CHARACTERIZATION OF ZIRCONIUM - DIAMOND INTERFACES

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ABSTRACT

Thin Zr films were deposited on natural single crystal diamond (100) substrates by ebeam evaporation in ultra-high vacuum (UHV). Before metal deposition the surfaces were cleaned by UHV anneals at either 500°C or 1150°C. Following either one of these treatments a positive electron affinity was determined by means of UV photoemission spectroscopy (UPS). Depositing 2Å of Zr induced a NEA on both surfaces. Field emission current - voltage measurements resulted in a threshold field (for a current of 0.1 μ A) of 79 V/ μ m for positive electron affinity diamond surfaces and values as low as 20 V/ μ m for Zr on diamond.

INTRODUCTION

Negative electron affinity (NEA) surfaces based on wide bandgap semiconductors like diamond could enable the development of cold cathodes. So far n-type doping of diamond remains a major challenge. The electron affinity of a semiconductor corresponds to the energy difference between the vacuum level and the conduction band minimum. Usually 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. 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 can induce or inhibit a NEA on diamond surfaces [1-6]. Such treatments include plasma cleaning as well as annealing in ultra high vacuum (UHV). Subsequent to a wet chemical etch the diamond surfaces are terminated by oxygen. 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. For the diamond (100) surface an anneal to 900°C - 1050°C or a H-plasma clean results in a NEA and a 2x1 reconstructed, oxygen free surface [3, 5, 6]. The different threshold temperatures are related to different wet chemical pre-treatments [3]. However for all these treatments a positive electron affinity and a 2x1 reconstruction are observed following a 1150°C anneal [6]. The diamond (100) surface has been proposed to be terminated by a monohydride subsequent to a 900°C - 1050°C anneal or a Hplasma exposure. Ab initio calculations for the 2x1 reconstructed surface predict a NEA for a monohydride terminated surface and a positive electron affinity for an adsorbate free surface [5].

Depositing a few Å of a metal like Ti, Ni, Co or Cu on diamond can induce a NEA [7, 8, 9, 10, 3]. The presence of a NEA or positive electron affinity has been correlated with different structures of the metal - diamond interface. Metal - diamond structures with a NEA have been found to exhibit lower Schottky barrier heights than those with a positive electron affinity. Schottky barrier height measurements have been reported for metals deposited on (100), (111) and polycrystalline diamond surfaces [3, 7-20]. No significant dependence of the Schottky barrier heights have been reported for metal films deposited on adsorbate free surfaces than for surfaces terminated by species such as hydrogen or oxygen.

Photoemission spectroscopy is found to be a very sensitive method to distinguish between a NEA or positive electron affinity. 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 [14, 21]. While photoemission spectroscopy determines the emission properties of the surface itself, 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 500°C or 1050°C. Thin Zr films were deposited on these diamond substrates. The surface properties were analyzed before and after Zr deposition.

EXPERIMENTAL DETAILS

Several natural p-type single crystal semiconducting diamond (100) substrates were used in this study. To remove nondiamond carbon and metal contaminants an electrochemical etch has been employed. Details of this technique have been described earlier [22, 3]. The samples were then loaded into a UHV system consisting of several interconnected chambers featuring capabilities for annealing, metal deposition, ARUPS and AES. Two different in vacuo cleaning processes were used to study the effect of surface treatment on the characteristics of the zirconium - diamond interface. One procedure involved annealing the wafers to 500°C for 10 minutes. And the other involved a 1150°C anneal for 10 minutes. The base pressure in the annealing chamber was ~ 1 x 10⁻¹⁰ Torr and rose to ~ 8 x 10⁻¹⁰ Torr and ~7 x 10⁻⁹ Torr during the anneals, respectively. Subsequent to the anneal a Zr e-beam evaporator was employed to deposit 2 Å thick films. A quartz crystal monitor was used to measure the thickness. During deposition the pressure was ~ 2 x 10⁻⁹ Torr. Following each annealing - and deposition step, UPS and AES were used to characterize the samples.

The presence of a Zr film was confirmed by means of AES. AFM images of the diamond wafers clearly display linear groves with a depth of ~ 20 Å. This surface structure is due to polishing the samples with diamond grit. No island structures were observed in AFM measurements after 2 Å of deposition, indicating a uniform 2D layer.

A discharge lamp was employed to excite HeI (21.21 eV) radiation to facilitate the photoemission and a 50 mm hemispherical analyzer with an energy resolution of 0.15 eV was used to detect the emitted electrons. To overcome the workfunction 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 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 . 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 $E_V + hv$ in the conduction band and are obviously detected at $E_V + hv$ in UPS spectra. This corresponds to the high kinetic energy of of the spectra. Therefore the spectral width for a NEA surface is $hv - E_G$. Using the value of hv = 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. This results in a smaller value for the spectral width as compared to the case of a NEA.

Photoemission spectra that exhibit features from both the semiconductor and the metal can be used to determine the Schottky barrier height Φ_B (Fig. 1).



Fig. 1 Schematic diagram of photoemission spectra for metal deposited on diamond. The Schottky barrier height $\Phi_{\rm B}$ is determined from the difference between the position of the valence band edge of diamond $E_{\rm V}$ and the metal Fermi level $E_{\rm F}$.

This method is only suitable for metal films with thicknesses equal to or less than the electron mean free path (≤ 5 Å). 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 . But 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. In our case a feature positioned at 8.3 eV below E_V has been chosen. For a NEA the position of the low energy turnon (which corresponds to E_C) can also be used as a reference to find E_V (which is the high energy turnon of the spectrum). The difference between E_C and E_V has to be $h\nu - E_G$.

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 to 1100V was applied between the sample and a 2 mm diameter platinum anode with a rounded tip. The distances were varied between 2 and 20 μ m.

RESULTS AND DISCUSSION

AES spectra of the as-loaded samples clearly exhibited oxygen peaks. 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 $\chi \equiv 1.4$ eV and of $\chi \equiv 0.7$ eV were observed for the crystals annealed to 500°C 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. Depositing 2Å of Zr onto oxygen terminated diamond (100) samples resulted in a NEA (Fig. 2a). A Schottky barrier height of $\Phi_B \equiv 0.9$ eV was determined by UPS. Subsequent to deposition of 2Å of Zr on clean diamond (100) surfaces a NEA was observed and the spectrum shifted ~ 0.3 eV toward lower energies (Fig. 2b). A lower Schottky barrier height of $\Phi_B \equiv 0.7$ eV was measured. This structure exhibited emission even below the conduction band minimum E_C . A summary of these results is shown in Table 1. The electron affinity of a p-type semiconductor following metal deposition is given by equation (1) [21].

$$\chi = (\Phi_{\rm M} + \Phi_{\rm B}) - E_{\rm G} \tag{1}$$

Using the bandgap of diamond $E_G = 5.47$ eV, the workfunction of Zr $\Phi_M = 4.05$ eV and the measured Schottky barrier heights one can calculate electron affinities of $\chi \cong -0.52$ eV for the oxygen terminated surface and $\chi \cong -0.72$ eV for the clean surface. These results are in agreement with the detection of metal induced NEA's by means of UPS. The emission detected below E_C for 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.

This simple workfunction model has been used successfully to explain NEA or positive electron affinity effects for systems like Ti or Ni layers on diamond (111) surfaces [7, 8] and Co or Cu films on diamond (100) surfaces [9, 10]. It has been found that Ni deposited on Ar plasma cleaned diamond (111) substrates induced a NEA. An Ar plasma or a 950°C anneal result in a (111) surface free of adsorbates [4]. In comparison, a positive electron affinity and a larger Schottky barrier were observed for thin Ni films on (111) surfaces terminated by hydrogen. Theoretical results of the Ni - diamond interface have been reported by Erwin and Pickett [24-27] and Pickett, Pederson and Erwin [28]. The most stable configuration for clean (111) and (100) surfaces resulted in a Schottky barrier height of less than 0.1 eV. Lambrecht calculated the Schottky barrier height for copper on diamond (111) surfaces. A value of less than 0.1 eV for a clean surface and greater than 1.0 eV for a surface terminated with hydrogen were found [29]. These results indicate that the Schottky barrier height depends on the interface termination. Lower values for the Schottky barrier height and a greater likelihood of inducing a NEA are expected for metals deposited on clean surfaces than on non adsorbate free surfaces. The Schottky barrier heights reported in this study for Zr on diamond are in agreement with this. It is significant that a metal induced NEA was observed for deposition of Zr on both clean and

oxygen terminated surfaces. Previously a positive electron affinity was found for Ti on a oxygen terminated diamond (100) surface [7]. Ti has a workfunction only 0.3 eV higher than that of Zr. So far only metal diamond interfaces with low workfunction metals like Cs have been reported to exhibit a NEA for non adsorbate fee diamond surfaces [30].

Field emission measurements were performed on diamond samples and on Zr films deposited on oxygen terminated and clean diamond surfaces. The emission threshold field was defined for a current of 0.1 μ A. Thresholds between 20 and 79 V/ μ m were measured. For a summary see Table 1. Values of the same magnitude have been reported previously for diamond samples [31, 32]. As an example I-V curves for the diamond surface are shown in Fig. 3. The results from the field emission measurements have been compared to the Fowler - Nordheim equation [33]:

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

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. By fitting the field emission data to equation (2) the effective barrier heights φ were obtained as shown in Table 1. Depositing Zr onto both oxygen terminated and clean diamond (100) surfaces improves the emission properties. The best results were obtained for Zr on the clean surface. Both UPS and field emission measurements show these trends consistently.



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



Fig. 3 Field emission current - voltage curves for a type IIb single crystal diamond (100) sample. Distances between the sample and the anode: a) $3.3 \ \mu m$, b) $4.3 \ \mu m$, c) $5.6 \ \mu m$, d) $8.5 \ \mu m$.

Sample	UPS		Field Emission Threshold (V/µm)	Barrier Height (eV)
C(100)	after 500°C anneal PEA, $\chi \cong 1.4 \text{ eV}$	after 1150°C anneal PEA, $\chi \cong 0.7 \text{ eV}$	79 ± 7	0.23 ± 0.01
Zr/C(100) oxygen	NEA, $\chi < 0$, $\Phi_B \cong 0.9 \text{ eV}$		49 ± 4	0.20 ± 0.01
Zr/C(100) clean	NEA, $\chi < 0$, $\Phi_B \cong 0.7 \text{ eV}$		20 ± 3	0.09 ± 0.01

Table 1 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 barrier height. The threshold current is $0.1 \,\mu A$.

CONCLUSIONS

Thin films of Zr were grown on diamond (100) surfaces annealed to 500°C or 1150°C. Using UPS the diamond samples were found to exhibit a positive electron affinity after either one of the heat treatments. Metal induced NEA's were observed for Zr deposition on either one of these surfaces. For Zr on clean surfaces emission even below E_C was detected. Depositing Zr on diamond reduced both the field emission threshold and the effective barrier height in a manner consistent with the UPS results.

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REFERENCES

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

- 2. B.B. Pate, M.H. Hecht, C. Binns, I. Lindau and W.E. Spicer, J. Vac. Sci. Technol. 21, 364 (1982).
- 3. P.K. Baumann, T.P. Humphreys and R.J. Nemanich, in Diamond, SiC and Nitride Wide Bandgap Semiconductors, edited by C.H. Carter, G. Gildenblat, S. Nakamura, R.J. Nemanich, (Mater. Res. Soc. Proc. 339, Pittsburgh, PA, 1994) 69-74.
- 4 J. van der Weide and R.J. Nemanich, Appl. Phys. Lett. 62 (1993) 1878.
- J. van der Weide, Z. Zhang, P.K. Baumann, M.G. Wensell, J. Bernholc and R.J. Nemanich, 5. Phys. Rev. B 50 (1994) 5803.
- 6. P.K. Baumann and R.J. Nemanich, Proc. of the 5th European Conference on Diamond, Diamond-like and Related Materials, edited by P.K. Bachmann, I.M. Buckley-Golder, J.T. Glass, M. Kamo: J. Diamond Rel. Mat., **4** (1995) 802. J. van der Weide and R.J. Nemanich, J. Vac. Sci. Technol. B **10** (1992) 1940.
- 7.
- J. van der Weide and R.J. Nemanich, Phys. Rev. B, 49 (1994) 13629. 8
- 9. P.K. Baumann and R.J. Nemanich, Appl. Surf. Sci., accepted for publication.
- P.K. Baumann and R.J. Nemanich, in <u>Diamond for Electronic Applications</u>, edited by C. Beetz, A. Collins, K. Das, D. Dreifus, T. Humphreys, P. Pehrsson, (Mater. Res. Symp. Soc. Proc. MRS, Pittsburgh, PA 1996), accepted for publication.
- 11. P.K. Baumann, T.P. Humphreys, R.J. Nemanich, K. Ishibashi, N.R. Parikh, L.M. Porter and R.F. Davis, Proc. of the 4th European Conference on Diamond, Diamond-like and Related Materials, edited by P.K. Bachmann, I.M. Buckley-Golder, J.T. Glass, M. Kamo: J. Diamond Rel. Mat. 3 (1994) 883.
- 12. C.A. Mead and T.C. McGill, Phys. Lett. 58A (1976) 149.
- 13. F.J. Himpsel, D.E. Eastman and J.F. van der Veen, J. Vac. Sci. Technol. 17 (1980) 1085.
- 14. F.J. Himpsel, P. Heimann and D.E. Eastman, Sol. State Commun. 36, 631 (1980).
- 15. J.W. Glesener, A.A. Morrish and K.A. Snail, J. Appl. Phys. 70 (1991) 5144.
- 16. M.W. Geis, D.D. Rathman, D.J. Ehrlich, R.A. Murphy and W.T. Lindley, IEEE Electron Device Lett. 8 (1987) 341.
- 17. H. Shiomi, H. Nakahata, T. Imai, Y. Nishibayashi and N. Fujimori, Jpn. J. Appl. Phys. 28 (1989) 758.
- 18. T. Tachibachi, B.E. Williams and J.T. Glass, Phys. Rev. B 45 (1992) 11975.
- 19. M.C. Hicks, C.R. Wronski, S.A. Grot, G.S. Gildenblat, A.R. Badzian, T. Badzian and R. Messier, J. Appl. Phys. 65 (1989) 2139.
- 20. S.A. Grot, S. Lee, G.S. Gildenblat, C.W. Hatfield, C.R. Wronski, A.R. Badzian, T. Badzian and R. Messier, J. Mater. Res. 5 (1990) 2497.
- 21. B.B. Pate, W.E. Spicer, T. Ohta and I. Lindau, J. Vac. Sci. Technol. 17 (1980) 1087.
- 22. M. Marchywka, P.E. Pehrsson, S.C. Binari and D. Moses, J. Electrochem. Soc., 140, No. 2 (1993) L19.
- 23. E.H. Rhoderick and R.H. Williams, Metal-Semiconductor Contacts Clarendon, Oxford, (1988).
- 24. S.C. Erwin and W.E. Pickett, Surf. Coat. Technol. 47 (1991) 487.
- 25. S.C. Erwin and W.E. Pickett, Solid State Commun. 81 (1992) 891.
- 26. W.E. Pickett and S.C. Erwin, Phys. Rev. B 41 (1990) 9756.
- 27. W.E. Pickett and S.C. Erwin, Superlatt. Microsruct. 7 (1990) 335.
- 28. W.E. Pickett, M.R. Pederson and S.C. Erwin, Mater. Sci. Eng. B 14 (1992) 87.
- W.R.L. Lambrecht, Physica B 185 (1993) 512.
- 30. M.W. Geis, J.C. Twichell, J. Macaulay, K. Okano, Appl. Phys. Lett. 67 (1995) 1.
- 31. W. Zhu, G.P Kockanski, S. Jin and L. Siebels, J. of Appl. Phys., in press
- 32. S.P. Bozeman, P.K. Baumann, B.L. Ward, M.J. Powers, J.J Cuomo, R.J. Nemanich and D.L. Dreifus, Proc. of the 6th European Conference on Diamond, Diamond-like and Related Materials, edited by P.K. Bachmann, I.M. Buckley-Golder, J.T. Glass, M. Kamo: J. Diamond Rel. Mat. (1996), accepted for publication.
- 33. R. Gomer, Field Emission and Field Ionization, Cambridge, MA, (1961).