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Comparison of electron affinity and Schottky barrier height of zirconium and copper-diamond interfaces

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In this study, the evolution from diamond surfaces to metal-diamond interfaces has been examined. The electron affinity and the Schottky barrier height of a few Å thick films of Zr and Cu deposited in ultrahigh vacuum (UHV) onto II*b* substrates were correlated. Prior to metal deposition, the diamond surfaces have been cleaned by different anneals and plasma treatments in UHV, and the surfaces were characterized by Auger electron spectroscopy and atomic force microscopy. The initial surfaces were terminated with oxygen, or free of chemisorbed species. Ultraviolet photoemission spectroscopy was employed to determine whether the samples exhibited a positive electron affinity or a negative electron affinity (NEA) before and after metal deposition. For Zr, the Schottky barrier height was found to change very little with the presence or absence of chemisorbed species at the interface. A NEA was observed for Zr on diamond independent of the surface termination. However, for Cu, the surface cleaning prior to metal deposition had a more significant effect. The Schottky barrier height changed strongly depending on the chemical species at the interface. A NEA was only detected for Cu on clean diamond surfaces. The differences between Zr on the one hand and Cu on the other are correlated with differences in interface chemistry and structure. © *1997 American Vacuum Society*. [S0734-211X(97)11604-3]

I. INTRODUCTION

Negative electron affinity (NEA) surfaces could enable the development of cold cathode devices. The electron affinity of a semiconductor corresponds to the energy difference between the vacuum level and the conduction-band minimum. For most materials, the vacuum level lies above the conduction-band minimum. This is called a positive electron affinity. As a wide bandgap semiconductor, diamond has the potential of exhibiting negative electron affinity surfaces since the conduction-band minimum lies near the vacuum level. Electrons from the conduction-band minimum then have sufficient energy to leave a NEA surface and be emitted into vacuum.

By employing different surface treatments, such as plasma cleaning or annealing in ultrahigh vacuum (UHV), the position of the conduction-band minimum can be shifted with respect to the vacuum level. This can induce a NEA or remove it.¹⁻⁶ Subsequent to precleaning the diamond (100) samples with a wet chemical etch, the diamond surfaces are oxygen terminated. This chemisorbed oxygen layer forms a surface dipole. Such a surface exhibits a positive electron affinity. For the diamond (100) surface, an anneal to 900-1050 °C or a H-plasma clean results in a NEA and a 2×1 reconstructed, oxygen-free surface.^{3,5,6} The different threshold temperatures are related to different wet chemical pretreatments.³ It was found that UHV annealing at 900 °C was sufficient for samples precleaned by an electrochemical etch. But a 1050 °C anneal was required for a preclean employing chromic acid. It has been proposed that the diamond (100) surface exhibits a monohydride termination subsequent to a 900-1050 °C anneal or a H-plasma exposure.^{3,5,6} A H surface layer results in a dipole resulting in a NEA. However, for all these treatments, a positive electron affinity and a 2×1 reconstruction are observed following a 1150 °C anneal.⁶ This surface is considered to be free of adsorbates. *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 This is in agreement with the experimental results.^{5,6}

Various studies have described metals on diamond.7-15 As-deposited metal contacts usually have been found to exhibit Schottky characteristics. Most of these reports are based on current-voltage (I-V) data. It is, however, difficult to deduce the Schottky barrier height from I-V measurements due to the large ideality factors of metal-diamond interfaces.^{13–15} Ultraviolet photoemission spectra can be used to measure the Schottky barrier height of metaldiamond interfaces. For this purpose, features from both the metal and the semiconductor need to be visible. This means the thickness of the metal has to be equal to or less than the electron mean-free path (≤ 5 Å). It has been demonstrated that depositing a few Å of metals such as Ti, Ni, Co, Cu, and Zr can induce a NEA on diamond surfaces.^{3,16–21} Also, submonolayer deposition of TiO has been reported to induce a NEA.²² The presence of a NEA or positive electron affinity has been correlated with different structures of the metaldiamond interface. Metal films deposited on adsorbate-free surfaces have been found to exhibit lower Schottky barrier heights and lower electron affinities than for surfaces terminated by species such as hydrogen or oxygen. And for some metal-diamond structures, the Schottky barrier heights have been low enough to induce a NEA.

Photoemission spectroscopy is a very sensitive technique to determine whether a surface exhibits a NEA or a positive

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electron affinity. Electrons are photoexcited from the valence band into states in the conduction band. These electrons can then quasithermalize down to the conduction-band minimum. For NEA surfaces, these secondary electrons from the conduction-band minimum can be emitted into vacuum and appear as a sharp peak at the low kinetic energy end of the photoemission spectra.^{23,24} In this study, diamond (100) surfaces have been cleaned by anneals to 1050 or 500 °C. Thin Zr or Cu films were deposited on these diamond substrates. The surface properties were analyzed before and after metal deposition.

II. EXPERIMENT

For this study, an UHV system was employed that consists of several interconnected chambers featuring capabilities for annealing, metal deposition, ultraviolet photoemission spectroscopy (UPS), and Auger electron spectroscopy (AES). Several natural type IIb single-crystal semiconducting, boron doped diamond (100) substrates $(3.0 \times 3.0 \times 0.25)$ mm) were used. Typical resistivities of these samples were $10^4 \ \Omega$ cm. To remove nondiamond carbon and metal contaminants, an electrochemical etch has been employed. Details of this method have been previously described.²⁵ The wafers were blown dry with N2, mounted on a Mo holder and transferred into the UHV system (base pressure ~ 1 $\times 10^{-10}$ Torr). Two different *in vacuo* cleaning processes were employed to study the effect of surface treatment on the characteristics of the metal-diamond interface. These processes consisted of an anneal to either 1150 or 500 °C both for 10 min. The pressure in the annealing chamber rose from 1×10^{-10} to 7×10^{-9} and 8×10^{-10} Torr during the anneals, respectively. After the heat treatment, 2 Å thick layers of Zr or Cu were deposited onto the diamond surface. The deposition was facilitatied by an e-beam evaporator. And the diamond substrates were kept at room temperature during metal deposition. The pressure in the chamber rose to 2 $\times 10^{-9}$ Torr during deposition. A quartz-crystal monitor was employed to determine the thickness of the metal films. Following the annealing, and the growth steps, UPS and AES were employed to characterize the surface properties.

The presence of Zr or Cu on the surface was confirmed by using AES. Atomic force microscopy (AFM) images of the diamond wafers clearly showed arrays of linear grooves parallel to each other with a depth of ~ 20 Å. This surface structure is a result of the commercial polishing procedure used to smoothen the surfaces. Subsequent to depositing 2 Å of metal, no island structures were observed in the AFM measurements. This is indicative of a uniform twodimensional layer for both Zr and Cu.

He I (21.21 eV) radiation from a discharge lamp was employed to facilitate the photoemission. The emitted electrons were measured using a 50 mm hemispherical analyzer with an energy resolution of 0.15 eV. The sample was biased by 1 V with respect to the analyzer. This was necessary so that the low-energy electrons from the NEA surfaces could be detected, despite the work function of the analyzer. The sharp



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

NEA peak appears at the low-energy end of the photoemission spectrum and corresponds to the energy position of the conduction-band minimum E_C (Fig. 1). Emission from E_C is positioned at $E_V + E_G$ in the spectrum. E_V is the energy position of the valence-band maximum and E_G the energy of the band gap. In a corresponding manner, emission from E_V appears at $E_V + h\nu$ in the UPS spectra. For semiconductors, this corresponds to the high kinetic energy cutoff of the spectra. Then, the spectral width for NEA surfaces, or the distance between emission from the valence-band maximum and the conduction-band minimum is given by $h\nu - E_G$. With the values for He I radiation $h\nu = 21.21$ eV and the band gap of diamond $E_G = 5.47$ eV, the width of the spectrum is 15.7 eV. However, for a surface with a positive electron affinity, the low-energy cutoff is determined by the vacuum level. Then, the spectral width will be smaller than for a NEA. In fact, the width will be reduced by the value of the positive electron affinity of the surface.

Consider photoemission spectra of a thin metal film on a semiconductor. Spectra exhibiting features from both the metal and the semiconductor can be used to determine the Schottky barrier height Φ_B (Fig. 2). For this to be the case, the thickness of the metal layer needs to be equal to or less than the electron mean-free path (≤ 5 Å). The Schottky barrier height for a metal on a *p*-type semiconductor, like diamond, is defined by the difference between the position of the Fermi level of the metal, E_F and the valence-band edge, E_V , of the semiconductor. It may, however, be difficult to detect the relatively weak onset of emission at E_V , even for metal layers thinner than the mean-free path. This is due to the fact that emission from the metal Fermi level may overshadow this weak onset. Often times it is, therefore, necessary to use an independent method to determine the position of the valence-band minimum. In particular, E_V can be referenced to some strong features in the diamond spectrum before metal deposition. Here, a peak positioned at 8.3 eV



FIG. 2. Schematic diagram of photoemission spectra for a metal (e.g., 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 .

below E_V was chosen as a reference. In the case of a NEA surface, the sharp low-energy peak corresponding to E_C can be used to find E_V , too. Then the difference between E_C and E_V corresponds to $h\nu - E_G$.

III. RESULTS AND DISCUSSION

First consider the diamond surfaces before metal deposition. After loading the samples into the vacuum system, AES scans were obtained. Features indicative of the presence of oxygen on the surface were detected. Subsequent to a 500 °C anneal, the oxygen peak was only slightly reduced. After a 1150 °C anneal, oxygen was no longer observed by means of AES. From UPS spectra, positive electron affinities of χ =1.4 eV and of χ =0.7 eV were found for the substrates heated to 500 and 1150 °C, respectively. These numbers are consistent



FIG. 3. UV photoemission spectra of 2 Å of Zr deposited on a diamond (100) surface annealed to (a) 1150 °C 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.



FIG. 4. UV photoemission spectra of 2 Å of Cu grown on a diamond (100) surface following an anneal to (a) 1150 $^{\circ}$ C and (b) 500 $^{\circ}$ C. A metal induced NEA is observed for (a), whereas a positive electron affinity is detected for (b).

with values reported previously.^{5,18} It is expected that chemisorbed oxygen on diamond results in a stronger surface dipole than for the clean surface. This would also lead to a larger work function for the oxygen terminated surface. Our observations are in agreement with that.

Following deposition of 2 Å of Zr on clean diamond surfaces, the width of the UPS spectrum increased consistently with the surface, exhibiting a NEA [Fig. 3(a)]. A Schottky barrier height of $\Phi_B = 0.70$ eV was measured. Emission below the conduction-band minimum E_C was observed. This phenomenon will be discussed further in another publication.²⁶ Deposition of 2 Å of Zr on oxygen terminated diamond surfaces also resulted in a NEA. A larger Schottky barrier height of $\Phi_B \cong 0.9$ eV was measured [Fig. 3(b)]. And the spectrum shifted~0.3 eV toward lower energies. Subsequent to depositing 2 Å of Cu on clean diamond surfaces, a NEA and a Schottky barrier height of $\Phi_B = 0.70 \text{ eV}$ were determined by means of UPS [Fig. 4(a)]. Also, the spectra shifted by 0.3 eV to lower energies. However, in the case of Cu on oxygen terminated surfaces, a positive electron affinity of $\chi = 0.75$ eV and a larger Schottky barrier height of $\Phi_B \cong 1.60 \text{ eV}$ were measured [Fig. 4(b)]. Also, a larger shift to lower energies of 0.6 eV was found. These results are summarized in Table I. Equation (1) is valid specifically for photoemission of thin metal layers (less than the electron

TABLE I. Results of UV photoelectron emission spectroscopy to measure electron affinity χ and Schottky barrier Φ_B . PEA: positive electron affinity, NEA: negative electron affinity.

| | UPS | |
|-----------|--|--|
| Sample | oxygen | Clean |
| C(100) | PEA, <i>χ</i> ≅1.40 eV | PEA, <i>χ</i> ≅0.70 eV |
| Zr/C(100) | NEA, $\chi < 0$, $\Phi_B \cong 0.90 \text{ eV}$ | NEA, $\chi < 0$, $\Phi_B \cong 0.70 \text{ eV}$ |
| Cu/C(100) | PEA, $\chi \cong 0.75 \text{ eV}$, $\Phi_B \cong 1.60 \text{ eV}$ | NEA, $\chi < 0$, $\Phi_B \cong 0.70 \text{ eV}$ |





FIG. 5. Band diagrams of the zirconium–diamond interface. For zirconium, on both the oxygen terminated (a) and the clean surface (b), the Schottky barrier height added to the metal work function is less than the diamond band gap. This corresponds to a NEA.

mean-free path) on semiconductors: The electron affinity can be expressed in terms of the Schottky barrier formed with a p-type semiconductor.²⁷

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

Using the band gap of diamond $E_G = 5.47 \text{ eV}$, the work function of Zr ($\Phi_M = 4.05 \text{ eV}$) and Cu ($\Phi_M = 4.59 \text{ eV}$), and the measured Schottky barrier heights Φ_B , the electron affinities can be calculated. For Zr, we obtain $\chi = -0.72 \text{ eV}$ for the clean surface and $\chi = -0.52 \text{ eV}$ for the oxygen terminated surface. In the same way, $\chi = -0.18 \text{ eV}$ and $\chi = 0.72$ eV are obtained for Cu on the clean and oxygenated surfaces, respectively. These results are consistent with the NEA and positive electron affinity effects that were observed by employing the UPS. Figures 5 and 6 show energy-band diagrams of the Zr-diamond and the Cu-diamond interfaces. These schematics illustrate the correlation of the Schottky barrier height with the electron affinity.

This simple work-function model has been used successfully to explain NEA or positive electron affinity effects for systems like Ti or Ni layers on diamond (111) surfaces.^{16,17} Other approaches may be used to interpret these results. The monolayer thick metal films could be considered as dipole layers. It has been found that Ni deposited on Ar-plasma cleaned diamond (111) substrates induces a NEA. An Ar plasma or a 950 °C anneal results in a (111) surface free of adsorbates.⁴ In comparison, a larger Schottky barrier and a

FIG. 6. Band diagrams of the copper-diamond interface. For copper on the oxygen terminated surface (a), the sum of the Schottky barrier height and work function for metal on diamond is greater than the band gap of diamond, resulting in a positive electron affinity. For copper on the clean surface (b), the Schottky barrier height added to the metal work function is less than the diamond band gap. This corresponds to a NEA.

positive electron affinity were measured for thin Ni films on hydrogen terminated (111) surfaces. In theoretical studies by Erwin and Pickett²⁸⁻³¹ and Pickett, Pederson, and Erwin,³² 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. Considering copper on diamond (111) surfaces, Lambrecht³³ 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. According to these results, the interface termination 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 non-adsorbate-free surfaces. The Schottky barrier heights reported in our study for Zr and Cu on diamond are consistent with this.

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 Cu. Both Zr on clean, as well as oxygen terminated diamond surfaces, tend to exhibit lower electron affinities than Cu on corresponding surfaces. This could be due to the higher reactivity of Zr with both C and O than Cu. It has been reported that Ti, as well as titanium oxide on diamond, exhibit a NEA.²² Zr 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. Zr, like Ti, does react with C. But this reaction is not expected to occur at room temperature. Ti was annealed to >400 °C before reaction with C was observed.³⁴ Cu, on the other hand, does not react as readily with C or O. Thus, the Cu–diamond interface structure for Cu on the clean diamond surfaces is different than for Cu on the oxygen terminated surfaces.

IV. CONCLUSIONS

The effects of depositing thin metal films onto clean and oxygen terminated diamond (100) substrates has been studied by UPS. It was found that Cu induced a NEA on clean surfaces but not on oxygen terminated surfaces. In comparison, Zr induced a NEA on both clean and oxygen terminated surfaces. The Schottky barrier height of Zr on diamond was less dependent on the termination of the diamond surface than was the case for Cu. This is attributed to the fact that Zr exhibits a strong affinity to the oxygen of the oxygen terminated diamond surfaces. In comparison, Cu does not exhibit a significant tendency to form oxides.

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