X-ray Photoelectron Diffraction Study of Bias-Treatment for the Growth of 1-Inch-Diameter Hetero-Epitaxial Diamond (001) Thick Films

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Abstract. Bias-treatment (BT) is widely used as an initial seeding process of chemical vapor deposition (CVD) growth of diamonds. In a BT, substrates are negatively biased by an order of hundred volts so that positive ions in the plasma of CVD gas source bombard the substrate to form ‘seeds’ of diamond growth. Bias-treated 1-inch-diameter (φ) Ir(001)/MgO(001) substrates were used as the substrates of the CVD growth of 1-inch-φ diamond (001) thick films. XPS (X-ray Photoelectron Spectroscopy) spectra and C 1s and Ir 4f XPD (X-ray Photoelectron Diffraction) patterns were measured for the BT 1-inch-φ samples. 5 typical portions on the sample were measured; one at the central portion and the other 4 were peripheral portions, 90° apart from each other and ~4 mm from the edge of the sample. The uniformity of the result over the 5 portions was confirmed. The coverage of carbon layers on the sample after BT was evaluated to be ~ 50 ML in the unit of monolayer of Ir(001)1x1 surface. A quantitative measure of the effect of BT, $A_{45°}$ (the degree of variation of XPD pattern as defined as $I_{\text{max}} - I_{\text{min}}/I_a$, where $I_{\text{max}}$, $I_{\text{min}}$, and $I_a$ are the maximum, minimum and average intensities of photoelectrons in an azimuthal diffraction pattern at the polar angle of 45°, respectively), was examined for C 1s and Ir 4f core-levels for the 1-inch-φ BT samples. The $A_{45°}$ values appeared to be ~3% and ~17% for C 1s and Ir 4f, respectively. The results were compared with those for other bias-treated smaller samples reported so far. The $A_{45°}$ value of ~3% for C 1s is found to be very small compared to the corresponding values for the smaller samples reported so far. Thus, the method of BT for the present 1-inch-φ sample was found to have a large margin of improvement in terms of $A_{45°}$ for C 1s XPD.
1. Introduction

Bias-treatment (BT) or bias-enhanced nucleation (BEN) is widely used as an initial seeding process of chemical vapor deposition (CVD) growth of diamonds. In a BT, substrates are negatively biased by an order of hundred volts so that positive ions in the plasma of CVD gas source bombard the substrate to form ‘seeds’ of diamond growth. A BT on an Ir(001) substrate has been first reported by Ohtsuka et al. [1] to grow hetero-epitaxial diamond (001) films on the Ir(001) substrate. Since then, growth of hetero-epitaxial diamond (001) films on Ir(001) substrates has been reported by many workers [2-8]. So far, the crystalline quality of hetero-epitaxial diamond films grown on Ir(001) substrates has been the best among other hetero-epitaxial diamond films in terms of the peak sharpness of diamond Raman shift and of X-ray diffraction locking curves [9, 10]. Application of the hetero-epitaxial diamond (001) films to devices has just started [11]. For the further application of CVD diamond to devices, hetero-epitaxial diamond films on Ir substrates with a sufficiently large size are desired. Fabrication of large size (typically larger than ~1 inch diameter) diamond films has been just tried [10, 12, 13].

The dependence of crystalline quality of hetero-epitaxial diamond films to the quality of BT has been studied previously [8, 9, 14]. In these studies, X-ray photoelectron diffraction (XPD) patterns of C 1s core-level appeared to be most sensitive to the quality of BT. In particular, the anisotropy, $A_{45°}$ (the degree of variation of XPD pattern as defined as $I_{\text{max}}-I_{\text{min}}/I_a$, where $I_{\text{max}}$, $I_{\text{min}}$, and $I_a$ are the maximum, minimum and average intensities of C 1s photoelectrons in an azimuthal diffraction pattern at the polar angle of 45°, respectively) appeared to be a good measure of the quality of BT. Actually, C 1s XPD patterns after BT have been first reported to be similar to the C 1s XPD patterns of single crystal diamond (001) surface [15]. The $A_{45°}$ corresponds to the degree of forward scattering peak between the nearest neighbor carbon atoms along <110> direction in nanometer scale diamond crystallites epitaxially grown on the Ir(001) substrate[15]. It was also found that there are non-oriented carbon layers that give no XPD peaks. The volume ratio of epitaxial diamond crystallites to the non-oriented carbon layers gives the variation in $A_{45°}$[8, 15]. It was recently suggested that, in addition to the epitaxial diamond crystallites, there are carbon atoms in a highly defective crystalline structure which can contribute to the XPD pattern [14]. In any cases, the $A_{45°}$ is a good measure of the quality of BT.

The $A_{45°}$ for a homoepitaxial diamond (001) wafer was ~32% [16] while that was ~67% for a thick hetero-epitaxial diamond (001) film[14]. The reason for this large difference is not certain but likely to be the difference in angular resolutions of electron spectrometers; A gray scale stereograph (Fig.4 of Ref.[16]) of C 1s XPD pattern has less fine structures than a corresponding stereograph (Fig.3b of Ref.[14]). A commercial electron spectrometer (CLAM4) was used in the former experiment and another commercial electron spectrometer (VG ESCALAB220) was used for the later. C 1s XPD patterns of a thick hetero-epitaxial diamond (001) films was later measured with the third electron spectrometer (ADES400) and $A_{45°}$ appeared to be ~50%[17]. Therefore, we can state that $A_{45°}$ value for a bulk diamond (001) can be a value between ~30% and ~70% depending on the angular resolution of electron spectrometer used.

After a BT using a three-electrode DC plasma apparatus, the $A_{45°}$ was ~46% with ADES400 spectrometer [15]. Thus, the BT using the three-electrode DC plasma apparatus gives almost perfect alignment of seeding diamond crystallites. However, the area of BT was limited only to a circle of ~2.5 mm in diameter[15]. The $A_{45°}$ value for a BT sample in a micro-wave (MW) plasma CVD chamber was ~12% with ESCALAB220 spectrometer which should be compared to the $A_{45°}$ value of ~67% for the thick epitaxial diamond film[14]. The area of BT region for this sample was not strictly described but the substrate size was 10x10mm$^2$. A BT method on an area of 10x10mm$^2$ was invented using a DC plasma apparatus [9]. The $A_{45°}$ values for the 10x10mm$^2$ area BT samples was examined with ADES400 to have typical values of 9-22% which should be compared to the $A_{45°}$ value of ~50% of the thick epitaxial diamond (001) film [8]. A free standing diamond wafer of a size of ~10x10mm$^2$ was made from a BT sample similar to the above and the FWHM (full width at half maximum) of (004) X-ray diffraction locking curve was found to be ~0.13° [9]. A one-inch $\phi$ free standing diamond wafer was made from a one-inch-\phi BT Ir(001)/MgO(001) substrate and the FWHM of (004) X-ray
diffraction locking curve was found to be ~0.35° [12]. Thus, the fabrication method of the one-inch-φ diamond (001) wafer has not reached the optimized stages for the 10x10 mm² substrates. The purpose of the present study is therefore to examine the goodness or badness of BT of one-inch-φ Ir(001)/MgO(001) substrates by measuring $A_{45°}$ value in C 1s XPD patterns.

2. Experimental

The samples used were 1-inch-φ Ir(001) films (thickness~500nm) which were epitaxially grown on mirror-polished 1-inch-φ MgO(001) substrates. BTs were performed on the substrates in a planar-diode DC-plasma chamber. Typical conditions of BT were: bias voltage-current, ~390V-1.35A; source gas/ratio and pressure, CH$_4$/(CH$_4$+H$_2$)=~2% at 120 Torr; duration, 30-45s. These conditions were the best so far in terms of crystalline quality of 1-inch-φ diamond (001) films [18]. The BT sample was then contained in a desiccator and transferred to a UHV photoelectron spectrometer (ADES400) which is the same apparatus used previously for the 10x10 mm² samples [8].

To facilitate XPS and XPD measurements of the 1-inch-φ samples, a special sample holder was made of a molybdenum (Mo) sheet. Inset of Fig.1 shows a photograph of the holder and a 1-inch-φ sample (a dark disk). The 1-inch-φ sample is loosely pressed by a Mo spring from the back-side outward the two straight stopper edges (as marked by two arrows) at the upper and lower sides. The position and area of XPS and XPD measurements are marked by a white circle on the right hand side of the dark disk, which is the midway between the two screw heads on the up and down sides. For XPD measurement, the whole the sample holder was rotated about an axis located at the center of the white circle and normal to the 1-inch-φ disk surface. To change the position of measurements, the sample disk was slid sideway and rotated about the surface normal by a flat tip end of a transfer-rod connected to the outside of vacuum. The sample position could be judged by several position markers made on the backside of the sample disk. Typical positions examined were a) central portion, 4 peripheral portions 90° apart from each other and ~4 mm from the edge of the sample disk.

![Figure 1. Wide-scan XPS spectrum measured at the photoelectron polar angle of 45° from the central portion of the 1-inch-φ BT sample. Inset shows a photograph of the sample holder and 1-inch-φ sample (a dark disk).](image-url)
3. Results and discussion

Figure 1 shows a typical wide-scan XPS spectrum (excited by Mg Kα lines) measured at photoelectron polar angle of 45° from the central portion of the sample; Wide-scan XPS spectra measured for the other 4 peripheral portions showed similar spectra. It must be noted that the mode (a constant pass energy mode) of wide-scan is different from that (a constant retard ratio mode) for Fig.2 of the previous similar study[8], thus the intensity distribution appears differently. The assignment of apparent peaks is given in Fig.1, where C 1s and Ir 4f peaks are the main components; C1s and Ir 4f peaks excited by O Kα X-ray from an oxidized Mg target in the X-ray tube are also seen. Impurity components, O 1s XPS and O KLL Auger peaks are also discernible. No other unexpected major impurity components can be seen in Fig.1. The coverage of oxygen can be roughly estimated assuming a uniform oxide overlayers and taking into account of the O1s/Ir4f photo-excitation cross-section ratio and electron attenuation length [19, 20]. The oxygen coverage turned out to be ~ 5 layers in the unit of Ir(001) layer, which is reasonable to be due to the air transfer of the BT sample.

Figure 2 shows a detailed XPS spectrum for C 1s, Ir 4d_{5/2} and Ir 4d_{3/2} core levels measured under the same condition as for Fig.1. Similar spectra were measured for the other 4 peripheral portions and the peak intensity ratios of C 1s to Ir 4d_{5/2} are summarized in Table I. The intensity ratios can be very roughly converted to the coverage of carbon layers assuming a uniform carbon overlayer and taking into account of C1s/Ir4d_{5/2} photo-excitation cross-section ratio and electron attenuation length [19, 20]. The result is summarized in Table I; the coverage is in the unit of monolayer (ML) of diamond (001) layer which is 0.089 nm in thickness.

![Figure 2](image)

**Figure 2.** Detailed XPS spectrum for C 1s, Ir 4d_{5/2} and Ir 4d_{3/2} core levels measured for the 1-inch-φ BT sample under the same condition as in Fig.1.

Figure 3 shows azimuth-dependent XPD patterns of C 1s (red circles) and Ir 4f (blue squares) core-levels measured on the central portion of the 1-inch-φ BT sample at the polar detection angle of 45°. The abscissa is the azimuthal angle of photoelectron detection and the <100> and <110> axes of substrate Ir(001) surface are marked in Fig.3. The ordinates on the right and left hand sides are the anisotropy of C 1s and Ir 4f XPD patterns, respectively. The anisotropy is defined as $I-I_a/I_a$, where $I$ is the electron intensity at an azimuthal angle and $I_a$ the average of electron intensity over the azimuthal scan. The $A_{45°}$ value for Ir 4f in Fig.3 is found to be ~17% and that for C 1s in Fig.3 is
found to be rather low of ~2.5%. Similar azimuthal XPD patterns were measured for the other 4 peripheral portions and the resulting $A_{45^\circ}$ values are summarized in Table I.

![Figure 3. Azimuthal dependent XPD patterns of C 1s (red squares) and Ir 4f (blue squares) core-levels measured on the central portion of the 1-inch-φ BT sample at the polar detection angle of 45°.](image)

As found in Figs.1-3 and in Table I, the uniformity of carbon coverages and $A_{45^\circ}$ values is expected to be good over the whole 1-inch-φ substrate. However, the mean $A_{45^\circ}$ value for C 1s is ~3 % which is far below the $A_{45^\circ}$ values of ~15-22 % found for 10x10 mm$^2$ substrate [8]. The carbon coverage of ~50 ML for the 1-inch-φ substrate is also slightly higher than that of ~36-40 ML for the 10x10 cm$^2$ substrate [8]. The fraction of epitaxial nano-diamond (001) crystallites to the whole carbon coverage may be roughly evaluated from the mean $A_{45^\circ}$ values of ~3 % for the 1-inch-φ sample using the $A_{45^\circ}$ value of ~50% for the hetero-epitaxial diamond (001) films [15]. For simplicity, we assume that there are only two kinds of carbon layers, one is non-oriented carbon layers and the other is nano-scale diamond (001) epitaxial crystallite layers which are present at the boundary between the Ir(001) substrate and the ~50 ML carbon layer. Reason for the $A_{45^\circ}$ value reduction is ascribed to the fact that non-oriented carbon layer shows no anisotropy. The fraction $x$ of $I_a(epi)$ from epitaxial layer to $I_a(non)$ from non-oriented carbon layer is defined as $I_a(epi)=xI_a(non)$ and $x$ can be evaluated as $0.03=0.5\times xL_a(non)/(xL_a(non)+L_a(non))$ which results that $x=0.064$. Taking into account the attenuation length (~2 nm [21]) of C 1s photoelectrons from the epitaxial diamond layers, the thickness of epitaxial layer can be evaluated to be ~1.6 nm (~18 ML). This rather large value indicates that most parts of the epitaxial layers are in reality in a highly defective crystalline structure as suggested previously [14]. The two dimensional density ($D$) of epitaxial crystallites can be indirectly evaluated from scanning electron microscopic image of a sample subjected to a short-time diamond CVD growth of the BT substrates [9]. The density appeared to be ~$10^{10}$ cm$^{-2}$ for a 10x10 mm$^2$ sample with 30s diamond CVD growth for a BT sample with $A_{45^\circ}$ of ~18% [9]. The density appeared to be ~$2\times10^6$ cm$^{-2}$ for a 10x10 mm$^2$ sample with 10 min diamond CVD growth for a BT sample with $A_{45^\circ}$ of ~18% [8]. The density $D$ appeared to be ~$2\times10^6$ cm$^{-2}$ for the present 1-inch-φ sample with 30 s diamond CVD growth [18]. Thus, the method of BT for the present 1-inch-φ sample has a large margin of improvement in terms of $A_{45^\circ}$ and $D$.

The $A_{45^\circ}$ values for Ir 4f are ~15-18% as found in Table I. The $A_{45^\circ}$ values for Ir 4d$^{5/2}$ was ~25% for a 10x10 mm$^2$ sample with C 1s $A_{45^\circ}$ of ~18% [17]. It was found that $A_{45^\circ}$ value for Ir 4f was not much
different from $A_{45^\circ}$ value for Ir 4d$_{5/2}$ [17]. Thus, the present 1-inch-ϕ BT sample is not much far from the 10x10 mm$^2$ BT sample in terms of $A_{45^\circ}$ values for Ir 4f or 4d$_{5/2}$.

4. Conclusion

XPS spectra and C 1s and Ir 4f XPD patterns were measured for bias-treated 1-inch-ϕ Ir(001)/MgO(001) samples which are the substrates of the CVD growth of 1-inch-ϕ diamond (001) thick films. 5 typical portions on the sample were measured; one at the central portion and the other 4 are peripheral portions, 90° apart from each other and ~4 mm from the edge of the sample. The XPS and XPD results over the 5 positions showed a good uniformity of the bias-treatment. The coverage of carbon layers on the sample after BT was evaluated to be ~50 ML in the unit of monolayer of diamond (001)₁⁻¹ surface. A quantitative measure of quality of BT, $A_{45^\circ}$, was examined for C 1s and Ir 4f core-levels for the 1-inch-ϕ BT samples. The $A_{45^\circ}$ values appeared to be ~3% and ~17% for C 1s and Ir 4f, respectively. The results were compared with those for other bias-treated smaller samples reported so far. The $A_{45^\circ}$ value of ~3% for C 1s is found to be very small compared to the corresponding values for the smaller samples reported so far. Thus, the method of BT for the present 1-inch-ϕ sample was found to have a large margin of improvement in terms of $A_{45^\circ}$ for C 1s XPD.

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