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Selective secondary nucleation controlled (001)-texture in boron doped diamond films by increasing the concentrations of tetramethylsilane and trimethylborane

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ABSTRACT

Diamond shows anisotropic physical and chemical properties, depending on its crystallographic orientations. Owing to the lack of large-scale single crystalline diamond substrates, however, the growth of textured diamond film becomes a popular way in tailoring its optical, electrical, mechanical, and thermal properties for specific applications. In the present study, we show that the (001)-texture of boron doped diamond (BDD) thin film can be controlled by a selective secondary nucleation process. To achieve this, a low concentration of tetramethylsilane (TMS) was introduced to induce a high secondary nucleation rate on the non-{001} diamond facets, hindering their lateral growth. In contrast, the continuous growth and expansion of the {001} facets are kept, which leads to the formation of (001)-textured diamond film. In addition, the orientation of the film can be continuously improved by increasing the concentration of either TMS or trimethylborane (TMB) in the gas phase within a relatively large parameter window. This study not only presents a new mechanism in controlling the textured of diamond, but also sheds some light on the fundamental research regarding the diamond growth.

1. Introduction

Diamond is well-known for its exceptional physical and chemical properties [1,2]. It has been considered as a promising candidate for numerous applications, i.e. cutting tools, sensors, and quantum computers [3–6]. From the material's point of view, however, its application should be always linked to its properties, which in turn are determined by its structure. Possessing a face-centered cubic (FCC) crystal structure, diamond shows orientation dependent physical and chemical properties [7–9]. Therefore, while coming to specific applications, it would be beneficial to choose the most suitable orientation to achieve the best device performance. Nevertheless, the complexities and difficulties involved in the fabrication of large-scale single crystalline diamond substrates become the major obstacle. Alternatively, the synthesis of highly oriented diamond thin films has thus become a research focus in the last decades [9–12]. Among all the possible textures in the diamond films, the (001)-texture is of particular interest to the scientific community owing to the superior properties of the (001)-oriented diamond over the others. It shows lower reflection index and extinction coefficient in comparison with the (111)-oriented diamond [13]. The {001} facets are also much smoother than the {011} and {111} facets, making them more suitable for tribological applications [10]. The stability of the {001} facets is higher under steam etching in comparison with that of the {111} facets [14]. Regarding the electrical properties, Schottky contact is more preferentially formed on the {001} facets [15]. Last but not the least, the (001)-oriented diamond can be also used as the raw material in fabricating sharp diamond tip for scanning probe microscopy application [16].

Owing to the great importance of texture, Wild et al. introduced a growth parameter, α, into the chemical vapor deposition (CVD) process to quantitatively describe the texture of the diamond films [17]. By adjusting the gas composition and deposition temperature, α can be controlled to a certain extent to form (001)-oriented diamond films [18]. Later on, they discovered that the addition of a small amount of N_2 into the gas phase could influence the formation of twinning on the {111} facets [18], which drastically improves the (001)-orientation of the films [19]. Even though intensive researches have been carried out later on [20–25], these (001)-textured diamond films have low practical value for electrical applications because of the deep donor level of nitrogen in diamond. In contrast, boron is able to form shallow acceptor level in diamond for semiconductor applications. Nevertheless, only very sporadic reports have stated so far the possible formation of (001)-textured boron doped diamond (BDD), unless (001)-textured or single crystalline diamond substrates were employed [26,27]. The reason might lie in the extremely narrow parameter window for the direct synthesis of (001)-textured BDD. In the present study, we show that the (001)-texture of BDD can be gradually improved within a relatively large parameter window by adding tetramethylsilane (TMS)

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into the gas phase. Unlike the selective twinning mechanism suggested by Wild et al. [18], a new mechanism based on the selective secondary nucleation on the non-{001} facets has been proposed. The present work not only offers us a new possibility in controlling the growth and texture of the diamond films, but also sheds some light on the fundamental research regarding the diamond growth.

2. Material and methods

Mirror polished single-crystalline p-type Si (100) wafers were used as substrates for the deposition of the films. The size of the substrate is 1×2 cm^2. Standard ultrasonic seeding is performed on the Si wafers to achieve a high diamond nucleation density (>10^{11}/cm^2) [28]. Before seeding, the Si wafer is cleaned in piranha solution (H_2SO_4:H_2O_2 = 3:1). After being cleaned in deionized water, the silicon wafer is immersed into aqueous solutions containing monodispersed detonation nanodiamonds (5 nm, New Metals & Chemicals Corporation, Japan) in an ultrasonic bath for 30 min. A MWCVD reactor was employed for the growth of the films. The reactive gas features a mixture of H_2, CH_4, tetramethylsilane (TMS, 1.15% diluted in H_2) and trimethylborane (TMB, 1.15% diluted in H_2). For all of the depositions, the microwave power is fixed at 700 W and the substrate temperature is maintained at ~800 °C which is measured by an optical pyrometer. During the deposition, CH_4 concentration is fixed at 2% with a total gas flow rate of 400 sccm (standard cubic centimeters per minute). TMS and TMB are added into the gas phase to improve the (001)-texture of the diamond film. Their concentrations vary from 0 to 345 ppm for TMS and from 0 to 144 ppm for TMB, respectively. The depositions were carried out for a total time of 6 h. Scanning electron microscope (SEM, Zeiss Ultra 55) was used to obtain the plane and cross-sectional microstructures of the samples. It is observed that the texture is uniformly formed on the substrate, except the edges of the wafer (~0.1 mm in width) and the thicknesses of the films are all around 6 μm. To determine the phase composition and orientation of the samples as well as their variation with different deposition conditions, X-ray diffraction (XRD) measurements are performed in the 2θ range of 34–125° with a step size of 0.05°. The standard JPCDS cards (card no. 65-0537 for diamond and card no. 29-1129 for β-SiC) were used for indexing the observed diffraction peaks. The spectra in the 2θ range of 65–75° are excluded due to the strong Si (400) diffraction peak. Micro Raman scattering studies are carried out to understand the structural order and boron incorporation into the diamond. The 532 nm line of a Nd:YVO_4 diode-pumped solid-state laser was used as the excitation source.

3. Results

Fig. 1(a) shows the surface SEM image of the BDD film deposited with a TMB addition of 86 ppm in the gas phase. Randomly oriented diamond crystals have been observed. The size of the diamond crystal is ~1 μm, showing good crystallinity. Fig. 1(b) shows the SEM image of the typical diamond/β-SiC composite film deposited by adding only 230 ppm TMS during the growth of undoped diamond film. The film consists of bright and dark regions corresponding to diamond and β-SiC phases, respectively. Nanometer sized diamond and β-SiC crystals are clearly observable owing to the high secondary nucleation, which has been systematically discussed in our previous publications [29,30].

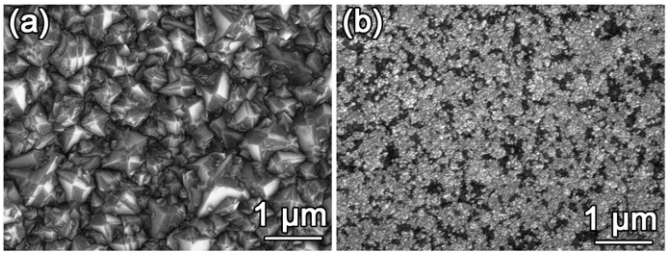

Fig. 1. SEM surface images of (a) BDD film deposited with TMB concentration of 86 ppm; (b) diamond/β-SiC composite film deposited with TMS concentration of 230 ppm.

The above observations clearly indicate that, no (001)-textured diamond films have been obtained when only TMB or TMS is introduced in the present study. However, this case can be changed when the TMS and TMB are co-introduced into the gas phase. Fig. 2(a)–(d) show SEM images of the films obtained by adding 115–345 ppm of TMS during the deposition of BDD. The TMB concentration is kept constant at 86 ppm for all the samples. It can be seen that, the addition of only 115 ppm TMS is capable of causing a drastic change in the morphology of diamond crystals (comparing Fig. 2(a) with Fig. 1(a)). Two kinds of diamond crystals with significant differences in their sizes can be clearly observed. The small diamond crystals feature a size of tens of nanometers while the large ones are about several micrometers. Moreover, the large diamond crystals apparently show their {001} facets parallel to the surface of the film, even though a slight tilt is observed. Such a phenomenon implies that (001)-textured growth of the diamond crystals has been achieved to a certain extent. Higher magnification SEM image shown in Fig. 2(a′) depicts that the {001} diamond facets are smooth and no microscopic defects present. In addition, no β-SiC phase is observable which might be due to the too low TMS concentration to form visible β-SiC phase in the film. Increase of TMS to 173 ppm leads to an increase in the amount of the large (001)-oriented diamond

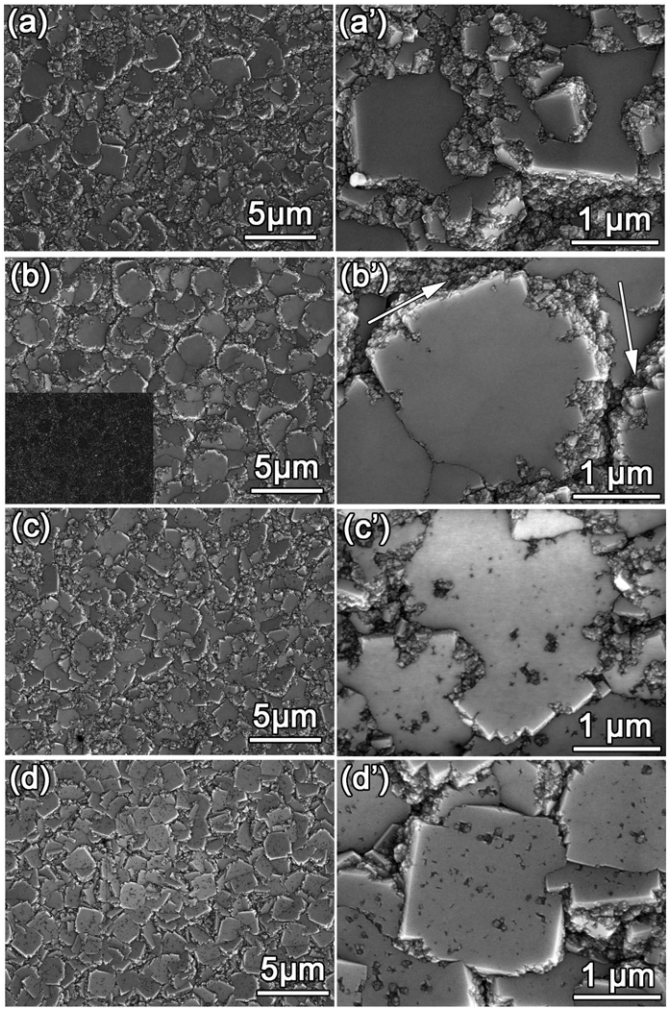

Fig. 2. SEM surface images of the BDD film deposited with different TMS concentrations. The TMB concentration is fixed at 86 ppm; (a) and (a′) TMS = 115 ppm; (b) and (b′) TMS = 173 ppm; (c) and (c′) TMS = 230 ppm; and (d) and (d′) TMS = 345 ppm. Inset of (b) shows the corresponding BSE image.