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Negative electron affinity effects on H plasma exposed diamond (100) surfaces

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Abstract

The effects of annealing and a H plasma exposure on natural type IIb diamond (100) were investigated by means of ultraviolet photoemission spectroscopy (UPS). The diamond (100) surface was found to exhibit a negative electron affinity (NEA) following a 900 °C anneal in ultrahigh vacuum. After a H plasma exposure the NEA peak in the UPS spectra had doubled in height. An anneal to 1100 °C resulted in the removal of the sharp NEA feature. A second H plasma treatment resulted in the reappearance of the NEA peak like after the first H plasma exposure. A 2×1 reconstructed low-energy electron diffraction (LEED) pattern was observed subsequent to the anneals as well as the H plasma treatments. The fact that a NEA can be induced or removed repeatedly by means of a H plasma exposure or a 1100 °C anneal respectively provides evidence to correlate the appearance of a NEA with the presence of a monohydride terminated surface.

Keywords: Diamond; Hydrogen; Substrate preparation; Surface characterization

1. Introduction

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, and corresponds to a positive electron affinity. Surfaces of wide bandgap semiconductors like diamond have the potential of exhibiting a negative electron affinity (NEA), since the conduction band minimum lies near the vacuum level. Electrons present in the conduction band have sufficient energy to overcome the work function of a NEA surface and can be emitted into vacuum. Indeed, different surface preparation techniques can shift the position of the vacuum level and therefore induce a NEA or remove it [1-3]. Photoemission spectroscopy is very sensitive to determine whether a surface exhibits a NEA or not. Secondary electrons appear as a sharp feature at the low-energy end of photoemission spectra for NEA surfaces [4,5].

Cleaning of diamond substrates for vacuum investigations often involves a chemical cleaning step followed by an in-vacuum treatment. A common chemical clean is based on using chromic acid and aqua regia. An electrochemical etch has been suggested as a suitable alternative approach [6]. Previously we have published comparative studies on the influence of this electrochemi-

0925-9635/95/\$09.50 © 1995 Elsevier Science S.A. All rights reserved SSDI 0925-9635(94)05228-X cal cleaning technique versus a conventional chromic acid clean on the diamond (100) surface [1]. In particular it was found that oxygen could be removed from the surface at lower annealing temperatures for samples cleaned by an electrochemical etch than for those cleaned by using chromic acid. Furthermore, we have used both techniques to clean diamond substrates prior to deposition of epitaxial Cu contacts [7]. Various metals like Ti, Ni and Cu have been shown to induce a NEA on diamond [1,8,9]. The vacuum cleaning step usually involves annealing the sample or exposing it to a plasma. The effects of annealing diamond (100) have been addressed in several studies [1,3,10-12]. Two different structures have been suggested for an unreconstructed, oxygen-terminated surface [11]. Arguments for a monohydride-terminated surface [1,3,12] or a hydrogen-free surface [10] after annealing to about 1000 °C have been presented. Plasma treatments have been used previously to clean diamond surfaces [2,3].

In this study natural type IIb diamond (100) crystals have been chemically cleaned by an electrochemical etch [6] and a HF dip [1]. Following the chemical cleaning step a series of anneals and H plasma exposures at 500 $^{\circ}$ C have been employed. Such a H plasma may be comparable to the environment of diamond growth at low temperatures [13].

2. Experimental details

The ultrahigh vacuum (UHV) system used in our studies consists of several chambers connected by a UHV transfer line featuring a rail-mounted cart to transport the samples between the chambers. In particular, the chambers used for this study included a UV photoemission spectroscopy (UPS) chamber, a chamber for low-energy electron spectroscopy (LEED) and Auger electron spectroscopy (AES), and a plasma cleaning chamber. The diamond samples used were natural type IIb single crystal C(100) $3.0 \times 3.0 \times 0.25$ mm wafers. An electrochemical etch was used to chemically clean the samples [6]. For this purpose they were suspended between two Pt electrodes in deionized (DI) water as an electrolyte. For a d.c. bias of 350 V between the electrodes a current of 0.5 mA could be measured. After the electrochemical etch the samples were exposed to UV ozone and rinsed in an HF solution to remove SiO₂ surface contaminants. The presence of SiO_2 has been observed previously following the electrochemical etch [1]. N_2 was used to blow the samples dry before they were mounted onto a Mo holder and transferred into the load lock of the UHV system. In vacuum the samples were annealed to 900 °C for 15 min. A pyrometer was used to determine the surface temperature of the Mo holder on which the diamond wafers were mounted. The base pressure was approx. 1×10^{-10} Torr and rose to approx. 4×10^{-9} Torr during annealing. Following the anneal the samples were exposed to a remote H plasma clean. During the clean the temperature of the sample was kept at 500 °C, and the H pressure was held at 50 mTorr. The plasma cleaning system has been described in detail in a previous publication [14]. After the plasma clean the samples were heated to 1100 °C, which caused the pressure in the annealing chamber to rise to approx. 7×10^{-9} Torr. Following this anneal the samples were reexposed to a H plasma.

Subsequent to each cleaning step the techniques of UPS, LEED and AES have been used to characterize the diamond surface. The photoemission was excited by HeI (21.21 eV) radiation. A 50 mm hemispherical electron analyzer with an angular resolution of 2° was used to analyze the photoemitted electrons. An energy resolution of 0.15 eV was used for these experiments. The sample was biased by 1.0 V to overcome the workfunction of the analyzer and to ensure that low-energy electrons from a NEA surface could be detected. 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, $E_{\rm C}$ (Fig. 1). Emission from $E_{\rm C}$ is positioned at $E_{\rm V} + E_{\rm G}$ 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 $E_{\rm v} + hv$ in the spectrum. The spectral width or the distance between



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

emission from the valence band maximum and the conduction band minimum is therefore $hv - E_G$. With the values for HeI radiation hv = 21.21 eV and the band-gap of diamond $E_G = 5.47$ eV, a spectral width of approx. 15.7 eV is determined for a NEA surface. However, in 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.

3. Results and discussion

Subsequent to the electrochemical etch and HF dip the as-loaded diamond crystals exhibited a positive electron affinity, as evidenced from photoemission spectra. In addition, a 1×1 unreconstructed surface and oxygen surface contaminations were detected by means of LEED and AES respectively. Upon annealing to 900 °C in UHV a sharp low-energy peak indicating a NEA surface could be observed in UPS spectra (Fig. 2). This peak is positioned 15.7 eV below the position of the valence band maximum E_V in the spectrum. Furthermore a weak feature at approx. 1.7 eV below $E_{\rm V}$ was also observed after annealing. The NEA effect coincided with the appearance of a 2×1 reconstructed LEED pattern and the removal of oxygen from the surface as seen from AES (Fig. 3). All the spectra in Fig. 2 have been scaled with respect to feature A. Following a hydrogen plasma clean the NEA peak in the UPS spectra was found to be doubled in intensity. Also, the peak at approx. 1.7 eV below $E_{\rm V}$ was no longer observed. Furthermore, the 2×1 LEED pattern could be retained and no changes in the AES spectra were detected.

After the diamond wafers were heated to 1100 °C, the sharp low-energy peak was removed from the UPS



Fig. 2. Photoemission spectra of C(100) cleaned by an electrochemical etch. The sequence of spectra follows from bottom to top: a 900 °C anneal, a H plasma, a 1100 °C anneal, a 1150 °C anneal and a second H plasma.



Fig. 3. Auger spectra of the diamond (100) surface cleaned by an electrochemical etch, as a function of annealing and H plasma exposure.

spectra, and the low-energy cutoff had moved toward higher energies by about 0.5 eV. However, a small lowenergy shoulder could still be observed. In addition, the whole spectrum was found to be shifted to lower energies by about 0.3 eV. Furthermore, the weak feature reappeared at approx. 1.0 eV below the valence band edge. Annealing to 1150 °C resulted in the removal of the lowenergy shoulder. The remaining small low-energy feature may still be an indication that the hydrogen has not been removed completely from the surface. Again, after the 1100 °C and 1150 °C anneals the surface remained 2×1 reconstructed, and the AES spectra did not change. Repeating the H plasma exposure resulted in the appearance of a sharp NEA peak similar to the one observed after the initial H plasma clean. In addition the feature at approx. 1.0 eV below $E_{\rm V}$ was removed.

The features at approx. 1.7 eV and 1.0 eV below E_V

that appeared subsequent to the 900 $^{\circ}$ C and 1100 $^{\circ}$ C anneal are suggested to be surface states. However, only a LEED pattern with weak secondary spots was observed following the second H plasma exposure. Evidently the second H plasma clean caused a reduction in the domain size of the reconstructed surface. Therefore only a weak secondary interference pattern could form.

From our experiments it is suggested that removing the oxygen from the surface can be correlated to the induction of a NEA effect and a 2×1 reconstruction. This has been described in previous publications [1,10-12]. It is interesting to note that the intensity of the NEA peak in the UPS spectra could be increased by employing a H plasma clean. Indeed, a H plasma could also induce a NEA on a positive electron affinity surface. However, a reconstructed (2×1) LEED pattern could be detected after every anneal (900 °C and 1100 °C) and H plasma exposure. It is therefore suggested that a reconstructed surface exhibiting a NEA is terminated by a monohydride, whereas a reconstructed positive electron affinity surface is believed to be free of hydrogen. 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 $\lceil 3 \rceil$.

Previously Yang et al. suggested that a dihydrideterminated surface is energetically unlikely due to stearic hindrance of the H atoms [10]. They proposed that a monohydride-terminated surface turns into a free surface upon annealing to about 1000 °C. However, Hamza et al. reported the presence of a monohydride-terminated surface after annealing to about 1000 °C based on electron-simulated desorption time-of-flight (ESD-TOF) measurements [12]. Furthermore, they report that even after annealing up to about 1260 °C the slow proton peak could be detected in the ESD-TOF spectra. Therefore they argue that large parts of the surface are still terminated by a monohydride. They did not anneal the samples beyond 1260 °C since diamond is expected to graphitize at higher temperatures. Our results, however, suggest that upon annealing to 1100 °C enough hydrogen has been desorbed from the surface to remove the sharp NEA peak from the photoemission spectra. However, if any significant portions of the surface were still terminated by a monohydride, a peak characteristic of a NEA could clearly be observed in the photoemission spectra (according to Weide et al. [3]). Indeed, spectra obtained upon heating to 900 °C exhibited a smaller NEA peak than those taken after a H plasma exposure.

It is suggested that the H plasma clean resulted in a uniform monohydride-terminated surface. From the size difference of the NEA peaks we therefore estimate that about half the surface was terminated by a monohydride following the 900 $^{\circ}$ C anneal. Furthermore, the remaining small low-energy feature in the photoemission spectra following the 1100 $^{\circ}$ C and 1150 $^{\circ}$ C anneals may be an

indication that the hydrogen has not been removed completely from the surface. It may be possible that the portions of the surface terminated by a monohydride were large enough to result in the slow proton peak seen in the ESD-TOF spectra up to approx. 1260 °C. However, these portions may have been too small to result in a distinctive low-energy peak in the photoemission spectra after heating to 1100 °C. It is however interesting to realize that Hamza et al. heated the diamond surface rapidly (up to 1130 °C in about 45 s). Typical heating rates used for our experiments were approx. 60 °C min⁻¹. It is, however, unclear whether the different annealing rates would influence the results significantly. Furthermore, it is difficult to measure the temperature of diamond due to its transparent nature. Therefore, the temperature values mentioned in this and other studies may be off somewhat with respect to each other. This may reconcile some of the apparent differences in the results. Also, different surface cleaning processes or the presence of H in the bulk may affect the surface characteristics. Further work will be necessary to clarify these issues.

4. Conclusions

A NEA effect was induced on the electrochemically cleaned diamond (100) surface by means of a 900 °C anneal. A H plasma exposure enhanced this effect. The NEA could be removed following a 1100 °C anneal. The UPS spectrum from the initial H plasma clean could be reproduced by reexposing the diamond surface to a H plasma. The surface was found to be 2×1 reconstructed following the 900 °C, 1100 °C anneals and after each H plasma exposure.

Acknowledgments

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