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Characterization of cobalt–diamond (100) interfaces: electron affinity and Schottky barrier

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Abstract

UV photoemission measurements were used to relate the electron affinity and Schottky barrier of thin Co layers on diamond (100) surfaces. Cobalt films of 2 Å thickness were deposited on natural single crystal diamond (100) substrates by hot filament evaporation in ultra-high vacuum (UHV). The surfaces were characterized with auger electron spectroscopy and atomic force microscopy. The study explores the properties of the cobalt–diamond interface as a function of different surface cleaning procedures. Prior to deposition the diamond samples have been cleaned by UHV anneals at either 500°C or 1150°C. Following either of these anneals a positive electron affinity was deduced from the ultraviolet photoemission measurements. The measurements indicate that the surface annealed at 500°C is terminated with oxygen while the surface annealed at high temperature is free of adsorbates. Upon deposition of Co on the surface heated to 1150°C, a negative electron affinity (NEA) was detected, and a Schottky barrier height of 0.35 eV was measured. However, for Co films deposited on substrates annealed to 500°C a positive electron affinity and a Schottky barrier height of 1.45 eV were observed. The results are discussed in terms of a model that relates the electron affinity to the metal workfunction and the Schottky barrier.

1. Introduction

The electron affinity of a semiconductor surface is defined as the energy difference between the vacuum level and the conduction band minimum. For most materials the conduction band minimum lies below the vacuum level resulting in a positive electron affinity surface. For wide bandgap semiconductors like diamond the conduction band minimum is likely to be close to the vacuum level. Different surface treatments can induce or inhibit a NEA on diamond surfaces [1–4]. Such treatments include annealing in UHV or plasma cleaning. Following a chemical etch the diamond (100) surface is terminated by oxygen. Chemisorbed oxygen forms a dipole layer on the surface that tends to increase the workfunction. Such a surface exhibits, therefore, a positive electron affinity. In addition it has been found that annealing the oxygen terminated diamond (100) crystals to 900–1050°C resulted in the removal of the oxygen which coincided with the appearance of a NEA and a 2×1 reconstructed surface [1,3,4]. We have found that different wet chemical pre-treatments raised or lowered the annealing temperature at which the chemisorbed oxygen was removed from the diamond (100) surface [1]. However heating these samples to

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1150°C resulted in a positive electron affinity while the surface remained 2×1 reconstructed [4]. It has been proposed that the diamond surfaces are terminated by a monohydride following a 900–1050°C anneal. A monohydride on the diamond (100) surface changes the surface dipole such that the workfunction of the surface is lowered. Whereas the removal of hydrogen leads to a clean surface and an increase in the workfunction. Indeed, ab initio calculations for the 2×1 reconstructed surface indicate a NEA for the monohydride terminated surface and a positive electron affinity for the clean surface [3].

The deposition of a few Å of metals like Ti, Ni or Cu on diamond has also been shown to induce a NEA [5,6,1]. 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 have lower Schottky barrier heights than those exhibiting a positive electron affinity [6]. Depositing a few Å of Ni on an Ar-plasma cleaned diamond (111) surface resulted in a NEA. A Schottky barrier height of 0.5 eV was measured for this interface. However, a positive electron affinity and a Schottky barrier height of 1.0 eV were found after growing a Ni layer of the same thickness on a hydrogen terminated diamond (111) surface.

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 [1,5–16]. It has been found that the Schottky barrier height of metals on diamond is virtually independent of the workfunction of the metal. But it has been reported that the Schottky barrier height clearly depends on the surface treatment of the diamond before metal deposition. In general, cleaning the diamond surfaces chemically in air results in a higher value for the Schottky barrier height than cleaning in vacuum.

Photoemission spectroscopy is 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 [10,17].

In this study diamond (100) surfaces were cleaned by two different in vacuo heat treatments. Subsequent to Co deposition on these diamond substrates the effects of the different surface treatments on the Co–diamond interface were examined.

2. Experimental details

Several natural type IIb semiconducting diamond (100) crystals ($3.0 \times 3.0 \times 0.25$ mm) were used in this study. To remove non-diamond carbon and metal contaminants an electrochemical etch has been employed [18]. This cleaning step involved placing the diamond samples between two Pt electrodes in deionized (DI) 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 SiO_2 contaminants. It has previously been reported that SiO_2 was present on the surface after an electrochemical etch [1]. Following this wet chemical cleaning step the samples were blown dry with N_2. The wafers were 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, metal deposition, UPS, AES and LEED.

Two different in vacuo cleaning processes were employed to assess the influence of surface preparation on the properties of the cobalt–diamond interface. One procedure involved annealing the samples to 500°C for 10 min. And the other involved a 1150°C anneal for 10 min. During the anneals the pressure increased to $\sim 8 \times 10^{-10}$ Torr and $\sim 7 \times 10^{-9}$ Torr, respectively. Before deposition on the substrate, 10 Å of Co was evaporated from the hot filament to clean surface contaminants from the source material. Then 2 Å of Co was deposited on the diamond substrates. The thickness was monitored by a quartz crystal oscillator. The pressure during deposition was typically $\sim 2 \times 10^{-9}$ Torr. The samples have been characterized by means of UPS, AES and LEED subsequent to the annealing and the deposition steps.

The presence of a cobalt layer was confirmed by AES. 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. For both cases of growing Co on diamond samples annealed to 1150°C and on those heated to 500°C, the cobalt layers replicated the surface morphology of the underlying diamond substrates. Indeed Co grew as uniform films on the polishing groves of the diamond surfaces (Fig. 1). A 1×1 unreconstructed LEED pattern was observed for the diamond samples subsequent to the 500°C anneal. Upon heating to 1150°C a 2×1 reconstruction was obtained.

The photoemission spectra were excited by HeI (21.21 eV) radiation. A 50 mm 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 workfunction of the analyzer a bias of 1 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 UPS spectra. The position of this feature corresponds to the energy position of the conduction band minimum, E_C (Fig. 2). 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 bandgap energy. Furthermore, electrons from E_V get photoexcited to an energy level at $E_V + h\nu$ in the conduction band and are

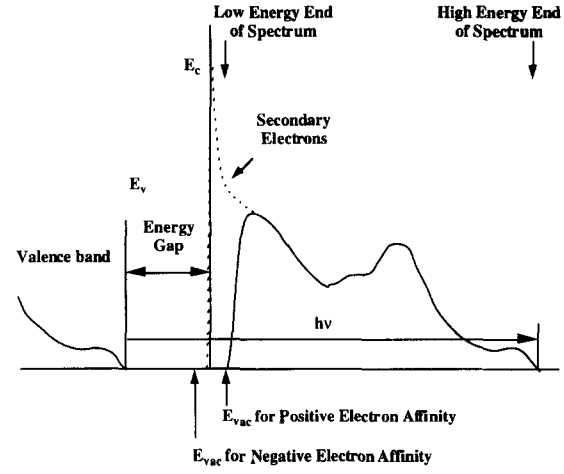

Fig. 2. Schematic diagram of photoemission spectra for a negative electron affinity surface (dotted line) and a positive electron affinity surface (solid line).

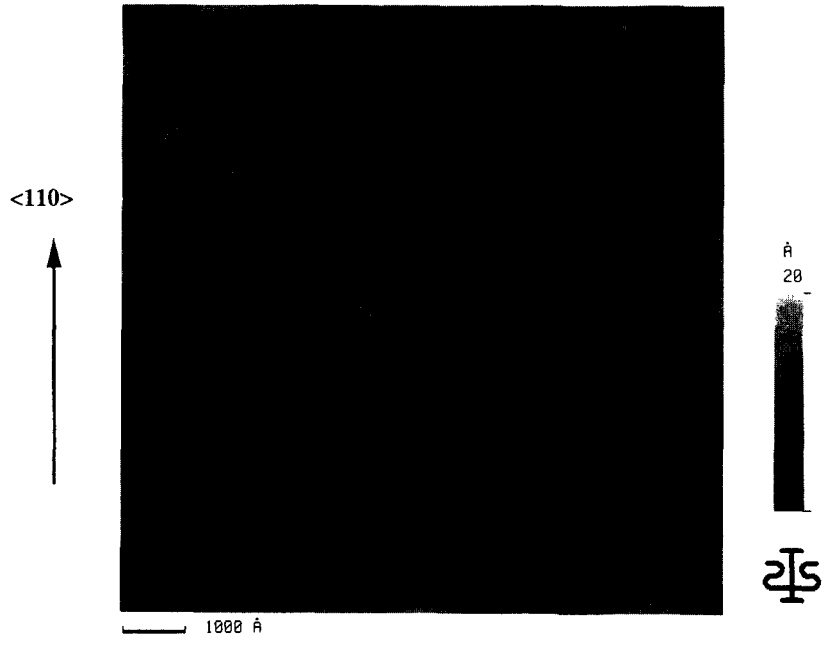

Fig. 1. AFM micrograph of 2 Å of Co deposited on diamond (100).

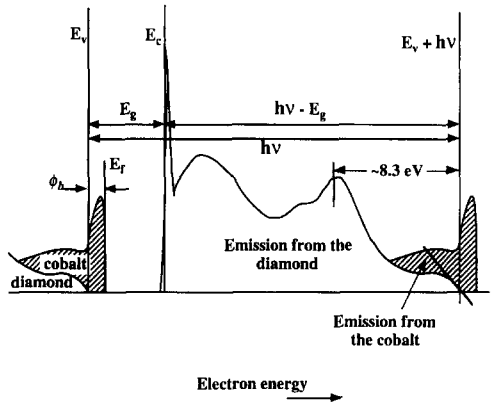

Fig. 3. Schematic diagram of photoemission spectra for cobalt deposited on diamond. The Schottky barrier height Φ_B is determined from the difference between the position of the valence band edge of diamond E_v and the metal Fermi level E_F.

obviously detected at $E_V + h\nu$ in UPS spectra. This corresponds to the high kinetic 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 bandgap 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. 3). 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, 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 case of a NEA the position of the low energy turnon (which corresponds to E_C) can also be used as a reference point to find E_V (which is the high energy turnon of the spectrum). The distance between E_C and E_V has to be $h\nu - E_G$ (Fig. 3).

3. Results and discussion

Consider first the termination of the surfaces prior to Co deposition. The AES spectra of the as-loaded diamond samples showed peaks indicative of the presence of oxygen (Fig. 4). Upon heating the crystals to 500°C the oxygen features were only slightly reduced. However as a result of the 1150°C anneal the amount of oxygen on the diamond surface dropped below the detection limit of the AES instrument. Crystals annealed to 1150°C as well as those heated to 500°C exhibited a positive electron affinity as evidenced by UPS (Fig. 5 and Fig. 6). By referencing the low energy turnon to a bulk feature in the spectrum (feature A in Fig. 5 and Fig. 6) an electron affinity of $\chi \cong 0.65$ eV was determined for the surfaces free of adsorbates and an electron affinity of $\chi \cong 1.50$ eV for the oxygen terminated surfaces. Indeed, oxygen chemisorbed to the diamond surface is expected to induce a stronger surface dipole and therefore cause an increase in the workfunction in

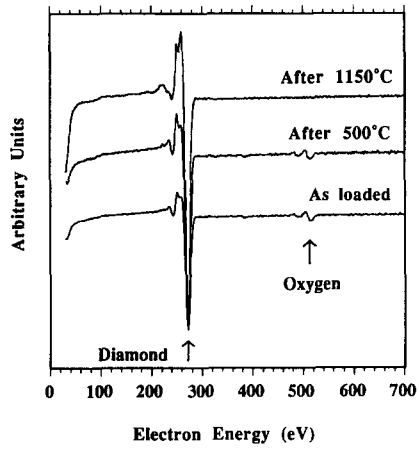

Fig. 4. AES spectra of diamond as a function of different surface cleaning processes. The as-loaded surface exhibits features indicative of oxygen which get only slightly reduced following a 500°C anneal. Subsequent to a 1150°C anneal the oxygen peak is removed.

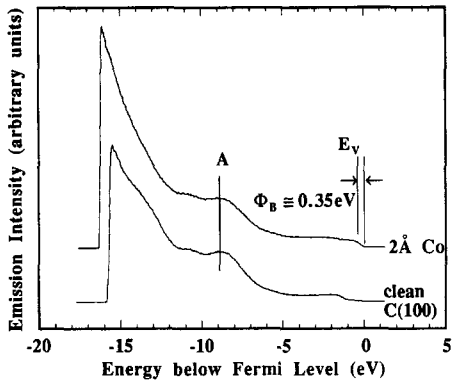

Fig. 5. UV photoemission spectra of diamond (100) following a 1150°C anneal and of Co deposited on diamond. A metal induced NEA is observed upon deposition of Co.

comparison with a clean surface. Our results are consistent with this.

Deposition of 2 Å of Co on the diamond samples heated to 1150°C induces a NEA. Indeed, the width of the UPS spectrum increased following the Co deposition (Fig. 4). Furthermore, a Schottky barrier height of $\Phi_B \cong 0.35$ eV was measured by means of UPS. The electron affinity of a p-type semiconductor subsequent to the formation of a Schottky barrier is given by [19]

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

In our study $\Phi_M = 5.00$ eV is the workfunction of cobalt and $E_G = 5.47$ eV the bandgap of diamond.

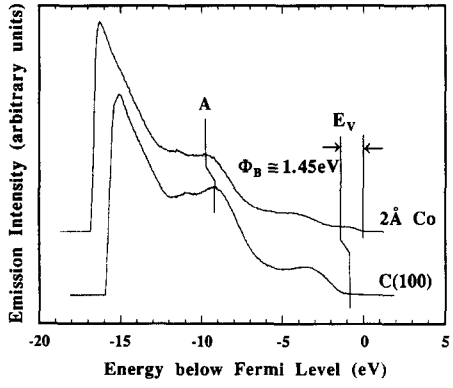

Fig. 6. UV photoemission spectra of diamond (100) following a 500°C anneal and of Co deposited on diamond. The diamond sample exhibits a positive electron affinity both after the 500°C anneal as well as the deposition of Co.

Using these values and the measured Schottky barrier height one can calculate an electron affinity of $\chi \cong -0.1$ eV. Indeed this is consistent with the experimental result of the formation of a NEA. In comparison, depositing 2 Å of Co on the diamond crystals annealed at 500°C resulted in a positive electron affinity, and the spectrum shifted ~ 0.6 V to lower energies (Fig. 6). Furthermore, a Schottky barrier height of $\Phi_B \cong 1.45$ eV was determined from the UPS spectra. By referencing the low energy turnon to a bulk peak in the spectrum an electron affinity of $\chi \cong 0.90$ eV was deduced for the cobalt diamond interface. Due to Co deposition the electron affinity was reduced by about 0.60 eV. From Eq. (1) an electron affinity of $\chi \cong 0.95$ eV is obtained for Co grown on oxygen terminated diamond surfaces. Again this result is in agreement with the experimental data.

The simple workfunction model described above (Eq. (1)) has been employed in previous studies to explain NEA or positive electron affinity effects of Ti or Ni deposited on diamond (111) surfaces [5,6]. Indeed it has been found that Ni grown on Ar plasma cleaned diamond (111) crystals induces a NEA, and a Schottky barrier height of 0.5 eV was measured. It has been demonstrated that an Ar plasma or a 950°C anneal can remove a NEA from a H plasma treated diamond (111) surface [2]. Therefore it has been proposed that an Ar plasma removes chemisorbed hydrogen and thus leads to a clean surface. However, depositing Ni on a hydrogen terminated diamond (111) surface resulted in a positive electron affinity. And a larger value for the Schottky barrier height ($\Phi_B \cong 1.0$ eV) was measured. Theoretical studies of the Ni–diamond interface have been performed by Erwin and Pickett [20–23] and Pickett et al. [24]. For the adsorbate free diamond (100) and (111) surfaces a Schottky barrier height of less than 0.1 eV was calculated for the most stable configurations. Lambrecht calculated the Schottky barrier height for copper on diamond (111) surfaces depending on the interface structure [25]. A Schottky barrier of less than 0.1 eV was determined for the clean surface and ≥ 1.0 eV for the hydrogen terminated surface. The values obtained for both Ni and Cu on clean surfaces are indeed similar. And these results indicate that the Schottky barrier depends on the interface termination.

We suggest that a 1150°C anneal removes chemisorbed atoms from sufficiently large portions of the diamond (100) surface, that a positive electron affinity is induced on the diamond surface itself, and that the Schottky barrier height due to metal deposition on this surface is significantly smaller than for metal deposition on a hydrogen or oxygen terminated surface. In fact the Schottky barrier height is small enough to result in a NEA from the metal–diamond interface. Furthermore, we note that an Ar plasma exposure or an anneal at 950°C of the diamond (111) surface has similar effects on the properties of the diamond surface and metal–diamond interface as a 1150°C anneal does pertaining to the diamond (100) surface [2,6]. In particular, the results on Co reported in this paper and the previous study on Ni clearly suggests that the value of the electron affinity is correlated with the Schottky barrier height. Metal–diamond interfaces with a lower Schottky barrier height also exhibit a lower electron affinity, and no clear dependence of the Schottky barrier height on the metal workfunction has been found. But the type of surface treatment of the diamond substrate prior to metal deposition is critical for the properties of the metal–diamond interface. It can be said that choosing an appropriate surface cleaning procedure is therefore crucial for obtaining a NEA. Treatments capable of removing chemisorbed atoms from diamond surfaces are necessary to obtain a minimum for both the Schottky barrier height and the electron affinity. Apparently a surface sufficiently free of adsorbates is necessary to minimize the Schottky barrier height enough to induce a NEA for most metals. Only metal–diamond interfaces with low workfunction metals such as Cs have been reported to exhibit a NEA for non adsorbate free diamond surfaces [26]. Overall, different types of surface treatments have been shown to influence the Schottky barrier height and the electron affinity significantly.

4. Conclusions

Thin cobalt films have been deposited on clean (after a 1150°C anneal) and oxygen terminated (following a 500°C anneal) diamond (100) substrates. Both the clean and oxygen terminated surfaces exhibited a positive electron affinity as evidenced by UPS. A metal induced NEA has been detected and a Schottky barrier height of 0.35 eV was measured by means of UPS for the clean diamond samples. Cobalt deposited on oxygen terminated surfaces resulted in a positive electron affinity and a Schottky barrier height of 1.45 eV. Furthermore, the Co films were shown to be uniform. The results discussed here indicate that surface cleaning can have a significant impact on the properties of the metal–diamond interface.

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