

## Lonsdaleite Diamond Growth on Reconstructed Si (100) by Hot-Filament Chemical Vapor Deposition (HFCVD)

Chu Van Chiem, Hyung-Kee Seo, Shafeeque G. Ansari, Gil-Sung Kim, Jae Myung Seo\* and Hyung-Shik Shin†

School of Chemical Engineering, \*Department of Physics,  
Chonbuk National University, Chonju 561-756, Republic of Korea  
(Received 23 April 2003 • accepted 12 July 2003)

**Abstract**—In this paper, the growth of Lonsdaleite diamond using hot-filament chemical vapor deposition (HFCVD) on flashed and reconstructed Si (100) is reported. Surface morphology studies using scanning electron microscopy (SEM) show that the film is composed of decahedron and icosahedron diamond particles. The X-ray diffraction (XRD) pattern has a strongest peak at  $47^\circ$  and a peak at  $41^\circ$ , which is indicative of Lonsdaleite nature of the grown diamond film. The Raman spectrum of the film shows a broadened diamond peak at wave number of  $1,329\text{ cm}^{-1}$ , which has shifted towards the peak position corresponding to Lonsdaleite nature of the diamond ( $1,326\text{ cm}^{-1}$ ).

Key words: Lonsdaleite, Diamond, HFCVD, Surface Reconstruction

### INTRODUCTION

Since the determination of X-ray structure of the diamond, it has been known that the diamond is a tetrahedral network of carbon atoms and these atoms are arranged in a cubic lattice. Furthermore, it is also well known that there exist two isomers of diamond, i.e., the cubic diamond and the hexagonal diamond (also called Lonsdaleite). The Lonsdaleite diamond is found only in the bulk natural diamond. It has broadbands and is mostly observed in shock wave produced diamonds. The peaks in the Raman spectra are positioned in the wave number range from  $1,315$  to  $1,326\text{ cm}^{-1}$ . In fact, various amorphous metastable and crystalline phases of carbon such as diamond, nano-tube, and fullerene like  $C_{60}$  can exist; and most of them have been grown under non-thermal equilibrium conditions [Spear and Dismukes, 1993]. Diamond is a metastable form of carbon compared to graphite at low pressure growth. The structure of graphite was formed by two-layer stacking sequences ...ABABAB... of flat hexagonal (0001) carbon atomic planes, but diamond structure was formed by three-layer stacking sequences ...ABCABCABC... of the same hexagonal, but puckered (111) carbon atomic planes. It has been reported that the Lonsdaleite diamond is detected in meteorites. Although Lonsdaleite was found in bulk diamonds of meteorites, but it is not clear whether it exists in the CVD diamond [Lawrence and Kania, 1995]. In thermal equilibrium conditions, the diamond phase is stable under a high temperature of about  $2,300^\circ\text{C}$  and a high pressure of about 40-50 KBar. But under a normal chemical vapor deposition (CVD) growth condition, i.e., under a low pressure of a few tens Torr, the nucleation and growth of diamonds can occur in non-equilibrium conditions, and hence the nucleation and growth will be controlled by kinetic laws rather than by thermodynamics. However, because of relatively large surface free energy of diamond and its small lattice constant compared to other semiconductors, diamond nucleation on semiconductor or non-diamond substrates is hardly achieved [Wurzinger et al., 1996]. Therefore,

various methods of nucleation enhancement, i.e., mechanical scratching (or grinding) and bias enhancement nucleation (BEN), surface carburization, ion-implantation, use of carbon seeding layer etc. are used [Yugo et al., 1991; Stoner et al., 1993]. The property of CVD-diamond strongly depends on the nucleation enhancement method and the depositing parameters. Therefore, such flexibility of CVD techniques can enable us to produce the CVD diamond film with various structures, properties and qualities. To our knowledge, reports are not available for the growth of Lonsdaleite diamond except the work of Lee et al. [1998] reporting the growth of Lonsdaleite-like Carbon using HFCVD. In this paper, we report the evidence of the Lonsdaleite diamond grown by HFCVD on clean (flashed and reconstructed) Si (100) at specific deposition condition based on SEM, XRD and Raman spectroscopy results.

### EXPERIMENT

Diamond films were deposited on Si (100)- $2\times 1$  surface using hot filament CVD technique. Prior to diamond growth Si surface was flashed and reconstructed. The p-type Si (100) wafers of dimensions  $13\times 7\times 0.5\text{ mm}$  were used as a substrate. For cleaning Si substrate, they were first degreased, then chemically etched by repeated oxidation and etching processes and finally protected by a thin oxide layer (using the so-called Shiraki method) [Ishizaka and Shiraki, 1986]. The cleaned substrate was then transferred to the high-vacuum chamber (pressure of  $\sim 1\times 10^{-7}$  Torr) by using a specially designed substrate holder suitable for passing current to the substrate for flashing purpose. Thin oxide layer was removed by heating (known as flashing process) the substrate to  $1,200^\circ\text{C}$  in  $\text{H}_2$  atmosphere (30 Torr pressure) until the oxygen species from the surface was completely removed. This was confirmed by X-ray photoelectron spectroscopic study (ESCALAB250, VG Microtech, UK) without exposing the substrate to ambient atmosphere. At the final flashing stage, the surface was reconstructed by slow cooling from  $1,000^\circ\text{C}$  to room temperature at the rate of  $2^\circ\text{C}/\text{sec}$ . The surface cleanliness was confirmed by XPS, and the surface reconstruction was confirmed by the two-fold  $2\times 1$  low electron energy dif-

†To whom correspondence should be addressed.  
E-mail: hsshin@chonbuk.ac.kr

fraction (LEED, model ESCALAB250) patterns. Previously we reported that the diamond could be nucleated on such a flashed and reconstructed Si (100) with high nucleation density of  $\sim 10^{10} \text{ cm}^{-2}$  by HFCVD where a detailed experimental description is also given [Chiem et al., 2002].

For this work, a 15 mm wide filament with 5 mm cross sectional diameter was used. A mixture of high purity  $\text{H}_2$  (99.999%) and  $\text{CH}_4$  (99.95%) gas was injected inside the chamber from the bottom. The reaction gas consisting of 1 vol% of  $\text{CH}_4$  was supplied in a total flow rate of 100 sccm, and the pressure (30 Torr) in the reaction chamber was kept constant throughout the deposition process. Filament temperature was monitored by optical pyrometer (Minolta TR-630, Japan), whereas the substrate temperature was measured by K-type thermocouple arranged in such way that its tip was in contact with the back side of the substrate. Filament temperature was maintained at 2,050 °C by using CV/CC source, and the substrates were kept at 900 °C by adjusting the distance between the filament and substrate. During growth process, substrate was heated by filament radiation and temperature was continuously monitored throughout the deposition period of 2 hours.

The deposited diamond films were analyzed by scanning elec-

tron microscope (JSM-6400, JEOL, Japan), X-ray diffraction (Rigaku III/A Type) and Micro Raman spectroscopy (Renishaw) using He-Ne laser ( $\lambda=632.8 \text{ nm}$ ).

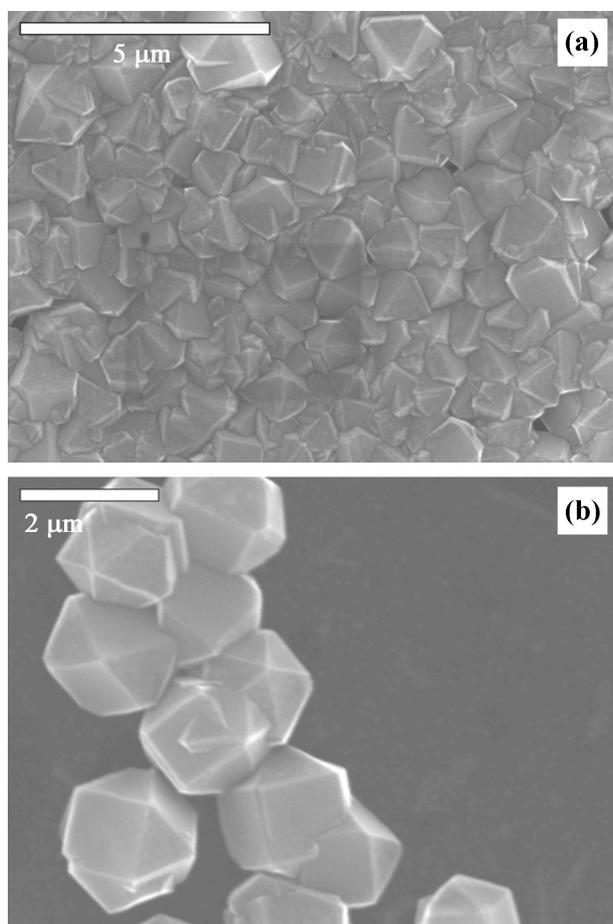
## RESULTS AND DISCUSSION

Fig. 1 shows the SEM images obtained from the samples grown on clean Si (100)- $2\times 1$  after flashing and surface reconstruction. In Fig. 1a, it can be clearly seen that the grown film is composed of particles of different sizes with the same (111) facet. This implies that the particles favor (111) growth direction. Existence of the diamond particles with various sizes implies that during the growth period either an additional diamond nucleates or generates defects such as twins and stacking faults. It can also be seen that there is secondary nucleation of diamond grains in between the existing diamond crystal, where surface energy is low. It can be said that the secondary nucleation fills up the surface irregularities and results in a smooth film. The secondary nucleation is expected to be due to methane gas since increase in methane gas pressure may result in secondary nucleation.

Fig. 1b shows the magnified image obtained from the periphery of the sample, where typical decahedrons and icosahedrons of diamond can be seen clearly. It is well known that these particles are not single crystals, but they are multiply twinned particles (MTPs) [Lawrence and Kania, 1995]. Therefore, the presence of these particles evidenced that the film is defective.

It is known that adsorption of foreign atoms on the surface can significantly modify its physical and chemical properties. In some cases impurities act as a "surfactants" can greatly modify the morphology of the film. An example is the heteroepitaxial growth of semiconductors. Hydrogen is a common impurity that plays a significant role in semiconductor growth as well as diamond growth. A conventional CVD diamond growth process typically consists of few stages, viz. (I) incubation period, (II) 3-D surface nucleation, (III) termination of nucleation and 3-D growth of nuclei to grains, (IV) faceting and coalescence of individual grains and formation of continuous film, and finally (V) growth of continuous film. In the first step of the growth process, carbon clusters are formed on the substrate surface and a change in the bonding structure from  $\text{sp}^1$  to  $\text{sp}^2$  occurs. In step II,  $\text{sp}^2$ -bonded carbon atoms are converted into a relatively stable network of  $\text{sp}^3$ -bonded carbon. The continuous molecular rain of activated hydrocarbon and atomic hydrogen on the substrate surface provides sufficient energy for  $\text{sp}^1 \rightarrow \text{sp}^2 \rightarrow \text{sp}^3$  conversion. After this, a transition of bonding state in the carbon network occurs from a disordered domain with  $\text{sp}^3$  bonded carbon to diamond with  $\text{sp}^3$ -bonded carbon. Crystallization also includes chemical reactions such as hydrogen abstraction, dehydrogenation of absorbed surfactants, recombination of hydrogen atoms etc. During crystallization, the carbon atoms rearrange towards {111} planes to achieve minimum surface energy and this crystallized region then acts as a nucleus for subsequent growth of diamond (i.e., further growth steps).

In Fig. 2, the corresponding X-ray diffraction (XRD) obtained from the film is shown. The peaks at  $28^\circ$  and  $69^\circ$  are due to the silicon substrate [Woo et al., 1998; Meng et al., 1999]. According to the JCPDS (the Joint Committee on Powder Diffraction Standards) card, the peaks at  $44^\circ$ ,  $75^\circ$ ,  $91^\circ$ ,  $119^\circ$ , and  $140^\circ$  (2-theta) characterize



**Fig. 1. SEM images obtained from the film grown on the flashed and reconstructed Si (100) (a) Image from the center of the sample, where the film is uniform and continuous; and (b) Magnified image from the periphery of the same sample, where the film is discontinuous.**

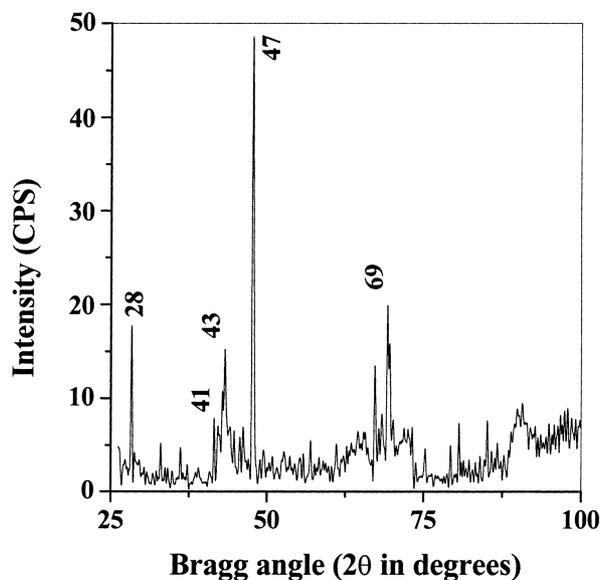


Fig. 2. X-ray diffraction pattern of the film grown on the flashed and reconstructed Si (100).

a cubic diamond but the Lonsdaleite diamond is characterized by additional peaks at  $41^\circ$ ,  $47^\circ$ ,  $61^\circ$ ,  $82^\circ$ , and  $93^\circ$  compared to the cubic diamond [Lee et al., 1998]. From Fig. 2, it is seen that there exist clear peaks at  $41^\circ$  and  $47^\circ$  in 2-theta angle. The peak at  $47^\circ$  is the strongest peak with 100% intensity ratio. Thus from the XRD pattern of the deposited diamond film shown in Fig. 2, it can be concluded that the nature of the grown film is mostly Lonsdaleite with a slight mix of cubic diamond grains.

The Raman spectrum obtained from the corresponding film is shown in Fig. 3. Two peaks at the wave numbers of  $1,329\text{ cm}^{-1}$  and  $1,600\text{ cm}^{-1}$  correspond to diamond and non-diamond phases, respectively [Stockel et al., 1996]. The peak at  $940\text{ cm}^{-1}$  is due to the Silicon substrate. Considering that the Raman scattering efficiency from

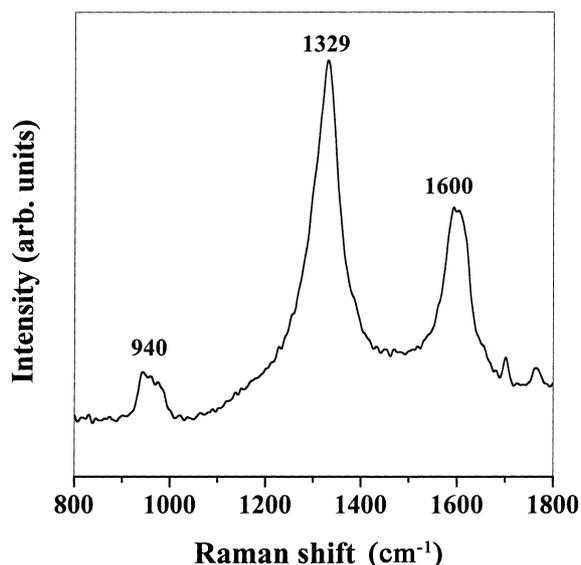


Fig. 3. Micro-Raman spectrum obtained from the film grown on the flashed and reconstructed Si(100).

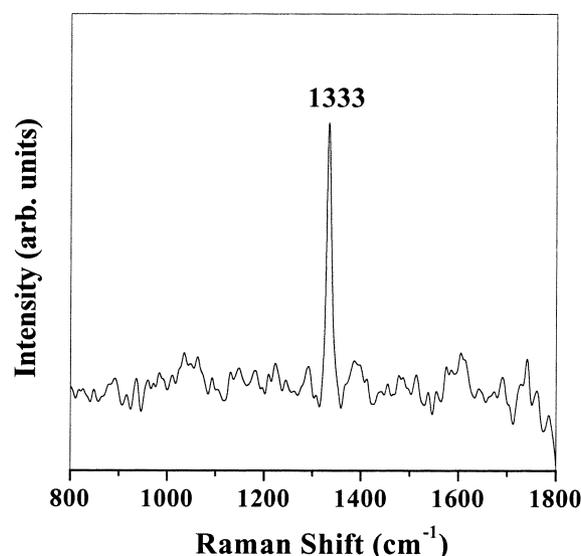


Fig. 4. Micro-Raman spectrum, obtained from the film prepared by BEN growth process with bias voltage of  $-280\text{ V}$  ( $25\text{ mA}$ ) for 30 min.

the  $sp^3$ - bonds of diamond is about 50 times smaller than that from the  $sp^2$ - bonds of non-diamond (graphite or diamond-like) [Glass et al., 1990], the fact that the peak height at  $1,600\text{ cm}^{-1}$  is smaller than that at  $1,329\text{ cm}^{-1}$  implies that the film is mostly composed of diamond phase even though there also exists a small portion of non-diamond phase. This shows the possibility of formation of a non-diamond phase between the diamond planes and thus causes a shift in positions of all surrounding carbon atoms and introduces strains in the grown film. This intrinsic strain therefore causes broadening in the diamond peak (at  $1,329\text{ cm}^{-1}$  wave number), which can be seen in the spectra and a slight shift in peak position from the expected Lonsdaleite position ( $1,326\text{ cm}^{-1}$ ).

Fig. 4 shows the Raman spectrum obtained from the film grown by using the BEN method under the deposition conditions as mentioned in experimentation. In the BEN method, the substrate was negatively biased with a bias voltage of  $-280\text{ V}$  ( $25\text{ mA}$ ) and the bias period was 30 min (for initial nucleation). The experimental configurations were kept the same in order to compare the two kinds of diamond film grown by different nucleation enhancement methods. It can be noted that the Raman spectrum (shown in Fig. 4) has only a very sharp cubic diamond peak at a wave number of  $1,333\text{ cm}^{-1}$ .

Comparing spectra shown in Figs. 3 and 4, it is clearly observed that the Raman peaks appear at different positions, i.e., at  $1,329\text{ cm}^{-1}$  and  $1,333\text{ cm}^{-1}$  and with different peak widths (FWHM=53 and  $10\text{ cm}^{-1}$ ), respectively. These two distinct differences, i.e., shift in peak position and peak broadening, in Raman peaks imply that the film with hexagonal diamond structure (Lonsdaleite) has more defects than the film with cubic diamond structure as the optical phonon frequency of hexagonal structure is different from that of cubic structure. It was previously proposed that the nucleation of Lonsdaleite layers on a diamond surface is equivalent to nucleation of a stacking fault or twin plane during diamond growth [Spear and Dismukes, 1993; Lawrence and Kania, 1995]. In general, such a process causes intrinsic strains during the growth process. Hence, the

intrinsic strain causes broadening of the Raman peak as shown in Fig. 3. Therefore, the broadened Raman peak shown in Fig. 3 also evidences the Lonsdaleite nature of the present film.

### CONCLUSION

In the present experiment, diamond film mostly consisting of Lonsdaleite structure was successfully grown for the first time on flashed and reconstructed Si(100) by hot-filament chemical vapor deposition (HFCVD). SEM, X-ray diffraction (XRD) pattern and Raman spectra obtained from this film commonly evidence the unique Lonsdaleite nature obtained.

### ACKNOWLEDGMENT

The authors wish to acknowledge the financial support received from KOSEF basic research grant No. 1999-2-307-003-3 and post-doc program of Chonbuk National University.

### REFERENCES

- Chiem, C. V., Kim, J. H., Shin, H. S. and Seo, J. M., "Diamond Nucleation Enhancement on the Reconstructed Si(100)," *J. Vac. Sci. & Tech. A*, **20**(1), 202 (2002).
- Glass, J. T., Messier, R. and Fujimori, N., "Diamond, Silicon Carbide and Related Wide Bandgap Semiconductors," MRS (1990).
- Ishizaka, A. and Shiraki Y., "Low Temperature Surface Cleaning of Silicon and its Application to Silicon MBE," *J. Electrochem. Soc.*, **133**, 666 (1986).
- Lawrence, S. P. and Kania, D. R. (Eds.), "Diamond: Electronic Properties and Applications," Kluwer Academic Publisher (1995).
- Lee, Y. H., Chen, C. H., Chung, S. R., Chen, S. H. and Wung, Y. T., "Preparation and Properties of Lonsdaleite-like Carbon by HFCVD," International Symposium of Carbon, 554-555, 1998 (Tokyo).
- Meng, Q. B., Fei, Y. J., Kang, J., Xiong, Y. Y., Lin, Z. D., Feng, K.-A., Wu, Z. J. and Zhang, S. Y., "Study on the Interface Structure: Diamond Thin Film Epitaxy on (001) Silicon Substrate," *Modern Physics Letters B*, **13**, 125 (1999).
- Spear, K. E. and Dismukes, J. P., "Synthetic Diamond: Emerging CVD Science and Technology," John Wiley & Sons, New York (1993).
- Stockel, R., Janischowsky, K., Rohmfeld, S., Ristein, J., Hundhausen, M. and Ley, L., "Diamond Growth During Bias Pre-treatment in the Microwave CVD of Diamond," *Diamond Relat. Mater.*, **5**, 321 (1996).
- Stoner, B. R., Sahaida, S. R., Bade, J. P., Southworth, P. and Ellis, P. J., "Highly Oriented, Textured Diamond Films on Silicon via Bias-enhanced Nucleation and Textured Growth," *J. Mater. Res.*, **8**, 1334 (1993).
- Woo, H. K., Lee, C. S., Bello, I. and Lee, S. T., "Epitaxial Growth of B-SiC on Silicon by Bias-assisted Hot Filament Chemical Vapor Deposition from Solid Graphite and Silicon Sources," *J. Mater. Res.*, **13**, 1738 (1998).
- Wurzinger, P., Pongratz, P., Gerber, J. and Ehrhardt, H., "Bias-Enhanced Diamond Nucleation on Silicon-A TEM Study," *Diamond Relat. Mater.*, **5**, 345 (1996).
- Yugo, S., Kanai, T., Kimura, T. and Muto, T., "Generation of Diamond Nuclei by Electric Field in Plasma Chemical Vapor Deposition," *J. Appl. Phys. Lett.*, **58**, 1036(1991).