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Characterization of copper-diamond (100), (111), and (110) interfaces: Electron affinity and Schottky barrier

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In this study ultraviolet photoemission spectroscopy was employed to correlate the electron affinity and Schottky barrier height of Cu films on type-IIb (p-type) diamond (100), (111), and (110) surfaces. Furthermore, field emission measurements were correlated with the effective electron affinity of the samples. Prior to deposition the diamond samples were cleaned by various annealings and plasma treatments in ultrahigh vacuum. Annealing the diamond substrates to 1150 °C resulted in adsorbate-free surfaces with a positive electron affinity. A negative electron affinity (NEA) was induced after depositing 1 Å of Cu on the clean surface. The Schottky barrier heights for the clean surfaces ranged from 0.30 eV for the (111) surface to 0.70 eV for the (100) surface. Depositing Cu onto H-terminated surfaces exhibiting a NEA still resulted in a NEA on all surfaces. However, the Schottky barrier heights were larger, ranging from 0.50 eV for the (111) surface to 0.90 eV for the (100) and (110) surfaces. The metal-induced NEA has been found to be stable to exposure to air. Following a 500 °C annealing an oxygen-terminated (100) surface with a positive electron affinity was obtained. Cu deposition resulted in a positive electron affinity and the largest Schottky barrier height with 1.60 eV. A field emission threshold field of 79 V/μm was obtained for an oxygen-terminated diamond (100) surface. Values of 20, 25, and 53 V/μm were measured for Cu on clean, H- and O-terminated surfaces, respectively. Based on these experiments, it is suggested that chemisorbed species such as H or O on diamond surfaces cause an increase in the Schottky barrier as well as in the field emission threshold field after Cu deposition. [S0163-1829(98)04627-X]

I. INTRODUCTION

The properties of metal-diamond interfaces are of interest for possible applications in electronic devices based on diamond. Previous studies have reported Ohmic and rectifying characteristics on oriented as well as polycrystalline diamond surfaces.[1–9] Diamond has also been considered for cold cathode electron-emission applications.

Copper is of interest since it exhibits a fcc crystal structure with a close lattice match with diamond [$a(\text{dia}) = 3.567$ Å, $a(\text{Cu}) = 3.615$ Å]. Epitaxial deposition of Cu on diamond (100) surfaces has been reported.[10] There have also been attempts to grow heteroepitaxial diamond on copper. In addition, the relatively low work function of Cu (4.48 eV) could enable the formation of a negative electron affinity (NEA) on diamond surfaces prepared with different surface terminations.

To understand both rectifying and Ohmic contacts it is necessary to determine the Schottky barrier height of the metal-semiconductor interface. Because current-voltage characteristics of metal-semiconductor junctions often exhibit high ideality factors, these measurements are often not suitable to obtain the Schottky barrier height. Photoemission spectroscopy has been employed successfully to determine the Schottky barrier height of metal-diamond interfaces.[11–19]

It has been found that in some instances diamond exhibits a negative electron affinity. This situation implies that electrons in the conduction band can be emitted directly into vacuum without overcoming an energy barrier. In essence the electron affinity of a semiconductor represents the band offset between free electrons in the vacuum and the conduction band of the semiconductor and a NEA represents the situation when the vacuum level is situated below the conduction-band minimum. Photoemission has been found to be a very sensitive technique to distinguish between a NEA or positive electron affinity.

Prior studies have shown that deposition of a few angstrom of a metal such as Ti, Ni, Co, Cu, or Zr on diamond can induce a NEA.[11–19] In particular it has been found that thin layers of Ti or Ni on clean (111) surfaces resulted in a NEA. Reports of preliminary studies of films of Cu, Co, and Zr on diamond have also indicated the possibility of a NEA and these results suggested that the initial diamond surface preparation played a role in the effect. Furthermore, lower Schottky barrier heights have been reported for metal films deposited on adsorbate-free surfaces than for surfaces terminated by species such as hydrogen or oxygen.

Interfaces between metals and semiconductors can be described in general by different models. An ideal metal-semiconductor interface is often described by the Schottky-Mott model, also called the work-function model. Then for a p-type semiconductor the Schottky barrier height is described by[20]

$$\Phi_B = E_G - (\Phi_M - \chi), \tag{1}$$

where E_G is the band gap and χ the electron affinity of the semiconductor and Φ_B is the metal work function. Other models are based on interface dipoles.[20]

A theoretical study of Cu on clean and H-terminated diamond (111) surfaces has been presented by Lambrecht.[21] A value of the Schottky barrier height of less than 0.1 eV was predicted for the most stable configuration for the clean sur-

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face, whereas a Schottky barrier of greater than 1.0 eV was calculated for Cu on a hydrogenated surface.

The formation of a cold cathode structure will typically require a field emission structure. In the experiments described here, field electron emission measurements are obtained by bringing a metal anode in close proximity to the sample and applying a bias between the two. Then the emission current vs applied voltage is recorded. The mechanism for field emission is more complicated than for photoemission spectroscopy. Here the injection of electrons into the semiconductor, the transport of these electrons through the bulk to the emitting surface, and the actual emission from the surface into vacuum need to be considered. Consider the case of a NEA surface. If the field emitted electrons are emitted from the conduction-band minimum then the electrons do not encounter a barrier when leaving the surface. The field electron emission would be limited only by the injection and transport processes.

For the diamond (111) 1×1:H surface simultaneous photoemission and field emission measurements have been reported.[22] This surface exhibits a NEA, but it was found that the field emitted electrons originated from the valence band. Assuming this is the case, then the electrons still may have to overcome (or tunnel through) a surface barrier when being emitted into vacuum even for a NEA surface. A NEA would only contribute to lowering this surface barrier, but may not entirely remove it.

We report here a comprehensive study of thin Cu films deposited on diamond (100), (111), and (110) surfaces. Before deposition the diamond surfaces have been cleaned by various annealing and plasma cleanings. These treatments result in surfaces terminated with oxygen, hydrogen, or free of surface adsorbates. The surface properties were analyzed before and after Cu deposition. The UV photoemission results are employed to understand the relationship of the Schottky barrier height with the presence of a NEA. In addition, the results from UV photoemission and field electron emission are compared.

II. EXPERIMENTAL DETAILS

Natural type-IIb single-crystal semiconducting, boron-doped diamond (100), (111), and (110) substrates were used. Typical resistivities of these samples were $10^4\ \Omega$ cm. The wafers were $3\times3\times0.25\ \text{mm}^3$ in size and were polished with 0.1-μm diamond grit.

An electrochemical etch has been employed to remove nondiamond carbon and metal contaminants.[23,24] After the wet chemical etch the substrates were blown dry with N_2, mounted on a Mo holder, and transferred into the ultrahigh vacuum (UHV) system. This UHV system consists of several chambers connected by a UHV transfer system. These capabilities include annealing, H plasma treatment, metal deposition, angle-resolved ultraviolet photoemission spectroscopy, Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED).

To study the effect of surface preparation on the characteristics of copper-diamond interfaces three different *in situ* cleaning processes were used. Each of these treatments was employed on the diamond substrates before copper deposition. One procedure included an annealing to 500 °C for 10 min. Another involved annealing the substrates to 1150 °C for 10 min. The base pressure in the annealing chamber was 1×10^{-10} Torr and rose to 8×10^{-10} and 7×10^{-9} Torr during the 500 °C and 1150 °C annealings, respectively. The temperature was measured using an optical pyrometer focused on the Mo plate holding the sample. The third surface cleaning process consisted of a H plasma exposure. During this process the sample was held at 500 °C. The H plasma was remotely excited by a rf induction coil. Remote excitation results in significantly lower ion and electron densities at the surface of the samples. The details of the plasma system have been discussed previously.[25] The surface morphology was characterized with atomic force microscopy (AFM). Linear grooves ~20 Å in depth were detected on the diamond substrates. These are attributed to the polishing process with diamond grit.

The photoemission spectra were excited with He I (21.21-eV) radiation. A 50-mm VSW HAC50 hemispherical analyzer with an energy resolution of 0.15 eV and an acceptance angle of 2° was employed to measure the emitted electrons. A bias of up to 1 V was applied to the sample to overcome the work function of the analyzer. This enabled the detection of the low-energy electrons emitted from the NEA surfaces. These electrons appear as a sharp peak at the low-energy end of ultraviolet photoemission spectroscopy (UPS) spectra. The position of this feature corresponds to the energy position of the conduction-band minimum.[17]

Photovoltaic effects may cause shifts in the UPS spectra, especially for wide-band-gap semiconductors such as diamond or for low-temperature measurements.[27] These effects have been demonstrated recently for the diamond (111) surface.[28] These shifts are, however, uniform for the entire spectrum and the relative distance between the valence-band maximum and the low-energy cutoff will not change.

For p-type semiconductors such as diamond, the Schottky barrier height, Φ_B, is determined by the difference between the position of the valence-band maximum of the semiconductor and the Fermi level of the metal. See Ref. 11 for more details on obtaining the Schottky barrier from UPS spectra of metal-diamond interfaces.

Field emission measurements were carried out in a separate vacuum chamber with a base pressure of 2×10^{-8} Torr. The I-V characteristics were determined by applying a bias of 0–1100 V between the sample and a 2-mm-diam stainless-steel anode with a rounded tip. A Keithley 237 source-measuring unit was employed for the I-V measurements. The distance between the sample and the anode could be varied in vacuum by a stepper motor. Typical distances were 2–30 μm.

Cu films of 1, 2, 3, 6, and 10 Å thickness have been deposited by electron-beam evaporation. AES was employed to confirm the presence of a Cu layer. Following each deposition step the samples were characterized by means of UPS. In the metal deposition chamber the pressure was 1×10^{-10} Torr and the pressure rose to 8×10^{-9} Torr during deposition. The growth rate was determined by a quartz crystal monitor. Typical values were ~0.1 Å/s for thicknesses up to 3 Å and ~0.2 Å/s for thicknesses of 6 and 10 Å. Most of the samples were held at room temperature during deposition. To check if the morphology or epitaxy of the Cu films depended on the substrate temperature during deposition, some samples were heated to 500 °C during Cu overgrowth. We also studied the effects of air exposure on the samples. For this purpose the UPS measurements were repeated on samples that were taken out of the UHV system. It was of particular technological interest to determine whether the NEA characteristics of some samples would be stable in air.

III. RESULTS

A. Diamond surfaces

The photoemission of diamond surfaces has been reported elsewhere but is briefly summarized here.[1,26,29–33] Consider first the termination of the surfaces before Cu deposition. Annealing the C(100) samples to 500 °C does not significantly reduce the oxygen peak in the AES spectra and the LEED measurements indicated a 1×1 unreconstructed or bulk pattern. After annealing to 1150 °C the oxygen feature could no longer be detected, a 2×1 LEED pattern is observed, and the surface is presumed clean of adsorbates. A H-terminated 2×1 surface could be induced by H plasma exposure either after the 500 °C or after the high-temperature anneal. The electron affinity was deduced from the UPS measurements. An electron affinity of $\chi=0.7$ eV was found for the adsorbate-free and of $\chi=1.45$ eV for the oxygen-terminated surfaces. A NEA was detected subsequent to the H plasma exposure. In addition, an emission feature at 0.4 eV below the conduction-band minimum (E_C) was observed in the spectrum of the H-terminated surface. It was suggested that this feature could be due to emission sites near the conduction band or due to spatial variations in the surface Fermi level.

For the diamond (111) samples, annealing to 1050 °C results in an adsorbate-free surface with a 2×1 LEED pattern. A positive electron affinity of $\chi=0.5$ eV was measured from the UPS spectra. A H plasma cleaning results in a NEA. These results are consistent with previous studies on surface cleaning and UV photoemission measurements of diamond (111) samples.[1,2,4] Following the H plasma exposure, we also measured emission at 0.4 eV below E_C.

For the diamond (110) surfaces, an adsorbate-free surface was observed after a 1150 °C annealing. The UPS indicated a positive electron affinity of $\chi=0.7$ eV. After a H plasma exposure the UPS indicated a NEA and again the low-energy end of the spectrum extended to 0.4 eV below E_C.

B. Copper on diamond

Subsequent to depositing 1 Å of Cu onto the clean (100) surface, the width of the photoemission spectrum increased consistently with a NEA (Fig. 1). A bulk feature of the diamond (labeled B) was used as a point of reference to determine shifts of the spectra. The error in determining the position of feature B was typically 0.1 eV. After the initial 1-Å deposition, the spectrum was observed to shift by 0.3 eV to lower energies with respect to the Fermi level. The energy difference between feature B and the valence-band maximum was observed to be unchanged. This difference is expected to remain constant for thicker copper layers. The spectral shift is indicative of a change in Fermi level pinning at the surface. As the Cu thickness is increased, the emission from the copper d bands is observed and the Fermi level is easily detectable. A Schottky barrier height of $\Phi_B=0.70$ eV was determined from the UPS spectra. This value remained constant for the different thicknesses of the Cu films. Thus the pinning position of the Fermi level did not change with the thickness of the Cu layer. The thicker layers of Cu up to 10 Å still resulted in a NEA; however, the intensity of the low-energy emission was reduced. In addition, the bulk features of diamond became less pronounced with increased Cu coverage.

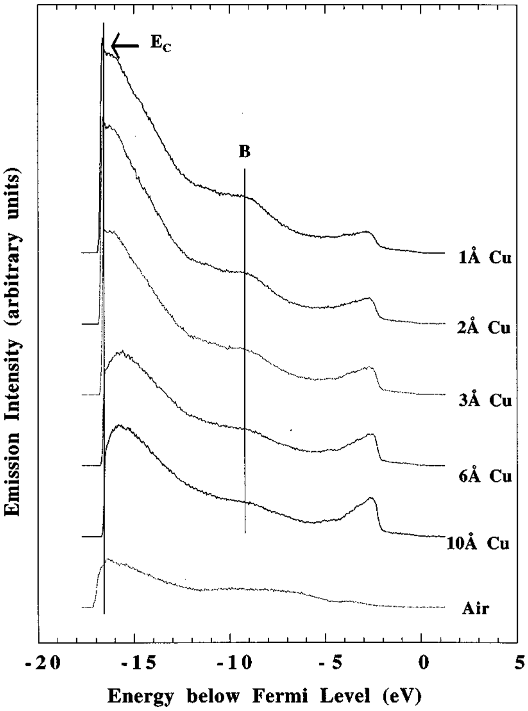

FIG. 1. UV photoemission spectra of copper on a clean diamond (100) surface. The diamond surface exhibits a positive electron affinity before Cu deposition. Subsequent to Cu deposition the width of the spectrum increases and a NEA is detected. After air exposure the NEA is still observed.

For the H-terminated (100) surface the NEA peak was still observed after Cu deposition for all Cu thicknesses. However, the peak intensity continued to decrease with increasing Cu coverage. In addition, the emission below E_C was reduced with increasing thickness of the Cu film until it was no longer detected for a thickness of 10 Å of Cu. In fact, the low-energy cutoff was reduced by 0.4 eV in the spectra for 10 Å of Cu as compared to 1 Å of Cu. The Schottky barrier height was found to be $\Phi_B=0.90$ eV and the shift in the spectra following metal deposition was 0.6 eV towards lower energies.

In comparison to Cu on the clean and H-terminated C(100) surfaces, 1 Å of Cu on the oxygen-terminated (100) surfaces resulted in a positive electron affinity (Fig. 2). The electron affinity was, however, reduced from $\chi=1.45$ eV for the oxygen-terminated surface to $\chi=0.75$ eV after Cu deposition. The spectrum was observed to shift by 0.6 eV to lower energies. A value of 1.60 eV was determined for the Schottky barrier height. The intensity of the bulk diamond features decreased for increasing thickness of the Cu layers. LEED patterns could still be observed following deposition.

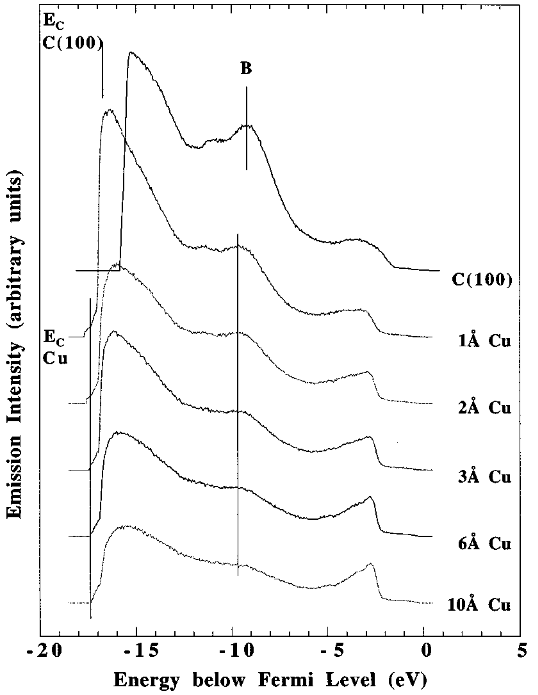

FIG. 2. UV photoemission spectra of copper on an oxygen-terminated diamond (100) surface. The diamond surface exhibits a positive electron affinity prior to Cu deposition. Subsequent to Cu deposition the width of the spectrum increases somewhat, but the spectra still exhibit a positive electron affinity.

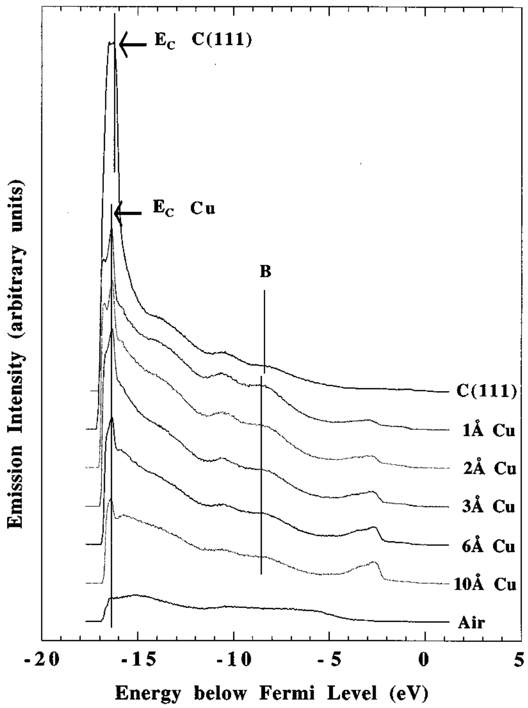

FIG. 3. UV photoemission spectra of copper on a hydrogen-terminated diamond (111) surface. The diamond surface exhibits a NEA before Cu deposition. Also emission below E_C is detected. Following Cu deposition the NEA is still observed; however, the emission below E_C gets reduced with increasing thickness of Cu. After air exposure the NEA is still detected.

Depositing Cu on the clean (111) surface did not result in a shift of the UPS spectra. The low-energy edge of the spectrum extended to lower energies, consistent with a NEA. The NEA was still observed for 10-Å-thick Cu films, however, with decreased intensity. A Schottky barrier of $\Phi_B = 0.30$ eV was measured, which did not change for increasing thickness of the Cu films.

After depositing Cu onto the H-covered (111) surface, the UPS spectra still indicated the presence of a NEA, even for 10-Å-thick layers (Fig. 3). However, the emission below decreased significantly with increasing Cu coverage and was no longer observable for 10 Å of Cu. The spectra shifted 0.2 eV to lower energies upon Cu deposition and a Schottky barrier of $\Phi_B = 0.50$ eV was determined. The Cu-on-diamond films exhibited 1×1 LEED patterns.

Similar to the (100) and (111) samples, the deposition of Cu on the clean (110) surface resulted in the indication of a NEA that was still observable for 10-Å-thick films (Fig. 4). A shift of 0.2 eV to lower energies due to Cu was determined and the Schottky barrier was deduced to be $\Phi_B = 0.60$ eV.

Corresponding to the (100) and (111) surfaces, the NEA peak could still be detected after deposition of Cu onto the H-terminated (110) surface, even for layers of 10 Å in thickness. A shift in the spectra of 0.6 eV was observed following Cu deposition. Also the low-energy cutoff shifted, reducing the width of the spectrum by 0.4 eV for the thick Cu layers. Subsequent to Cu deposition LEED patterns were still detected.

Consider the case of Cu deposition on clean diamond (100) substrates at 500 °C (Fig. 5). Deposition of 1 Å of Cu resulted in a shift of the spectra by 0.1 eV to lower energies. While the width of the spectrum increased, only weak emission was detected at the energy position of the conduction-band minimum. Subsequent to depositing more Cu an additional increase in the width of the spectrum consistent with a NEA was observed. For 10-Å-thick layers of Cu, the spectra still indicated a NEA. The spectra shifted by an additional 0.2 eV and the measured Schottky barrier height of $\Phi_B = 0.75$ eV corresponds to the value obtained for Cu deposition on the clean diamond (100) surface at room temperature. 1×1 LEED patterns were detected from the Cu-on-diamond films. All UPS results are summarized in Table I.

We have previously reported that 300 and 2000 Å of Cu deposited on diamond (100) substrates at 500 °C exhibited 1×1 LEED patterns. By using AFM, islands oriented with respect to the substrate were detected.[10] In particular well-defined islands about 10000×5000 Å^2 in size were observed for the 2000-Å-thick Cu layers. By means of Rutherford backscattering we have confirmed that these Cu films were epitaxial.[10]

AFM scans of the diamond surfaces before Cu deposition exhibited linear grooves parallel to each other. These features are attributed to the polishing process with diamond grit. Consider first the Cu layers on diamond deposited at room temperature. After depositing 2 Å of Cu on diamond no islands could be resolved by AFM [Fig. 6(a)]. Following the overgrowth of 6 Å of Cu, islands of about 50 Å in diameter were detected on the grooves of the diamond substrate [Fig. 6(b)]. For a 40-Å-thick Cu layer, islands ~100–200 Å in size were observed [Fig. 6(c)] and LEED did not show clear diffraction patterns for 40 Å of Cu deposited at

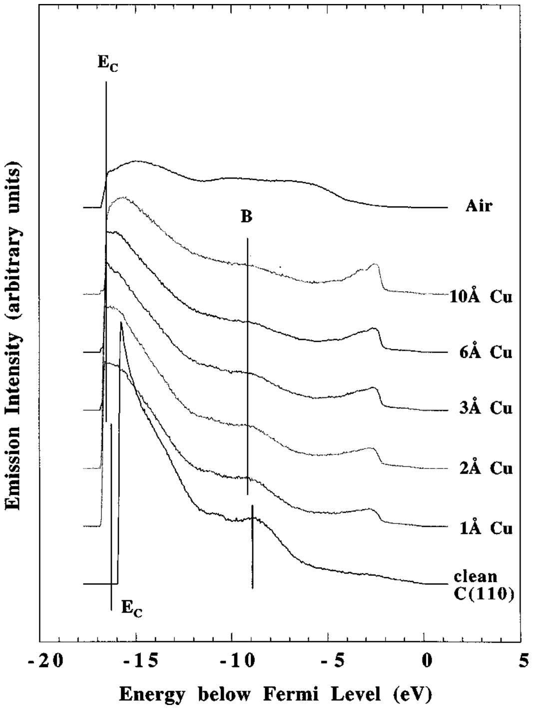

FIG. 4. UV photoemission spectra of copper on a clean diamond (110) surface. The diamond surface exhibits a positive electron affinity before Cu deposition. Subsequent to Cu deposition the width of the spectrum increases and a NEA is detected. After air exposure the NEA is still observed.

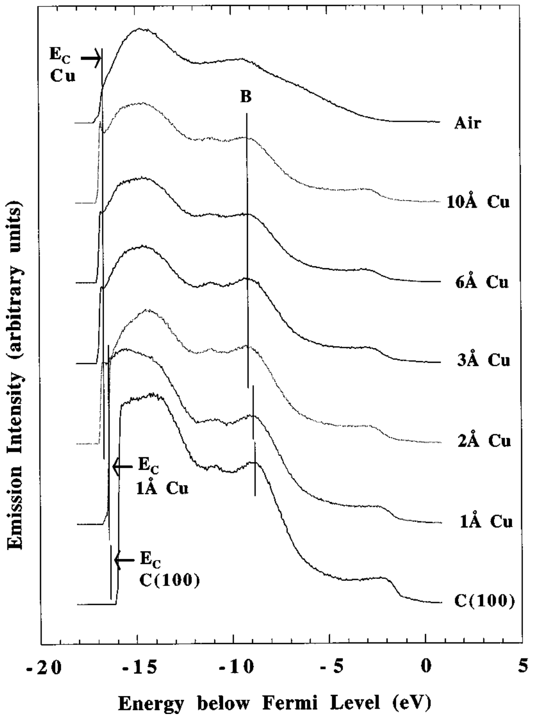

FIG. 5. UV photoemission spectra of copper on a clean diamond (100) surface. The substrate was kept at 500 °C during Cu deposition. The diamond surface exhibits a positive electron affinity before Cu deposition. Subsequent to Cu deposition the width of the spectrum increases and a NEA is detected. After air exposure the NEA is still observed.

room temperature. For the case of Cu grown at 500 °C islanding could be observed after 2 Å had been deposited [Fig. 7(a)]. The islands were ~50–100 Å in size. An AFM scan after 100 Å of Cu on diamond deposited at 500 °C displayed oriented islands about 500–1000 Å in size. The islands were oriented along the ⟨110⟩ directions of the underlying diamond (100) substrate [Fig. 7(b)]. The observation of oriented islands is an indication of epitaxial alignment. LEED patterns could be detected for 2 and 100 Å of Cu deposited at 500 °C.

The samples of Cu on both clean and H-terminated diamond (100), (111), and (110) surfaces were exposed to air and reintroduced for UPS measurements. Even after air exposure, the width of the UPS spectra still corresponded to a NEA. However, the intensity of the low-energy emission was reduced. Such a reduction in intensity may be consistent with the presence of physiadsorbed species that are expected to be on the surface from the air exposure. Indeed, AES scans indicated the presence of oxygen following air exposure.

C. Field emission results

Field emission measurements were performed on diamond (100) and (110) samples and on the 10-Å-thick Cu films deposited on clean, hydrogen-terminated, or oxygen-terminated diamond (100) surfaces. The I-V data for Cu on the hydrogen-terminated diamond surface is shown in Fig. 8. For the measurements presented here, the emission threshold voltage has been defined to corresponded to a current of 0.1 μA. This is necessary since the measured current-voltage curves did not exhibit an absolute threshold. Oftentimes the voltage per micrometer is also called the average field. The average field emission threshold field and corresponding standard deviation were calculated from the values of the emission threshold voltage for different distances. For the distances used here, it was found that the average field was relatively independent of distance.

The results and the standard deviations for the different surface terminations are summarized in Table II. Thresholds between 25 and 81 V/μm were determined. For the oxygen-terminated diamond (100) and (110) surfaces values of 79 and 81 V/μm were measured, respectively. The hydrogen-terminated diamond (110) surface exhibited a lower value of 25 V/μm. It needs to be noted that oxygen-terminated diamond surfaces exhibit a positive electron affinity while hydrogenated diamond surfaces show NEA characteristics.

Consider now Cu deposited on diamond surfaces. The lowest threshold of 25 V/μm was obtained for Cu deposited on the clean surface. The next highest value of 35 V/μm was measured for Cu on the hydrogen-terminated surface. These two surfaces also exhibited a NEA as determined from UPS spectra. For Cu on the oxygen-terminated surface, the measurements indicated the highest value of 53 V/μm for the different Cu-diamond surfaces. Note that the surface exhibited a positive electron affinity.

These results indicate that surfaces exhibiting a NEA also exhibit a lower field emission threshold than those with a positive electron affinity. The threshold value decreased with decreasing electron affinity. Since the actual value of the electron affinity cannot be determined by UPS for a NEA,

TABLE I. Summary of the UPS measurements. PEA, positive electron affinity; NEA, negative electron affinity. Also the values of the electron affinity χ calculated according to the work-function model are listed. The error margins are 0.1 eV.

Sample surface	UPS before Cu growth	UPS after Cu growth	NEA stable in air	Calculated χ (eV)
C(100)				
clean	PEA, $\chi = 0.7$ eV	NEA, $\chi < 0$, $\Phi_B = 0.70$ eV, 0.3-eV shift	yes	−0.20
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.90$ eV, 0.6-eV shift	yes	0
O terminated	PEA, $\chi = 1.45$ eV	PEA, $\chi = 0.75$ eV, $\Phi_B = 1.60$ eV, 0.6-eV shift		0.70
C(111)				
clean	PEA, $\chi = 0.5$ eV	NEA, $\chi < 0$, $\Phi_B = 0.30$ eV, no shift	yes	−0.20
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.50$ eV, 0.2-eV shift	yes	0
C(110)				
clean	PEA, $\chi = 0.7$ eV	NEA, $\chi < 0$, $\Phi_B = 0.60$ eV, 0.2-eV shift	yes	−0.40
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.90$ eV, 0.6-eV shift	yes	−0.10
C(100)		deposition at 500 °C		
clean	PEA, $\chi = 0.7$ eV	NEA, $\chi < 0$, $\Phi_B = 0.75$ eV, 0.3-eV shift	yes	−0.15

we may correlate the threshold field with the Schottky barrier height of the Cu-diamond interfaces. From Table II it is evident that the threshold field does decrease with declining values of the Schottky barrier height.

The values for the field emission threshold reported here are of the same order of magnitude as previously reported for diamond samples.[34,35] The data from the field emission measurements have been fit to the Fowler-Nordheim equation[36]

$$I = k\left(\frac{\beta V}{d}\right)^2 \exp\left(\frac{-6.530 d \varphi^{3/2}}{\beta V}\right), \tag{2}$$

where I is the current in amps, V is the bias in volts, d is the distance between the sample and the anode in microns, k is a constant, φ is the Fowler-Nordheim barrier height in eV, and β is the field enhancement factor. For perfectly flat surfaces β is equal to 1 and can be neglected. It should be noted that different surface terminations could lead to changes in the actual work function and therefore give the appearance of different β values. In our case the rms roughness of the diamond surfaces as well as the metal films on diamond was of the order of a few angstroms. We therefore do not expect the surface roughness to have a significant impact on the field electron measurements. Based on this consideration, a value of 1 has been assumed for β. The Fowler-Nordheim barrier heights φ were obtained by fitting the field emission data to Eq. (2). Figure 9 shows this fitting of the field emission data for Cu on the hydrogen-terminated surface. The fitted graphs exhibit different slopes, which correspond to different distances between the anode and the sample. After correcting for the distance, the curves all resulted in about the same value for the effective barrier height. The values and the standard deviations are listed in Table II.

IV. DISCUSSION

From the UPS spectra of the diamond surfaces before copper deposition different Fermi level positions were determined for the different surface terminations. Values between 0.3 and 0.4 eV were measured for $E_F - E_V$ for the clean or hydrogen-terminated surfaces. This corresponds to the position of the boron impurities in the band gap. Furthermore, it did not appear to change for the (100), (111), and (110) surface orientations. A larger value of 1.0 eV for $E_F - E_V$ due to surface pinning was found for oxygen termination. After copper deposition the position of the Fermi level increased, except for the clean (111) surface where no change has been found. The observed increase in $E_F - E_V$ corresponded to shifts to lower energies in the spectra of the same magnitude. The Schottky barrier height of copper on clean surfaces was determined to be about 0.2–0.3 eV, smaller than for copper on hydrogen-terminated surfaces with the same orientation.

For photoemission of thin metal layers (less than the electron mean free path) on semiconductors, the electron affinity can be expressed in terms of the metal work function and the Schottky barrier formed with a p-type semiconductor according to Eq. (1):[20] The model assumes that the structure can be characterized with two interfaces: vacuum-metal and metal-diamond.

Using the band gap of diamond $E_G = 5.47$ eV, the work function of Cu for the (100) surface $\Phi_M = 4.59$ eV, and the measured Schottky barrier height, the electron affinity can be calculated [see Eq. (1) and Fig. 10]. For the clean surface a value of the electron affinity $\chi = -0.2$ eV is obtained while 0 and 0.7 eV are obtained for the hydrogen- and oxygen-terminated surfaces, respectively. These results are consistent with observing a NEA for Cu on the clean (100) surface and a positive electron affinity of $\chi = 0.75$ eV for Cu on the surface covered with oxygen.

For the H-terminated surface a NEA was detected. The question may be asked whether the observation reflects the properties of the Cu-diamond (100) interface or the initial H termination of the diamond (100) surface. Subsequent to deposition of 10 Å of Cu the NEA peak was still measured and the width of the spectra was reduced by 0.4 eV. This spectral change is inconsistent with a superposition of the substrate H induced NEA and the spectra of the Cu layer. We

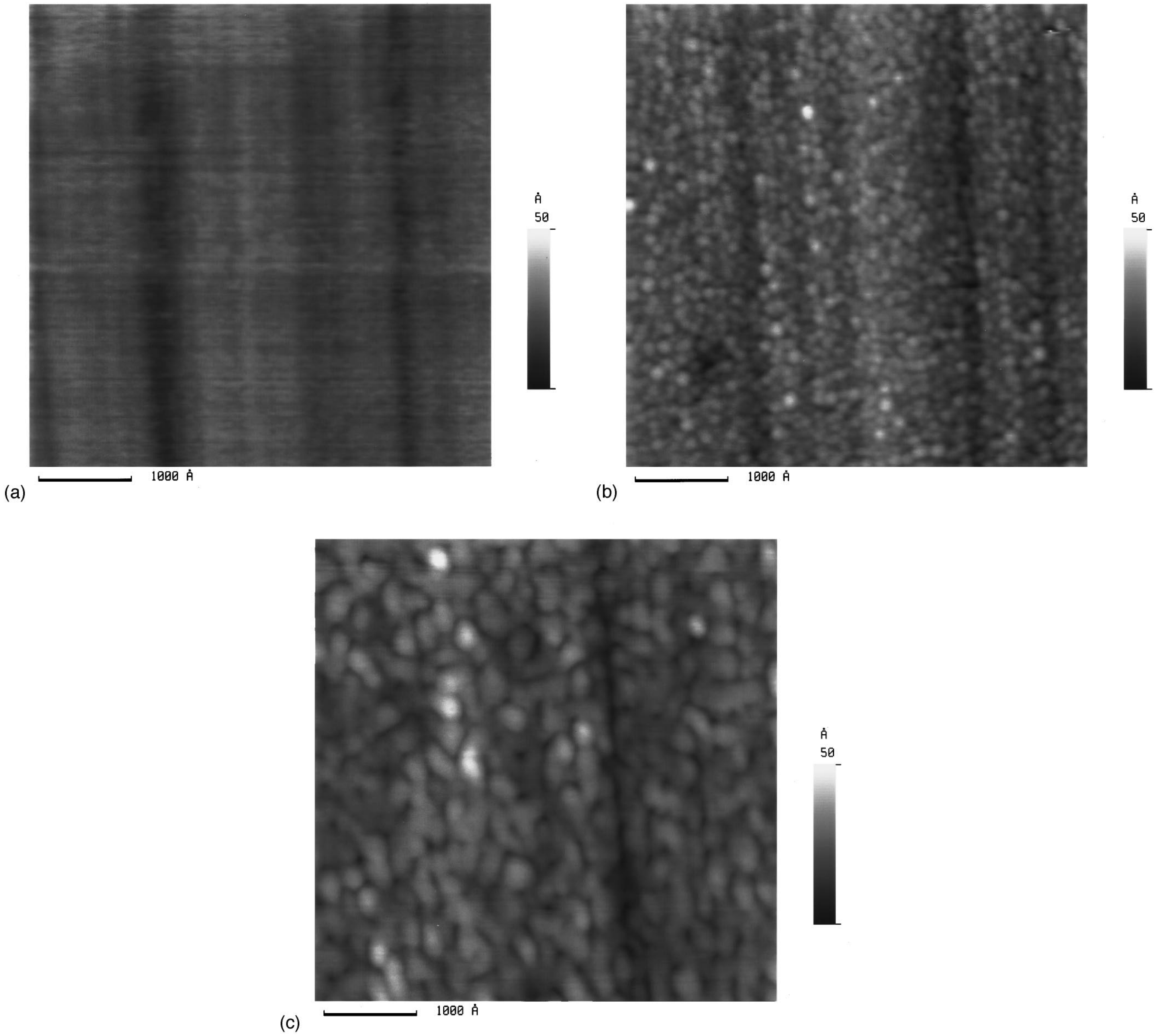

FIG. 6. (a) Atomic force micrograph of 2 Å of Cu on diamond. No island formation is resolved on the polishing groves of the diamond substrate. (b) AFM scan of 6 Å of Cu on diamond. Islands ~50 Å in diameter are observed. (c) AFM scan of 40 Å of Cu on diamond. Islands ~100–200 Å in size are detected.

therefore suggest that the Cu-diamond (100) interface itself exhibits a NEA. The calculated value of $\chi = 0$ eV is still in essential agreement with measuring a NEA after Cu deposition.

Applying this model to Cu on the (111) surface and assuming a work function of $\Phi_M = 4.94$ eV, we calculate values of $\chi = -0.2$ and 0 eV for the clean and H-terminated surfaces, respectively. Similar to the (100) surface, this is in agreement with observing a NEA for the clean surface. It may also be consistent with measuring a NEA for the surface covered with hydrogen. In the same manner using the work function of Cu, $\Phi_M = 4.48$ eV for the (110) surface, we obtain electron affinities of $\chi = -0.4$ eV for Cu on clean and $\chi = -0.1$ eV for Cu deposited on H-terminated samples. Both values are consistent with the experimentally observed NEA from these surfaces. These values for the electron affinity are summarized in Table I.

Also it has been reported that carbon contaminations can lower the work function of Ni.[37] The first layer of Ni deposited on diamond may have a different work function due to the carbon of the diamond. This effect may also occur for Cu on diamond, but such an effect would only lead to a larger calculated reduction of the electron affinity for Cu on the clean and H-terminated surfaces. This would be consistent with our results. For Cu on the oxygen-terminated surface the measured and calculated values for the electron affinity are consistent with each other. Thus, at least for the latter case this effect is not expected to be significant.

Previously Eq. (1) has been used successfully to relate the electron affinity and Schottky barrier of Ti, Ni, Co, Cu, and Zr deposited on diamond.[11–19] In these studies it has been found that the Schottky barrier height for clean surfaces was

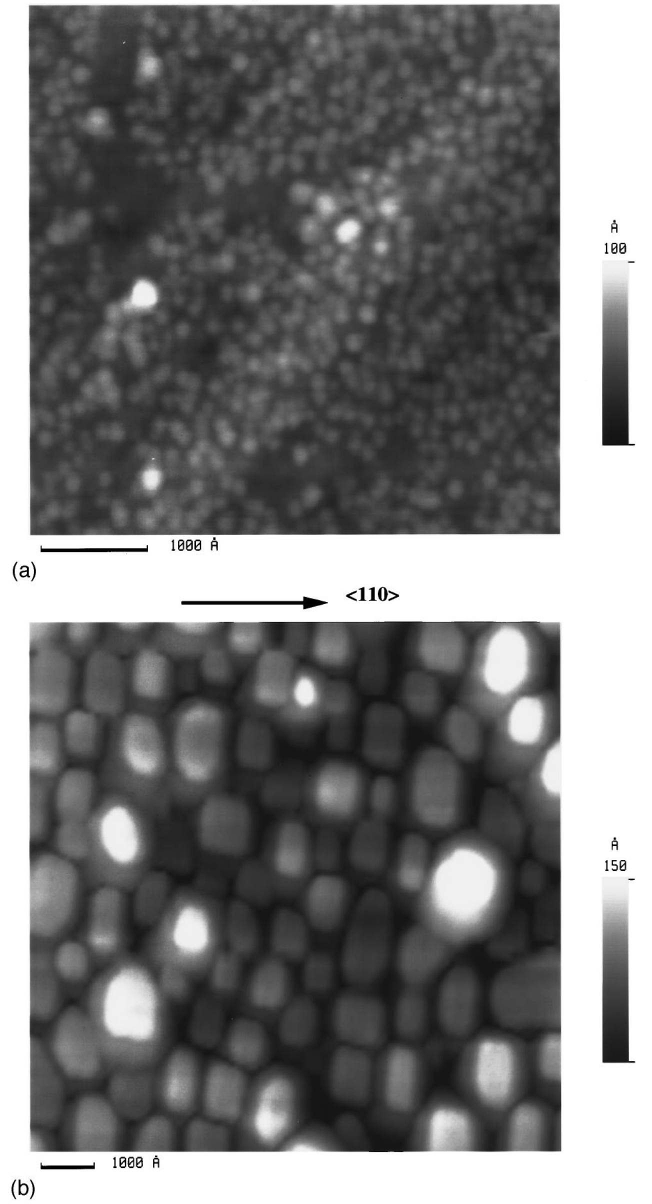

FIG. 7. (a) AFM scan of 2 Å of Cu on diamond deposited at 500 °C. Islands ~50–100 Å in size are detected. (b) AFM scan of 100 Å of Cu on diamond deposited at 500 °C. Oriented islands ~500–1000 Å in size are detected. The islands are oriented along the ⟨110⟩ directions of the underlying diamond (100) substrate.

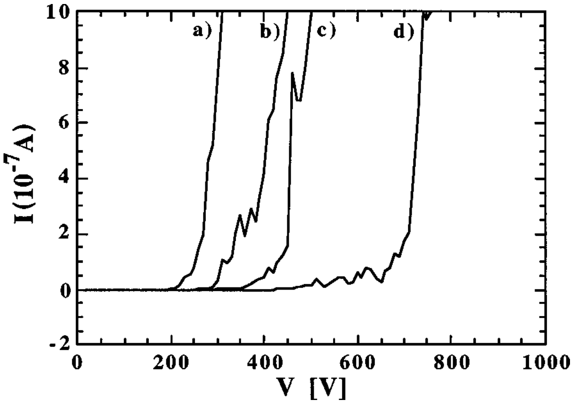

FIG. 8. Field emission current-voltage curves for Cu on a hydrogen-terminated type-IIb single-crystal diamond (100) sample. The distances between the sample and the anode are; (a) 5.4 μm, (b) 8.8 μm, (c) 13.2 μm, and (d) 26.4 μm.

lower than for surfaces terminated by oxygen or hydrogen. Indeed, metal-diamond interfaces exhibiting a NEA have a lower Schottky barrier height than those exhibiting a positive electron affinity. Surface preparation apparently has a significant impact on the properties of the interface subsequent to metal deposition.[11–19] For Ni deposited on clean (111) surfaces a NEA has been observed.[12] In comparison, for Ni on H-terminated (111) surfaces, a positive electron affinity and a larger Schottky barrier height were measured. Erwin and Pickett[38–41] and Pickett, Pederson, and Erwin[42] calculated a Schottky barrier height of less than 0.1 eV for the most stable configuration for Ni on clean (100) and (111) surfaces. A theoretical study of Cu on the (111) surface by Lambrecht[21] considered different interface structures. For the clean surface the tetrahedral position for the Cu atoms was found to be most favorable energetically. This structure led to a Schottky barrier height of less than 0.1 eV. In comparison, for the in-hollow position a Schottky barrier of 0.5 ±0.2 eV was calculated. These results indicate a strong dependence of the Schottky barriers on the actual interface formation. The formation energies are somewhat different with 2.3 ± 0.5 J/m^2 for the tetrahedral structure and 3.8 ± 0.5 J/m^2 for the in-hollow position. Taking these uncertainties into account, the values for the formation energies may be quite similar. The value of 0.3 eV for the Schottky barrier of Cu on the clean diamond (111) surface measured in our study does fall between the values for the two geometries considered in the calculations and it may be suggested that both geometries actually form at the interface.

For Cu on the H-terminated (111) surface Lambrecht calculated a Schottky barrier greater than 1.0 eV. This value is considerably larger than the measured value of 0.5 eV from our experiments. The Schottky barrier measured for Cu on the H-terminated surface is, however, larger than the value measured for the clean (111) surface. One explanation may be that the Cu-diamond interface was not completely H saturated. Portions of the interface could be adsorbate free. Therefore, the measured Schottky barrier would be an average of the values from different interface structures. We did, however, observe a NEA following the H plasma clean and it is questionable whether significant portions of the (111) surface would remain adsorbate free after a H plasma exposure. It is also possible that H may have been displaced from the interface during the Cu deposition.

Overall for the (100), (111), and (110) surfaces the Schottky barrier increases from the clean surface to the H-terminated surface. For the oxygen-terminated (100) surface an even greater Schottky barrier has been measured and the value of the electron affinity is correlated with the Schottky barrier. Metal-diamond interfaces exhibiting a lower Schottky barrier also exhibit a lower electron affinity. The surface termination of the diamond substrate before metal deposition is important for determining the properties of the metal-diamond interface. In order to obtain a minimum for the Schottky barrier and the electron affinity, a surface treatment removing surface chemisorbed species is necessary.

In a previous study of Ti on diamond it has been found that the metal-induced NEA peak was significantly reduced

TABLE II. Results of electron emission measurements. PEA, positive electron affinity; NEA, negative electron affinity. The error margins for χ and Φ_B from the UPS measurements are 0.1 eV. The averages and standard deviations of the field emission measurements at different distances are shown as the field emission threshold and the Fowler-Nordheim barrier height. The threshold current is 0.1 μA.

Sample	UPS	Field emission threshold (V/μm)	Fowler-Nordheim barrier height (eV)
C(100)	oxygen terminated PEA, $\chi = 1.4$ eV	79 ± 7	0.23 ± 0.01
Cu/C(100) clean	NEA, $\chi < 0$, $\Phi_B = 0.70$ eV	25 ± 3	0.10 ± 0.01
Cu/C(100) hydrogen	NEA, $\chi < 0$, $\Phi_B = 0.90$ eV	35 ± 4	0.15 ± 0.02
Cu/C(100) oxygen	PEA, $\chi = 0.75$ eV, $\Phi_B = 1.60$ eV	53 ± 4	0.21 ± 0.01

once the uniform metal film reached several angstroms in thickness. In particular, the intensity was reduced by about 50% for an increase in the thickness of the Ti layer from 2 to 3 Å.[11] Only electrons from within a few scattering lengths of the surface will get emitted into vacuum and can be detected. In our study we have determined reductions by about 10% for an increase in the Cu thickness from 2 to 3 Å. We have also observed island formation for the Cu layers by AFM. This is consistent with a NEA peak still being more pronounced for thicker Cu films than for the case of uniform Ti layers.

For 1 Å of Cu deposited onto clean surfaces at room temperature strong NEA-type emission could be clearly observed. However, 1 Å of Cu deposited onto a clean surface at 500 °C resulted in only very little intensity at the position of the conduction-band minimum. Only after 2 Å of Cu was a clear NEA feature detected. This can be correlated with the stronger tendency of islanding for deposition of up to 2 Å of Cu at 500 °C, as observed by AFM. For 1 Å of Cu deposited

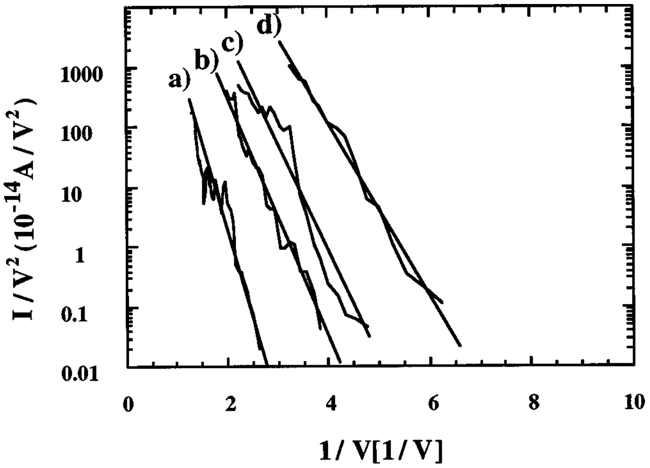

FIG. 9. Fitting field emission current-voltage curves [for Cu on a hydrogen-terminated type-IIb single-crystal diamond (100) sample] to the Fowler-Nordheim equation. The distances between the sample and the anode are (a) 5.4 μm, (b) 8.8 μm, (c) 13.2 μm, and (d) 26.4 μm.

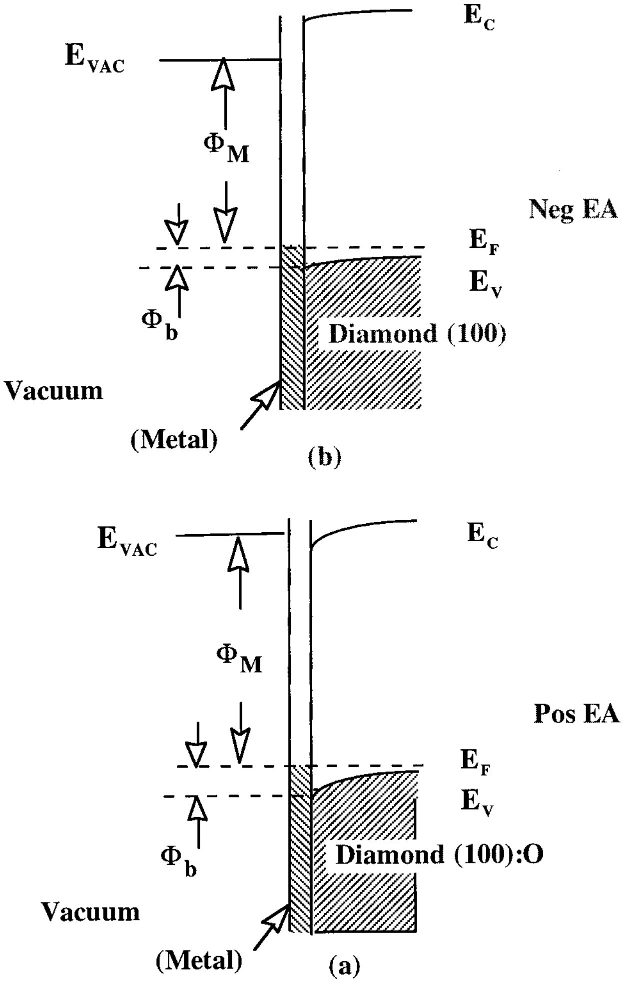

FIG. 10. Band diagrams of the copper-diamond interface. For copper on the oxygen terminated surface (a) the sum of the Schottky barrier height and work function for metal on diamond is greater than the band gap of diamond resulting in a positive electron affinity. For copper on the clean or hydrogenated surface (b) the Schottky barrier height added to the metal work function is less than the diamond band gap. This corresponds to a NEA.

at 500 °C only a few islands would be expected to form. We found that already for 2 Å of Cu deposited at 500 °C the islands were higher than the electron mean free path ($\leqslant 5$ Å). Electrons originating from the buried interface could not get emitted. Only NEA effects from around the edges of the islands could be detected. This would result in NEA emission from only a small fraction of the surface area. This is consistent with the very weak NEA emission observed by UPS. For further Cu deposition a larger number of islands would be formed. This would be expected to lead to an increase in the NEA emission intensity. For Cu deposited on clean diamond substrates at room temperature no island formation has been detected up to 2 Å. This would correspond to a larger part of the surface area exhibiting a NEA for 1 Å of Cu. For more than 2 Å of Cu a large number of islands were observed and again NEA emission would occur from a significant part of the surface. These considerations are in agreement with our observations from the UPS spectra.

We have found that a few angstroms thick Cu films deposited on diamond at room temperature exhibit LEED patterns corresponding to the orientation of the underlying surface. For thicker Cu layers (40 Å) the diffraction patterns faded. The first few monolayers of Cu on the different diamond surfaces are apparently epitaxial. This could be correlated with the fcc lattice structure of Cu and the close lattice match with diamond. In comparison, Cu deposited while the substrates were held at 500 °C resulted in LEED patterns even for the thickest films grown [100 and 2000 Å (Ref. 10)]. AFM scans of thick Cu films [100 and 2000 Å (Ref. 10)] showed islands oriented with respect to the underlying diamond substrates and Rutherford backscattering experiments[10] confirmed that the Cu films grow epitaxially with the diamond.

It is significant that the copper on diamond samples with a NEA retained this characteristic following air exposure. We also found that the NEA characteristics of hydrogenated diamond surfaces were somewhat stable in air. However, a deterioration of this NEA effect was observed over a relatively short period of time, resulting eventually in a positive electron affinity. The NEA effect of copper-coated diamond surfaces was not found to exhibit such a deterioration. A corresponding air stability of the NEA characteristics was observed for Co or Zr on diamond surfaces.[19] The air stability may be important for the development of cold cathode devices stable in a technical vacuum and may also simplify their production process.

Lower field emission thresholds have been observed for p-type diamond surfaces with a lower electron affinity. For Cu on the clean surface or for hydrogen-terminated diamond the lowest field emission values have been found, 25 V/μm. The experiments presented here were on similarly prepared natural diamond surfaces with a low surface roughness particularly as compared to diamond films. The roughness of the surfaces before and after metal deposition was comparable and of the order of a few angstroms. The field enhancement factor β may not be expected to be significantly different for the various surfaces considered. While field emission is often described by the Fowler-Nordheim expression, it should be noted that this expression was derived for emission from metal surfaces, assuming no field inside the bulk of the material. An equation for microscopic dielectric regions has been proposed,[43] but this approach would not be a reasonable model for our case with a diamond substrate thickness of 0.25 mm.

Bandis and Pate[22] have performed simultaneous field emission and photoemission measurements from (111) 1×1:H natural p-type diamond to determine the origin of the field emitted electrons. This surface exhibited a NEA that allowed the determination of the position of the conduction-band minimum. They report that the electrons due to field emission originate from the valence-band maximum.

The diamond samples used in our study were p type also. Electrons that originate from the conduction-band minimum can freely leave a NEA surface. This is the case for electrons detected in UPS measurements. From our results we expect the energy of the vacuum level for Cu on clean and H-terminated surfaces to be near the conduction band of the diamond. Then even for a small NEA, the field emitted electrons would have to overcome a significant barrier at the surface to be emitted into vacuum, assuming that they came from the valence-band maximum. Inducing a NEA on a positive electron affinity diamond surface would then reduce the surface energy barrier but not entirely remove it for field emitted electrons. The actual reduction of this surface barrier may still have a significant impact on the field emission results. Considering the case of depositing copper onto an oxygen-terminated diamond surface, the lowering of the field emission threshold from 79 to 53 V/μm may be attributed to the measured reduction of the electron affinity from 1.4 eV for an oxygen-terminated surface to 0.75 eV for Cu on this surface. Deposition of copper onto a clean or a hydrogen-terminated diamond surface results in even lower values for the field emission threshold. This may be due to lower values for the electron affinity. The threshold value is the smallest for copper on clean diamond surfaces. In addition, for this case the NEA is expected to be the most negative, as calculated from the Schottky barrier height (see Table I). This is consistent with the correlation of the lowering of the field emission threshold with the reduction in electron affinity and correspondingly in surface energy barrier height.

Both the UPS and field emission measurements show consistent trends for Cu on the clean and H- and O-terminated surfaces. The lowest Schottky barrier heights and lowest electron affinities have been found for Cu on the clean surfaces. The same is the case for the lowest field emission threshold fields. Whereas interfacial hydrogen or oxygen caused all these values to increase. The barrier for field emission is, however, expected to be near the band-gap value of the diamond while significantly lower values were deduced from the field emission. This substantial difference may be an indication that $\beta=1$ is an incorrect assumption or other aspects affect the field emission.

V. CONCLUSIONS

In this study UV photoemission and field emission have been employed to characterize the copper-diamond (100), (111), and (110) interfaces. The lowest values for the Schottky barrier height were obtained for copper deposited on adsorbate-free surfaces. Hydrogen at the interface led to an increase in Schottky barrier height. The highest value of the Schottky barrier was obtained for an oxygen-terminated surface. The measured values were consistent with a theoretical model for Cu on the clean and hydrogen-terminated (100) surface. A NEA was detected for thin layers of copper deposited on clean and H-terminated surfaces. The NEA was found to be stable in air. A lower Schottky barrier height generally leads to a lower electron affinity. The results were consistent with a model in which the Cu-diamond structure was described in terms of the measured Schottky barrier and the Cu work function appropriate to the surface. From the field emission measurements it was observed that metal deposition tends to lower the threshold field compared to the oxygen-terminated diamond surface. The lowest value was measured for Cu on the clean diamond surface. Surface cleaning of the diamond samples before metal deposition is therefore suggested to be critical in determining the Schottky barrier height and thus the electron emission properties. From field emission and photoemission measurements it can be deduced that a lowering in field emission threshold is correlated with a reduction in the electron affinity. Photoemitted electrons originate from the conduction-band minimum while the results indicate that field emitted electrons are emitted from the valence-band maximum for *p*-type diamond.

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