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Characterization of metal–diamond interfaces: electron affinity and Schottky barrier height

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Abstract

In this study, the electron affinity and Schottky barrier height of thin Cu and Zr films on diamond (100) substrates were correlated by means of UV photoemission spectroscopy (UPS) measurements. Prior to metal deposition the diamond crystals were cleaned by a 1150°C or 500°C anneal in UHV, and the surfaces were characterized by AES and AFM. This resulted in surfaces terminated with oxygen or free of chemisorbed species. By means of UPS it was found that whether a metal did induce a negative electron affinity (NEA) on a diamond surface was dependent on the surface preparation before metal deposition and on the metal work function. In particular, the Schottky barrier height for clean surfaces was lower than for surfaces terminated by oxygen. Metal–diamond interfaces exhibiting a NEA had a lower Schottky barrier height than those exhibiting a positive electron affinity. These effects were attributed to different interfacial layers. Field emission measurements were performed before and after metal deposition. For all cases a reduction in the threshold electric field was observed upon metal overgrowth. © 1997 Elsevier Science S.A.

Keywords: metal–diamond interfaces; electron affinity; Schottky barrier height

1. Introduction

Negative electron affinity (NEA) surfaces based on wide bandgap semiconductors such as diamond may be important for the development of cold cathode devices. However n-type doping of diamond still poses a major challenge. The electron affinity of a semiconductor is defined as the energy difference between the vacuum level and the conduction band minimum. For most materials the vacuum level lies above the conduction band minimum, corresponding to a positive electron affinity. Surfaces of wide bandgap semiconductors, such as diamond, have the potential of exhibiting a NEA since the conduction band minimum lies near the vacuum level. For a NEA surface, the electrons from the conduction band minimum have sufficient energy to overcome the surface potential and can be emitted into vacuum.

Various surface treatments such as plasma cleaning, as well as annealing in ultra high vacuum (UHV), can shift the position of the vacuum level and therefore induce a NEA or remove it [1–6]. Pre-cleaning the diamond (100) samples with a wet chemical etch results in an oxygen termination of the surface. This chemisorbed oxygen layer forms a surface dipole that results in an increase in the surface workfunction. It is found that such a surface exhibits a positive electron affinity. Annealing these samples to 900–1050°C or exposing them to a H-plasma results in the removal of oxygen from the surface, a 2×1 reconstruction and a NEA [3,5,6]. The different threshold temperatures are related to different wet chemical pre-treatments [3]: it was found that 900°C was sufficient for samples pre-cleaned by an electrochemical etch. But 1050°C was required for a pre-clean employing chromic acid. The diamond (100) surface has been proposed to exhibit a monohydride termination subsequent to a 900–1050°C anneal or a H-plasma exposure. A H surface layer results in a dipole such that the work function is reduced resulting in a NEA. Heating these samples to 1150°C resulted in a 2×1 reconstructed surface with a positive electron affinity [6]. This surface has been suggested to be free of adsorbates. In agreement with the experimental results, ab initio calculations for the 2×1 reconstructed surface predict a NEA for a monohydride terminated surface and a positive electron affinity for an adsorbate-free surface [5].

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Furthermore it has been demonstrated that metals like Ti, Ni, Co, Cu and Zr can induce a NEA on diamond surfaces [7–11]. Also no significant dependence of the Schottky barrier height on the metal work function has been found [3,7–12]. Metal films deposited on adsorbate-free surfaces tend to result in lower Schottky barrier heights and lower electron affinities than for surfaces terminated by species such as hydrogen or oxygen [8,9]. Photoemission spectroscopy is found to be a very sensitive method to determine whether a surface exhibits a NEA or not. Electrons get photoexcited from the valence band into states in the conduction band and can quasi-thermalize to the conduction band minimum. Secondary electrons from the conduction band minimum appear as a sharp peak at the low kinetic energy end of photoemission spectra for NEA surfaces [13,14].

Photoemission spectroscopy determines the emission properties of the surface itself. In comparison, field emission data reflect a combination of carrier injection, transport and emission processes. In this study diamond (100) surfaces have been cleaned by anneals to 1050 or 500°C. Thin Cu or Zr films were deposited on these diamond substrates. The surface properties were characterized before and after metal deposition.

2. Experimental details

The UHV system used in this study consists of several interconnected chambers, including systems used for annealing, metal deposition, UPS and AES. Natural type IIb single-crystal diamond (100) substrates ($3.0 \times 3.0 \times 0.25$ mm) were used in this study. First, the samples were electrochemically etched to remove non-diamond carbon and metal contaminants [15]. This etch included applying a d.c. bias of 350 V between two Pt electrodes that were placed in deionized (DI) water as an electrolyte. The samples were suspended in water between the two electrodes. Following the electrochemical etch, a h.f. dip was employed to remove SiO_2 from the surface [3]. Then the wafers were mounted on a Mo holder and transferred into the UHV system (base pressure $\sim 1 \times 10^{-10}$ Torr). As an in vacuo cleaning step, the wafers were annealed to 1150 or 500°C for 10 min. This caused the pressure to rise to $\sim 7 \times 10^{-9}$ Torr. Subsequent to annealing 2 Å thick films of Cu or Zr were deposited by means of e-beam evaporation. The thickness of the metal layers was determined by a quartz crystal oscillator. During deposition the pressure rose to $\sim 2 \times 10^{-9}$ Torr. Following the annealing, and the growth steps, UPS and AES were employed to analyze the surface properties.

The presence of a Cu or Zr film was confirmed by using AES. AFM images of the diamond wafers clearly showed arrays of linear groves parallel to each other with a depth of ~ 20 Å. This surface structure is due to the commercial polishing of the samples. No island structures were observed in AFM measurements after 2 Å of deposition, which may be indicative of a uniform 2D layer for both Cu and Zr.

HeI (21.21 eV) radiation was used to excite the photoemission of electrons. A 50 mm hemispherical analyzer was employed to measure the emitted electrons with an energy resolution of 0.15 eV. A bias of 1 V was applied to the sample to overcome the workfunction of the analyzer and thus to detect the low energy electrons emitted from the NEA surface. The position of the sharp NEA peak at the low energy end of photoemission spectra corresponds to the energy position of the conduction band minimum, E_C. Emission from E_C is positioned at $E_V + E_G$ in the spectrum, where E_V is the energy of the valence band maximum and E_G that of the bandgap. Emission from the valence band maximum appears at $E_V + h\nu$ in the spectrum. The spectral width or the distance between emission from the valence band maximum and the conduction band minimum is therefore $h\nu - E_G$. With the values for HeI radiation $h\nu = 21.21$ eV and the bandgap of diamond $E_G = 5.47$ eV a spectral width of ~ 15.7 eV is determined for a NEA surface. However, for the case of a positive electron affinity surface the low energy cutoff will be determined by the position of the vacuum level and the spectral width will be smaller.

The base pressure in the field emission chamber was $\sim 2 \times 10^{-7}$ Torr. To determine the current–voltage characteristics a bias of 0–1100 V was applied between the sample and a 2 mm diameter platinum anode with a rounded tip. The distances were varied between 2 and 20 μm.

3. Results and discussion

AES spectra of the as loaded samples exhibited features indicative of the presence of oxygen on the surface. Following a 500°C anneal the oxygen feature was only slightly reduced. Upon heating the samples to 1150°C oxygen could no longer be detected by means of AES. By employing UPS, a positive electron affinity of $\chi \cong 1.4$ eV and of $\chi \cong 0.7$ eV were observed for the crystals annealed to 500 and 1150°C, respectively. These values correspond to previous results [5,9]. Oxygen chemisorbed to diamond is expected to induce a stronger surface dipole and therefore cause an increase in the workfunction compared to a clean surface. Our results are consistent with this. Upon deposition of 2 Å of copper on clean surfaces, a Schottky barrier height of $\Phi_B \cong 0.70$ eV and a NEA were observed by UPS (Fig. 1(a)). In comparison, depositing 2 Å of Cu onto oxygen-terminated diamond (100) surfaces resulted in a positive electron affinity of $\chi \cong 0.75$ eV, and a corre-

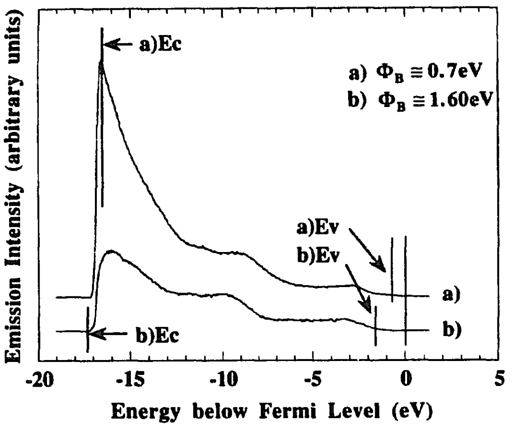

Fig. 1. UV photoemission spectra of 2 Å of Cu grown on a diamond (100) surface following an anneal to (a) 1150 and (b) 500°C. A metal-induced NEA is observed for (a), whereas a positive electron affinity is detected for (b).

sponding Schottky barrier of $\Phi_B \cong 1.60$ eV was obtained (Fig. 1(b)). Depositing 2 Å of Zr onto clean diamond (100) samples resulted in a Schottky barrier height of $\Phi_B \cong 0.7$ eV and a NEA (Fig. 2(a)). Emission below the conduction band minimum E_C was observed. Subsequent to deposition of 2 Å of Zr on oxygen-terminated diamond (100) surfaces, a NEA was observed. A larger Schottky barrier height of $\Phi_B \cong 0.9$ eV was measured (Fig. 2(b)). These results are summarized in Table 1. Eq. (1) gives an expression for the electron affinity of a p-type semiconductor subsequent to metal deposition [16].

$$\chi = (\Phi_M + \Phi_B) - E_G \qquad (1)$$

Using the workfunction of Cu for the (100) surface $\Phi_M = 4.59$ eV, the bandgap of diamond $E_G = 5.47$ eV and the measured Schottky barrier heights one can calculate the electron affinities of $\chi \cong -0.18$ eV for the clean surface and $\chi \cong 0.72$ eV for the oxygen-terminated surface. With the value of $\Phi_M \cong 4.05$ eV for the workfunction of Zr and the observed Schottky barrier heights, electron affinities of $\chi \cong -0.72$ eV for the clean surface and $\chi \cong -0.52$ eV for the oxygen-terminated surface are obtained. These results are in agreement with the NEA and positive electron affinity effects that were observed by means of UPS. The emission detected below E_C for Zr on the clean surface is consistent with the calculated value of $\chi \cong -0.72$ eV. The fact that no emission below E_C was observed for Zr on oxygen-terminated diamond may be due to a different interface structure. It has been reported that carbon contaminants lower the workfunction of Ni [17]. The workfunction of the 2-Å thick films in our study may be affected by the carbon of the diamond. But such an effect would only lead to a stronger NEA effect for Cu on the clean surface and both Zr on the clean and oxygenated surface, and 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.

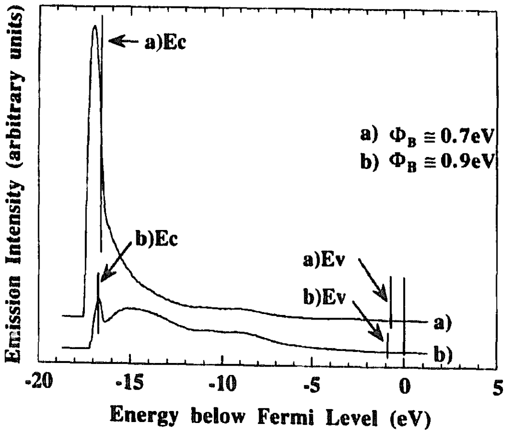

Fig. 2. UV photoemission spectra of 2 Å of Zr deposited on a diamond (100) surface annealed to (a) 1150 and (b) 500°C. Metal-induced NEAs are observed upon deposition of Zr for both (a) and (b). For (a) emission below E_C is detected.

For systems like Ti or Ni layers on diamond (111) surfaces [7,8] this simple workfunction model has been used successfully to explain NEA or positive electron affinity effects. It has been observed that Ni deposited on an adsorbate-free (111) surface induced a NEA [8]. In comparison, a positive electron affinity and a larger Schottky barrier were obtained for thin Ni films on (111) surfaces terminated by hydrogen. In theoretical studies by Erwin and Pickett [18–21] and Pickett et al. [22] it was reported that the most stable configuration for Ni on clean (111) and (100) surfaces resulted in a Schottky barrier height of less than 0.1 eV. Regarding copper on diamond (111) surfaces, Lambrecht [23] obtained 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. According to these results the interface termination appears to be crucial for 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 non-adsorbate-free surfaces. The Schottky barrier heights reported in this study for Cu and Zr on diamond are in agreement with this. Zr and Ti have a stronger affinity to C than is the case for Cu and Ni. This may play a role in the interface formation of the thin films on diamond. Both Zr or Ti on clean as well as oxygen-terminated diamond surfaces tend to exhibit lower electron affinities than Cu or Ni on corresponding surfaces. This can be determined from the results of this study as well as previous reports [7,8]. The workfunction of Ti is only 0.3 eV higher than that of Zr. Apparently the relatively small difference between Zr and Ti is sufficient to induce a NEA for Zr on the oxygen-terminated surface but not for the case of Ti. It

Table 1
Results of electron emission measurements

Sample	UPS	Field emission threshold ($V\ \mu m^{-1}$)	Barrier height (eV)
C(100)	after 500 C anneal. PEA, $\chi \cong 1.4$ eV	79 ± 7	0.23 ± 0.01
Cu/C(100) clean	NEA, $\chi < 0$, $\Phi_B \cong 0.70$ eV	25 ± 3	0.10 ± 0.01
Cu/C(100) oxygen	PEA, $\chi \cong 0.75$ eV, $\Phi_B \cong 1.60$ eV	53 ± 4	0.21 ± 0.01
Zr/C(100) clean	NEA, $\chi < 0$, $\Phi_B \cong 0.7$ eV	20 ± 3	0.09 ± 0.01
Zr/C(100) oxygen	NEA, $\chi < 0$, $\Phi_B \cong 0.9$ 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.

is significant that a metal-induced NEA was observed for deposition of Zr on both clean and oxygen-terminated surfaces. Prior to this work only low workfunction metals like Cs have been found to induce a NEA on non-adsorbate-free diamond surfaces [24].

Field emission measurements were performed on diamond samples and on Cu or Zr films deposited on clean and oxygen-terminated diamond surfaces. For a current of 0.1 μA values between 20 and 79 V μm^{-1} were measured for the emission threshold field. A summary of the results is shown in Table 1. Previous studies have reported comparable values for diamond samples [11,25,26]. As an example *I–V* curves for the diamond surface are shown in Fig. 3. For comparison one *I–V* curve for Zr on a clean diamond surface has been included also. These results have been compared to the Fowler–Nordheim equation [27]:

$$I = k\left(\frac{V}{d}\right)^2 \exp\left(\frac{-6530 d\phi^{3/2}}{V}\right) \qquad (2)$$

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 and ϕ is the effective barrier height in eV. The field enhancement factor has been neglected since the surfaces have been found to be essentially flat by means of AFM. The effective barrier heights, ϕ, were obtained by fitting the field emission data to Eq. (2) (see Table 1). Depositing Cu or Zr onto both clean and oxygen-terminated diamond (100) surfaces improves the emission properties. The case of Zr on clean surfaces gave the best results. Both UPS and field emission measurements show these trends consistently.

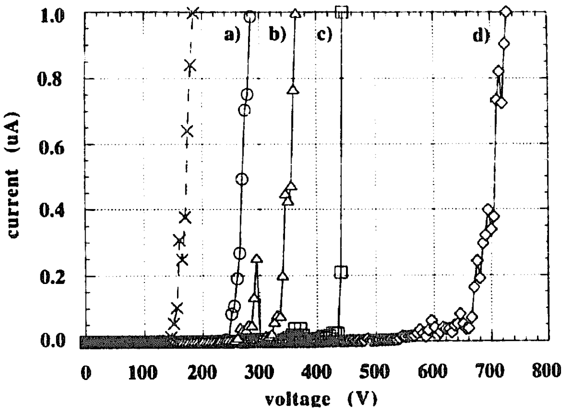

Fig. 3. Field emission current–voltage curves for a type IIb single crystal diamond (100) sample. Distances between the sample and the anode: (a) 3.3 μm, (b) 4.3 μm, (c) 5.6 μm, (d) 8.5 μm. For comparison one current–voltage curve for Zr on a clean diamond (100) surface is also shown (dashed line) with a distance between the sample and the anode of 7.8 μm.

4. Conclusions

The effects of depositing thin metal films onto clean and oxygen-terminated diamond (100) substrates has been studied by UPS. Cu only induced a NEA on clean surfaces. In comparison, Zr induced a NEA on both clean and oxygen-terminated surfaces. Emission even below E_C was detected for Zr on clean surfaces. Both the field emission threshold and the effective barrier height were reduced in a manner consistent with the UPS results by depositing metals on diamond.

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References

[1] F.J. Himpsel, D.E. Eastman, P. Heimann and J.F. van der Veen, *Phys Rev., B 24* (1981) 7270.

[2] B.B. Pate, M.H. Hecht, C. Binns, I. Lindau and W.E. Spicer, *J. Vac. Sci. Technol., 21*, (1982) 364.

[3] P.K. Baumann, T.P. Humphreys and R.J. Nemanich, in C.H. Carter, G. Gildenblat, S. Nakamura and R.J. Nemanich (eds.), *Diamond, SiC and Nitride Wide Bandgap Semiconductors*, Mater. Res. Soc. Proc. 339, Pittsburgh, PA, 1994, pp. 69–74.

[4] J. van der Weide and R.J. Nemanich, *Appl. Phys. Lett., 62* (1993) 1878.

[5] J. van der Weide, Z. Zhang, P.K. Baumann, M.G. Wensell, J. Bernholc and R.J. Nemanich, *Phys. Rev.*, *B 50* (1994) 5803.

[6] P.K. Baumann and R.J. Nemanich, in P.K. Bachmann, I.M. Buckley-Golder, J.T. Glass and M. Kamo (eds.), *J. Proc. of the 5th European Conference on Diamond, Diamond-like and Related Materials*, in *Diamond Relat. Mater.*, *4* (1995) 802.

[7] J. van der Weide and R.J. Nemanich, *J. Vac. Sci. Technol.*, *B 10* (1992) 1940.

[8] J. van der Weide and R.J. Nemanich, *Phys. Rev.*, *B 49* (1994) 13629.

[9] P.K. Baumann and R.J. Nemanich, *Appl. Surf. Sci.*, *104/105* (1996) 267.

[10] P.K. Baumann and R.J. Nemanich, in C. Beetz, A. Collins, K. Das, D. Dreifus, T. Humphreys and P. Pehrsson (eds.), *Diamond for Electronic Applications*, Mater. Res. Symp. Soc. Proc. 416, Pittsburgh, PA, 1996, pp. 157–162.

[11] P.K. Baumann, S.P. Bozeman, B.L. Ward and R.J. Nemanich, in C. Brandt, D.K. Gaskill and R.J. Nemanich (eds.), *III-Nitride, SiC, and Diamond Materials for Electronic Devices*, Mater. Res. Soc. Proc., Pittsburgh, PA, 1996, in press.

[12] P.K. Baumann, T.P. Humphreys, R.J. Nemanich, K. Ishibashi, N.R. Parikh, L.M. Porter and R.F. Davis, in P.K. Bachmann, I.M. Buckley-Golder, J.T. Glass and M. Kamo (eds.), *Proc. of the 4th European Conference on Diamond, Diamond-like and Related Materials*, in *Diamond Relat. Mater.*, *3* (1994) 883.

[13] F.J. Himpsel, P. Heimann and D.E. Eastman, *Sol. State Commun.*, *36*, (1980) 631.

[14] B.B. Pate, W.E. Spicer, T. Ohta and I. Lindau, *J. Vac. Sci. Technol.*, *17* (1980) 1087.

[15] M. Marchywka, P.E. Pehrsson, S.C. Binari and D. Moses, *J. Electrochem. Soc.*, *140(2)* (1993) L19.

[16] E.H. Rhoderick and R.H. Williams, *Metal-Semiconductor Contacts*, Clarendon, Oxford, 1988.

[17] C. Weiser, *Surf. Sci.*, *20* (1970) 143.

[18] S.C. Erwin and W.E. Pickett, *Surf. Coat. Technol.*, *47* (1991) 487.

[19] S.C. Erwin and W.E. Pickett, *Solid State Commun.*, *81* (1992) 891.

[20] W.E. Pickett and S.C. Erwin, *Phys. Rev.*, *B 41* (1990) 9756.

[21] W.E. Pickett and S.C. Erwin, *Superlatt. Microsruct.*, *7* (1990) 335.

[22] W.E. Pickett, M.R. Pederson and S.C. Erwin, *Mater. Sci. Eng.*, *B 14* (1992) 87.

[23] W.R.L. Lambrecht, *Physica*, *B 185* (1993) 512.

[24] M.W. Geis, J.C. Twichell, J. Macaulay and K. Okano, *Appl. Phys. Lett.*, *67* (1995) 1.

[25] W. Zhu, G.P Kockanski, S. Jin and L. Siebels, *J. Appl. Phys.*, in press.

[26] S.P. Bozeman, P.K. Baumann, B.L. Ward, M.J. Powers, J.J Cuomo, R.J. Nemanich and D.L Dreifus, in P.K. Bachmann, I.M. Buckley-Golder, J.T. Glass and M. Kamo (eds.), *Proc. of the 6th European Conference on Diamond, Diamond-like and Related Materials*, in *Diamond Relat. Mater.*, *5* (1996) 802.

[27] R. Gomer, *Field Emission and Field Ionization*, Cambridge, MA, 1961.