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Annealing effects in H- and O-terminated P-doped diamond (111) surfaces

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Abstract

The annealing induced effects on hydrogen (H)- and oxygen (O)-terminated P-doped (111) diamond surfaces were investigated by X-ray photoelectron spectroscopy (XPS). Thermally triggered systematic shift of carbon 1s (C1s) peaks was observed for both the surface terminations. The shift is characterized by H- and O-desorption kinetics until a clean surface is produced and then by the non-diamond carbon layer formation on the diamond surface. Desorption induced shift of binding energy (BE) in H-terminated surface is larger than O-terminated diamond surface since the surface bonding configuration of H and O is different. The clean surface emerges at a lower temperature for O-terminated surface than it turned out in H-terminated surface. The growth of non-diamond carbon layer was analysed through loss spectrum of C1s core levels.

Keywords: Diamond; Phosphorus-doping; Annealing; X-ray photoelectron spectroscopy; Field emission

1. Introduction

Phosphorus (P)-doped diamond requires low threshold voltage for the electron emission from its surface [1–3]. This is an attractive feature of diamond for cold cathode applications. The field emission process in diamond depends largely on the surface potential barrier [1,4–6] which are defined by the surface dipoles like C–H, C–O, etc. Among various surface terminations on P-doped diamond, the lowest threshold voltage and stable field emission current were obtained from vacuum annealed surface [4–5]. An appropriate, stable and reliable potential barrier is the key for the steady field emission process. However, the relationship between the annealing effects, the surface residuals and the energy band diagram, is not investigated yet in P-doped diamond. Although the annealing induced effects are comprehensively established for H-terminated boron (B)-doped (111) diamond surfaces [7–12], a very limited attention has been paid on the O-terminated (111) surface [13–14]. In this paper, ex-situ annealing effects in H- and O-terminated P-doped (111) diamond surfaces, studied through X-ray photoelectron spectroscopy (XPS), are reported for a wide high-temperature range. The binding energy (BE) shift is presented as a function of annealing temperature and the cause for the shift is explained.

2. Experiment

Nearly, 2 μm thick P-doped diamond films were grown on $2\times2\times0.5$ mm^3 dimension (111) oriented Ib diamond substrates by microwave plasma chemical vapour deposition (MPCVD) method [15]. The secondary ion mass spectroscopy (SIMS) measurement on the grown layers showed a typical phosphorus concentrations in the order of 10^{19}/cm^3. To oxidize the surface, diamonds were boiled in an acid mixture of H_2SO_4 and HNO_3 (3:1) at 200 °C for an hour. Hydrogen plasma treatment was carried out in MPCVD reactor at a substrate temperature of 800 °C for 10 min to produce H-terminated surface. Both H- and O-terminated surfaces were ex-situ annealed in high-vacuum for 10 min in the temperature range of 700–1150 °C at several intermediate steps. After every annealing process, the XPS measurement was carried out at room temperature in UHV (1×10^{-8} Pa) using a ThermoVG Scientific ESCALAB Theta Probe spectrometer. A monochromatized AlK_α radiation from a twin anode X-ray source with photon energy of 1486.6 eV was used to excite the diamond C1s core levels. The incident area was 400 μmφ. The analyzer pass energy was set to 50 eV. The energy step size was 50 meV. To prevent the charge-up effects, we employed the flood gun in our experiments.

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The reproducibility of the XPS results under the aforementioned sample preparation conditions was verified.

3. Results and discussion

The wide survey scan showed carbon 1s (C1s) and oxygen 1s (O1s) peaks on the surface. A close scan of C1s peak from H-terminated surface, at a take-off angle of 55° with respect to the surface normal, in the temperature range of 750–1150 °C is shown in Fig. 1a. As it can be seen, a shift in the C1s peak position towards higher BE side was observed up to 900 °C annealing temperature. After 1000 °C, the peaks shift towards lower BE side. Around 850 °C, a satellite peak nearly 1 eV below the original peak started to appear. The intensity of the satellite peak grows with further raise of annealing temperature and becomes equivalent to the original peak at 1150 °C. Hereafter, we call the original peak as C1 and the new satellite peak as C2 for reference. The conductivity of the sample was good enough to disseminate the charge-up effect and the consequent shift of the peak maxima. However, we performed the XPS measurements with and without the employment of charge neutralizing flood gun and we hardly see any noticeable change in the spectra or the peak BE values. XPS experiments similar to that of H-terminated surface were also performed on oxidized diamond surface. The C1s peaks recorded after every annealing in the temperature range 700–1150 °C is shown in Fig. 1b. C1s peak BE shift was also observed in O-terminated surface. Compared to H-terminated surface, the C1s peaks are rather broad for O-terminated surface. The BEs corresponding to C1 peaks are plotted in Fig. 2 for both H- and O-terminated diamond surfaces for the annealing temperature range 700–1150 °C. The BEs of both H- and O-terminated diamond surfaces increase and then reach a small plateau region and later decrease. For H-terminated surface, the maximum shift of the BE is nearly 1 eV and it is 0.5 eV for O-terminated surface. After 1000 °C annealing, the BE decreases for both the terminations. Irrespective of the surface termination, a systematic change in the C1s peak position occurs upon increasing the annealing temperature. The observed sequential BE shift in other words, the valance band bending near the surface must be a consequence of some systematic change on the surface structure/dynamics of chemical species.

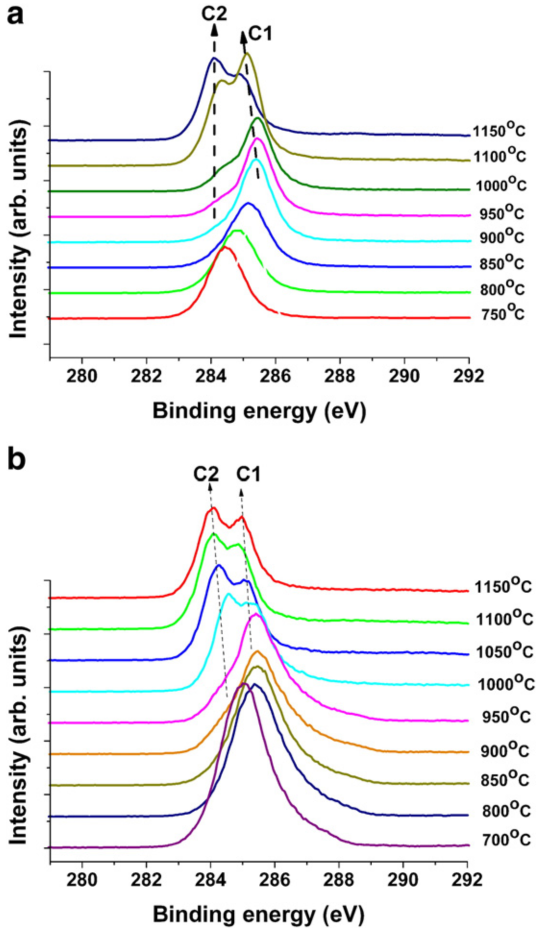

Fig. 1. The C1s spectra recorded after vacuum annealing a) H-terminated and b) O-terminated P-doped (111) diamond surface at different temperatures.

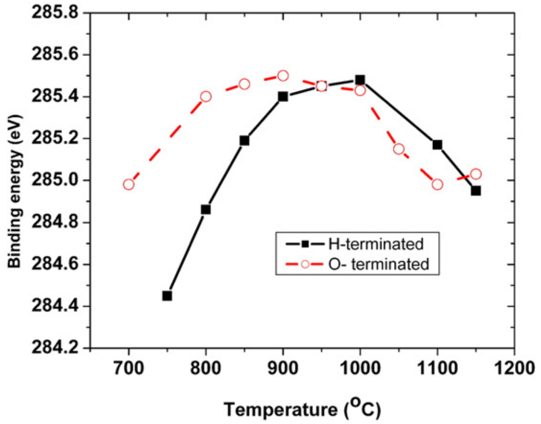

Fig. 2. Shift of binding energy (corresponding to C1 peaks) as a function of temperature for O- and H-terminated P-doped diamond (111) surfaces.

The annealing effects and the consequent band bending in H-terminated IIb diamonds have been widely reported [7–10]. It is well known that H desorbs in the form of H_2 from diamond surface around 850°C annealing and eventually, an adsorbate-free surface is produced. Soon after the desorption process, the unsaturated C atoms at the surface undergo a reconstruction from the initial (1 × 1) to (2 × 1) structure [7–8]. Therefore, the rise of BE for H-terminated diamond surface in Fig. 2 could be attributed to the dehydrogenation process and consequently the emergence of the clean surface. Our previous reflection high energy electron diffraction (RHEED) experiment on 850 °C annealed (initially H-terminated) surface showed a distinct half-order (2 × 1) and Kikuchi pattern in the [112] azimuth which is characteristic of the clean surface [16–17].

The oxygen desorption characteristics of (111) diamond are very limited in the literature [13–14]. Temperature programmed desorption (TDS) experiment on (100) oriented diamond revealed that O-desorption takes place in a broad temperature range with a maximum at 600 °C [18–19]. The main desorption