**Morphology and Electron Emission Properties of
Nanocrystalline CVD Diamond Thin Films***

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MORPHOLOGY AND ELECTRON EMISSION PROPERTIES OF NANOCRYSTALLINE CVD DIAMOND THIN FILMS

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ABSTRACT

Nanocrystalline diamond thin films have been produced by microwave plasma-enhanced chemical vapor deposition (MPECVD) using $C_{60}/Ar/H_2$ or $CH_4/Ar/H_2$ plasmas. Films grown with H_2 concentration $\leq 20\%$ are nanocrystalline, with atomically abrupt grain boundaries and without observable graphitic or amorphous carbon phases. The growth and morphology of these films are controlled via a high nucleation rate resulting from low hydrogen concentration in the plasma. Initial growth is in the form of diamond, which is the thermodynamic equilibrium phase for grains ≤ 5 nm in diameter. Once formed, the diamond phase persists for grains up to at least 15-20 nm in diameter. The renucleation rate in the near-absence of atomic hydrogen is very high ($\sim 10^{10} \text{ cm}^{-2} \text{ sec}^{-1}$), limiting the average grain size to a nearly constant value as the film thickness increases, although the average grain size increases as hydrogen is added to the plasma. For hydrogen concentrations less than $\sim 20\%$, the growth species is believed to be the carbon dimer, C_2 , rather than the CH_3^* growth species associated with diamond film growth at higher hydrogen concentrations. For very thin films grown from the C_{60} precursor, the threshold field (2 to ~ 60 volts/micron) for cold cathode electron emission depends on the electrical conductivity and on the surface topography, which in turn depends on the hydrogen concentration in the plasma. A model of electron emission, based on quantum well effects at the grain boundaries is presented. This model predicts promotion of the electrons at the grain boundary to the conduction band of diamond for a grain boundary width $\sim 3\text{-}4 \text{ \AA}$, a value within the range observed by TEM.

INTRODUCTION

Diamond Film Growth

Bulk diamond is unstable relative to graphite except at extremely high pressures and temperatures. Therefore, the growth of diamond films via low pressure chemical vapor deposition (CVD) requires a means of kinetically allowing the growth of the diamond phase while suppressing the formation of the graphitic phase. This is typically achieved by using atomic hydrogen to preferentially etch the graphitic phase and stabilize the diamond surface structure via hydrogen termination of the carbon dangling bonds. Additionally, since the growth species in this process is the CH_3^* radical, it is necessary to both prepare a carbon atom insertion site at the surface, and to remove the extra hydrogen atoms from the growth species in order to permit migration of the adsorbed carbon to the diamond lattice site. These functions are accomplished through atomic hydrogen abstraction reactions [1]. The presence of a large excess of atomic hydrogen is therefore considered essential to the conventional method of low pressure growth of diamond films, which is restricted to a region of the C-H-O phase diagram (Fig. 1) close to the line extending from the hydrogen corner to the middle of the C-O line [2]. The region below this line corresponds to a net etching of the diamond, and therefore no growth is observed. The region above this line corresponds to the growth of non-diamond phases. By growing close to the H-CO line, phase pure, large grain, textured diamond films may be produced.

These films however, generally make poor electron emitters [3], and changes in the growth conditions which result in improved electron emission properties generally result in the

simultaneous variation of a number of film properties. Increasing the carbon/hydrogen ratio in the CVD plasma tends to enhance the electron emission, but it can be seen by referring to Figure 1, that the result will be to enhance the growth of non-diamond phases, typically as intergranular graphitic or amorphous carbon inclusions. Additionally, the grain size decreases, preferred orientation is lost, and a larger number of atoms are located along grain boundaries. Consequently, there is an intrinsic linkage between grain size, growth rate, surface morphology, and the presence of intergranular non-diamond phases which makes it very difficult to either sort out the basic physics of the electron emission process or to significantly improve the performance of carbon-based cold cathode electron emission materials in a systematic manner.

Figure 1. The H-C-O phase diagram showing the predicted [1] region of diamond film growth as the solid line connecting the H corner to the middle of the C-O line, the experimentally observed region of film growth [2] as the shaded area surrounding the theoretical line, and the growth method reported here [4], located at the carbon apex and extending along the C-H leg of the triangle as hydrogen is added to the plasma.

We have developed a new method of diamond film deposition based on direct insertion of gas phase carbon dimers (C_2) into the diamond lattice without the assistance of atomic hydrogen abstraction reactions. The relation between the morphological, compositional and electronic properties of these films differs significantly from that of conventionally grown diamond films. It is possible to control the ratio of C_2 / CH_3^* growth species and the resulting character of the dominant growth process by tailoring the amount of H_2 in the plasma. Films grown by this new method display a correlation between readily identifiable topographic, electrical, and morphological properties which are predictive of the electron emission properties of the films.

The growth process involves either C_{60} or CH_4 precursors in an argon microwave plasma [4] with little or no added atomic hydrogen [5], and permits growth of equiaxed, nanocrystalline diamond films [6]. It has been predicted [7], and experimental results indicate [8] that the growth species is the carbon dimer, and atomic hydrogen abstraction reactions do not seem to play a role in the film growth. Diamond growth by the new method occurs in the region indicated by the shaded area near the carbon vertex of Figure 1. Both x-ray photoabsorption spectroscopy [9] and UV excitation Raman spectroscopy [10] show that the electronic bonding character is almost entirely sp^3 . High resolution TEM studies [11] reveal equiaxed nanocrystalline diamond grains with atomically abrupt grain boundaries and no trace of inter-granular non-diamond phases. Because of the relative absence of atomic hydrogen in the plasma, there is little etching of the nascent diamond grains, and continuous renucleation occurs, resulting in an average grain size of ~ 15 nm [11], and surface roughness of 20-40 nm, regardless of film thickness [12]. For very small grains, there is evidence [13, 14] that the grain boundary energy is sufficient to make the diamond phase stable relative to graphite, and we conclude that the dimer growth species gives rise to a high nucleation rate which limits the grain size, and grows diamond as the thermodynamically stable phase of carbon.

If the ambient hydrogen pressure is low, the C_2 growth species can be produced via two possible routes using either a C_{60} gas phase precursor;

or a hydrocarbon precursor such as CH_4 ;

By increasing the amount of hydrogen in the plasma, reactions 1 and 2 can be shifted to the left;

Figure 2. ChemKin Calculation at 100 Torr, 1% CH_4 in Ar vs. % H_2 , $T_{vib} = 2500$ K

Equations 1 and 2 correspond to the growth of diamond via direct insertion of the carbon dimer into the diamond lattice site [7], whereas equation 3 corresponds to diamond film growth from the CH_3 species [1, 2]. If thermodynamic equilibrium conditions are assumed, it is possible to calculate the C_2/CH_3^* ratio using the Chemkin code [16]. The calculated C_2 and CH_3^* concentrations in the plasma are shown in Figure 2 for a plasma in thermodynamic equilibrium at 2500 K. In reality however, the plasma is not in thermodynamic equilibrium, and preliminary optical absorption measurements [17, 18] indicate that the effective temperature may be lower than 2500 K. However, the general result that the C_2 concentration decreases and the CH_3^* concentration increases as the plasma hydrogen concentration increases remains valid. Since these two growth species give rise to films with very different properties with regard to grain size and orientation, surface morphology, and the formation of inter-granular non-diamond phases, it is possible to controllably produce films with a wide range of morphological and electronic characteristics by varying the plasma hydrogen concentration.

Cold Cathode Electron Emission

Some diamond and diamond-like carbon thin films exhibit cold cathode electron emission [19] for moderately low applied voltages. This requires a means for (I) transferring electrons from the substrate into the diamond, (II) transferring charge through the diamond layer to the surface, and (III) ejecting electrons into the vacuum. The experimentally observed current-voltage relation fits the Fowler-Nordheim expression (Eq. 4) corresponding to tunneling through a barrier [20].

However, it is not clear whether the tunneling occurs at the interface between the substrate and the diamond [21, 22], or between the diamond and the vacuum [23]. There is additional disagreement as to whether the electrons tunnel from the valence band [24], the conduction band [23], or from interband [25] states either associated with graphitic or DLC phases, or induced by damage or dopants [3], intentional or otherwise. Assuming that the electron mechanism consists of tunneling through a barrier associated with an effective work function ϕ , the emission current density can be expressed in the form [21]

$$J = 154 E^2 F / \phi \exp\{-6830 \phi^{3/2} / E\} \quad (4)$$

where J is the current density in amps/cm², E is the electric field in volts/micron, ϕ is measured in eV, and F is the effective fraction of the free surface area which gives rise to electron emission. In general, $E = \beta \times E_{fp}$, where E_{fp} is the field corresponding to a parallel flat plate geometry, and the quantity β reflects the geometric enhancement of the electric field, presumably by surface asperities. The effective work function and emission area can be determined from the slope and intercept, respectively, of a plot of $\ln(J/E^2)$ vs $1/E$, assuming a known value of β . The value of the effective work function tends to be quite low [26], typically less than 0.1 eV, and the emission comes from isolated, discrete sites [20] which are often very low in density.

It has been demonstrated via ultra-violet photoelectron spectroscopy [20, 27] that under certain circumstances, diamond is a negative electron affinity (NEA) material (i. e., the bottom of the conduction band lies above the vacuum level) with a 5.5 eV band gap. Consequently, conduction electrons which reach the surface would experience little or no barrier to emission into the vacuum. A back-injection model has been hypothesized [21, 22] in which the observed current-voltage characteristic relates to tunneling through a barrier between the substrate and the diamond film, followed by transport to the NEA surface and ejection without further energy loss. The voltage drop across the diamond film results in a shift of the conduction and valence bands such that tunneling through the substrate-diamond interface barrier may result in injection of substrate electrons into the conduction band [21, 23]. Recent studies of the kinetic energy distributions of electrons emitted from Mo tips cathodically coated with diamond powder confirm this picture, although the energy distribution of electrons emitted from natural p-type diamond suggests that emission occurs from the diamond valence band [28], and there may not be a single tunneling mechanism [29].

However, diamond is an insulator with a large band gap, and the transport mechanism through the film is not clear. The best electron emitting thin film materials are usually either a highly damaged polycrystalline diamond [3], or various forms of diamond-like carbon (DLC) [4] (amorphous carbon with a high degree of sp³ bonding), and almost certainly do not meet the conditions under which NEA has been observed. It is not clear at this point what role NEA has in the electron emission process in diamond and diamond-like carbon films. If the barrier is at the diamond-vacuum interface, then damage may be required simply to provide conductive paths through the film, although Xu, Tzeng, and Latham [20] argue that such conducting paths are inconsistent with the observed low density of emitting sites. They have proposed a model in which the intergranular regions of graphite which typically form between diamond grains act as antennas which give rise to a local field enhancement sufficient to form conducting channels within the diamond matrix. The emission sites are conjectured to be a "triple-point" at which a diamond grain and graphitic inclusion intersect at the vacuum interface.

The "triple point" model however, does not seem plausible for the more uniform DLC films. A model proposed by Robertson [30] describes both the observed low effective work function values and the low effective emission area in DLC films. Eq. 4 yields the quantity $\phi^{3/2} / E$ as the slope of the Fowler-Nordheim (F-N) plot ($\ln J/E^2$ vs $1/E$). In general, it is not possible to separate the effect of the work function from that of the local electric field, which is very sensitive to surface structures with small radii of curvature. The effective low work function of conventionally grown diamond films could be attributed to field enhancement at surface asperities and/or sharp-edged crystalline facets associated with these typically very rough surfaces. However, DLC films are

quite smooth, and it is therefore difficult to explain low effective work function values in topographic terms. A "patch effect" model based on a largely hydrogen-terminated surface with small bare patches at defect sites has been proposed [30]. Hydrogen is an electropositive adsorbate, which results in the formation of surface dipoles with the positive end pointing outward. Small regions of the surface which are hydrogen-deficient experience the effects of the adjacent negative image charge, resulting in a lowering of the electron affinity and a large normal component of the electric field, i. e. a non-topographic field enhancement effect. The key ingredients of this model are a high density of very small hydrogen-depleted surface defect sites.

There are still a number of issues which remain to be resolved before the cold cathode electron emission mechanism in diamond and DLC films is understood. The complexity of the process and variability of materials properties leads to poor reproducibility which has hindered the development of applications based on cold cathode electron emission from diamond films. In particular, it has not been possible to provide definitive morphological or electronic bonding criteria which would make it possible to predict whether a given diamond or diamond-like carbon film will emit electrons, except by direct testing. We have developed a class of phase-pure nanocrystalline diamond which has properties characteristic of both microcrystalline diamond and DLC, and therefore provides a new means of examining the electron emission process.

EXPERIMENTAL

Nanocrystalline diamond films were grown on $\langle 100 \rangle$ n-type Si substrates with resistivity in the range 0.01-1.0 ohm-cm, using an ASTeX PDS-17 microwave (2.45 GHz) CVD reactor. Diamond nucleation was accomplished by applying a 100-200 volt negative bias to the substrate in a 10% CH_4 / 90% H_2 plasma with a total pressure of 5 Torr. The substrate temperature was maintained at 800 °C, and the microwave power level was 500 watts. Laser interferometry [31] was used to determine when diamond film growth begins, with an estimated reproducibility of 300-400 Å. Once the initial growth has begun, the gas composition and pressure are altered to grow the films using the desired processes corresponding to equations 1, 2, or 3. For growth using the dimer insertion process (Eqs. 1 or 2), Ar is introduced at a pressure of 98-100 Torr at a flow rate of 100 sccm, with carbon provided via either 1-2 sccm of CH_4 , or by turning on the C_{60} sublimation source described elsewhere [5]. In most cases, at least 1-2 sccm of H_2 was required to reduce the electron density and stabilize the predominantly Ar plasma, which otherwise tends to form at the quartz microwave window, rather than wetting the substrate. The hydrogen flow rate was varied up to 20 sccm by connecting two of the system's flowmeters in parallel. The growth rate at a microwave power level of 800 watts is in the range 0.4-0.6 $\mu\text{m/hr}$.

Electron emission was measured using an anode 1.89 mm in diameter with rounded edges to prevent spurious emission at anode asperities. The initial anode-cathode spacing was measured using a high magnification CCD camera. A series of current-voltage measurements were made at various distances, set by computer control of a calibrated micro-step motor. The cathode voltage was increased under computer control until the emission current reached 10 μA , and then decreased to zero. The sequence was typically repeated three times to verify reproducibility. The gap was then increased, typically in five micron steps, and the whole sequence was repeated until the distance was so large that a current of 0.1 μA could not be obtained with an applied voltage of 3 kV. The samples were also analyzed by atomic force microscopy (AFM) using a Burleigh ARIS 3300 microscope. Transmission electron microscopy was performed using a JEOL 4000 EX. Electrical conductivity measurements were made using a two-point probe, and are intended for comparison purposes only.

RESULTS

The surface morphology as a function of plasma composition is shown in the SEM images of Fig. 3 for four films grown in a plasma containing 1% CH_4 and various amounts of Ar and H_2 . For high H_2/Ar ratio (Fig. 3(a)), the growth species is CH_3^* , and the resulting film consists of large, faceted diamond grains. Total gas pressure was 100 Torr, with a gas flow rate of 100 sccm.

The microwave power was 800 watts, and the substrate temperature was 800 °C. As the H₂ concentration drops toward ~20%, a new morphology, consisting of equiaxed, very small, non-faceted grains develops, as shown in Fig. 3 (b-d). X-ray photoabsorption measurements at the C_{1s} edge [9] have been used to characterize the relative amounts of diamond vs graphitic material in the films, showing that for both CH₄ and C₆₀ precursors, the films grown with the smallest amount of hydrogen are indistinguishable from single crystal natural diamond, with a well defined diamond σ^* exciton at 289 eV, as shown in Fig. 4. As the hydrogen content of the plasma increases, the diamond exciton becomes less well-defined, and there is evidence of H-C localized bonding, although diamond remains the predominant phase.

Fig. 3 Scanning electron micrograph images of diamond films grown in a microwave plasma consisting of 1% CH₄ and (a) 2% Ar, 97% H₂, (b) 80% Ar, 19% H₂, (c) 90% Ar, 9% H₂, (d) 97% Ar, 2% H₂.

Figure 4. C_{1s} x-ray photoabsorption spectra of a single crystal diamond and graphite reference samples, and nanocrystalline diamond films grown from C₆₀ and CH₄ precursors in an Ar microwave plasma containing either 2% or 10% added hydrogen.

The electron emission properties for twelve 60 and 120 nm thick samples, as well as that of a 1 μm thick reference film deposited using a 2% CH_4 -98% Ar microwave plasma are listed in Table I. The conventionally grown film has an rms roughness value > 500 nm, very high electrical resistance as measured by a two point probe, and a high threshold field (defined as the flat plate field at which an emission current of 0.1 μA was measured). The films made using the Ar- CH_4 - H_2 plasma exhibited increasing roughness as the plasma hydrogen concentration increased, but there was little change in electrical resistivity, and none of these films emitted at fields up to 60 V/ μm (assuming $\beta=1$). The films derived from the C_{60} precursor exhibited very different behavior. The rms roughness, electrical resistance and threshold field were strong functions of the plasma hydrogen content, with threshold fields ranging from 2 V/ μm to more than 60 V/ μm .

Table I: Electron Emission Properties of Diamond Films Grown in H_2 - CH_4 , Ar- CH_4 - H_2 , and Ar- C_{60} - H_2 Microwave Plasmas

Sample	Carbon Precursor	% H_2	Thickness (nm)	Resistance (Kilohms)	Turn-on Field (V/ μm)	roughness (nm rms)
950111	CH_4	98	1000	250-400	60-70	>500
950707c	CH_4^*	2	60	0.8	NE	
950707a	CH_4^*	2	120	5.0	NE	65
950724	CH_4^*	10	60	0.8	NE	15
950725b	CH_4^*	10	120	0.8	NE	70
950725d	CH_4^*	20	60	--	NE	26
950725c	CH_4^*	20	120	2.7	NE	153
950726a	C_{60}^*	2	60	--	NE	
950726b	C_{60}^*	2	120	400	50-65	28
950727b	C_{60}^*	10	60	13.0	30	16
950727a	C_{60}^*	10	120	1.8	12-35	70
950731	C_{60}^*	20	60	186	10	15
960807	C_{60}^*	20	120	500	2	140

* Balance of the gas is argon

Figure 5. Plan view and line scan AFM image of two 120 nm thick diamond films grown in a CH_4 (1%)-Ar plasma with (a) 2% added H_2 , and (b) 20% added H_2 .

Figure 5 shows the atomic force microscope (AFM) images for films corresponding to (a) growth in a 2% H_2 - CH_4 (1%) - Ar plasma, and (b) growth in a 20% H_2 - CH_4 (1%) - Ar plasma. Both films exhibit a faceted topography with a 5-10 μm lateral modulation distance. Neither film emitted electrons at fields up to 70 V/ μm

Figure 6 shows the atomic force microscope (AFM) images for films corresponding to (a) growth in a 2% H_2 - C_{60} (1%) - Ar plasma, and (b) growth in a 20% H_2 - C_{60} (1%) - Ar plasma. The rms roughness values are similar to those of Figs. 5(a) and 5(b), but there is no well-defined crystallinity, and the lateral modulation length is much shorter, varying from roughly 1.5 to 2 μm with little change as the plasma hydrogen concentration varies, although the rms roughness varies significantly as shown in Table I. The origin of this lateral modulation is not known but it superficially resembles stress relief-related topography observed in strained epilayer growth of [SiGe/Ge]. The modulated structure which appears in Figs. 6a and 6b seems to be closely correlated to field electron emission in these films.

Figure 6. plan view and line scan AFM image of (a) a film grown in a plasma containing 2% H_2 in a C_{60} -Ar plasma, (b) a film grown in a plasma containing 20% H_2 in a C_{60} -Ar plasma.

The effect of increasing plasma hydrogen content on grain morphology of 120 nm thick nanocrystalline diamond films grown from CH_4 and C_{60} precursors is shown in Figs. 7 and 8. A TEM image of a film grown using the CH_4 precursor in an Ar plasma with 2% H_2 added (Fig. 7a) shows very small grains with extremely low defect density, consisting almost entirely of twinning. Increasing the plasma hydrogen content (Fig. 7b and 7c) to 20% results in a relatively small degree of grain coarsening resulting from etching by atomic hydrogen, but there is no detectable formation of intergranular graphitic phase in this range of hydrogen concentration. 120 nm thick films grown from an Ar- H_2 plasma into which C_{60} has been sublimed (Fig. 8) show for low plasma hydrogen concentration (Fig. 8a), a structure similar to that of Fig. 7a. However, as the plasma hydrogen content increases, there is a considerable increase in both the defect density and grain size, which reaches a diameter of $\sim 1 \mu m$ for 20% added H_2 . It should be emphasized that the lateral topographic modulation observed in Figs. 5 and 6 do not correspond to the individual diamond grains, although for the film corresponding to Fig. 8c, the defect density has become so high that it is difficult to identify individual grains.

UV Raman spectroscopy [10] has shown that the films grown from C_{60} precursors in an Ar microwave plasma with relatively low added hydrogen have electronic bonding character which is $\sim 2-3\%$ sp^2 in character. However, atomic resolution TEM has failed to reveal any significant presence of non-diamond phase in these films. Generally, non-diamond phases in diamond films occur as intergranular inclusions of sp^2 -bonded amorphous carbon or graphite. Figure 9 shows a boundary between 2 grains of a diamond film grown under the same conditions as that of Fig. 7(a). The individual grains are found to be nearly defect-free, with extremely narrow grain boundaries, estimated to be 0.25-0.4 nm in width [11]. As the hydrogen in the plasma is varied

over the range 2-20%, there is no evidence of the formation of non-diamond intergranular phases, and the grain boundary width remains near-atomic in sharpness.

Fig. 7 TEM images of diamond films grown from CH_4 in (a) Ar-2% H_2 , (b) Ar-10% H_2 , and (c) Ar-20% H_2 plasmas.

Fig. 8 TEM images of diamond films grown from C_{60} in (a) Ar-2% H_2 , (b) Ar-10% H_2 , and (c) Ar-20% H_2 plasmas.

Figure 9. High resolution TEM image of the grain boundary in a nanocrystalline diamond film grown from a C_{60} precursor in an Ar microwave plasma with 2% added hydrogen.

Figure 10 shows the current density vs flat plate electric field for two films grown from the C_{60} precursor in an Ar plasma using 2% and 20% added H_2 . There is a considerable difference in both the threshold field and the abruptness of the current rise with electric field. Both films however, show a smooth turn-on, with little apparent need for conditioning [32], little or no hysteresis, and excellent reproducibility from one cycle to the next. Plotting the same data in "Fowler-Nordheim" (FN) units ($\ln [J/E^2]$ vs $1/E$) as shown in Figure 11, results in a straight line plot in which the slope can be interpreted in terms of the effective work function. For the film grown using 2% added H_2 , the corresponding value of ϕ is 0.17 eV, assuming $\beta=1$. According to the x-ray photoabsorption data of Fig. 4, this sample has a near-edge electronic structure virtually

indistinguishable from that of single crystal diamond, and it would therefore be reasonable to expect the work function to be close to that of pure diamond, namely 5.5 eV. If this value is assumed, the corresponding field enhancement factor turns out to be $\beta=185$. This value is consistent with that of microtip arrays such as reported by McCauley et. al. [33] in these proceedings, but is not consistent with AFM images of Fig. 6(a). The FN plot for the sample grown using 20% added H_2 yields even more extreme values. If it is assumed that $\beta=1$, the corresponding value for ϕ is 0.02 eV. It must be assumed that such a low value is unphysical since such a material would result in room temperature thermionic emission. If a value of 5.5 eV is assumed for ϕ , the requisite field enhancement factor is $\beta=5300$. This value is totally inconsistent with AFM image Fig. 6b.

Fig. 10 J vs E plot of nanocrystalline diamond films grown in an Ar plasma with 2% and 20% added hydrogen.

Fig. 11 "FN" plot of nanocrystalline diamond films grown in an Ar plasma with 2% and 20% added hydrogen.

DISCUSSION

A recent model [34], based on a pseudopotential method for describing grain boundaries in silicon, has been extended to diamond. Starting from the two assumptions of a nanocrystalline microstructure and randomly oriented grain boundaries, and by observing that unlike silicon, the grain boundary energy for carbon can be minimized either by forming disordered 4-fold bonds, or 3-fold bonds with a lower degree of disorder, it is predicted that the grain boundary width will be typically less than one lattice parameter (0.36 nm), and that approximately 80% of the atoms at the grain boundary will be *locally* sp^2 -bonded in the sense that bonds across the boundary are 3-fold coordinated, but there is no long range connectivity along the grain boundary unless some impurity such as hydrogen is present in the grain boundary. This result both agrees well with experimentally observed properties of the C_{60} nanocrystalline diamond, and provides a basis for a model of electron emission from these films. As noted previously, the grain boundary width has been determined to be 0.25-0.4 nm. UV Raman spectroscopy has determined that 2-3% of the carbon atoms are sp^2 in character, and the mean grain size has been determined to be [11] 10-15 nm, with the result that 2-3% of the carbon atoms are located at the grain boundary. we have seen that both the electrical conductivity and the electron emission properties are strongly dependent on plasma hydrogen concentration, and it may therefore be postulated that the presence of hydrogen at the grain boundaries is necessary to provide conducting paths to the surface. Band bending associated with the IR drop in the film may then be responsible for tunneling into the conduction band.

A recent model proposed by Robertson [30] attempts to describe field emission from DLC as the result of a non-uniform image dipole distribution associated with adsorbed hydrogen covering most of the surface except for a few very small surface defects of unspecified origin. Since hydrogen is an electropositive adsorbate on carbon, hydrogen termination of the surface results in a dipole layer with the positive end pointing into the vacuum, and an induced accumulation of negative image charge just below the surface. At sites which are denuded of hydrogen, the

neighboring image charge results in an enhanced electric field and a focusing mechanism for electrons ejected from the surface. We note in this context, that the grain boundaries in the phase-pure nanocrystalline films described here constitute a sink for hydrogen which may give rise to the hydrogen-depleted surface sites required by Robertson's model.

Figure 12. The allowed energy levels in a one dimensional quantum well 26.5 eV deep as a function of well width for a particle with effective mass equal to that of the free electron.

It should also be noted that a conducting region 0.25-0.4 nm in width but unbounded in the other two dimensions constitutes a one dimensional quantum well. A simple calculation of the allowed energy wells for such a system as a function of grain boundary width is presented in Fig. 12. For a width of 0.36 nm or less, it is not possible to accommodate the four valence electrons of carbon since the highest state lies in the continuum. For a well width of 0.36 nm, all four valence electrons are in bound states, but the highest lying state is at the bottom of the conduction band, which, depending on the crystal face and adsorbed gas, is within a few tenths of an eV of the vacuum level. Finally, we note that a very thin conducting sheet between insulating media gives rise to a very high field enhancement factor without the need for surface asperities.

SUMMARY

Previous attempts to find correlations between the physical properties of diamond and diamond-like carbon films and their electron emission behavior have been largely unsuccessful. The films studied in this work are not typical of either conventionally grown CVD diamond or diamond-like carbon. They show a clear correlation between film morphology and field-induced electron emission. This grain morphology is associated with a characteristic non-faceted surface topography. Several mechanisms have been presented which are expected to increase the electric field, lower the tunneling barrier, and provide a means for enhancing the interband density of electronic states at the grain boundaries, making the intersection of the grain boundaries with the surface a likely candidate for the electron emission site in these materials.

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REFERENCES

1. D. N. Belton and S. J. Harris, *J. Chem. Phys.* **96**, 2371 (1992); S. J. Harris and D. G. Goodwin, *J. Phys. Chem* **97**, 23 (1993)

2. P. K. Bachmann, H. J. Hagemann, H. Lade, D. Leers, D. U. Weichert, H. Wilson, D. Fournier, and K. Plamann, *Diamond and Related Materials*, **4**, 820 (1995)
3. W. Zhu, G. P. Kochanski, S. Jin, L. Seibles, D. C. Jacobson, M. McCormack, and A. E. White *Applied Phys. Lett.*, **67**, 1157, 1995
4. D. M. Gruen, S. Liu, A. R. Krauss, J. Luo, and X. Pan, *Appl. Phys. Lett.* **64**, 1502 (1994)
5. D. M. Gruen, S. Liu, A. R. Krauss and X. Pan, *J. Appl. Phys.* **75**, 1758 (1994)
6. R. Csencsits, D.M. Gruen, A.R. Krauss and C. Zuiker, *Mat. Res. Soc. Symp. Proc.* **403**, 291 (1996)
7. P.C. Redfern, D.A. Horner, L.A. Curtiss and D.M. Gruen, *J. Phys. Chem.* **100**, 11654 (1996)
8. D.M. Gruen, C.D. Zuiker, A.R. Krauss, and X. Pan, *J. Vac. Sci. Technol.* **A13**, 1628 (1995)
9. D. M. Gruen, A. R. Krauss, C. D. Zuiker, L. Terminello, J. A. Carlisle, I. Jiminez, D. G. J. Sutherland, D. K. Shuh, W. Tong, and F. J. Himpsel, *Appl. Phys. Lett.* **68**, 1640 (1996)
10. C. D. Zuiker, A. R. Krauss, D. M. Gruen, J. A. Carlisle, L. J. Terminello, S. A. Asher, and R. W. Bormett. *Mat. Res. Soc. Proc.* **437**, 211 (1996)
11. R. Csencsits, C.D. Zuiker, D.M. Gruen, A. R. Krauss, *Sol. St. Phenom.* **51-52**, 261 (1996)
12. C.D. Zuiker, D.M. Gruen and A.R. Krauss, *Proc. 187th Symp. Electrochem Soc., Reno Nevada, May 21-26, 1995*
13. Y. Bar-Yam and T. D. Moustakas, *Nature* **342**, 786 (1989)
14. J. Bernholc, A. Antonelli, T. M. Sel-Sole, Y. Bar-Yam, and S. T. Pantelides, *Phys. Rev. B* **61**, 2689 (1988)
15. K. R. Lykke, *Phys. rev. A* **52**, 1354 (1995)
16. R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia National Laboratories Report No. SAND-8215B and SAND 89-8009B
17. A. N. Goyette, J. E. Lawler, L. W. Anderson, D. M. Gruen, T. G. McCauley, D. Zhou, and A. R. Krauss, submitted to *Plasma Sources Science and Technology*, in press
18. A. N. Goyette, J. E. Lawler, L. W. Anderson, D. M. Gruen, T. G. McCauley, D. Zhou, and A. R. Krauss, submitted to *J. Phys. D*
19. C. Wang, A. Garcia, D.C. Ingram, M. Lake, and M.E. Kordesch, *Electron Lett.* **27**, 1459 (1991)
20. N. S. Xu, Y. Tzeng, and R. V. Latham, *J. Phys.* **D26**, 1776 (1993)
21. M. W. Geis, J. C. Twichell, N. N. Efremov, K. Krohn, and T. M. Lyszczarsz, *Appl. Phys. Lett.* **68**, 2294 (1996)
22. E. I. Givargizov, V. V. Shirnov, A. N. Stepanova, E. V. Rakova, A. N. Kiselev, and P. S. Plekhanov, *Appl. Surf. Sci.* **87/88**, 24 (1995)
23. R. Schlessler, M.T. McClure, W.B. Choi, J.J. Hren, and Z. Sitar, *Appl. Phys. Lett.* **70**, 1596 (1997)
24. C. Nützenadel, O.M. Küttel, O. Gröning, and L. Schlapbach, *Appl. Phys. Lett.* **69**, 2662, (1996)
25. J. Bruley, D. B. Williams, J. J. Cuomo and D. P. Pappas, *J. Microscopy* **180**, 22 (1995)
26. J. Robertson and W. I. Milne, *Mat. Res. Soc. Symp* **424**, 381 (1997)
27. F.J. Himpsel, J.A. Knapp, J.A. Van Vechten and D.E. Eastman, *Phys. rev. B* **20**, 624 (1979)
28. C. Bandis and B.B. Pate, *Appl. Phys. Lett.* **69**, 366 (1996)]
29. W.B. Choi, M.T. McClure, R. Schlessler, Z. Sitar and J.J. Hren, *J. de Physique IV* **6**, C5-97 (1996)
30. J. Robertson, *Phys. Rev. B*, in press
31. C. D. Zuiker, D. M. Gruen and A. R. Krauss, *J. Appl. Phys.* **79**, 3541 (1996)
32. O. Gröning, O.M. Küttel, E. Schaller, P. Gröning, and L. Schlapbach, *Applied Physics Letters*, **69**, 476 (1996)
33. T.G. McCauley, T.D. Corrigan, A.R. Krauss, O. Auciello, D. Zhou, D.M. Gruen, D. Temple, R.P.H. Chang, S. English, and R. Nemanich, In press: *Proc. Mater. Res. Soc. 1997 Fall Meeting, Boston, MA Dec. 1-5, 1997*
34. P. Keblinsky, D. Wolf, S. Philpott, and H. Gleiter, *J. Mater. Resch.*, in press