

Highly oriented diamond growth on $\text{Si}_x\text{Ge}_{1-x}$ (100) thin films

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Abstract

Highly oriented (100) diamond films have been successfully grown on $\text{Si}_x\text{Ge}_{1-x}$ (100) thin films by bias enhanced nucleation (BEN) in microwave plasma chemical vapor deposition (MPCVD) system. Raman spectra show the 1332 cm^{-1} peak which proves the formation of diamond. Diamond nucleation density on $\text{Si}_x\text{Ge}_{1-x}$ substrate estimated by scanning electron microscopy is higher than 10^9 cm^{-2} . The interface between diamond and $\text{Si}_x\text{Ge}_{1-x}$ substrate was characterized by transmission electron microscopy (TEM). About 20 nm decrease in thickness of the $\text{Si}_x\text{Ge}_{1-x}$ film was observed after bias enhanced nucleation step. TEM shows the existence of silicon carbide and heteroepitaxial diamond grains grown on $\text{Si}_x\text{Ge}_{1-x}$ substrate. Characterization from high-resolution TEM on the specimen of short time deposition reveals that a number of epitaxial diamond grains were directly nucleated on $\text{Si}_x\text{Ge}_{1-x}$ with {111} interplanar spacing ratio of diamond and $\text{Si}_x\text{Ge}_{1-x}$ of 2:3. The diamond nucleation is found to be preferred on the ridge position of the rough substrate surface. Diamond {100} facets were quickly developed in the early stage of growth.

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1. Introduction

Diamond is a promising material for high power and high frequency devices, due to its several excellent properties, such as high thermal conductivity, high hole mobility and wide band gap. In order to use diamond on several electronic applications, it is necessary to produce a single crystalline diamond film. However, a single crystalline diamond film is hard to form, so that highly oriented or heteroepitaxial diamond films are the nearest way to reach this aim. Recently, high quality heteroepitaxial diamond grown on iridium has been successfully achieved [1–6]. However, for the consideration of commercial usage, iridium material cost is very expensive even in the forms of thin films which normally needs a bulk target. Highly oriented or heteroepitaxial diamond films grown on silicon substrate have been studied in the past [7–12]. It is necessary to have a high nucleation density on silicon for achieving smooth and epitaxial diamond. However, without any surface pre-treatment, the nucleation density of diamond on mirror polished Si is rarely low, which is hard to gain for the

continuous diamond films. Yugo et al. [13] first proposed a bias enhanced nucleation (BEN) process to increase the nucleation density on Si. By applying negative dc bias on silicon substrate, the nucleation density higher than 10^9 cm^{-2} can be reached. Stoner et al. [14] reported the formation of an interfacial layer of $\beta\text{-SiC}$ and amorphous carbon on Si during the negative bias treatment. Stoner et al. [15,16] and Kawarada et al. [17–19] have demonstrated that epitaxial diamond films can be successfully obtained on $\beta\text{-SiC}$. Stöckel et al. [20] also reported a thin layer of $\beta\text{-SiC}$ formed under bias condition and played a crucial role for diamond nucleation. However, Jiang and Jia [11] have reported that diamond can directly deposit on Si with {111} interplanar spacing ratio of diamond and Si of 2:3, which demonstrated that $\beta\text{-SiC}$ is not necessary for growth of heteroepitaxial diamond on Si. However, it is hard to prevent the carbide formation on silicon surface during the bias pretreatment process. In order to reduce the formation of carbide on the substrate surface and increase the amount of diamond deposition directly on substrate, silicon germanium was chosen as the substrate. As the solubility of carbon in germanium is rarely low and hardly form germanium carbide, it is promising that the possibility for carbide formation during diamond deposition on silicon germanium will be less than on silicon. Since lattice constant of silicon

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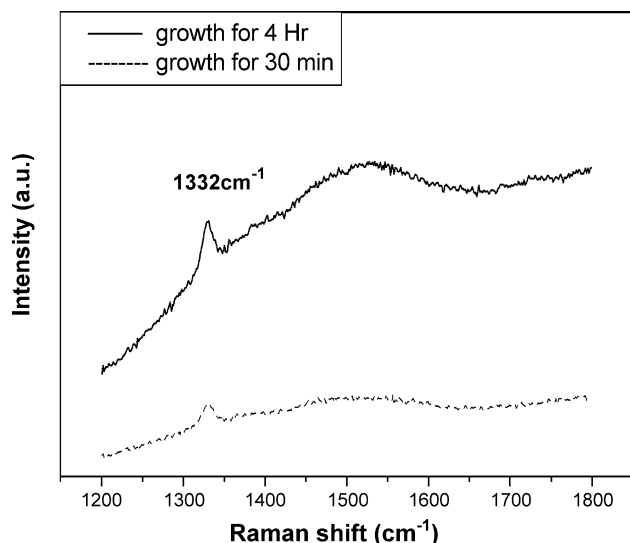


Fig. 1. Raman spectra ($\lambda=514.5$ nm, wavelength of laser) of oriented diamond films grown on $\text{Si}_x\text{Ge}_{1-x}$ for (a) 30 min and (b) 4 h.

germanium is very close to that of silicon, it is still possible for diamond to be directly grown on silicon germanium in epitaxy.

2. Experiment

$\text{Si}_x\text{Ge}_{1-x}$ (100) thin films deposited on 6-in. mirror polished silicon wafer in an ultrahigh vacuum chemical vapor deposition system were selected as substrate. The composition of $\text{Si}_x\text{Ge}_{1-x}$ thin films estimated by microanalysis of X-ray energy dispersive spectroscopy in transmission electron microscopy (TEM) is about 70 at.% Si and 30 at.% Ge. The $\text{Si}_x\text{Ge}_{1-x}$ (100) thin films characterized by selected area diffraction pattern and high resolution transmission electron microscopy were heteroepitaxially deposited on Si with thickness of about 60 nm. The substrates were cut in the size of 10 mm in square, ultrasonically cleaned by acetone for 10 min to remove contamination, dipped in HF for 1 min to remove native oxides, and ultrasonically cleaned in deionized water before inserting into the microwave plasma chemical vapor deposition (MPCVD) reactor. An ASTeX MPCVD system with microwave frequency of 2.45 GHz was used to deposit diamond. For the purpose of diamond deposition, methane and hydrogen were chosen as the reactant gases. The $\text{Si}_x\text{Ge}_{1-x}$ (100) substrate was put on a 2 cm diameter-disk molybdenum holder during the deposition process. Microwave power of 800 W and pressure at ~ 2700 Pa were applied during diamond deposition. Before diamond deposition, hydrogen plasma with -80 V applied bias was used to clean and preheat the substrate surface. In the bias enhanced nucleation (BEN) process, -200 V dc bias was applied to substrate with 3% methane diluted in hydrogen as gas source for 30 min. It was then followed by 0–4 h textured

growth with 1% methane. A sample only treated with the BEN process was covered with a thin layer of silicon nitride by low-temperature plasma enhanced chemical vapor deposition to protect the surface for TEM sample preparation. Conventional method consisting of mechanical grinding to thin foil and Ar ion milling was used for the preparation of cross-sectional TEM samples. JEOL JEM 2010F and Philips Tecnai 20 microscopes equipped with an EDX spectrometer and a Gatan image filter were used for microstructural and compositional characterization. Raman spectroscopy with laser wavelength of 514.5 nm was used to study the existence and quality of the diamond films.

3. Results and discussion

Fig. 1 shows Raman spectra of diamond films deposited with 30 min bias pretreatment followed by growth for 30 min and 4 h. In the spectra, the diamond peak at 1332 cm^{-1} is clearly observed. The full width half maximum (FWHM) of the diamond peaks grown for 30 min and 4 h is approximately 16 and 13 cm^{-1} , respectively. It reveals that the crystal quality of diamond films was improved after long period growth. SEM micrographs of diamond films grown for 30 min and 4 h are shown in Fig. 2a and b, respectively. As shown in Fig. 2, the grain size with (100) texture is about

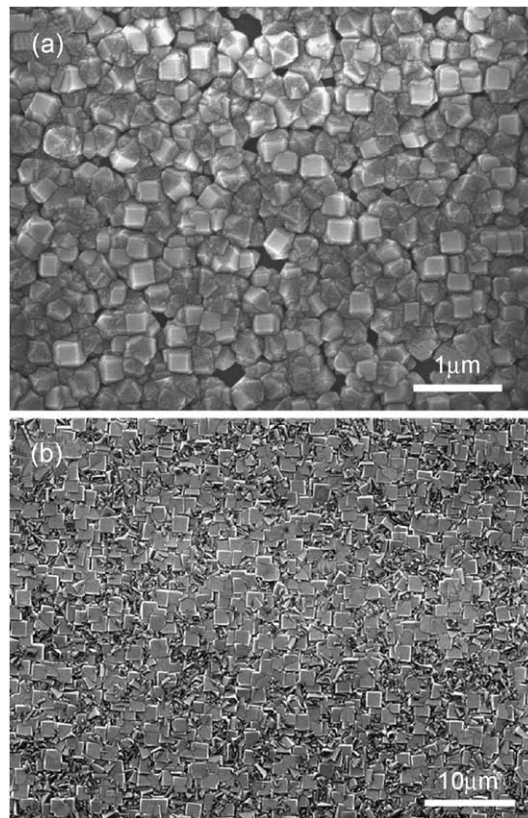


Fig. 2. SEM images showing (100) textured diamond films grown on $\text{Si}_x\text{Ge}_{1-x}$ for (a) 30 min and (b) 4 h.

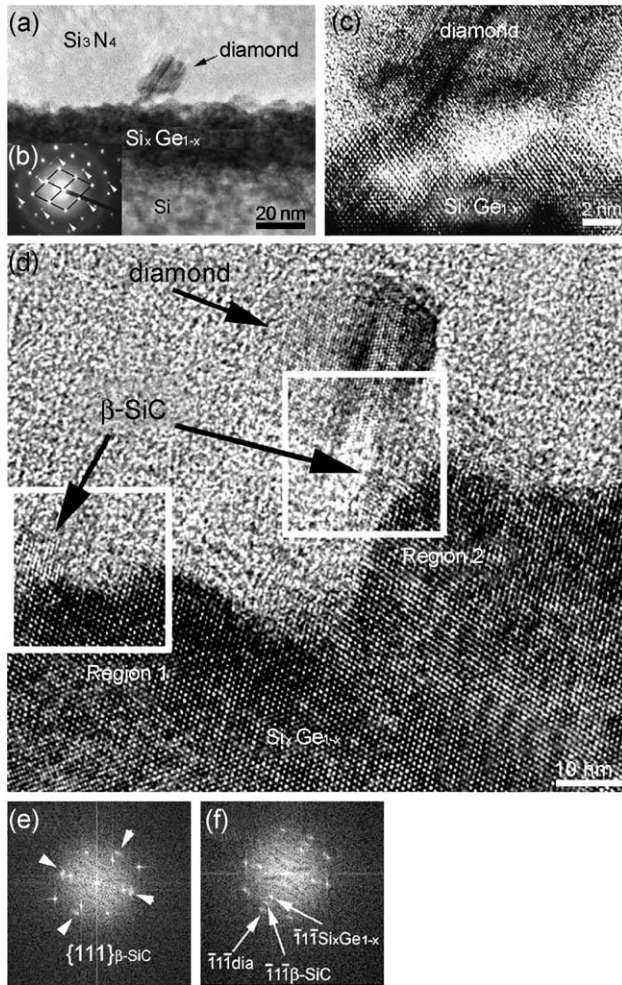


Fig. 3. Cross-sectional TEM micrographs showing diamond on $\text{Si}_x\text{Ge}_{1-x}$ (100) substrate with deposition condition of only biasing pretreatment at -200 V for 30 min. (a) Bright-field image, (b) the corresponding selected area diffraction pattern in $\text{Si}_x\text{Ge}_{1-x}$ [011] zone axis drawn as a parallelogram in dark lines which is parallel to diamond [011] zone axis with reflections as pointed by white arrows, (c) high-resolution image of diamond/ $\text{Si}_x\text{Ge}_{1-x}$ interface in (a), and (d) high-resolution image of another area in the same TEM sample. (e) and (f) are FFT images of regions 1 and 2 in (d), respectively.

200 nm after 30 min growth and 2 μm after 4 h growth, suggesting that the lateral growth rate of diamond grains are about 0.5–0.6 $\mu\text{m}/\text{h}$. Estimated from Fig. 2a and b, the overall grain density is about $2 \times 10^9 \text{ cm}^{-2}$ after 30 min growth and about $3.8 \times 10^7 \text{ cm}^{-2}$ after 4 h growth. Apparently, there exists a number of diamond grains which nearly have the same orientation in (100) texture as shown in Fig. 2a. Observation from Fig. 2b shows that the ratio of diamond (100) facet area increases with growth time. The coverage ratio of (100) oriented diamond facet area is about 7.4% in total area after 30 min growth and increases to 64% after 4 h growth. Furthermore, estimated from Fig. 2a and b, the apparent density of (100) oriented diamond grains is about $3 \times 10^8 \text{ cm}^{-2}$ after 30 min growth and decreases to $1.5 \times 10^7 \text{ cm}^{-2}$ after 4 h growth. As the result, only about

5% of initial oriented diamond grains were survived after 4 h growth; it suggests that the decrease of oriented diamond grain density results from coalescence and overgrowth of diamond grains after long period growth which has been reported by Wild. et al. [21] and Jiang et al. [12]. To understand how diamond nucleates on the substrate, deposition with only the bias-enhanced nucleation pretreatment was carried out before formation of a continuous film. Cross-sectional TEM micrographs in Fig. 3a and d show the microstructure of diamond deposition on $\text{Si}_x\text{Ge}_{1-x}$ (100) substrate with only biasing pretreatment at -200 V for 30 min, {111} facets on the diamond grains can be seen in high-resolution TEM. All the diamonds that can be observed from high-resolution TEM from several different areas also show the same facet. The thickness of the $\text{Si}_x\text{Ge}_{1-x}$ substrate after bias-enhanced nucleation step is about 30–40 nm, which is nearly 20 nm decrease from the initial 60 nm. It is believed that the substrate surface has been etched because of ion bombardment during the bias-enhanced nucleation pretreatment. Consequently, a rough and uneven surface is observed. Fig. 3b shows the corresponding selected area diffraction pattern of the diamond nucleus shown in Fig. 3a. It appears that diamond [011] zone axis is parallel to $\text{Si}_x\text{Ge}_{1-x}$ [011] zone axis and diamond (100) plane is parallel to $\text{Si}_x\text{Ge}_{1-x}$ (100) plane. The result demonstrates that the diamond grain is in epitaxy with the $\text{Si}_x\text{Ge}_{1-x}$ substrate. As shown in Fig. 3c, the diamond is directly deposited on $\text{Si}_x\text{Ge}_{1-x}$ with the {111}

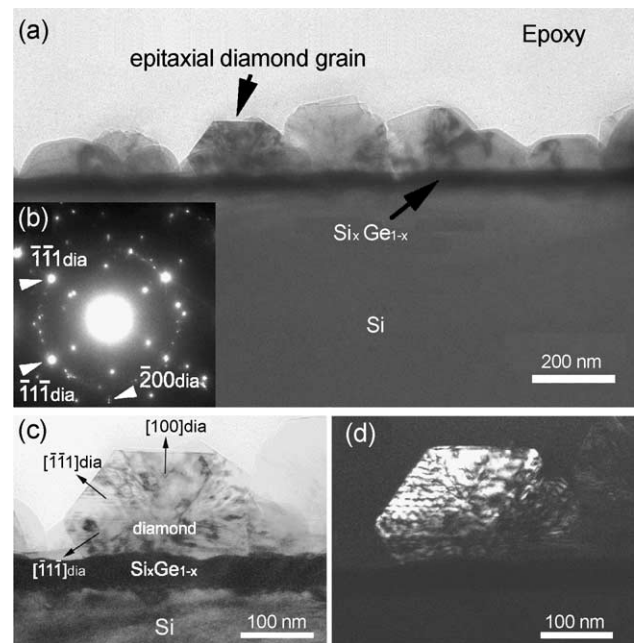


Fig. 4. (a) Cross-sectional TEM micrograph of diamond deposited on $\text{Si}_x\text{Ge}_{1-x}$ (100) substrate with deposition condition of bias pretreatment process and textured growth for 10 min. (b) The corresponding selected area electron diffraction pattern in $\text{Si}_x\text{Ge}_{1-x}$ [011] zone axis with a set of diamond reflections as pointed by white arrows. (c) Bright-field image and (d) dark-field image of the epitaxial diamond grain in (a).

interplanar spacing ratio between diamond and $\text{Si}_x\text{Ge}_{1-x}$ of about 2:3. The result is similar to that diamond grown on Si reported by Jiang et al. [11]. Fig. 3d shows the high-resolution TEM image from another area in the same TEM specimen. Fig. 3e and f are fast Fourier transformation (FFT) patterns of Region 1 and Region 2 shown as white boxes in Fig. 3d. Both FFT patterns show the existence of β -SiC which has epitaxial relationship with $\text{Si}_x\text{Ge}_{1-x}$ substrate. As shown in Fig. 3f, diamond is epitaxially deposited on the β -SiC as well. Examination of Fig. 3d reveals that the β -SiC crystallites in both regions are on the substrate surface, while the diamond is on the β -SiC in Region 2. As a result, nucleation of diamond on the substrate can be directly grown and through epitaxial β -SiC during the bias pretreatment condition. Observation of Fig. 3c and d reveals that both diamond and β -SiC were deposited on positions near the ridges instead of the grooves. Hence, it is supposed that the top of the ridge is the possible nucleation site [22], in contrast with diamond nucleation on Si and SiC steps reported by Lee et al. [23] and Kawarada et al. [17]. The diamond grain size in average observed from different areas is in the range of 10–20 nm.

Fig. 4a shows the cross-sectional TEM micrograph of diamond deposited on $\text{Si}_x\text{Ge}_{1-x}$ (100) substrate after bias pretreatment process and 10 min growth. The average grain size is about 100 nm. It is clear that growth has resulted in fast development of facets of diamonds with some of which have the top surface parallel to $\{001\}$. Estimated from Fig. 4a, the diamond nucleation density is about $1.4 \times 10^9 \text{ cm}^{-2}$, in good agreement with the estimation from SEM observation in Fig. 2a. The diffraction pattern in Fig. 4b, obtained from the arrowed diamond in Fig. 4a, shows the orientation relationship to be diamond $[011]$ parallel to $\text{Si}_x\text{Ge}_{1-x}$ $[011]$ and diamond (100) approximately parallel to $\text{Si}_x\text{Ge}_{1-x}$ (100). A high-magnification bright-field image of the epitaxial diamond grain is shown in Fig. 4c. Apart from the (100) facet on the top surface of the diamond, it clearly shows that all the side facets are bounded by $\{111\}$. The dark-field image taken from diamond ($\bar{1}\bar{1}1$) spot in Fig. 4b is shown in Fig. 4d. It confirms that the strong reflections of diamond in Fig. 4b are mainly contributed from the epitaxial diamond grain.

In summary, highly oriented (100) diamond films deposited on $\text{Si}_x\text{Ge}_{1-x}$ (100) thin films have been achieved. Both epitaxial β -SiC and diamond nuclei were formed on the $\text{Si}_x\text{Ge}_{1-x}$ surface during bias pretreatment step. Diamond grains were directly nucleated on the ridges of grooved $\text{Si}_x\text{Ge}_{1-x}$ surface with $\{111\}$ interplanar

spacing ratio of diamond and $\text{Si}_x\text{Ge}_{1-x}$ of 2:3. Moreover, the percentage of (100) oriented diamond grains have reached to 60% of total area of the diamond film after 4 h growth.

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