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Valence-band photoemission of the H-plasma annealed (100) textured CVD diamond surface

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Abstract

A (100) textured chemical vapor deposited (CVD) diamond thin film was exposed to a hydrogen plasma at 850°C as a cleaning procedure and was subsequently investigated by X-ray absorption spectroscopy (XAS) and ultraviolet photoelectron spectroscopy (UPS) with synchrotron radiation in the range $30\ \mathrm{eV} < h\nu < 150\ \mathrm{eV}$. The dominant feature of the UPS spectra between 30 and 60 eV excitation energy is the presence of a distinct peak at around 1.8 eV below the Fermi level. This feature can be identified as a surface state of the reconstructed diamond (100) surface. In analogy to reported UPS measurements of reconstructed natural diamonds of (100) orientation reported earlier, the results are discussed in terms of a surface reconstruction of the (100) textured CVD diamond film. The electronic properties of the (100) textured CVD diamond thin film are compared to the ones of annealed or H-plasma exposed natural diamond (100). The UPS measurements of a hydrogen-plasma exposed, reconstructed (100) textured CVD diamond surface discussed here are, to our knowledge, the first reported.

Keywords: Diamond; Near edge extended X-ray absorption fine structure (NEXAFS); Photoemission; Plasma processing; Polycrystalline surfaces; Soft X-ray photoelectron spectroscopy; Surface electronic phenomena; Surface relaxation and reconstruction

1. Introduction

The manifold applications of diamond especially in the field of semiconductor applications have raised growing interest in depositing diamond films with increasing quality and defined texture. The possibility of growing thin diamond films with a defined crystallographic texture is an encouraging breakthrough. However, the growth mechanism is still poorly understood, which is caused, at least to some extent, by lack of understanding of the diamond surface and its electronic properties. We have conducted several experiments focusing on the electronic properties of natural diamond (100) and (111) surfaces [1–4]. While the natural diamond surfaces proved to be often contaminated with oxygen, chemical vapor deposited diamond thin films were absolutely clean, as a result of the exposure to atomic hydrogen during the growth process. Regarding this and the relatively complicated polishing and cleaning procedures for natural diamond together with the fact that CVD diamond may be important for device applications we decided to investigate the CVD diamond (100) surface more closely by ultraviolet photoelectron

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spectroscopy (UPS) and X-ray absorption spectroscopy (XAS).

2. Experimental

The diamond film was deposited on a p-doped (100) silicon wafer in a standard downstream microwave plasma enhanced chemical vapor deposition setup (MPECVD) [5–7]. A gas composition of 1.5% CH_4 in H_2 and a pressure of 50 mbar was used for the deposition step. The sample was polished in a nucleation step with diamond powder. The set of growth conditions employed leads to preferred growth along the [100] direction and the angular spread of the nuclei orientation is rather small, amounting to 3°–5° in both polar and azimuthal directions as characterized by X-ray texture diffractometry [5–7]. The surface thickness is estimated to about 30 μm which is thick enough to conceal the underlying silicon. The film was exposed to a hydrogen microwave plasma for about 15 minutes at 850°C as a cleaning procedure, cooled down in vacuum and was then transported through air. Core level photoelectron spectroscopy of the hydrogen plasma exposed films indicated no surface contamination by oxygen after transportation through air.

Ultraviolet photoelectron spectroscopy (UPS) and X-ray absorption spectroscopy (XAS) of the CVD diamond film were carried out in a Vacuum Generator (VG) double-chamber UHV system with base pressures of 5×10^{-11} mbar. The photon-energy-dependent UV-photoemission measurements and the X-ray absorption spectroscopy (XAS) were performed at the SX700-I beamline at the Berlin Synchrotron Radiation source BESSY. The photon energy ranges from 10 to 2000 eV, and the monochromator was operated with a resolution of 0.2 eV at 150 eV photon energy and of 0.5 eV at the C K-edge. The photon energy was calibrated using the HOPG sample (Union Carbide) by taking the value of the lowest energy C 1s π transition from EELS data (285.4 eV). A VG CLAM electron energy analyzer was used for the photoemission experiments and a partial-electron-yield detector equipped with two commercial multichannel plates (Hamamatsu) for the XAS spectroscopy.

For comparison, ultraviolet photoelectron spectra of an annealed or H-plasma exposed natural (100) diamond crystal measured on a Fisons Escalab 210, and UPS spectra of the H-plasma treated (100) textured CVD film measured on a Leybold EA10/100 spectrometer are shown in some figures.

3. Results and discussion

Fig. 1 reflects the UPS HeII spectra before and after exposure of the CVD diamond film to the H-plasma (curves e and c, respectively), which was performed ex-situ in a microwave plasma CVD chamber with downstream configuration. A dramatic change in the valence band spectra can be observed, especially the appearance of two peaks near the valence band maxima, named S1 and B1 in the following. The letter S stands for surface related features, while the letter B is used for bulk

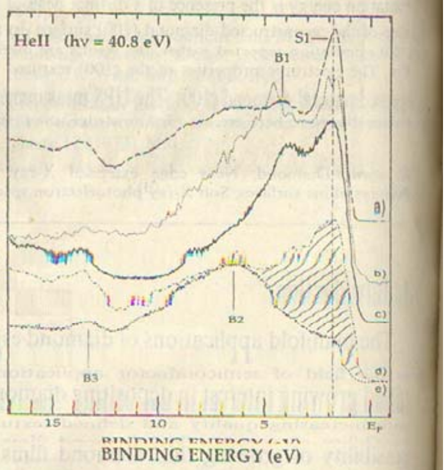

Fig. 1. Valence band spectra of: (a) natural diamond (100) after H-plasma at 870°C; (b) natural diamond (100) annealed at 955°C; (c) (100) textured CVD diamond after H-plasma at 850°C; (d) same film measured with 40.8 eV synchrotron radiation; (e) same CVD diamond film as received; The shaded area reflects the additional intensity after hydrogen plasma annealing.

related features. For comparison the UPS spectra of a natural diamond (100) crystal annealed at 955°C (curve b), the spectra of the same diamond after H-plasma exposure at 870°C (curve a) and the UPS spectra of the (100) textured CVD film measured with 40.8 eV synchrotron radiation (curve d) are displayed. The striking similarity between the valence band spectra of the CVD film and the natural diamond [1] implies that the surface of the H-plasma cleaned/annealed CVD diamond film is reconstructed.

Fig. 2 displays the valence band spectra of the (100) textured CVD diamond film measured with synchrotron radiation and excitation energies ranging from 30 to 150 eV after leaving the H-plasma cleaned film exposed in air for one week. In comparing the valence band spectra, the major trend was the emergence of a narrow, dispersionless peak around 1.8 eV (S1, in Fig. 2) binding energy. Its intensity steadily increases from 35 to 45 eV and abruptly decreases at 60 eV excitation energy. The second major trend was a slow variation in the carbon 2s-to-2p cross section. It is known that the cross section of the lower 2s-like portion of the valence band is enhanced with respect to the upper 2p-like portion at high excitation energies [8], while at low excitation energies the situation is reversed. From the close correspondence of the 140–150 eV spectra to the valence-band density of states, calculated by Painter et al. [9], the ratio of the carbon 2s-to-2p cross section can be approximately taken for unity at $h\nu = 140$–150 eV. This cross section is consistent with the ones of Pate et al. [10] and Bianconi et al. [11] who found that, in their photoemission studies of the valence band of diamond (111) and graphite, the 2s-to-2p cross section ratio is unity at $h\nu = 160$ eV and $h\nu = 120$ eV, respectively. We have observed several features highlighted by tic marks, and tagged by the letter B for bulk related features and S for surface related features. For comparison the UPS spectra of the same film measured with the unpolarized light of a helium discharge lamp (HeII: $h\nu = 40.8$ eV) immediately after H-plasma cleaning are inserted. The spectrum labeled (A) is taken from the film after cooling in a hydrogen atmosphere while spectrum (B) is taken from the same film cooled while evacuating the plasma chamber.

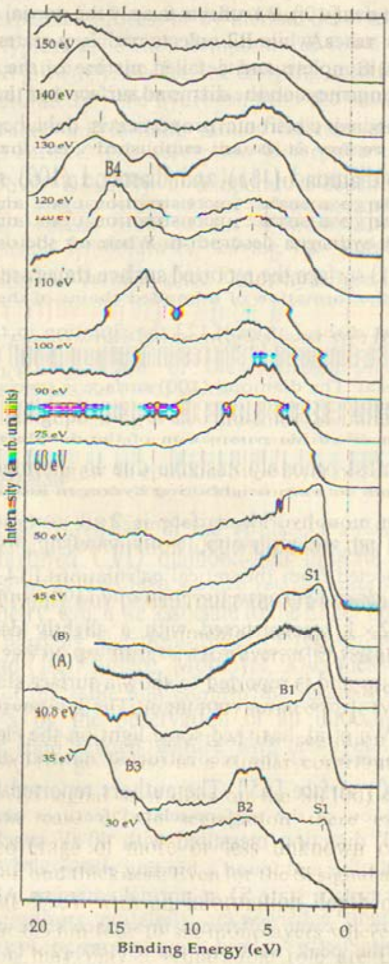

Fig. 2. A series of valence band spectra of a (100) textured CVD diamond film after H-plasma annealing at 850°C, recorded with photon energies from 30 to 150 eV. S1 marks the surface state, while bulk features are indicated by the letter B.

The peak B3 at 13.5 eV is characteristic for the sp^3-bonded diamond and its maximum was used for aligning the spectra, because of charging which occurs when performing photoelectron spectroscopy on highly insulating samples. Justification of this method comes from recognizing that his peak remains dispersionless over a wide range of photon energies [10]. B4 reflects mainly the partial density of s-states, while B2 reflects mainly p-states.

A complete and detailed picture of the atomic arrangement on the diamond surface and the corresponding electronic properties is only beginning to evolve. It is an established fact that both the diamond (111) and diamond (100) surfaces undergo a surface reconstruction upon annealing and hydrogen desorption. While on the diamond (111) surface the reported surface states are caused by the formation of π-bonded chains of the outermost carbon atoms [12] the situation in the case of the diamond (100) reconstruction is still controversial. The diamond (100) surface is special, as its surface carbon atoms have two dangling bonds. The dihydride passivation of the dangling bonds is most probably unstable due to the high steric forces between neighboring hydrogen atoms [13]. The monohydride surface is 2 × 1 reconstructed, but no surface states in the bandgap are to be expected from theoretical calculations [14], while the clean hydrogen-free diamond (100) surface still is 2 × 1 reconstructed with a slightly decreased distance between the dimer forming surface carbon atoms and is reported to show a surface state near the valence band maximum. The landmark study of Wu et al. has shed some light on the electronic properties of the reconstructed natural diamond (100) surface [15]. The authors reported the dispersion of the surface-related features along the Γ–J' direction measured with 40 eV synchrotron radiation and found a binding energy of 1.5 eV for the surface state S1 at normal emission. Although there is some difference in surface state intensity of the peak S1 from the C(100)-(2 × 1) surface reported by Wu et al. compared to our measurements, the position of the peaks, namely S1 and B1, are in good agreement. Theoretical calculations of the surface band structure of reconstructed diamond (100) surface [16,17] show positions of the surface state which are consistent with our measurements.

Recently, it was reported by Thoms and Butler [19] that the natural diamond (100) surface exhibits the monohydride dimer formation after cleaning in a 800°C hydrogen plasma as probed by high resolution electron energy loss spectroscopy (HREELS) and low energy electron diffraction (LEED) measurements. The authors report a two-domain 2 × 1 reconstruction as observed by LEED for the hydrogen (deuterium) saturated and for the 1050°C annealed diamond surface. The annealed surface exhibits no peaks in the CH stretching region indicating desorption of all surface hydrogen, while the hydrogen plasma treated and hydrogenated (or deuterated) surface clearly shows peaks due to C–H (C–D) stretching. The ratio between monohydrogenated and clean surface regions after the hydrogen plasma treatment is not given however. Regarding the theoretical calculations of Yang et al. [20] and Frauenheim et al. [21], which indicate no surface state related feature in the electronic density of states in the case of the monohydride diamond (100) surface and the observations of Thoms and Butler it is highly probable that the observed surface state S1 is caused by hydrogen-free diamond (100) 2 × 1 surface regions.

UPS measurements of the CVD diamond film after H-plasma treatment at increasing temperatures show a decrease in, and at 1000°C the total absence of, the negative electron affinity peak, normally seen on the H-saturated (100) diamond surface [22]. Simultaneously the surface state related peak S1 increases in intensity [23]. There is also a difference visible in the case of the natural (100) diamond surface after exposing the crystal to a H-plasma at 870°C or 920°C (see Fig. 3). The intensity of the feature S1 is strongly increased, suggesting a more complete reconstruction of the surface at higher temperatures. Moreover it was reported earlier [18] that cooling of CVD diamond films after deposition in a hydrogen atmosphere preserves the surface-state related structure around 2 and 4 eV binding energy. As known from other experiments, molecular hydrogen does not influence the electronic states, or the surface reconstruction.

The exposure of the reconstructed surface to atomic deuterium produced by a hot filament reverses the effect of the last H-plasma treatment at 920°C, as can be seen by the decrease in intensity of the surface state S1 (chained line).

Carbon K-edge XAS which is sensitive to the chemical environment of the carbon atoms was also performed for the first time on a (100) textured CVD diamond film (for a more detailed discussion

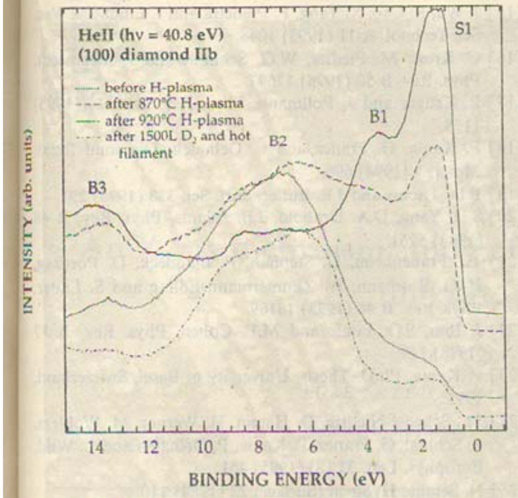

Fig. 3. Valence band spectra of natural type IIb (100) diamond before and after hydrogen plasma exposure at 870°C and 920°C, and after deuterium exposure.

see Ref. [24]). In the XAS spectra an absorption feature is observed at 284.6 eV in the bulk band gap, which is associated with a transition from the C 1s surface core level to an unoccupied state with π symmetry. The results confirm the above model for the H-plasma annealed diamond (100) surface. In particular, the well known assignment of the spectra of carbonaceous material combined with the information from the polarisation dependence of π^*, (C–H)*, and σ^* resonances, indicates that the surface region of the CVD diamond exhibits (C=C) groups as well as (C–H) groups. The assumption of an at least partially clean hydrogen-free 2 × 1 reconstructed surface therefore seems to be justified.

The most common model for diamond growth by microwave plasma CVD, which was first proposed by Setaka [25], deals with the desorption of hydrogen atoms saturating the dangling bonds of the diamond surface. In this model a H atom leaves the surface by reaction with an atomic hydrogen from the gas phase, forming molecular hydrogen. The free dangling bond is then resaturated by another H atom or by a hydrocarbon radical. Our experiments would indicate that the hydrogen leaves the diamond surface, either by the above explained process or by thermal desorption, at the typical deposition temperatures for CVD diamond growth. However, the dangling bonds are not resaturated by the hydrogen from the plasma, instead they are forming dimers on the reconstructed surface. The desorption–adsorption process, which is surely a temperature-dependent dynamic process, could be out of equilibrium at high plasma temperatures, leaving the diamond (100) surface reconstructed and hydrogen-free. Future experiments, hopefully, will give more information concerning this possibility and the exact atomic configuration of the hydrogen-plasma annealed diamond (100) surface.

4. Conclusion

UPS measurements of the H-plasma annealed (100) textured CVD diamond-film indicate the presence of an occupied surface related state with π symmetry, which we associate to the dimer bonds of the partially hydrogen-free 2 × 1 reconstructed diamond (100) surface. Moreover, XAS measurements of the same film confirm the results found by UPS by the observation of an unoccupied surface state related feature with π^* symmetry [24].

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