Chemical vapor deposition of uniform and high-quality diamond films by bias-enhanced nucleation method

Jhih-Kun Yan *, Li Chang

Department of Materials Science and Engineering, National Chiao Tung University, 1001 Ta Hsueh Rood, Hsinchu 300, Taiwan, ROC

Available online 22 August 2005

Abstract

Diamond films on 1×1 cm^2 Si (100) substrates were synthesized by microwave plasma chemical vapor deposition (MWCVD) using mixture of methane and hydrogen gases. Bias-enhanced nucleation method was used to avoid any mechanical pretreatments. Distribution of deposited diamond crystallites in terms of density, size, and morphology has been significantly improved over all the Si substrate surface area by using a novel designed Mo anode. Films were characterized from the center to the edges of substrates using scanning electron microscopy, transmission electron microscope, and Raman analysis. The results also show that uniform diamond films can be obtained by short bias nucleation period using a dome-shaped Mo anode. The diamond crystallites were directly deposited on Si substrate. Using 2% CH$_4$ in the growth stage, high quality diamond films in the <100> texture can be obtained with relatively smooth surface.
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Keywords: Diamond; Chemical vapor deposition; Nucleation; Growth

1. Introduction

Diamond is an excellent material for many important applications, due to its extreme physical and chemical properties such as extreme hardness, highest thermal conductivity, wide band gap energy, high breakdown field and chemical inertness [1,2]. For industrial applications, uniform deposition of high-quality diamond with low cost of production is essential to enhance efficiency. Chemical vapor deposition (CVD) of diamond has been intensively studied for the past decade [3,4]. In CVD processes for diamond films, few nuclei grow on mirror-polished silicon substrates because of the large lattice mismatch between diamond and Si and the large surface energy of diamond. Yugo et al. [5] developed a method to enhance the growth of diamond on untreated silicon substrate by applying a bias-enhanced nucleation (BEN) method to the substrate at the beginning of the deposition. Because the nucleation

density and film morphology of diamond film can be controlled by the BEN method, many studies used this method to investigate deposition of heteroepitaxial diamond on Si substrate [6–8]. However, the excellent results generally appear at a small local area of the sample. It has been described that the BEN step is the superposition of a microwave plasma and a modified dc glow discharge [9–13]. Stöckel et al. [13] have shown the spatiotemporal evolution of the dc glow discharge according to the formed diamond nuclei moving from the edge to the sample center. As a result, uniform deposition of diamond is difficult to be obtained by the BEN method. The extent of non-uniformity of nucleation and growth of deposited diamond along the radial direction which depends on the processing conditions results in difficulty to understand the exact mechanism of nucleation and its effect on epitaxy. Surprisingly, few studies devoted to improve uniform deposition of diamond. Recently, Barrat et al. showed a promising approach to obtain a uniform diamond film using an modified BEN method [9,14]. In the present study, we design a Mo anode which improves the distribution of microwave plasma and dc glow discharge to deposit uniform diamond films on Si

* Corresponding author. Tel.: +886 3 5712121x55373; fax: +886 3 5724727.

E-mail address: zhikun.mse91g@nctu.edu.tw (J.-K. Yan).

substrate. Also, the effects of various processing parameters are evaluated based on characterization of Raman spectroscopy and electron microscopy.

2. Experimental details

Deposition of diamond was carried out in a 2.45-GHz ASTeX microwave plasma CVD reactor as shown in Fig. 1(a). In order to optimize the microwave discharge and the extension of the bias discharge over the whole substrate, we designed a dome-shaped Mo anode which was located above the substrate as counter-electrode. The diameter of the anode is 15 mm. The distance between the disk anode and substrates was varied in the range from 15 to 30 mm. In Fig. 1(b), the optical photograph shows the distribution of the dc glow discharge with the Mo anode using +100 V bias on anode (corresponding to −100 V on substrate) and 4% CH_4 during the bias stage. It can be seen that the glow discharge has uniformly enveloped the entire surface of the silicon substrate. The
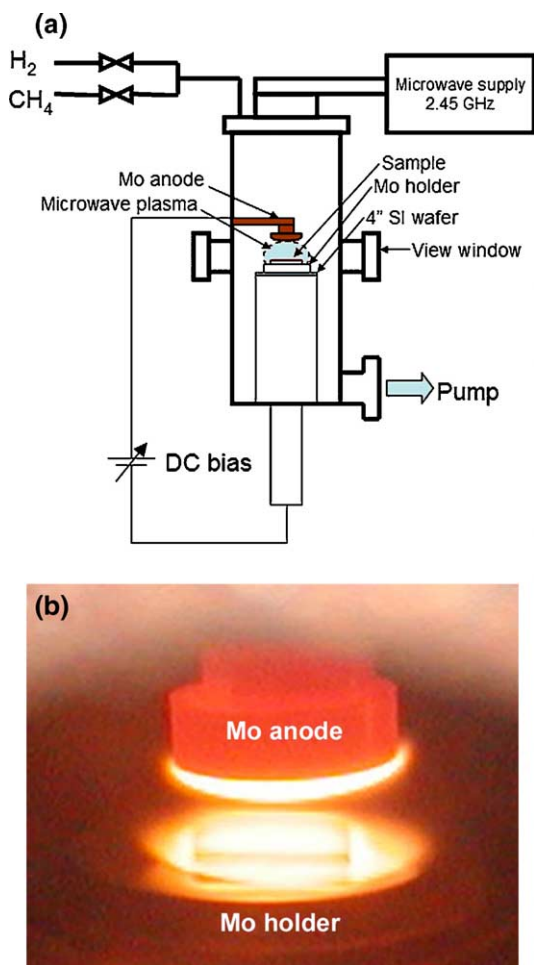

Fig. 1. (a) Schematic diagram of the MPCVD reactor, (b) optical photograph of the bias discharge for $V = -100$ V (substrate) and 4% CH_4 around the Mo anode and the substrate.

Table 1
Experimental parameters for diamond deposition

	Heating	Bias	Growth
Power, W	800	800	800
Pressure, Torr	20	20	20
CH_4 in H_2, %	0	4	0.667~2
Bias voltage ,V	0	−100	0
Flow rate, sccm	300	300	300
Duration	10 min	1 min	20 min~10 h

morphology of dc glow discharge is disk-shaped with diameter of about 20 mm.

The substrate was mirror-polished p-type (100) silicon wafer with dimension of 1×1 cm^2 without any mechanical pretreatment. Before deposition of diamond, the substrate was etched in hydrofluoric acid for 60 s to remove native oxide of Si, and ultrasonically cleaned with acetone for 10 min to remove contamination. The substrate was then placed on a Mo disk holder. A hydrogen plasma was initially applied to the substrate for 10 min for heating to the required temperature and to remove any residual of native oxide on the Si substrate surface. The detailed experimental conditions for biasing and subsequent growth steps are listed in Table 1. Further growth of 10 h with 0.667% and 2% CH_4 concentration are designated as Samples A and B, respectively. Scanning electron microscopy (SEM), Raman spectroscopy, secondary ion mass spectrometry (SIMS), and transmission electron microscopy (TEM) were used for microstructural characterization. The 514.5 nm line of an Argon ion gas laser with 20 mW power was employed for acquisition of Raman spectra. The composition depth profiles were analyzed with a CAMECA IMS-5F secondary ion mass spectrometer with a Cs^+ primary ion beam (accelerating voltage 10.5 kV, bias −4.5 kV).

3. Results and discussion

The morphology of diamond after deposition for 1 min negative bias treatment using 4% CH_4, followed by further growth for 20 min with 0.667% CH_4 is shown in Fig. 2. The photograph of Fig. 2(a) shows uniform color over all the Si substrate surface. The SEM image in Fig. 2(b) shows that crystallites have faceted morphologies with cubo-octahedral, icosahedral, and five-fold symmetries. The size and nucleation density of the deposited diamonds estimated from SEM images are approximately 400 nm and 2×10^8 cm^{-2}, respectively. In Fig. 2(c), the bright-field TEM micrograph in cross-section shows that diamond crystallites are preferentially deposited on the hillock regions of the Si. In the corresponding selected-area diffraction (SAD) pattern of Fig. 2(d), only diamond reflections can be seen in addition to Si diffraction spots, implying that diamonds are directly formed on Si.
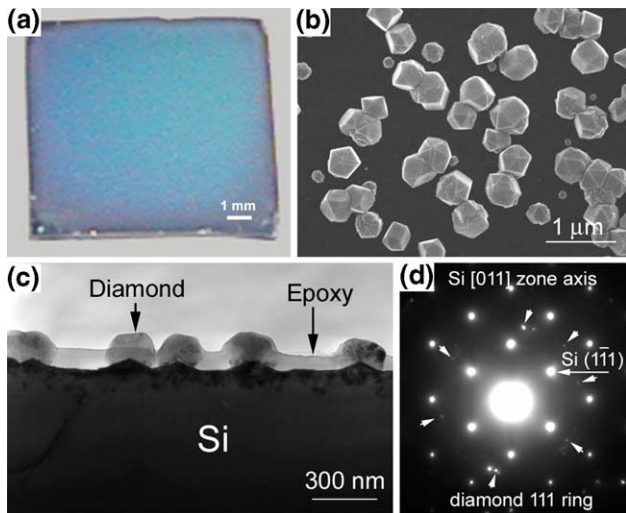
Fig. 2. (a) Optical photograph of the sample surface after BEN and growth, (b) SEM micrograph, (c) cross-sectional bright-field TEM image of diamond on Si(100) substrate, and (d) the corresponding selected area electron diffraction pattern. Deposition condition: Mo anode, bias -100 V, 4% CH_4/60 s and growth 0.667% CH_4/20 min.

For further growth of 10 h with 0.667% CH_4 concentration (Sample A), the morphologies observed at different local areas from the center to the edges of substrates are shown in Fig. 3. It is apparent that the distribution of diamond is quite uniform in terms of the density, size and shape. Similar results are also observed for the case of 2% CH_4 concentration (Sample B). Fig. 4(a) and (b) show the enlarged view of Samples A and B for comparison of the surface morphology. The surface is rough with <111> facets for growth with 0.667% CH_4 concentration (Sample A). From observation of the rough surface, it can be estimated that the average diamond grain size is about 2 μm. With 2% CH_4 concentration, the morphology changes to square-like facets of (100) with a relatively smooth surface. The (100) faceted diamond grains have a larger size. The corresponding Raman spectra of the two samples are presented in Fig. 4(c) and (d). The diamond peak at 1332 cm^{-1} appears in both samples. Sample A has three additional three peaks at 1440, 1180 and 1110 cm^{-1} in the spectrum. Similar peaks related with the bonding in transpolyacetylene have been observed in nanocrystalline diamond films in a-C:H containing nanocrystalline diamond [15–17]. Detailed examination of SEM micrographs in Figs. 2 and 4(a) shows that there exists quite a number of small crystallites on the facets for the case of Sample A. The high intensity of the diamond peak in Raman spectrum of Sample B implies the high quality of the deposited film. Therefore, it is evident that the methane concentration used in the growth stage has a strong influence on the development of the film morphology.

As the Mo anode was placed above the Si substrate, it is not certain if Mo atoms or its carbide might incorporate
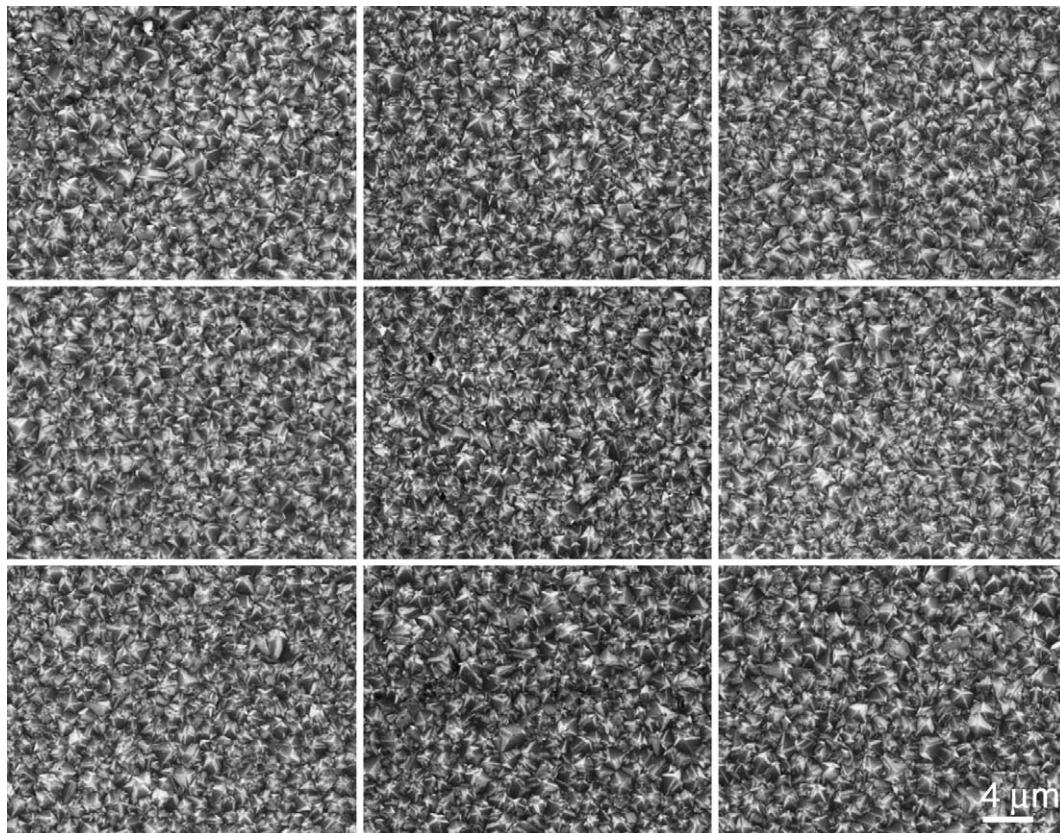

Fig. 3. SEM images of Sample A corresponding to the nine local divisions on the substrate from the center to the corners and the edges.
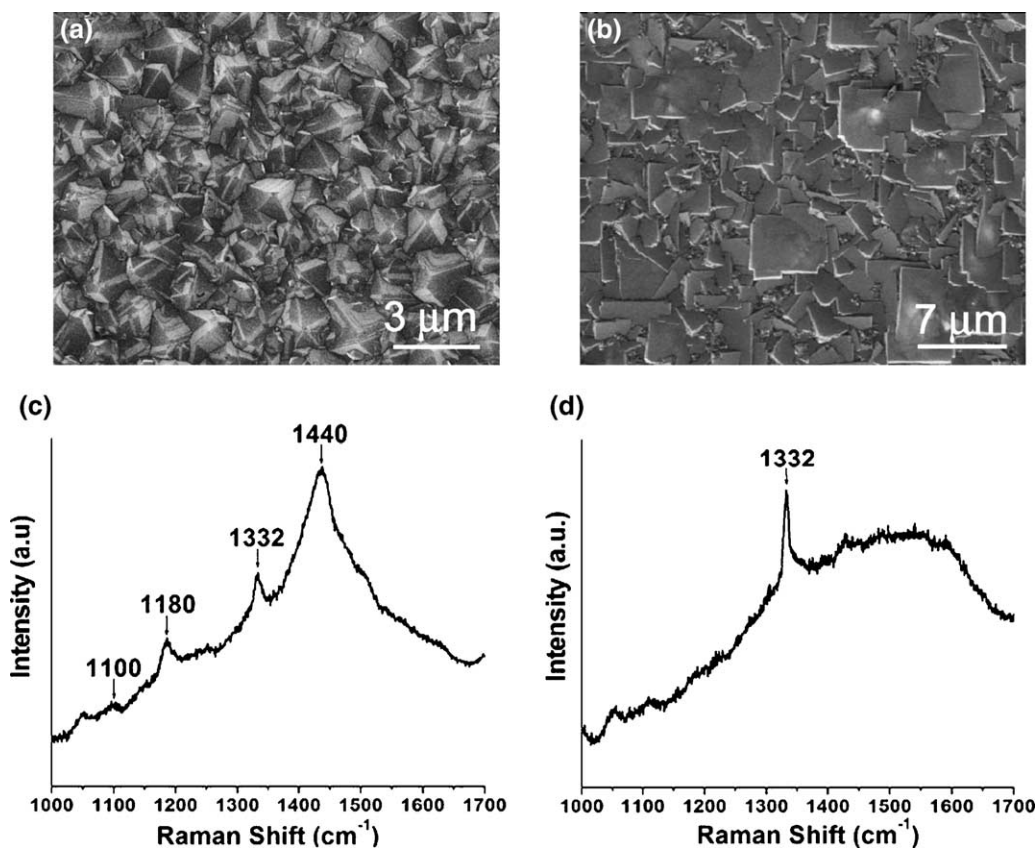
Fig. 4. SEM images and Raman spectra of the diamond films synthesized by the different conditions during 10 h growth process: (a and c) Sample A; (b and d) Sample B.

into the diamond during growth. The SIMS depth profiles of Samples A and B are shown in Fig. 5(a) and (b), respectively. After calibration with a Mo-doped Si standard, it is believed that no Mo impurity exists in the diamond films. Thus, the Mo anode has a negligible effect on the film chemistry in the growth stage.

4. Summary

The results show that uniform diamond films can be obtained by short bias nucleation period using a dome-shaped Mo anode with which the glow discharge can be uniformly produced over the substrate. Diamond crystal-
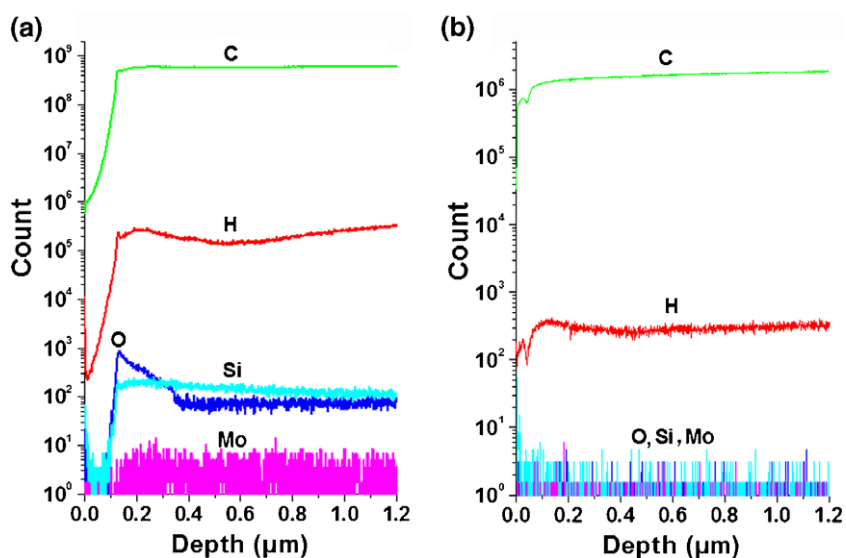

Fig. 5. Depth profiles showing the distribution of C, H, O, Si and Mo: (a) Sample A and (b) Sample B.

lites were directly deposited on Si substrate. Using 2% CH_4 in the growth stage, the <100> highly oriented diamond films with relatively smooth surface were uniformly formed. Thus, it is promising that high-quality heteroepitaxial diamond films can be obtained in large area in the near future.

Acknowledgements

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