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Electron affinity and Schottky barrier height of metal-diamond (100), (111), and (110) interfaces

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The electron emission properties of metal-diamond (100), (111), and (110) interfaces were characterized by means of UV photoemission spectroscopy (UPS) and field-emission measurements. Different surface cleaning procedures including annealing in ultrahigh vacuum (UHV) and rf plasma treatments were used before metal deposition. This resulted in diamond surfaces terminated by oxygen, hydrogen, or free of adsorbates. The electron affinity and Schottky barrier height of Zr or Co thin films were correlated by means of UPS. A negative electron affinity (NEA) was observed for Zr on any diamond surface. Co on diamond resulted in NEA characteristics except for oxygen-terminated surfaces. The lowest Schottky barrier heights were obtained for the clean diamond surfaces. Higher values were measured for H termination, and the highest values were obtained for O on diamond. For Zr, the Schottky barrier height ranged from 0.70 eV for the clean to 0.90 eV for the O-terminated diamond (100) surface. Values for Co ranged from 0.35 to 1.40 eV for clean- and O-covered (100) surfaces, respectively. The metal-induced NEA proved to be stable after exposure to air. For the oxygen-terminated diamond (100) surface a field-emission threshold of 79 V/ μ m was measured. Zr or Co deposition resulted in lower thresholds. Values as low as 20 V/ μ m were observed for Zr on the clean diamond (100) surface. Results for Zr or Co on H- or O-terminated surfaces were higher. H or O layers on diamond tend to cause an increase in the Schottky barrier height and the field-emission threshold field of Zr- and Co-diamond interfaces. The value of the electron affinity and Schottky barrier were correlated with work function and different initial surface preparation. The results were largely consistent with a model in which the vacuum level was related to the metal work function and the measured Schottky barrier. © 1998 American Institute of Physics. [S0021-8979(98)03604-4]

I. INTRODUCTION

Metal-diamond interfaces may be useful for potential applications in electronic devices based on diamond. These may include metallic surface coatings exhibiting a negative electron affinity (NEA) for use in cold cathode devices, or for more traditional electronic devices, carrier injecting or rectifying electrical contacts will be necessary. For these applications, a fundamental understanding of the Schottky barrier and the relationship to the vacuum level is necessary.

Ultraviolet photoemission spectroscopy (UPS) can be used to measure Schottky barrier heights of rectifying contacts. The technique can even be employed for accurate measurements of contacts with high ideality factors, for which I-V measurements would be unsuitable. UPS is also very sensitive to determine whether a surface exhibits a NEA. Electrons from the valence band are photoexcited into states in the conduction band and some will quasithermalize to the conduction-band minimum. Indeed, these secondary electrons can escape freely from a NEA surface. The spectra then exhibit a sharp feature at the low-kinetic-energy end of the photoemitted electrons.^{1,2} By means of UPS the surface emission properties can be characterized independent of carrier injection and conduction mechanisms.

Field-emission measurements integrate the effects of injecting electrons into the semiconductor, transporting the carriers through the bulk and emission from the surface into vacuum. To facilitate these measurements a bias is applied between a metal anode and the sample. Then the emission current is detected.

It has been reported that depositing a few Å of metals like Ti, Ni, Cu, Co, or Zr on diamond can to induce a NEA.^{3–8} The presence of a NEA or positive electron affinity has been correlated with different structures of the metal– diamond interface. Indeed, metal–diamond interfaces exhibiting a NEA have been found to exhibit lower Schottky barrier heights than those exhibiting a positive electron affinity.

The primary focus of this paper is on the relationship of the vacuum level to the diamond conduction band when thin metal layers are deposited on the surface of the diamond. The configuration may be modeled as two separate interfaces, namely the vacuum-metal and metal-diamond interfaces. For very thin metal layers, electrons could travel through the metal layer without scattering. Thus, the Schottky barrier height of the metal-diamond interface plays a critical role in determining the relationship of the diamond conduction band and the vacuum level and whether the structure exhibits a NEA.

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A number of studies have dealt with Schottky barrier height measurements of metals deposited on (100)- and (111)-oriented diamond surfaces as well as polycrystalline diamond films.^{1,5–19} It has been found that the Schottky barrier height of metals on diamond is virtually independent of the work function of the metal. But, it has been reported that the Schottky barrier height clearly depends on the surface treatment of the diamond surfaces chemically in air results in a higher value for the Schottky barrier height than cleaning in vacuum. For Cu, it has also been observed that a reduction in the field-emission threshold is correlated with a lowering in electron affinity.⁵

Zirconium has been chosen since the material exhibits a low work function which may be useful for inducing a NEA. It is also in the same column of the periodic table as Ti, and the Ti-diamond interface has been studied previously. Ti has been found to be reactive with C and O. Cobalt is next to nickel and copper in the periodic table. The work function of Co (5.0 eV) is higher than for Zr (4.05 eV) or Ti (4.33 eV)and comparable to Ni (5.04-5.35 eV) and Cu (4.48-4.65 eV). Another aspect that is important is that Co may be less reactive than Zr or Ti.

Various approaches may be used to model metal– semiconductor interfaces. The Schottky–Mott model describes an ideal interface, assuming that the difference between the metal work function and the electron affinity of the semiconductor does not change during interface formation. For a p-type semiconductor one can write

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

where Φ_B is the Schottky barrier height, E_G is the band gap, Φ_M is the metal work function, and χ the electron affinity of the semiconductor.

In many instances the Schottky–Mott model is not realized in practice. For instance, an insulating layer or an interface reaction may cause a high density of interface states in the semiconductor band gap. This may result in pinning of the Fermi level, and the Schottky barrier height is then independent of the metal work function.

Thin metal films (less than the electron mean-free path) can be thought of as a dipole layer on the semiconductor surface. For such a structure to exhibit a NEA the conduction-band minimum has to lie above the vacuum level. Adsorbates or states on the semiconductor surface prior to metal deposition as well as the metal itself may have an impact on whether the metal–semiconductor interface exhibits a NEA or a positive electron affinity.

In this study, results are described for thin Zr or Co films deposited on diamond (100), (111), and (110) surfaces. Prior to metal deposition, different *in vacuo* cleaning procedures were employed to obtain clean, hydrogen-terminated or oxygen-terminated diamond surfaces. Subsequent to Zr or Co deposition, the effects of the different surface treatments on the Zr– or Co–diamond interface were examined. In particular, the results of UV photoemission and field electron emission were correlated. The results were compared to previous reports on the properties of thin metal layers on diamond.

II. EXPERIMENTAL DETAILS

Several natural-type-IIb *p*-type (boron-doped) semiconducting single-crystal diamond (100), (111), and (110) crystals $(3.0 \times 3.0 \times 0.25 \text{ mm})$ were employed. Typical resistivities were $10^4 \ \Omega$ cm. To remove nondiamond carbon and metal contaminants an electrochemical etch has been employed.²⁰ This cleaning step involved placing the diamond samples between two Pt electrodes in deionized water as an electrolyte. A dc voltage of 350 V was applied between the electrodes. A typical value for the current was 0.5 mA. The crystals were then exposed to UV/ozone and rinsed in a HF solution to clean the surface from SiO₂ contaminants. It has previously been reported that SiO2 was present on the surface after an electrochemical etch.²¹ Small amounts of these contaminants may be released into the water from the ion exchanger matrix. Subsequent to the wet chemical cleaning step the samples were blown dry with N₂, mounted on a Mo holder and then transferred into the loadlock of the ultrahigh-vacuum (UHV) system. This UHV system consists of several interconnected chambers including capabilities for annealing, H-plasma cleaning, metal deposition, angleresolved ultraviolet photoemission spectroscopy (ARUPS), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED).

Three different in vacuo cleaning procedures were employed to assess the influence of surface preparation on the properties of the metal-diamond interfaces. One procedure involved annealing the samples to 500 °C for 10 min while another included a 1150 °C anneal for 10 min. An optical pyrometer was used to measure the temperature of the Mo holder on which the samples were mounted. During the anneals the pressure increased to 8×10^{-10} Torr and 7 $\times 10^{-9}$ Torr, respectively. The third surface cleaning procedure consisted of an exposure to a remotely excited rf H plasma. The plasma cleaning chamber has been described in an earlier report.²² The remote plasma process results in significantly lower electron and ion densities at the surface of the sample. This reduces the possibility of damaging the surface. Atomic force microscopy (AFM) was employed to characterize the morphology of the diamond samples. Linear groves of ~ 20 Å in depth were detected on the diamond substrates. These are attributed to the polishing process with 0.1 μ m diamond grit.

The photoemission spectra were excited by HeI (21.21 eV) radiation. A 50 mm VSW HAC50 hemispherical analyzer was employed to measure the emitted electrons. In this study, the energy resolution was 0.15 eV and the acceptance angle was 2°. To overcome the work function of the analyzer a bias of 2 V was applied to the sample. It was, therefore, possible to detect the low-energy electrons emitted from the NEA surface. These electrons appear as a sharp peak at the low-energy end of the UPS spectra. The position of this feature corresponds to the energy position of the conduction-band minimum, E_C (Fig. 1). Electrons emitted from E_C appear at $E_V + E_G$ in the spectra, where E_V is the energy of the valence-band maximum and E_G the band-gap energy. Electrons from E_V get photoexcited to an energy level at $E_V + h\nu$ in the conduction band and are then detected at E_V



FIG. 1. Schematic diagram of photoemission spectra for a negative electron affinity surface (dotted line) and a positive electron affinity surface (solid line).

 $+h\nu$ in the UPS spectra. This corresponds to the highkinetic-energy end of the spectra. Therefore, the spectral width for a NEA surface is $h\nu - E_G$. Using the value of $h\nu = 21.21$ eV for HeI radiation and $E_G = 5.47$ eV for the band gap of diamond, a spectral width of ~ 15.7 eV is obtained. For a surface with a positive electron affinity, the low-energy cutoff is determined by the vacuum level and will, therefore, be shifted to higher energies in the spectra compared to the case of a NEA surface. This results in a smaller value for the spectral width.

Photoemission spectra can also be used to determine the Schottky barrier height Φ_B . For *p*-type semiconductors like diamond, Φ_B corresponds to the difference between the position of the valence-band edge E_V of the semiconductor and the Fermi level of the metal E_F (Fig. 2). Since features from both the semiconductor and the metal need to be visible, this method is only suitable for metal films with thicknesses equal to or less than the electron mean-free path (≤ 5 Å). The relatively weak onset of emission at E_V may, however,



FIG. 2. Schematic diagram of photoemission spectra for copper deposited on diamond. The Schottky barrier height Φ_B is determined from the difference between the position of the valence-band edge of diamond E_V and the metal Fermi-level E_F .

be obscured by the metal Fermi level even for metal layers thinner than the mean-free path. As an independent method E_V can be referenced to some strong features in the diamond spectrum before metal deposition. These features can still be detected following the overgrowth of a thin metal layer. Here, we have chosen a peak positioned 8.3 eV below E_V . In the case of a NEA, the position of the low-energy turn-on (which corresponds to E_C) can also be used as a reference point to find E_V (which is the high-energy turn-on of the spectrum). The distance between E_C and E_V has to be $h\nu$ $-E_G$ (Fig. 2). A change in band bending (e.g., due to metal deposition) can be detected as a shift of the spectrum with respect to the Fermi level. Again, since the position of E_V may be difficult to discern, such a shift can be detected from the position of bulk features in the spectra.

The UPS spectra of wide-band-gap semiconductors may be shifted due to photovoltaic effects.²³ A recent study showed such shifts for diamond (111) surfaces.²⁴ However, these shifts are uniform for the entire spectrum. This means that the relative distance between the Fermi level and the valence-band maximum will not change.

A separate vacuum chamber with a base pressure of $\sim 2 \times 10^{-8}$ Torr was used to carry out the field-emission measurements. To determine the I-V characteristics a bias of 0-1100 V was applied between the sample and a 2 mm diam stainless-steel anode with a rounded tip. The I-V measurements were conducted with a Keithley 237 source measure unit. The distance between the sample and the anode could be varied in vacuum by means of a stepper motor. The distances ranged from 2 to 30 μ m. The mechanism of electron emission by field emission is more complex than by photoemission spectroscopy. With photoemission, only the emission properties of the surface are characterized. The samples only need to be sufficiently electrically conducting to avoid charging due to electron emission. For field emission, injection of electrons from an electrical contact into the semiconductor, transport of the electrons through the bulk to the emitting surface, and the emission from the surface into vacuum contribute to the overall emission properties.

An e-beam evaporator has been employed to deposit Co or Zr films of 1, 2, 3, 6, and 10, Å thicknesses onto the diamond (100), (111), and (110) surfaces. Before deposition, the metal sources were melted to clean surface contaminants from the source material. The thickness was monitored by a quartz-crystal oscillator. The growth rate was 0.1 Å/s up to 3 Å in thickness and 0.3 Å/s for 6 and 10 Å in thickness. The deposition was done at room temperature. The base pressure in the chamber was 1×10^{-10} Torr and the pressure rose to 5×10^{-9} Torr during deposition. The samples were characterized before and after metal deposition using ARUPS, AES, LEED, and AFM. The UPS measurements were also repeated following air exposure of the metalized diamond samples. This was done to examine whether the NEA characteristics were stable in air. Such an air stability would be of technological interest.

The presence of a zirconium or cobalt layer was confirmed by AES. AFM images of the diamond wafers used in this study clearly showed arrays of linear grooves parallel to each other. Typical depths of about 20 Å were observed for these grooves. This surface structure is due to the commercial surface polishing of the diamond samples. For metal thicknesses of 1 and 2 Å, the Zr layers replicated the surface morphology of the underlying diamond substrates as observed by AFM. For thicker layers nonuniform growth was detected. Similar characteristics were observed for Co.

III. RESULTS

A. Diamond surfaces

We first consider the properties of the diamond (100), (111), and (110) surfaces before Co or Zr deposition. Diamond (100) samples annealed to 500 °C exhibited a 1×1 LEED pattern and an AES oxygen feature. An 1150 °C anneal or a H-plasma exposure resulted in 2×1 reconstructed surfaces and the removal of oxygen according to AES. As evidenced by the UPS spectra, the surfaces annealed to 500 and 1150 °C showed a positive electron affinity of 1.45 and 0.75 eV, respectively. A NEA was induced by the H-plasma clean.

For diamond (111) surfaces, annealing to 1150 °C or exposure to a H plasma resulted in a 2×1 LEED pattern and caused the amount of surface oxygen contaminants to drop below the detection limit of the AES system. By means of UPS a positive electron affinity around 0.55 eV was measured for the 1150 °C anneal and a NEA was determined for the H-plasma clean.

A 700 °C anneal or a H-plasma removed the oxygen from the diamond (110) surfaces according to AES, and NEA characteristics as evidenced by UPS. Subsequent to a 1150 °C anneal the NEA was removed and a positive electron affinity of 0.55 eV was determined. Another H-plasma clean resulted in a NEA again.

Furthermore, emission below the conduction-band minimum was observed for (100), (111), and (110) surfaces following a H-plasma treatment.

All of these results are consistent with previous studies on surface cleaning and UPS measurements of diamond (100), (111), and (110) surfaces.^{1,2,25–28} In particular, the effect of emission below the conduction-band minimum for H-terminated surfaces has been discussed in a recent report.²⁸

B. Zirconium on diamond

The deposition of 1 Å of Zr onto clean diamond (100) surfaces resulted in an increase in the width of the photoemission spectrum consistent with a NEA. The energy between the bulk feature from the diamond (labeled B) and the valence-band maximum did not change subsequent to 1 Å of Zr deposition [Fig. 3(a)]. This energy is expected to remain constant for thicker Zr layers. Feature B is used as a point of reference to determine whether there is a shift in the spectra after metal deposition or other processing. This shift is indicative of a change in Fermi-level pinning in the gap. Thicker layers of Zr up to 10 Å still resulted in a NEA, however, the intensity of the spectrum was reduced. A Schottky barrier height of $\Phi_B = 0.70 \text{ eV}$ was determined from the UPS spectra. This value remained constant for the different thicknesses of the Zr films. The Fermi-level pinning did not change with increasing thickness of the Zr layer. Also, the bulk features of the diamond became less intense with increased Zr coverage.

Zr deposition on H- and O-terminated (100) surfaces resulted in NEA characteristics, too [Figs. 3(b) and 3(c)]. Schottky barrier heights of $\Phi_B = 0.75$ eV and $\Phi_B = 0.90$ eV were measured, respectively.

Subsequent to depositing Zr onto clean (111) surfaces, a Schottky barrier height of $\Phi_B = 0.85 \text{ eV}$ and a NEA were measured [Fig. 3(d)]. These characteristics did not change for increasing Zr thickness.

A NEA was still observed after growing Zr on the Hterminated (111) surface, even for a 10 Å thick film. A Schottky barrier height of $\Phi_B = 0.95 \text{ eV}$ and a shift in the spectra of 0.6 eV were measured upon Zr deposition.

Corresponding to (100) and (111) surfaces, a NEA was observed following Zr deposition on both the clean and H-terminated (110) surfaces. A Schottky barrier height of $\Phi_B = 0.70 \text{ eV}$ was determined for both the clean and H-covered surface. The low-energy edge of the spectra extended to below the conduction-band minimum.

In several cases an additional feature was observed at the low-energy end of the spectrum, especially for 6 and 10 Å thick films. This peak may be attributed to emission from Zr. For Zr on the O-terminated (100) and clean (111) surface the emission extended to 0.5 and 0.6 eV below the conduction-band minimum, respectively. For several cases [see Fig. 3(b), for example] the emission below the conduction-band minimum due to the NEA effect was so strong that it could not be determined whether there was also low-energy emission due to the Zr or not. All these results have been summarized in Table I.

After exposing the samples of Zr on clean, H-, and Oterminated diamond surfaces to air, the width of the UPS spectra still corresponded to a NEA. However, the intensity of the spectra was reduced. Such a reduction in intensity may be consistent with the presence of physiadsorbed species. These are expected to be on the surface due to the air exposure. Indeed, the presence of oxygen was detected by means of AES subsequent to air exposure. Overall, the NEA characteristics proved to be stable following air exposure.

C. Cobalt on diamond

A NEA and Schottky barrier heights of $\Phi_B = 0.35 \text{ eV}$ and $\Phi_B = 0.45 \text{ eV}$ were detected for Co on clean and Hcovered diamond (100) surfaces, respectively. However, a positive electron affinity of $\chi = 0.80 \text{ eV}$, and a Schottky barrier of $\Phi_B = 1.40 \text{ eV}$ were measured for Co on the oxygenterminated (100) surface.

Similar to the (100) surface, NEA characteristics were observed for Co on clean as well as H-terminated (111) and (110) surfaces. Schottky barrier heights between $\Phi_B = 0.40$ and 0.50 eV were measured. In Fig. 4 the UPS spectra of Co on a H-terminated (110) surface are shown as an example. The details of the measurements are listed in Table II. Also, the NEA of the Co-diamond interfaces proved to be stable following air exposure.



FIG. 3(a). UV photoemission spectra of Zr on a clean diamond (100) surface. The diamond surface exhibits a positive electron affinity before Zr deposition. Subsequent to Zr deposition the width of the spectrum increases and a NEA is detected. Emission below E_c is observed. After air exposure the NEA is still observed. (b) UV photoemission spectra of Zr on a hydrogen-terminated diamond (100) surface. The diamond surface exhibits a NEA before Zr deposition. Also, emission below E_c is detected. Following Zr deposition the NEA is still observed, however, the emission below E_c gets reduced with increasing thickness of Zr. After air exposure the NEA is still detected. (c) UV photoemission spectra of Zr on an O-terminated diamond (100) surface. The diamond surface exhibits a positive electron affinity before Zr deposition. Subsequent to Zr deposition the width of the spectrum increases and a NEA is detected. (d) UV photoemission spectra of Zr on a clean diamond (111) surface. The diamond surface exhibits a positive electron affinity before Zr deposition. Subsequent to Zr deposition the width of the spectrum increases and a NEA is detected. After air exposure the NEA is still observed.

D. Field-emission results

Field-emission measurements were performed on diamond (100) and (110) samples as well as on 2 and 10 Å thick Zr or Co films deposited on clean, hydrogen-or oxygenterminated diamond (100) surfaces. The measurements were used to determine the applied voltage per μ m where detectable emission was observed. The voltage per μ m is sometimes termed the average field. Since the measured current–

TABLE I. Summary of the UPS measurements on diamond (100), (111), and (110) surface before and after Zr deposition. PEA: positive electron affinity, NEA: negative electron affinity. Also, the values of the effective electron affinity χ_{eff} calculated according to Eq. (3). The experimental uncertainties are 0.1 eV.

Sample surface	UPS before Zr growth	UPS after Zr growth	NEA stable in air	Calculated $\chi_{\rm eff}$
C(100) Clean H terminated O terminated	PEA, $\chi = 0.75 \text{ eV}$ NEA, $\chi < 0$ PEA, $\chi = 1.40 \text{ eV}$	NEA, $\chi < 0$, $\Phi_B = 0.70 \text{ eV}$, no shift NEA, $\chi < 0$ $\Phi_B = 0.75 \text{ eV}$, 0.3 eV shift NEA, $\chi < 0$ $\Phi_B = 0.90 \text{ eV}$, 0.1 eV shift	Yes Yes Yes	$\chi_{\rm eff}$ =-0.7 eV $\chi_{\rm eff}$ =-0.65 eV $\chi_{\rm eff}$ =-0.5 eV
C(111) Clean H terminated	PEA, $\chi = 0.45 \text{ eV}$ NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.85$ eV, 0.1 eV shift NEA, $\chi < 0$, $\Phi_B = 0.95$ eV, 0.6 eV shift	Yes Yes	$\chi_{\rm eff} = -0.55 \ {\rm eV}$ $\chi_{\rm eff} = -0.45 \ {\rm eV}$
C(110) Clean H terminated	PEA, χ =0.5 eV NEA, χ <0	NEA, $\chi < 0$, $\Phi_B = 0.70$ eV, 0.2 eV shift NEA, $\chi < 0$, $\Phi_B = 0.70$ eV, 0.4 eV shift	Yes Yes	$\chi_{\rm eff} = -0.70 {\rm eV}$ $\chi_{\rm eff} = -0.70 {\rm eV}$

voltage curves did not exhibit an absolute threshold, it was necessary to define the emission threshold voltage per μ m for a specific current, and in this study a value of 0.1 μ A was employed. The I-V data for Zr on the O-terminated diamond surface are shown in Fig. 5. The average field-emission threshold field was calculated from the values for different distances.

Average threshold fields between 20 and 81 V/ μ m were measured for the different surface preparations. A value of 79 V/ μ m was determined for the threshold field of the oxygen-terminated diamond 100 surface. For the oxygenated-C(110) surface a value of 81 V/ μ m was mea-



FIG. 4. UV photoemission spectra of Co on a H-terminated diamond (110) surface. The diamond surface exhibits a NEA before Zr deposition. Also, emission below E_c is detected. Following Zr deposition the NEA is still observed, however, the emission below E_c gets reduced with increasing thickness of Zr.

sured. In comparison, a field-emission threshold of 25 V/ μ m was observed for the hydrogen-terminated-C(110) surface. According to the UPS measurements, oxygen-terminated diamond surfaces exhibit a positive electron affinity while hydrogenated-diamond surfaces show NEA characteristics.

For both Zr and Co deposition the lowest threshold has been obtained for the clean surface, and here average values of 20 and 30 V/ μ m have been determined for Zr and Co, respectively. The next highest values of 23 V/ μ m for Zr and 39 V/ μ m for Co were measured on the hydrogen-terminated surface. Zr or Co films on clean and H-terminated surfaces also exhibited a NEA as determined from the UPS spectra. Higher threshold average field values were obtained for the Co and Zr on the oxygen-terminated diamond. A value of 49 V/ μ m was determined for Zr on the oxygenated surface, and this surface still exhibited a NEA. The Co on the oxygenterminated surface resulted in the highest average field value of 52 V/ μ m for the different metal–diamond interfaces studied here. This surface exhibited a positive electron affinity.

The general trend of the results is that the threshold value decreased with decreasing electron affinity. The surfaces exhibiting a NEA also exhibited a lower field-emission threshold than those with a positive electron affinity. Since the actual value of the electron affinity cannot be determined by UPS, for a NEA one could correlate the threshold with the Schottky barrier height of the Zr-diamond or Co-diamond interfaces. The threshold does decrease with declining values of the Schottky barrier height for both Zr and Co. The results and the standard deviations for the different surface terminations are summarized in Table III.

The values for the field-emission threshold reported here are of the same order of magnitude as previously reported for diamond samples.^{29–31} The data from the field-emission measurements have been fitted to the Fowler–Nordheim equation.³²

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

In this equation, I is the current in amps, V is the bias in volts, d is the distance between the sample and the anode in μ m, k is a constant, φ is the Fowler–Nordheim barrier height

TABLE II. Summary of the UPS measurements on diamond (100), (111), and (110) surfaces before and after Co deposition. PEA: positive electron affinity, NEA: negative electron affinity. Also, the values of the effective electron affinity χ_{eff} calculated according to Eq. (3). The experimental uncertainties are 0.1 eV.

Sample surface	UPS before Co growth	UPS after Co growth	NEA stable in air	Calculated $\chi_{\rm eff}$
C(100) Clean H terminated O terminated	PEA, $\chi = 0.75 \text{ eV}$ NEA, $\chi < 0$ PEA, $\chi = 1.45 \text{ eV}$	NEA, $\chi < 0$, $\Phi_B = 0.35$ eV, no shift NEA, $\chi < 0$, $\Phi_B = 0.45$ eV, 0.15 eV shift PEA, $\chi = 0.80$ eV, $\Phi_B = 1.40$ eV, 0.55 eV shift	Yes Yes	$\chi_{\rm eff}$ = -0.2 eV $\chi_{\rm eff}$ = -0.1 eV $\chi_{\rm eff}$ = 0.90 eV
C(111) Clean H terminated	PEA, χ =0.50 eV NEA, χ <0	NEA, $\chi < 0$, $\Phi_B = 0.40$ eV, no shift NEA, $\chi < 0$, $\Phi_B = 0.50$ eV, 0.1 eV shift	Yes Yes	$\chi_{ m eff}$ =-0.05 eV $\chi_{ m eff}$ =-0.05 eV
C(110) Clean H terminated	PEA, $\chi = 0.6 \text{ eV}$ NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.40 \text{ eV}$, 0.1 eV shift NEA, $\chi < 0$, $\Phi_B = 0.45 \text{ eV}$, 0.1 eV shift	Yes Yes	$\chi_{\rm eff} = -0.10 {\rm eV}$ $\chi_{\rm eff} = -0.05 {\rm eV}$

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 Å. 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 effective barrier heights φ were obtained by fitting the field-emission data to Eq. (3). Figure 6 shows this fitting of the field-emission data for Zr on the clean surface. The fitted graphs exhibit different slopes corresponding to different distances between the anode and the sample. They resulted in about the same value for the Fowler-Nordheim barrier height. The values and the standard deviations are listed in Table III.

IV. DISCUSSION

It was found that the Schottky barrier height of Zr on H-terminated surfaces was about the same or only 0.1 eV higher than for Zr on clean surfaces of the same orientation. In addition, the Schottky barrier height for Zr on the oxygen-



FIG. 5. Field-emission current-voltage curves for Zr on a oxygenterminated type-IIb single-crystal diamond (100) sample. Distances between the sample and the anode: (a) 5.7 μ m, (b) 9.7 μ m, (c) 12.4 μ m, and (d) 17.2 μ m.

ated (100) surface is only 0.2 eV larger than for the clean (100) surface. For Co on diamond, the differences in Schottky barrier height for the H-covered and clean surfaces are comparable to Zr. In contrast, for Co on the oxygenterminated (100) surface, the Schottky barrier height was found to be larger by 1.05 eV than for the Co on the clean (100) surface.

The basic assumption in this study has been that it is necessary to consider both the metal–vacuum and metal–semiconductor interfaces to characterize the photoemission properties. With this in mind, the equation below gives an expression for the effective electron affinity for a thin metal overlayer on a semiconductor. The equation is a function of both the metal work function and the Schottky barrier height for the metal on the *p*-type semiconductor.³³ It is specific for photoemission of thin metal layers (less than the electron mean-free path) on semiconductors:

$$\chi_{\rm eff} = (\Phi_M + \Phi_B) - E_G. \tag{3}$$

With the band gap of diamond $E_G = 5.47 \text{ eV}$, the work function of Zr, $\Phi_M = 4.05 \text{ eV}$ or of Co, $\Phi_M = 5.00 \text{ eV}$ and the measured Schottky barrier height, the effective electron affinities can be calculated using Eq. (3). The results are listed for Zr in Table I and for Co in Table II. In comparing the photoemission measurements, the deduced effective electron affinities are consistent with the photoemission measurements. A NEA was observed for Zr on the clean, H-, and O-terminated diamond surfaces as well as detecting a NEA for Co on clean and hydrogenated-diamond surfaces and a positive electron affinity for the O-terminated surface.

Other effects may contribute to the observations. For instance, it has been reported that carbon contamination can lower the work function of Ni.³⁴ The first layer of Ni deposited on diamond may have a different work function due to an interface reaction or interdiffusion. This effect may also occur for Zr or Co on diamond. But, such an effect could only lead to a stronger NEA for Zr on diamond and Co on the clean and H-terminated diamond surfaces and would be consistent with our results. For Co on the oxygen-terminated surface, the measured and calculated values for the electron affinity are consistent with each other. Thus, at least for the

TABLE III. Results of electron emission measurements. PEA: positive electron affinity, NEA: negative electron affinity. 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 $0.1 \ \mu$ A.

Sample	UPS	Field-emission threshold (V/µm)	Fowler–Nordheim barrier height (eV)
C(100) after 500 °C anneal		79±7	0.23±0.01
	PEA, $\chi \cong 1.4 \text{ eV}$		
Zr/C(100) clean	NEA, $\chi < 0$, $\Phi_B \cong 0.70 \text{ eV}$	20±3	0.09 ± 0.01
Zr/C(100) hydrogen	NEA, $\chi < 0$, $\Phi_B \cong 0.75 \text{ eV}$	23±3	0.11 ± 0.01
Zr/C(100) oxygen	NEA, $\chi < 0$, $\Phi_B \cong 0.90 \text{ eV}$	49±4	0.20 ± 0.01
Co/C(100) clean	NEA, $\chi < 0$, $\Phi_B \cong 0.35 \text{ eV}$	30±3	0.11 ± 0.01
Co/C(100) hydrogen	NEA, $\chi < 0$, $\Phi_B \cong 0.45 \text{ eV}$	39±4	0.16 ± 0.02
Co/C(100) oxygen	PEA, $\chi \cong 0.75 \text{ eV}$, $\Phi_B \cong 1.40 \text{ eV}$	52±4	0.20±0.02

latter case this effect is not expected to be significant. Since all of the Zr-diamond interfaces investigated in our study exhibit a NEA, we cannot determine if such an effect could play a significant role for Zr. But, one effect may give some clues on this issue: For Zr on the O-terminated (100) and clean (111) surface, emission is observed below the conduction-band minimum, especially for 6 and 10 Å thick Zr films. We may suggest that this emission is due to the thin metal layer, and the cutoff is determined by the metal work function. This feature extends to 0.5 and 0.6 eV below the conduction-band minimum, respectively. These values are comparable to the calculated effective electron affinity χ of 0.5 eV for Zr on an oxygenated (100) and 0.55 eV for Zr on a clean (111) surface. From these considerations, the work function of Zr does not appear to be changed.



FIG. 6. Fitting field-emission current–voltage curves (for Zr on a oxygenterminated type-IIb single-crystal diamond (100) sample) to the Fowler– Nordheim equation. Distances between the sample and the anode: (a) 5.7 μ m, (b) 9.7 μ m, (c) 12.4 μ m, and (d) 17.2 μ m.

From results here and previously, Eq. (3) has been used successfully to describe photoemission of Ti, Ni, Co, Cu, and Zr deposited on diamond.^{3–6} In these studies, it has been found that the Schottky barrier height for clean surfaces was



FIG. 7. Band diagrams of the metal-diamond interface. (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 Co on the oxygen-terminated surface). (b) The Schottky barrier height added to the metal work function is less than the diamond band gap. This corresponds to a NEA. (Zr on clean, H- and O-terminated surfaces. Co on clean and H-terminated surfaces.)



FIG. 8. Diagram of the Schottky barrier height vs metal work function for Ti, Zr, Cu, Co, and Ni. The dashed line represents the limit for which a NEA is expected for metal-diamond interfaces according to Eq. (3). Thus, a NEA is expected for data points below this dashed line and a positive electron affinity for those above. The experimental data are plotted for Ti, Zr, Cu, Co, and Ni on diamond surfaces terminated with O, H, or adsorbate free. The filled markers correspond to an experimentally observed NEA and the empty markers indicate an experimentally observed positive electron affinity.

lower than for surfaces terminated by hydrogen or oxygen. Indeed, metal-diamond interfaces exhibiting a NEA have a lower Schottky barrier height than those exhibiting a positive electron affinity. The band schematic of the metal-diamond interface is shown in Fig. 7(a). In Fig. 7(a), the Schottky barrier height is sufficiently small to result in a NEA. Figure 7(b) shows the case for a larger Schottky barrier and a positive electron affinity. Surface preparation apparently has a significant impact on the properties of the interface subsequent to metal deposition.³⁻⁶

There have been several recent theoretical studies of Schottky barriers on diamond. Studies by Erwin and Pickett³⁵⁻³⁸ and Pickett, Pederson, and Erwin³⁹ described two configurations with very similar values for the formation energy for Ni on clean (111) surfaces. One resulted in a Schottky barrier height of less than 0.1 eV, the other of 0.8 eV. Experimental results measured the Schottky barrier height to be 0.5 eV, which is between the two calculated values.⁴ It was suggested that both configurations exist on the surface resulting in the observed intermediate value. Considering copper on diamond (111) surfaces, Lambrecht⁴⁰ calculated a value for the Schottky barrier height of less than 0.1 eV for clean surfaces and greater than 1.0 eV for hydrogen-terminated surfaces. Copper-diamond interfaces have been investigated previously by UPS.⁵ The Schottky barrier heights were the lowest for clean surfaces and the highest for oxygen-terminated surfaces. The values for H termination fell between. Furthermore, for thin Cu overlayers a NEA has been found for Cu on clean or H-terminated diamond (100), (111), and (110) surfaces while a positive electron affinity was found for Cu on oxygenated-diamond surfaces.

According to these results, the surface termination prior to metal deposition appears to have a significant effect on the Schottky barrier height. For metals deposited on clean surfaces, lower values for the Schottky barrier height and a greater likelihood of inducing a NEA are expected than for metals on nonadsorbate free surfaces. The Schottky barrier heights reported in our study for Zr and Co on diamond are consistent with this. Also, the results of Ti, Ni, or Cu on diamond^{3–5} follow this pattern. In Fig. 8 the measured Schottky barrier heights of the different metal–diamond interfaces are plotted versus the metal work function for Zr, Ti, Cu, Co, and Ni. The data are experimental results from this study for Zr and Co as well as from previous publications for Ti, Cu, and Ni.^{3–5} Apparently, the Schottky barrier height for Zr on diamond does not depend on the surface termination of the diamond substrate as strongly as is the case for Co, Cu, or Ni.

The variations in the Schottky barrier for the different surface preparations may be due to the reactivities of the metal layers with the diamond or the surface adsorbate. For instance, Zr, like Ti does react with C. In a prior study it was found that if a 30 Å thick Ti layer was annealed to >400 °C, a reaction with diamond was observed.³ This reaction was not evident at room temperature, but it is likely that the reaction could affect the first few monolayers for Zr or Ti on diamond. In our experiments, Zr may have also reacted with the oxygen from the oxygen-terminated surface. In contrast, Co, Cu, or Ni do not react as readily with C or O. Thus, the metal-diamond interface structure for Co, Cu, or Ni on the clean diamond surfaces is different than for the oxygenterminated surfaces. Consider now the Schottky barrier heights for a metal on H-terminated diamond surfaces compared to clean surfaces. While relatively smaller differences were observed, the Schottky barrier changes were significant for Cu or Ni. Hardly any changes were detected for Zr, and the results for Co fall between the cases of Cu or Ni on the one hand and Zr on the other. Values for the Schottky barrier height of Ti on a H-terminated surface were not available. But, these values may be expected to be similar to the case of Ti on a clean surface due to the high reactivity of Ti. The overall trend seems to be that Zr and Ti will displace both oxygen and hydrogen, Co will displace hydrogen but not oxygen and both O and H will be present at the interface of Cu or Ni.

The dashed line in Fig. 8 represents the limiting value of the Schottky barrier for which a NEA is expected for metaldiamond interfaces according to Eq. (3). Thus, a NEA is expected for data points below this dashed line and a positive electron affinity for those above. As is evident from Fig. 8, the experimental results for the electron affinity agree with this model except for Ni. For this case, a NEA has been observed for Ni on the clean diamond surface while a positive electron affinity would be expected for the measured Schottky barrier value of 0.5 eV. As discussed above, the measured NEA may be indicative of the presence of two configurations of Ni on the surface with Schottky barrier heights of 0.1 and 0.8 eV, respectively. The model would predict that the regions with a Schottky barrier of 0.1 eV would exhibit a NEA while the other regions would exhibit a positive electron affinity.

For Ti on diamond it has been found earlier that the intensity of the metal-induced NEA peak in the photoemission spectrum was significantly reduced once the uniform metal film reached several Å 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.³ Only electrons from within a few scattering lengths of the surface will be emitted into vacuum and then be detected. In our study, we have measured an emission reduction of $\sim 10\%$ for an increase in the Zr thickness from 2 to 3 Å. We have also observed non-uniform metal layers by AFM. This is consistent with a NEA peak still being more pronounced for thicker Zr or Co films than for the case of more uniform Ti layers.

It is significant that the Zr or Co on diamond samples that exhibited a NEA retained this characteristic after air exposure. In particular, the NEA did not show any signs of deterioration over time. We found that hydrogen-terminated diamond surfaces exhibit a NEA that is stable in air for a short period of time before it deteriorates, resulting in a positive electron affinity. The air stability of metal layers on diamond may be important for the development of cold cathode devices required to be stable in a technical vacuum. It has also been reported that Ti as well as titanium oxide on diamond exhibit a NEA.⁴¹ Since Zr has properties similar to Ti, this may be indicative that Zr as well as zirconium oxide on diamond could exhibit a NEA. A stability to air exposure similar to Zr or Co on diamond has been reported for Cu on diamond.⁵

The field-emission data indicate that reducing the electron affinity of surfaces of p-type diamond results in a lowering of the field-emission threshold. The lowest values obtained here for metal on clean diamond surfaces were 20 $V/\mu m$ for Zr and 30 $V/\mu m$ for Co, respectively, and 25 $V/\mu m$ was measured for hydrogen-terminated diamond. 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. This also needs to be considered when discussing how meaningful the values calculated for the Fowler-Nordheim barrier height may be. In particular, these values are lower than may be expected from the measured field-emission thresholds and the electron affinities. An equation for microscopic dielectric regions has been proposed,⁴² but this approach would not be a reasonable model for our case with a diamond substrate thickness of 0.25 mm.

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 Å. Therefore, the field enhancement factor, β , may not be expected to be significantly different for the various surfaces considered.

Simultaneous field-emission and photoemission measurements from a (111) 1×1 :H *p*-type natural diamond surface were reported by Bandis and Pate.⁴³ From these experiments it was found that the field-emitted electrons originated from the valance-band maximum. In contrast, the photoemission process involved emission from the conduction band.

For a surface in which the vacuum level aligns in the band gap of the semiconductor (i.e., a NEA), electrons at the conduction-band minimum can be freely emitted. In contrast, electrons emitted from the valence-band edge would still have to overcome a significant energy barrier even for this NEA surface. Theoretical calculations have indicated that the electron affinity for some H-terminated diamond surfaces can be as low as -3.4 eV.⁴⁴ A NEA would then result in a reduced barrier at the surface even for valence-band emission. For instance, we have found in this study a reduction of the electron affinity from +1.45 eV for the oxygenateddiamond surface to +0.80 eV for Co on oxygen-terminated diamond, and a corresponding reduction in the field-emission threshold from 79 to 52 V/ μ m. An even lower value for the field-emission threshold has been found for Co on the clean surface. The smallest value of 20 V/ μ m for the threshold has been determined for Zr on the clean surface. The NEA should also be the most negative for this case. In these studies, it appears that a decrease in the field-emission threshold is correlated with a reduction of the electron affinity. The threshold values for each of the metals studied [Zr, Co, Cu (Ref. 5)] decrease from the oxygen-to-hydrogen-terminatedto-clean surface. While effects due to the interface and transport through the bulk may be important in some instances, the results presented here suggest that the field emission from *p*-type diamond is most strongly affected by the surface preparation.

V. CONCLUSIONS

In this study, the Zr-diamond and Co-diamond (100), (111), and (110) interfaces were analyzed with UPS and field-emission measurements. The metals were deposited on clean diamond surfaces as well as diamond terminated with oxygen or hydrogen. The results examined and correlated the Schottky barrier, the effective electron affinity, and the fieldemission threshold.

The Schottky barrier value was found to depend on surface termination. The results were compared with previous studies on metal-diamond interfaces. A general trend was that the barrier was greatest for metals on oxygen-terminated surfaces and lowest on the clean surfaces. The Schottky barrier values for metal on H-terminated surfaces were similar to or slightly higher than those from the clean surface. The Schottky barrier heights of Zr-diamond interfaces were much less dependent on the surface termination before deposition than was the case for Co. We suggest that this is due to the higher reactivity of Zr, which will displace either O or H from the interface.

The electron affinity was found to depend on both the metal and diamond surface preparation. NEA characteristics were observed for all metal-diamond interfaces except for Co on oxygen-terminated diamond. The NEA was stable following air exposure, which may prove to be a technologically relevant aspect. The effective electron affinity for a thin metal layer on the diamond was modeled in terms of two interfaces: the vacuum metal and the metal diamond. In this model, a lower Schottky barrier height would result in a lower effective electron affinity, and this is consistent with the experimental results.

Metal deposition on diamond resulted in a decrease in the field-emission threshold as compared to the oxygenterminated diamond surface. The results of the field-emission threshold and electron affinity showed a similar trend in which the field-emission threshold decreased as the electron affinity decreased. The results showed that the emission threshold was dependent on the surface conditions. It was found that for p-type diamond, photoexcited electrons are emitted from the conduction-band minimum and field-emitted electrons apparently originate from the valence-band maximum.

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