsui, A. Yuuki, M. Sahara and Y. Hirose, J. Appl. Phys. 28, 1718 (1989).

12. Y. Matsui, H. Yabe and Y. Hirose, J. Appl. Phys. (Jpn) 29, 1552 (1990).
13. S. J. Harris, J. Appl. Phys. 65, 3044 (1989).
14. S. J. Harris and A. M. Weiner, Appl. Phys. Lett. 55, 2179 (1989).
15. R. S. Yalamanchi and K. S. Harashavardhan, J. Appl. Phys. 68, 5941 (1990).
16. Richard Phillips, Dept. of Elect. Engr., Auburn, Diamond Synthesis in Combustion Flames - Review (1991).

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 ion implantation [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 iden-

tified 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].

Figure 34. Typical diamond Raman spectrum for dopant implantation studies at three sample locations.

The Raman spectrum of diamond utilized in several implantation studies is shown in Figure 34. The characteristic peak of diamond at approximately 1333 cm^{-1} indicates sp^3 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 35, 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 36.

Figure 35. Current-voltage characteristics of $(\text{CH}_3\text{O})_3\text{P}$ implanted and non-implanted diamond on several locations.

Figure 36. Current-voltage characteristics of $(\text{CH}_3\text{O})_3\text{P}$ implanted samples at six sample positions.

Figure 37. Junction capacitance, measured at 50 kHz 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 37 and 38 for frequencies of 50kHz and 500kHz, respectively. This data indicates a built-in potential of ap-

proximately 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].

Figure 38. Junction capacitance, measured at 500 kHz 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.

Nitrogen implantation was performed in order to make comparisons to samples implanted with trimethyl phosphite. These samples similarly exhibited rectifying behavior, shown in Figure 39. However, voltage stressing of samples (3×10^5 v/cm) converted junctions to ohmic contacts, shown in Figure 40. 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 41. An increase to four times that field caused an increased reverse leakage current, shown in Figure 42.

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.

References

1. V. S. Vavilov, et. al. Sov. Phys.-Sol. State, 8 (1966)1560.
2. V. S. Vavilov, Rad. Eff., 37 (1978) 229.
3. K. Okano, et. al. Appl. Phys. Lett. 58 (1991) 840.
4. D. G. Beanland, Solid-State Electron. 21 (1978) 537.
5. E. J. Caine and E. J. Charlson, J. Electronic Materials, 13 (1984) 341.
6. G. Zhao, et. al., Appl. Phys. Lett., 61 (10), Sept.1992.
7. G. Braunstein and R. Kalish, J. Appl. Phys. 54 (1983) 2106, and references contained therein.
8. S. Albin and L. Watkins, IEEE El. Dev. Lett., 11 (1990)159.
9. M. I. Landstrass and K. V. Ravi, Appl. Phys. Lett., 55(1989) 975.
10. Y. Muto et. al., Appl. Phys. Lett., 59 (1991) 843.
11. G. S. Gildenblat, S. A. Grot, and A. Badzian, Proc. IEEE 79 (1991) 647, and references contained therein.
12. G. I. Roberts and C. R. Crowell, Solid-State Electron. 16(1973) 29.

VII GROWTH OF ORIENTED ALUMINUM NITRIDE FILMS ON SILICON BY CHEMICAL VAPOR DEPOSITION

A. H. Khan, M. F. Odeh, J. Meese, E. M. Charlson, E. J. Charlson, T. Stacy.
G. Popovici and M. A. Prelas.

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°-1300°C 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°- 800°C) 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

Figure 43. Diagram of CVD apparatus.

AlN films were grown on Si substrates using linear tube CVD method. AlN was formed by the chemical reaction of AlCl_3 with NH_3 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.43. The aluminum chloride container was maintained at 150°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°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 H_2 at approximately 500°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°C .

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 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. 44 (a) and Fig. 44 (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.45 (a) and Fig.45 (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 45 (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.46(b) and Fig.46(d)).

Figure 46 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.46-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.46b). 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.47a) 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.46-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 46 (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.48 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 50. 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 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 (4.5 kV) to a dose of approximately 10^{18} ions/cm^2 . 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.

Conclusions

The following conclusions can be drawn from this study.

1. AlN layers were grown on Si by CVD using AlCl₃ and NH₃ 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 whereas the large weak band is due to LO phonons.

References

1. ASTM card 25-1133.
2. W.M.Yim, E.J.Stofko, P.J. Zanzucchi, J.I.Pankove, M.Ettehberg, and S.L.Gilbert: J. Appl. Phys. 44, 292 (1973).
3. M.T.Duffy, C.C.Wang, G.D.O,Clock Jr., S.H.Mc Farlane III and P.J. Zanzucchi: J. Electron. Matter 2, 359 (1973).
4. A.J. Shuskus, T.M. Reeder and E.L. Paradis: Appl. Phys. Lett. 24, 155 (1974).
5. S. Yoshida, S. Misawa, Y. Fujii, S. Takada, H. Hayakawa, S. Gonda and A. Itoh: J. Vac. Sci. & Technol. 16, 990 (1979),
6. A.J. Noreika and D.W. Ing: J. Appl. Phys. 39, 5578 (1968).
7. M. Matloubian and M. Gershenson: J. Electron. Matter 14, 633 (1985).
8. J.L. Dupuie and E. Gulary: Appl. Phys. Lett. 59, 549 (1991).
9. M. Morita, S. Isogai, N. Shimizu, K. Tsubouchi and N. Mikoshiba; Jap. J. Appl. Phy. 20, L173 (1981).
10. L.M. Sheppard: Ceram. Bull. 69, 1801 (1990).
- 11.M.Morita, N. Uesugi, S. Isogai, K. Tsubouchi and N. Mikosiba: Jap. J. Appl. Phy. 20, 17 (1981).
12. T.L. Chu, D.W. and A.J. Noreika: Solid-State Electronics 10, 1023 (1967).
13. H. Komiyama and T. Osawa: Jap. J. Appl. Phys. 24, L795 (1985).
14. Y. S. Toulouvian, R.K. Kiby, R.E. Taylor and T.Y.R. Lee: Thermophysical properties of matter. v. 13, p.873 and p.154, IFI/Plenum, NY-WA., 1977.
15. B E Warren, X-Ray Diffraction, Dover Publ., N.Y., 1990, pp 298-305.
16. O. Brafman, G. Lengyel, S.S. Mitra, P.J. Gielisse, J.N. Plendl and L.C. Mansur: Solid State

Commun. 6, 523 (1968).

17. W. Changwen and L. Ling: J. Non-Cryst. Solids 112, 296 (1989).

18. A. T. Collins, E.C. Linghuwlers and P. J. Dean: Phys. Rev. 158, 833 (1967).

19. I. Akasaki and M. Hashimoto: Solid State Commun. 5, 851 (1967).