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Electron emission from metal–diamond (100), (111) and (110) interfaces

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Abstract

Electron emission characteristics of Cu, Co or Zr films on diamond (100), (111) and (110) surfaces were measured by employing ultraviolet photoemission spectroscopy (UPS) and field emission measurements. Prior to metal deposition, the diamond substrates were terminated with oxygen, hydrogen or were free of adsorbates. Deposition of thin Cu or Co films induced a NEA on clean and H-terminated surfaces. A positive electron affinity was observed for Cu or Co on oxygenated surfaces, and depositing thin Zr films resulted in a NEA on all surfaces considered. UPS can be used to correlate the electron affinity and Schottky barrier height. Schottky barriers of metals on clean surfaces were the lowest, whereas they were the highest on oxygen-covered surfaces. Values for the Schottky barrier height ranged from 0.70 eV to 1.60 eV for Cu, 0.35 eV to 1.40 eV for Co and 0.70 eV to 0.95 eV for Zr. A field emission threshold of 79 V μm^{-1} was measured for oxygenated (100) surfaces. The lowest value of 20 V μm^{-1} was observed for Zr on the clean (100) surface. For all the metals studied, it was found that a lower Schottky barrier height results in a lower electron affinity, and a lower electron affinity results in a lower field emission threshold. © 1998 Elsevier Science S.A.

Keywords: Electron emission; Metal–diamond interface; Electron affinity; Schottky barrier

1. 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. Also, carrier injecting electrical contacts will be necessary.

Ultraviolet photoemission spectroscopy (UPS) can be employed to determine Schottky barrier heights of rectifying contacts. It can also be used 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 quasi-thermalize 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 photoemission [1,2]. By means of UPS, the surface emission properties can be characterized independent of carrier injection and conduction mechanisms.

The mechanism of electron emission by field emission is more complex than by photoemission spectroscopy. 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. To facilitate these measurements, a bias is applied between a metal anode and the sample. Then, the emission current is detected. In comparison with photoemission, the emission properties of the surface itself are characterized. The samples only need to be sufficiently electrically conducting to avoid charging due to electron emission.

Several studies have dealt with Schottky barrier height measurements of metals on (100), (111) and (110) oriented diamond surfaces as well as polycrystalline diamond films [3–19]. It has been found that the Schottky barrier height of metals on diamond is virtually independent of the work function of the metal [11–14,17–19]. However, it has been reported that the Schottky barrier height clearly depends on the surface treatment of the diamond before metal deposition. Overall, cleaning the diamond surfaces chemically in air results in a higher value for the Schottky barrier height than cleaning in vacuum.

Zirconium has been chosen since it has a low work

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function that may be useful for inducing a NEA. It is also next to Ti in the periodic table of elements, which has been studied previously. Titanium has been found to be reactive with C and O. Cobalt and Cu are next to nickel in the periodic table. Their work functions are higher than for Zr or Ti and comparable to Ni. Copper and Co are also much less reactive than Zr or Ti.

For these studies, thin Cu, Co or Zr films have been deposited on diamond (100), (111) and (110) surfaces. Before metal deposition, various in-vacuo cleaning processes were used to obtain clean, hydrogen-terminated or oxygen-terminated diamond surfaces. Subsequent to metal deposition, the effects of the different surface treatments on the metal–diamond interfaces were examined. In particular, the results of UV photoemission and field electron emission were correlated. The results obtained here were compared to previous reports on the properties of thin metal layers on diamond.

2. Experimental details

In these studies, several boron-doped natural type IIb semiconducting single crystal diamond (100), (111) and (110) crystals (3.0 × 3.0 × 0.25 mm) were employed. An electrochemical etch has been used to remove non-diamond carbon and metal contaminants from the surfaces [20,21]. Subsequently, the samples were blown dry with N_2, mounted on a Mo holder and then transferred into the loadlock of the UHV system. This UHV system consists of several interconnected chambers, including capabilities for annealing, H plasma cleaning, metal deposition, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and angle-resolved ultraviolet photoemission spectroscopy (ARUPS).

Three different in-vacuo cleaning steps were employed to assess the influence of surface preparation on the properties of the metal–diamond interfaces. One process involved annealing the samples to 500 °C for 10 min, and another included a 1150 °C anneal for 10 min. The temperature of the Mo holder on which the samples were mounted was measured by means of an optical pyrometer. During the anneals, the pressure increased to $\sim 8 \times 10^{-10}$ Torr and $\sim 7 \times 10^{-9}$ 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 photoemission spectra were excited by HeI (21.21 eV) radiation. A 50-mm VSW HAC50 hemispherical analyzer was employed to measure the emitted electrons. 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 indicative of a NEA.

Photoemission spectra can be used to measure 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. This method can only be employed for metal films with thicknesses equal to or less than the electron mean free path (a few angstroms), since features from both the semiconductor and the metal need to be detected in the spectra. UPS spectra of wide bandgap 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-diameter 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 μm.

An e-beam evaporator has been employed to deposit Co or Zr films of 1, 2, 3, 6, 10 Å thickness on to 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^{-1} up to 3 Å in thickness and 0.3 Å s^{-1} for 6 and 10 Å in thickness. The depositions were done with the substrates 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 UPS, AES, LEED and atomic force microscopy (AFM). AFM images of the diamond wafers used in this study clearly showed arrays of linear groves 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.

3. Results and discussion

Consider first the properties of the diamond (100), (111) and (110) surfaces before deposition of Cu, Co or Zr. Diamond (100) samples heated to 500 °C exhibited a 1 × 1 unreconstructed LEED pattern and an AES oxygen peak. A 1150 °C anneal or a H plasma exposure resulted in 2 × 1 reconstructed surfaces and the removal of oxygen according to AES. By means of UPS, a positive electron affinity of 1.45 eV and 0.75 eV was found for the surfaces annealed to 500 °C and 1150 °C, respectively. A NEA was detected for surfaces treated with a H plasma.

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. As evidenced by UPS spectra for the 1150 °C anneal, a positive electron affinity around 0.55 eV was measured, and following the H plasma treatment a NEA was determined.

A 700 °C anneal or a H plasma removed the oxygen from the diamond (110) surfaces as evidenced by AES and resulted in NEA characteristics according to UPS. Following a 1150 °C anneal, the NEA was removed, and a positive electron affinity of 0.55 eV was detected. Another H plasma clean resulted in a NEA again. All these results are consistent with previous studies on surface cleaning and UPS measurements of diamond (100), (111) and (110) surfaces [1,2,25–28].

The deposition of Cu on to clean diamond (100) surfaces resulted in an increase in the width of the photoemission spectrum consistent with a NEA. The distance between bulk feature from the diamond (labeled B) and the valence band maximum shifted to lower energies by 0.3 eV. Feature B is used as a point of reference to determine the shift. This shift is indicative of a change in Fermi level pinning in the gap. A Schottky barrier height of $\Phi_B = 0.70$ eV was determined from the UPS spectra. This value stayed constant for the different thicknesses of the Cu films. Copper deposition on H-terminated (100) surfaces resulted in NEA characteristics, too, but a positive electron affinity was determined for oxygen terminated (100) surfaces (Fig. 1). Schottky barrier heights of $\Phi_B = 0.90$ eV and $\Phi_B = 1.60$ eV were measured, respectively. Corresponding to (100) surface, a NEA was observed following Cu deposition on both the clean and H-terminated (111) and (110) surfaces. For a summary of these results, see Table 1.

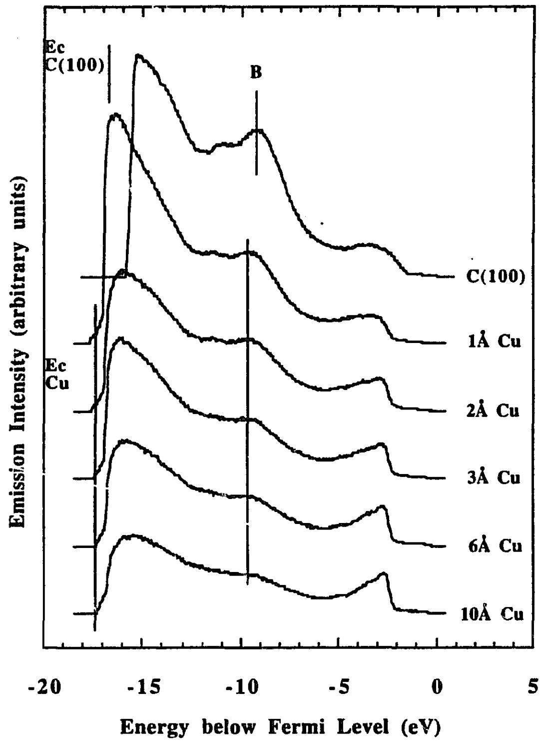

Fig. 1. UV Photoemission spectra of Cu on an oxygen-terminated diamond (100) surface. The diamond surface exhibits a positive electron affinity prior to Cu deposition. Subsequent to Cu deposition, the width of the spectrum increases somewhat, but the spectra still exhibit a positive electron affinity.

For Co on clean and H-terminated diamond (100) surfaces, a NEA and Schottky barrier heights of $\Phi_B = 0.35$ eV and $\Phi_B = 0.45$ eV were measured, respectively. In comparison, a positive electron affinity of $\chi = 0.80$ eV, and a Schottky barrier of $\Phi_B = 1.40$ eV were detected for Co on oxygen-terminated (100) surfaces.

Similar to the (100) surface, NEA characteristics were observed for Co on clean as well as H-terminated (111) and (110) surfaces. In Fig. 2, UPS spectra of Co on H terminated (110) surfaces are shown. Schottky barrier

Table 1
Summary of the UPS measurements

Sample surface	UPS before Cu growth	UPS after Cu growth	NEA stable in air	Calculated χ_{eff}
C(100)				
Clean	PEA, $\chi = 0.70$ eV	NEA, $\chi < 0$, $\Phi_B = 0.70$ eV, 0.30 eV shift	Yes	$\chi_{eff} = -0.20$ eV
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.90$ eV, 0.60 eV shift	Yes	$\chi_{eff} = 0$ eV
O terminated	PEA, $\chi = 1.45$ eV	PEA, $\chi = 0.75$ eV, $\Phi_B = 1.60$ eV, 0.60 eV shift	Yes	$\chi_{eff} = 0.70$ eV
C(111)				
Clean	PEA, $\chi = 0.50$ eV	NEA, $\chi < 0$, $\Phi_B = 0.30$ eV, no shift	Yes	$\chi_{eff} = -0.20$ eV
H terminated	PEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.50$ eV, 0.20 eV shift	Yes	$\chi_{eff} = 0$ eV
C(110)				
Clean	PEA, $\chi = 0.70$ eV	NEA, $\chi < 0$, $\Phi_B = 0.60$ eV, 0.20 eV shift	Yes	$\chi_{eff} = -0.40$ eV
H terminated	PEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.90$ eV, 0.60 eV shift	Yes	$\chi_{eff} = -0.10$ eV

PEA: positive electron affinity, NEA: negative electron affinity. Also the values of the electron affinity χ calculated according to Eq. (1) are listed. The error margins are 0.1 eV.

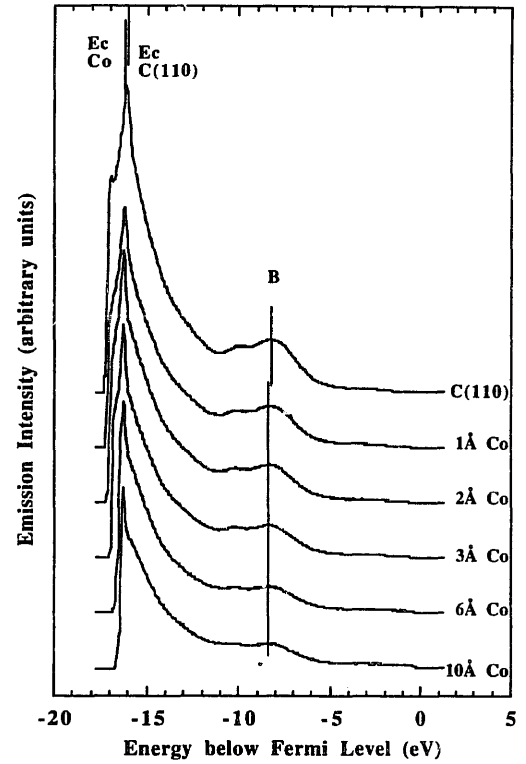

Fig. 2. UV photo emission spectra of Co on the H-terminated diamond (110) surface. The diamond surface exhibits a positive electron affinity before Co deposition. Subsequent to Co deposition, the width of the spectrum increases, and a NEA is detected.

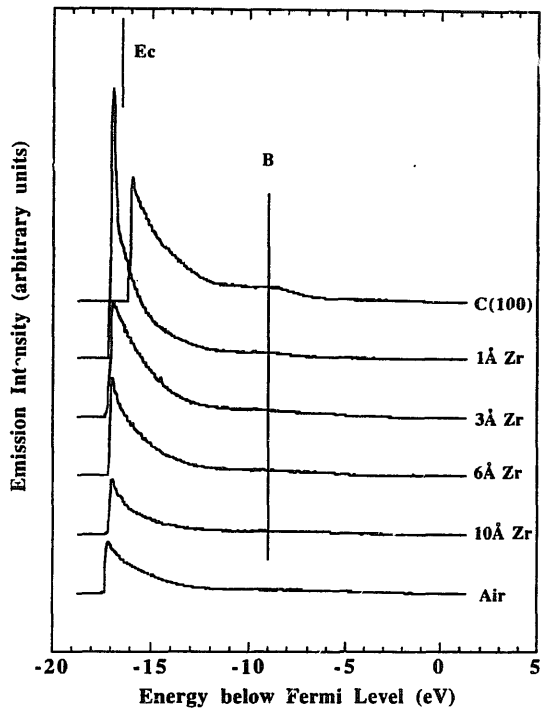

Fig. 3. UV photoemission spectra of Zr on a clean diamond (100) surface. Before Zr deposition, the diamond surface exhibits a positive electron affinity. Subsequent to Zr deposition, the width of the spectrum increases, and a NEA is detected. Following air exposure, the NEA is still observed.

heights between $\Phi_B = 0.40$ eV and 0.50 eV were measured. All these results have been summarized in Table 2.

Zirconium resulted in a NEA on all the surfaces considered. The Schottky barrier ranged from $\Phi_B = 0.70$ eV for clean (100) surfaces to 0.90 eV for oxygenated (100) surfaces. For Zr on the clean and H-terminated (111) and (110) surfaces, values between 0.70 eV and 0.95 eV were measured. In several cases, emission below the conduction band minimum was detected. As an example, UPS spectra of Zr on clean (100) surfaces are shown in Fig. 3. The details of the measurements are listed in Table 3.

As indicated in Tables 1–3, the NEA characteristics of Cu, Co or Zr on diamond surfaces were found to be stable following air exposure. In comparison to these metalized diamond surfaces, we have also observed that the NEA effect due to hydrogen on diamond surfaces showed some stability in air. However, this NEA effect was found to degrade over a short period of time, and eventually a positive electron affinity was detected. No such degradation was observed for the NEA characteris-

Table 2
Summary of the UPS measurements on diamond (100), (111) and (110) surfaces before and after Co deposition

Sample surface	UPS before Co growth	UPS after Co growth	NEA stable in air	Calculated χ_{eff}
C(100)				
Clean	PEA, $\chi = 0.75$ eV	NEA, $\chi < 0$, $\Phi_B = 0.35$ eV, no shift	Yes	$\chi_{eff} = -0.20$ eV
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.45$ eV, 0.15 eV shift	Yes	$\chi_{eff} = -0.10$ eV
O terminated	PEA, $\chi = 1.45$ eV	PEA, $\chi = 0.80$ eV, $\Phi_B = 1.40$ eV, 0.55 eV shift	Yes	$\chi_{eff} = 0.90$ eV
C(111)				
Clean	PEA, $\chi = 0.50$ eV	NEA, $\chi < 0$, $\Phi_B = 0.40$ eV, no shift	Yes	$\chi_{eff} = -0.15$ eV
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.50$ eV, 0.10 eV shift	Yes	$\chi_{eff} = -0.05$ eV
C(110)				
Clean	PEA, $\chi = 0.60$ eV	NEA, $\chi < 0$, $\Phi_B = 0.40$ eV, 0.10 eV shift	Yes	$\chi_{eff} = -0.10$ eV
H terminated	NEA, $\chi < 0$	NEA, $\chi < 0$, $\Phi_B = 0.45$ eV, 0.10 eV shift	Yes	$\chi_{eff} = -0.05$ eV

PEA, positive electron affinity; NEA, negative electron affinity. Also, the values of the effective electron affinity χ_{eff} were calculated according to Eq. (1). The experimental uncertainties are 0.1 eV.

Table 3
Summary of the UPS measurements on diamond (100), (111) and (110) surfaces before and after Zr deposition

Sample surface	UPS before Zr growth	UPS after Zr growth	NEA stable in air	Calculated χ_{eff}
C(100)				
Clean	PEA, $\chi=0.75$ eV	NEA, $\chi<0$, $\Phi_B=0.70$ eV, no shift	Yes	$\chi_{\text{eff}}=-0.70$ eV
H terminated	NEA, $\chi<0$	NEA, $\chi<0$, $\Phi_B=0.75$ eV, 0.30 eV shift	Yes	$\chi_{\text{eff}}=-0.65$ eV
O terminated	PEA, $\chi=1.40$ eV	NEA, $\chi<0$, $\Phi_B=0.90$ eV, 0.10 eV shift	Yes	$\chi_{\text{eff}}=-0.50$ eV
C(111)				
Clean	PEA, $\chi=0.45$ eV	NEA, $\chi<0$, $\Phi_B=0.85$ eV, 0.1 eV shift	Yes	$\chi_{\text{eff}}=-0.55$ eV
H terminated	NEA, $\chi<0$	NEA, $\chi<0$, $\Phi_B=0.95$ eV, 0.60 eV shift	Yes	$\chi_{\text{eff}}=-0.45$ eV
C(110)				
Clean	PEA, $\chi=0.50$ eV	NEA, $\chi<0$, $\Phi_B=0.70$ eV, 0.20 eV shift	Yes	$\chi_{\text{eff}}=-0.70$ eV
H terminated	NEA, $\chi<0$	NEA, $\chi<0$, $\Phi_B=0.70$ eV, 0.40 eV shift	Yes	$\chi_{\text{eff}}=-0.70$ eV

PEA, positive electron affinity; NEA, negative electron affinity. Also, the values of the effective electron affinity χ_{eff} were calculated according to Eq. (1). The experimental uncertainties are 0.1 eV.

tics of the metalized diamond surfaces. The NEA due to metal films on diamond proved to be stable in air.

The equation below describes the effective electron affinity for an interface between a metal and a p-type semiconductor as a function of the Schottky barrier height [29]. It is specific for photoemission of thin metal layers (less than the electron mean free path) on p-type semiconductors:

$$\chi_{\text{eff}}=(\Phi_M+\Phi_B)-E_G. \qquad (1)$$

With the bandgap of diamond $E_G=5.47$ eV, the metal work functions and the measured Schottky barrier height, the electron affinity can be calculated. The results are listed for Cu in Table 1, for Co in Table 2 and for Zr in Table 3. These results are consistent with detecting a NEA for Cu or Co on clean and hydrogenated diamond surfaces and a positive electron affinity for the O-terminated surface as well as observing a NEA for Zr on the clean H, and O-terminated diamond surfaces. Eq. (1) has been used successfully before to describe Ti, Ni, Co, Cu and Zr diamond interfaces [11–14,17–19]. In these studies, it has been found that the Schottky barrier height for clean surfaces was 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. Other approaches may be used to interpret these results. The monolayer thick metal films could be considered as dipole layers.

In Fig. 4, the Schottky barrier height of the metal–diamond interface is plotted vs. the metal workfunction for Zr, Ti, Cu, Co and Ni. The data are experimental results from this study for Cu, Co and Zr as well as from previous publications for Ti and Ni [11,12]. Apparently, the Schottky barrier height for Zr and Ti on diamond does not depend on the surface termination of the diamond substrate as strongly as is the case for Co, Cu or Ni. This could be due to the higher reactivity of Zr and Ti with both C and O than Cu, Co and Ni. It has been reported that Ti as well as titanium oxide on diamond exhibit a NEA [11,30]. Zirconium is next to Ti in the periodic table of elements and has properties similar to Ti. In our experiments, Zr could have reacted with the oxygen from the oxygen-terminated surface. This may be indicative that Zr as well as zirconium oxide on diamond could exhibit a NEA. Zirconium, like Ti, does react with C, but this reaction is not expected to occur at room temperature. Titanium was annealed to >400 °C before reaction with C was observed [11,31]. Copper, Co and Ni, however, do not react as readily with C or O. Thus, the metal–diamond interface structure for Cu, Co and Ni on the clean diamond surfaces is different than on the oxygen-terminated surfaces.

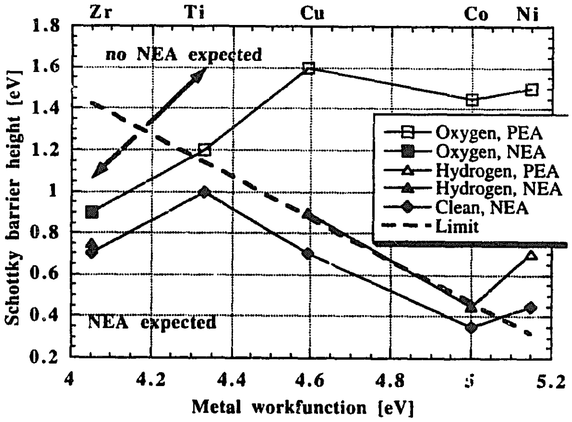

Fig. 4. Diagram of the Schottky barrier height vs. metal workfunction for Ti, Zr, Cu, Co and Ni. The dashed line represents the limit for which a NEA is expected for metal–diamond interfaces according to Eq. (1). Thus, a NEA is expected for data points below this dashed line and a positive electron affinity 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.

The dashed line in Fig. 4 represents the limit for which a NEA is expected for metal–diamond interfaces according to Eq. (1). Thus, a NEA is expected for data points below this dashed line and a positive electron affinity

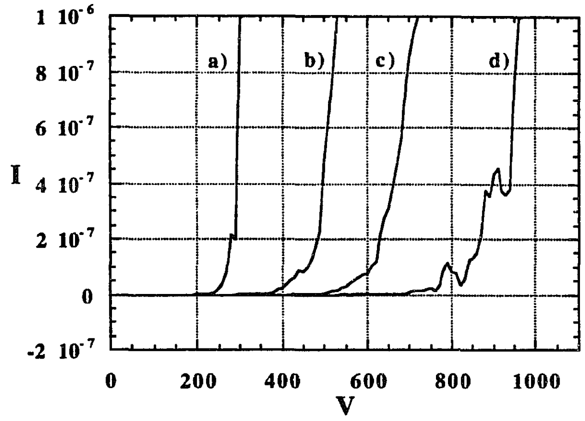

Fig. 5. Field emission current–voltage curves for Zr on a oxygen terminated type IIb single crystal diamond (100) sample. Distances between the sample and the anode: (a) 5.7 μm, (b) 9.7 μm, (c) 12.4 μm and (d) 17.2 μm.

for those above. The experimental results for the electron affinity agree with this model except for Ni on the clean surface where a NEA has been observed. However, theoretical studies by Erwin and Pickett [31–35] and Pickett et al. [36] reported two possible configurations for Ni on the clean surface with almost the same formation energy and Schottky barrier heights of 0.1 eV and 0.8 eV, respectively. Both may be present on the surface resulting in the measured value of 0.5 eV for the Schottky barrier height and leading to the detection of a NEA.

Field emission measurements were performed on diamond (100) samples as well as on 2 and 10-Å-thick Cu, Co and Zr films deposited on clean, hydrogen- or oxygen-terminated diamond (100) surfaces to determine the applied voltage per micrometer. The voltage per micrometer is also called the average field. Since the measured current–voltage curves did not exhibit an absolute threshold, it was necessary to define the emission threshold field. In this study, the voltage required to obtain an emission current of 0.1 μA was used. The I–V data for Zr on the O-terminated diamond surface are shown in Fig. 5. The average threshold field was calculated from the values for different distances. The highest value of 79 V μm^{1-} was measured for the diamond surface. For metal deposition, the lowest threshold has been obtained for the clean surface and the highest for the oxygenated surface. The results and the standard deviations for the different surface terminations are summarized in Table 4. The values for the field emission threshold reported here are of the same order of magnitude as previously reported for diamond samples [37–39]. The data from the field emission measurements have been fitted to the Fowler–Nordheim equation [40]:

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

where I is the current in amps, V is the bias in volts, d is the distance between the sample and the anode in micrometers, k is a constant, φ is the Fowler–Nordheim barrier height in eV, and β is the field enhancement factor. The roughness of the surfaces before and after metal deposition was comparable and of the order of a

Table 4
Results of electron emission measurements

Sample	UPS	Field emission threshold (V μm^{1})	Fowler–Nordheim barrier height (eV)
C(100)	After 500 C anneal PEA, $\chi \cong 1.40$ 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
Co/C(100) Clean	NEA, $\chi < 0$, $\Phi_B \cong 0.35$ eV	30 ± 3	0.11 ± 0.01
Co/C(100) Hydrogen	NEA, $\chi < 0$, $\Phi_B \cong 0.45$ eV	39 ± 4	0.16 ± 0.02
Co/C(100) Oxygen	PEA, $\chi \cong 0.75$, $\Phi_B \cong 1.40$ eV	52 ± 4	0.20 ± 0.02
Zr/C(100) Clean	NEA, $\chi < 0$, $\Phi_B \cong 0.70$ eV	20 ± 3	0.09 ± 0.01
Zr/C(100) Hydrogen	NEA, $\chi < 0$, $\Phi_B \cong 0.75$ eV	23 ± 3	0.11 ± 0.01
Zr/C(100) Oxygen	NEA, $\chi < 0$, $\Phi_B \cong 0.90$ eV	49 ± 4	0.20 ± 0.01

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 barrier height. The threshold current is 0.1 μA.

few angstrom as determined by AFM. The values for the Fowler–Nordheim barrier height listed in Table 4 were calculated assuming $\beta = 1$. These values do appear smaller than what may be expected from the measured field emission thresholds and electron affinities. A value of β larger than 1 may be more realistic, even for the smooth surfaces considered here. It should also be noted that the Fowler–Nordheim equation (Eq. (2)) describes the case of metals, assuming no field inside the bulk of the material. Another equation has been derived for microscopic dielectric inclusions [41], but the diamond samples used here had a thickness of 0.25 mm.

From simultaneous field emission and photoemission measurements from a (111) 1×1:H p-type natural diamond surface, Bandis and Pate [42] found that the field emitted electrons originated from the valance band maximum. Electrons at the conduction band minimum can be freely emitted from a NEA surface. However, electrons emitted from the valence band edge may still have to overcome a significant energy barrier for a NEA surface. A NEA would then result in a reduced barrier at the surface.

According to the data presented here, there is evidence 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 (Cu, Co, Zr) decrease from oxygen- to hydrogen-terminated to clean surface. It is, however, not clear why the field emission threshold value for Zr on the oxygenated surface (exhibiting a NEA) is similar to that of Cu on the oxygen-terminated surface (with a positive electron affinity). Other effects may play a role in this behavior, and further studies will be necessary to understand better field electron emission from various diamond surfaces.

4. Conclusions

Metal–diamond (100), (111) and (110) interfaces have been studied by UPS and field emission. It was found that Cu or Co induced a NEA on clean and H-terminated surfaces but not on oxygen-terminated surfaces. Zirconium induced a NEA on all surfaces considered. The Schottky barrier height of Zr on diamond was less dependent on the termination of the diamond surface than was the case for Cu or Co. This is attributed to the higher reactivity of Zr. A lower Schottky barrier height generally results in a lower electron affinity. A reduction in electron affinity led to lower field emission threshold fields. The results were compared with previous studies on metal diamond interfaces. Both the surface cleaning of the diamond samples prior to metal deposition as well as the type of metal influence the Schottky barrier height and the electron emission characteristics. The NEA characteristics of Cu, Co and Zr were found to be stable following air exposure. This may prove to be a technologically relevant aspect.

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