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Characterization of an epitaxial-grown diamond thin film

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Abstract. The epitaxial-grown diamond thin film on a natural diamond (111) substrate from a mixture of hydrogen and acetone by hot-filament-assisted CVD is studied. The deposited thin film is characterized by REM, RHEED, SEM, optical microscopy, the Laue method, Raman spectroscopy and x-ray topography. The deposited film is found to be completely epitaxial to the substrate with good crystallinity and a high degree of surface smoothness in a deposition area of about 4 mm^2. No grown defect is observed except regular cleaving grooves formed during growth. REM has been employed for the characterization of the surface fine structure. It is shown that the growth of the (111) thin film occurred by the lateral motion of two sets of straight steps of atomic height consisting of {112} and {110} planes in the surface normal. This lateral epitaxial-grown pattern accounts well for the formation of large-area (111) single-crystal thin film with high quality.

Research on diamond thin films is capturing worldwide attention because of the excellent physical properties of diamond. In particular the desirable electronic and thermal properties of diamond are very attractive in the fabrication of electronic devices. The epitaxial growth of high-quality diamond thin films is one of the key techniques for the application of deposited diamond to active electronics. Recently the approach of epitaxial growth of diamond films has been made on diamond and non-diamond substrates from a gaseous mixture of hydrogen and hydrocarbon by the CVD method [1–4]. It seems that diamond epitaxial thin films on diamond {111} substrates tend to be rough in surface and poor in quality by contrast with homoepitaxial diamond {100} thin films [5]. On the other hand, there are still many unresolved issues regarding both the growth characteristics and the growth mechanism of epitaxial diamond thin films. Thus it is very important to evaluate epitaxial diamond thin films via various effective and sensitive tools for the characterisation of the surface or near-surface regions of thin films.

In this paper, reflection electron microscopy (REM) which has recently been used for characterizing the atomic structures of surfaces [6–9], combined with scanning electron microscopy (SEM), optical microscopy, the Laue method and Raman spectroscopy, is employed to elucidate characteristics of a homoepitaxial thin film with a ⟨111⟩ orientation. We show for the first time that REM can be used to characterize the surface

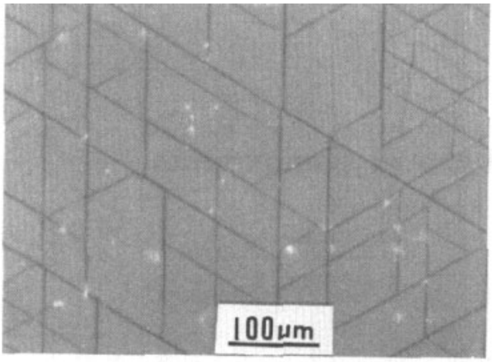

Figure 1. Optical micrograph of the deposited diamond thin-film surface.

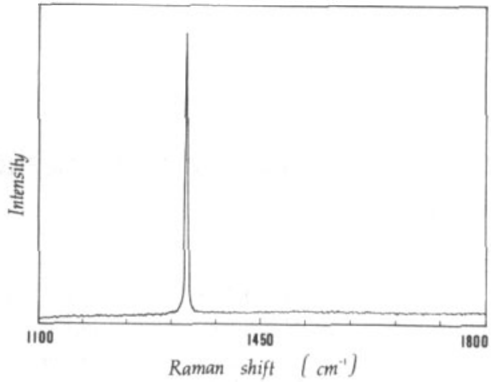

Figure 2. Raman spectrum of the deposited diamond thin film.

fine structure of the epitaxial film, which can provide important information on both epitaxial-grown characteristics and the mechanism of the diamond thin film.

A natural [111]-oriented single-crystal IIb diamond is used as the substrate which takes the shape of an equilateral triangle with a surface area of about 4 mm^2. The substrate surface was ultrasonically cleaned, and then the diamond thin film was deposited over the surface of the substrate from a gaseous mixture of hydrogen and acetone by hot-filament-assisted CVD. During deposition, the substrate temperature was held between 700 and 900 °C. The total gas flow rate was in the range of 200 to 300 sccm and the acetone concentration (CH_3COCH_3–H_2) was about 0.5 vol.%. The deposition time was 20 h, with a film thickness of 2–3 μm.

The structural characteristics of the deposited film surface can be seen using an optical microscope (figure 1). Three sets of sharp striations lie along the ⟨110⟩ directions, forming triangle and rectangle patterns over the smooth thin-film surface. The Raman spectrum measured for the thin films (figure 2) shows a rather sharp characteristic peak of diamond structure at 1332 cm^{-1}, the full width at half-maximum (FWHM) of which is 3.8 cm^{-1}, suggesting that the synthesized thin film is high-quality diamond. The laser beam wavelength used for measurement is the 514.5 nm line of an argon ion laser. To confirm whether the deposited diamond thin film is of single-crystal nature or not, back-reflection Laue photographs have been taken for the different regions of the thin-film surface; the exposure time is 7 h which is about five times longer than the usual exposure time of 1.5 h. One of the photographs is shown in figure 3, showing a good single-crystal diamond characteristic without any polycrystalline trace. The strong background in the centre zone is due to the over-exposure accumulation of scattered x-rays. An observation of x-ray topography is also indicative of the high degree of perfection of the diamond. Thus we can conclude that the deposited diamond thin film is completely epitaxial to the diamond (111) substrate with good crystallinity.

Figure 4 shows a reflection high-energy electron diffraction (RHEED) pattern of the diamond (111) film surface, electron beams being incident along the [112] azimuth with a glancing angle of about 20 mrad with the film surface. It should be emphasized that the reflection intensity information should come from the epitaxial film surface of only a few atomic layers because the electron beams are incident on the sample surface at a

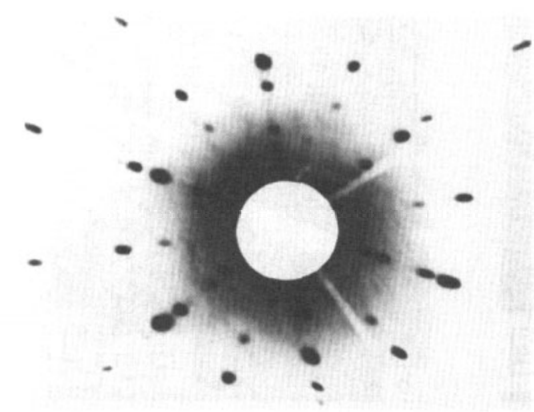

Figure 3. Back-reflection Laue photograph of the (111) diamond sample (operation conditions: copper target; 25 mA, 35 kV, 7 h). The deposited film faces the incident x-rays.

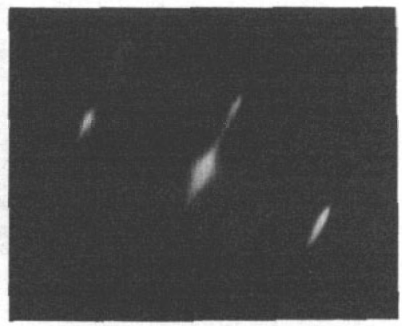

Figure 4. RHEED pattern of the deposited diamond thin-film surface with the beam azimuth [112].

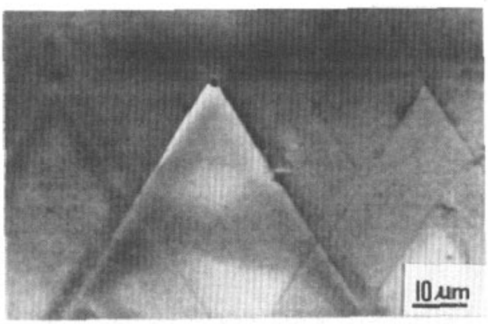

Figure 5. SEM micrograph of the deposited diamond thin film.

very small glancing angle. The sharp rod-shaped reflection spots in figure 4 are also indicative of both high crystallinity and smoothness of the thin film.

Figure 5 shows a SEM picture of the surface morphology of the epitaxial thin film. The surface morphology characteristic of figure 5, like that of figure 1, leaves us with a smooth impression except for some regular striations which are parallel to the ⟨110⟩ cleaving directions. It should be mentioned that no similar striations in the substrate surface were observed by SEM before deposition. These striations are believed to be cleaving grooves formed in the film surface during film growth. In fact, the epitaxy should cause strains between the substrate and the film due to the dimensional difference or mismatch of the lattices. The strain may be released to a large extent in the latter stage of the film growth so that the narrow grooves are formed in some parts of the film surface in the ⟨110⟩ cleaving directions. However, some residual strain may remain. The fact that some Laue spots (figure 3) are accompanied by 'weak tails' or to a certain extent are elongated indirectly confirms the above inference.

Since the study of crystal surfaces with REM has a relatively high resolution compared with SEM, REM observations are made to characterize the surface fine structures. To ensure that the sample surface was clean, it was both carefully and strictly treated before

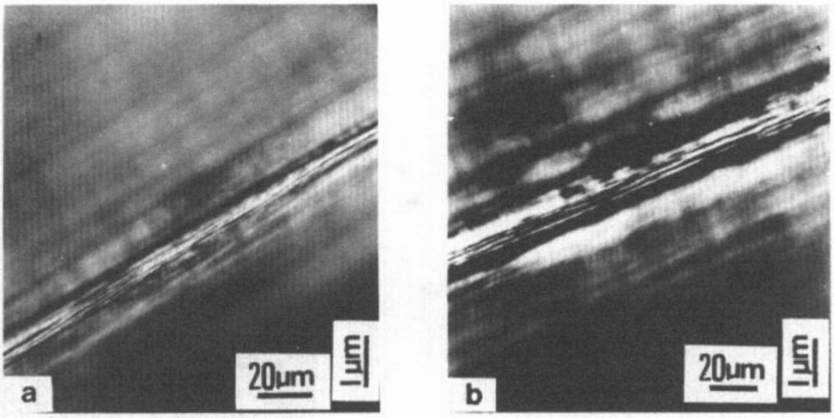

Figure 6. REM images of two different regions of the film surface. Two sets of modulated fringes are demonstrated in the thin film surface.

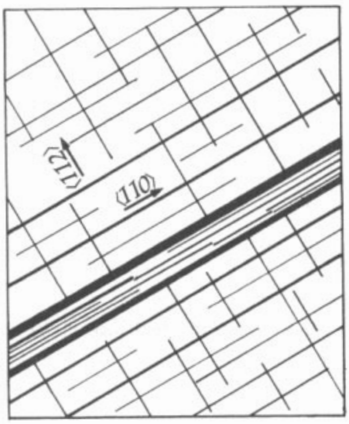

Figure 7. Schematic drawing of the structural characteristic in film surface: ———, steps of atomic height; ———, cleaving grooves.

observation. Figure 6 shows REM images of the epitaxial thin-film surface. Interestingly figures 6(*a*) and 6(*b*) reveal similar surface structural characteristics, i.e. two sets of modulated fringes (one stronger and the other weaker in contrast), although corresponding to two different regions of the surface. It should be mentioned that foreshortening of the images occurred in the beam direction, as shown in figure 6, because the electron beams are incident on the film surface at very small glancing angles. The contrast differences of the two respective sets of modulated fringes in figure 6 may result, in part, from this. According to the focus-dependent feature of the fringe contrast [10], the two sets of modulations are considered to be growth steps of atomic height in the surface normal. Also we can note that the formation of similar growth steps occurred in the surface of cleaving grooves, indicating that the cleaving grooves can promote the generation of growth steps during the latter growth. A schematic drawing of figure 6 is shown in figure 7, in which one set of straight growth steps, as well as a cleaving groove, lies along ⟨110⟩ directions, and the other along ⟨112⟩ directions. It seems uncertain whether these regularly straight steps can be considered as vicinal faces, but we can say from the observations of growth steps in the surface that the growth of the ⟨111⟩-oriented thin film occurred by the lateral motion of two sets of straight steps of atomic height and consisting of {112} and {110} planes in the surface normal. Moreover, the characteristics of surface growth steps suggest that the lateral epitaxial-grown rate is much higher than the vertical growth rate, which can account for the formation of a large-area ⟨111⟩-oriented single-crystal thin film with a smooth surface, since this growth pattern can effectively restrain or avoid the generation of polycrystalline grains and maintain a good crystallinity of the grown thin film.

In conclusion, the characterization of a diamond thin film deposited on a natural diamond (111) substrate from a gaseous mixture of hydrogen and acetone using hot-filament-assisted CVD has been made by REM, RHEED, SEM, the Laue method, optical microscopy, Raman spectroscopy and x-ray topography. The deposited thin film is found to be completely epitaxial to the substrate with both good crystallinity and a high degree of surface smoothness in a deposition area of about 4 mm^2. No grown defect is observed except cleaving grooves formed in the surface during growth. For the first time, REM is used to characterize the surface fine structure of the epitaxial thin film. It is shown that the growth of the ⟨111⟩-oriented thin film occurred by the lateral motion of two sets of straight steps of atomic height and consisting of {112} and {110} planes in the surface normal, which can account for the formation of large-area single-crystal thin film with high quality.

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