

# Deposition of heteroepitaxial diamond on 6H-SiC single crystal by bias-enhanced microwave plasma chemical vapor deposition

L. Chang<sup>a,\*</sup>, J.E. Yan<sup>b</sup>, F.R. Chen<sup>b</sup>, J.J. Kai<sup>b</sup>

<sup>a</sup> Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan 300

<sup>b</sup> Department of Engineering System and Science, National Tsing Hua University, Hsinchu, Taiwan 300

## Abstract

Deposition of heteroepitaxial diamond on substrates of 6H-SiC single crystal by a d.c. voltage biased-enhanced microwave plasma chemical vapor deposition method has been attempted. Various concentrations of methane (CH<sub>4</sub>) up to 10% in hydrogen (H<sub>2</sub>) was used to evaluate its effect on epitaxy. Characterization of cross-sectional transmission electron microscopy with electron energy loss spectroscopy shows that an interlayer can form between diamond 6H-SiC, depending on the CH<sub>4</sub> concentration. With low CH<sub>4</sub> concentration, diamond was directly nucleated on 6H-SiC with an orientation relationship of diamond {111}//6H-SiC {0001} and diamond <110>//6H-SiC <112̄0>. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Bias; Heteroepitaxy; Silicon carbide; Transmission electron microscopy

## 1. Introduction

Deposition of heteroepitaxial diamond is vital to electronic applications. In the past, heteroepitaxial diamond growth on Si and β-SiC has been demonstrated by the bias-enhanced nucleation method in microwave plasma chemical vapor deposition (MPCVD) [1–5]. It is often found that diamond growth on Si is preceded by the formation of β-SiC as an interlayer [3–5]. The β-SiC interlayer thus plays an important role on the orientation of subsequently nucleated diamond. Recently, diamond growth on a β-SiC substrate also has been shown to exhibit extremely high quality as a result of heteroepitaxy in which the epitaxial relationship of diamond with β-SiC is diamond [110]//SiC[110] and diamond (100)//SiC(100) [6]. Among SiC polytypes, β-SiC or 3C-SiC is a cubic structure in which the stacking sequence in the <111> direction is ABCABC..., and 6H-SiC is hexagonal in which the stacking sequence in [0001] is ABCACB.... As the β-SiC {111} plane has the same closed packing structure as 6H-SiC basal plane of {0001}, it is of interest to investigate diamond growth on 6H-SiC substrates. In particular, 6H-SiC substrates are more stable than Si during biasing, which may

clarify the nucleation process of diamond without SiC formation which occurs with deposition on Si substrates. In addition, 6H-SiC single crystal substrate is now commercially available, while β-SiC is not. The possibility of local epitaxy of diamond on 6H-SiC has been demonstrated in previous work using MPCVD [7,8]. Recently, Li et al. have shown heteroepitaxial growth of diamond on 6H-SiC using hot filament CVD [9]. In the present work, we report the results of diamond growth on 6H-SiC using the bias-enhanced method in MPCVD with different concentrations of CH<sub>4</sub>. The orientations and interfaces between diamond and 6H-SiC substrates were characterized by cross-sectional transmission electron microscopy (TEM).

## 2. Experimental details

Deposition was carried out in an ASTEX microwave plasma CVD reactor. The negative d.c. bias was applied on the sample holder at –200 V for 24 min. The pressure was at 20 Torr. The CH<sub>4</sub> concentration in H<sub>2</sub> was varied from 4% to 10% during biasing. The input microwave power was 700 W. The temperature on the substrate was measured to be in the range 760–790°C by an optical pyrometer. After biasing, continuous growth was followed for 30 min using 1% CH<sub>4</sub> without bias. The

\* Corresponding author. Fax: +886-3-5724727.

E-mail address: lichang@cc.nctu.edu.tw (L. Chang)

6H-SiC substrates in  $10 \times 3$  mm strips were obtained from Cree Research, USA. Prior to being loaded into the CVD reactor, the substrates were dipped into a 10% HF aqueous solution for 30 s to remove surface oxide. Before deposition, the substrates were further cleaned by  $H_2$  plasma for 30 min.

TEM characterization was performed on a JEOL JEM 2010F microscope. An electron beam with 0.5 nm diameter was used for nanobeam diffraction and electron energy loss spectroscopy (EELS). Cross-sectional TEM specimens were prepared by a conventional method consisting of gluing and grinding, followed by ion milling to perforation. TEM observations of each specimen were done at several positions where the thin areas were over a range of 10  $\mu\text{m}$ .

### 3. Results and discussion

Fig. 1 shows the typical TEM image of diamond deposited with 10%  $CH_4$ . The diamond film exhibits polycrystalline characteristics with randomly oriented diamond grains, as shown by the diffracted ring of the diamond  $\{111\}$  plane in the selected area diffraction (SAD) pattern. The average grain size in the lateral is

about 60 nm, suggesting that the nucleation density of diamond is close to  $10^{10} \text{ cm}^{-2}$ . An amorphous interlayer 40 nm thick can be seen between the diamond and the 6H-SiC substrate. EELS indicates that it is amorphous carbon. High resolution TEM (HRTEM) in Fig. 2 reveals the details around the interfacial region. From the lattice images, in which the  $\beta$ -SiC lattice stacking sequence is ABCABC, compared with ABCACB in 6H-SiC, it is identified that several  $\beta$ -SiC particles, in island shape, epitaxially grow on the 6H-SiC substrate. Nanobeam diffraction patterns from these areas also confirm that they are  $\beta$ -SiC. The orientation relationship is determined to be  $\beta$ -SiC  $\langle 110 \rangle \parallel$  6H-SiC  $\langle 11\bar{2}0 \rangle$  and  $\beta$ -SiC  $\{111\} \parallel$  6H-SiC  $\{0001\}$ . Also, a few nanocrystalline diamond particles are found embedded within the amorphous layer. For 5%  $CH_4$  specimens, diamond grains are in a columnar structure with lateral size 100 nm, as shown in Fig. 3. Similar to the 10%  $CH_4$  case, a 30–40 nm thick interlayer of amorphous carbon is seen around the interfacial region. Also, there are some epitaxial  $\beta$ -SiC regions on the 6H-SiC, and some diamond grains are nucleated on  $\beta$ -SiC as seen in the HRTEM micrograph in Fig. 4. In contrast with 5% and 10%  $CH_4$  conditions, the diamond films formed with 4.5%  $CH_4$  concentration show a distinct grain morphol-

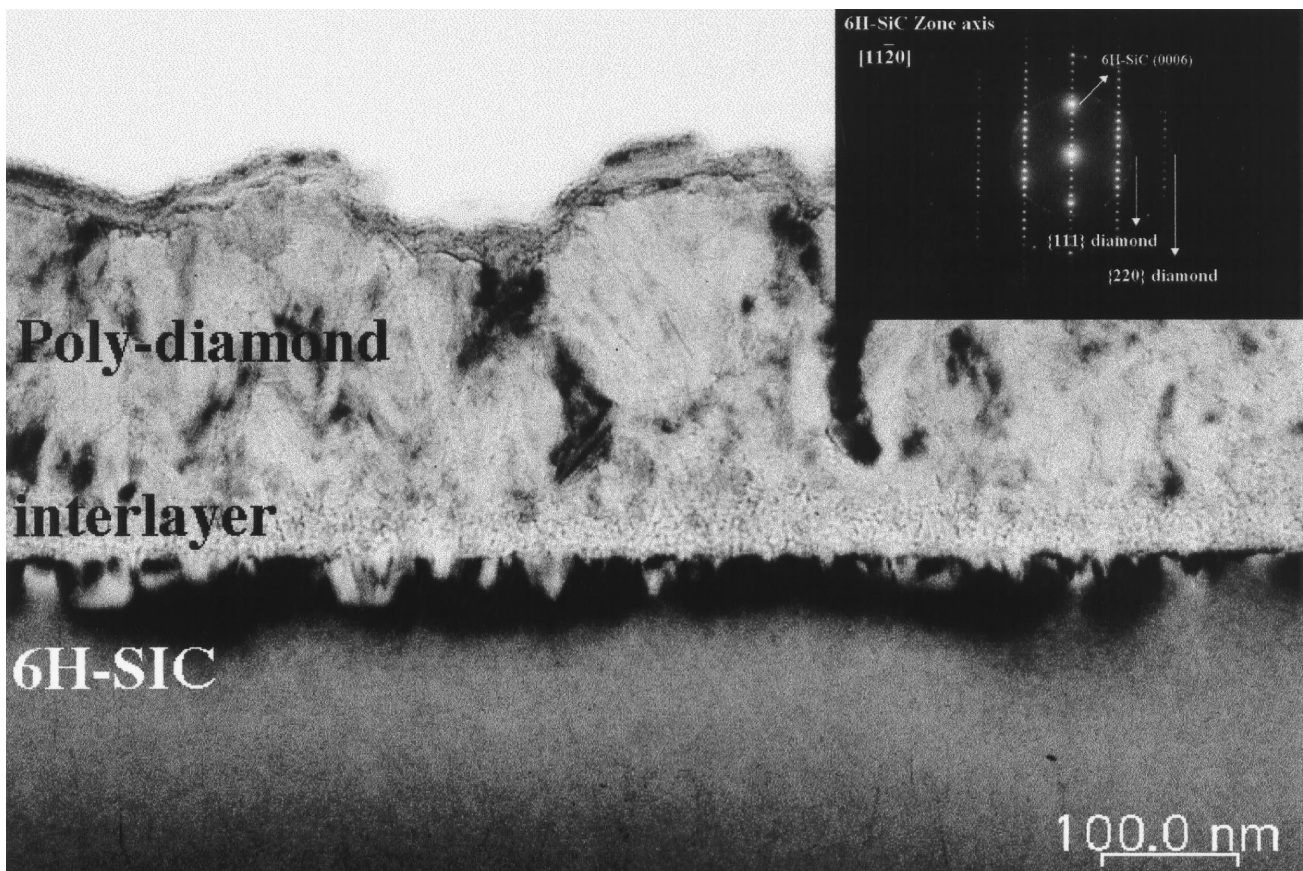


Fig. 1. TEM micrograph showing the microstructure of diamond deposited with 10%  $CH_4$ . The SAD pattern is given in the inset.

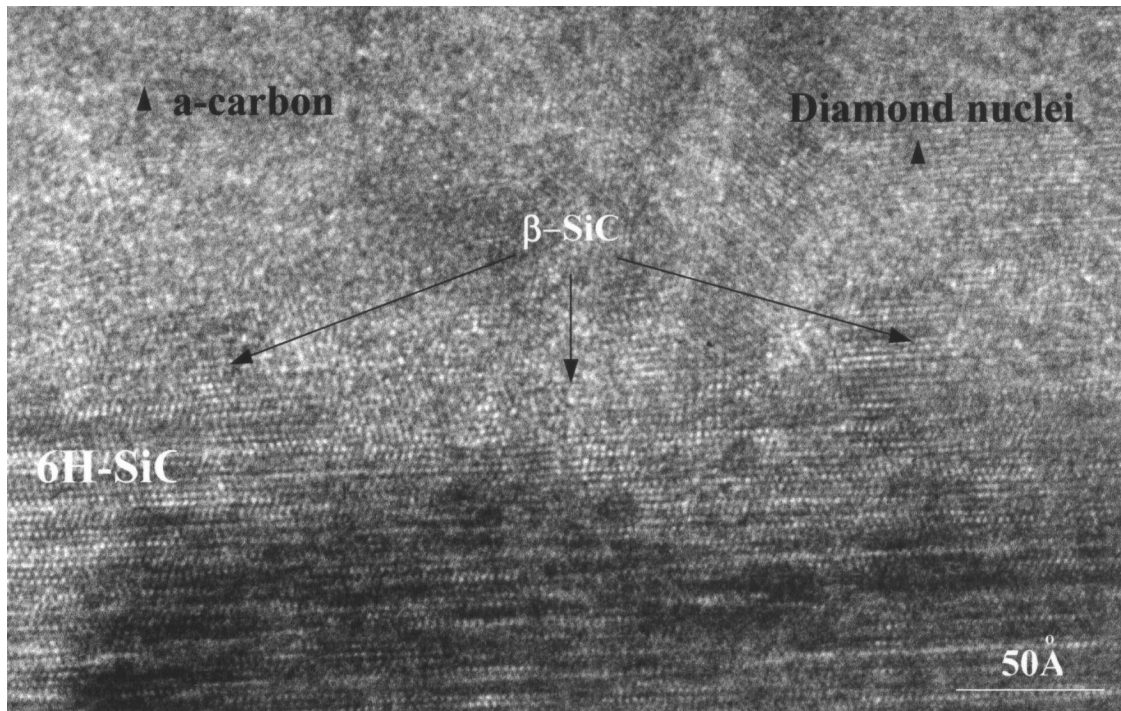


Fig. 2. HRTEM micrograph from a specimen deposited with 10% CH<sub>4</sub>.

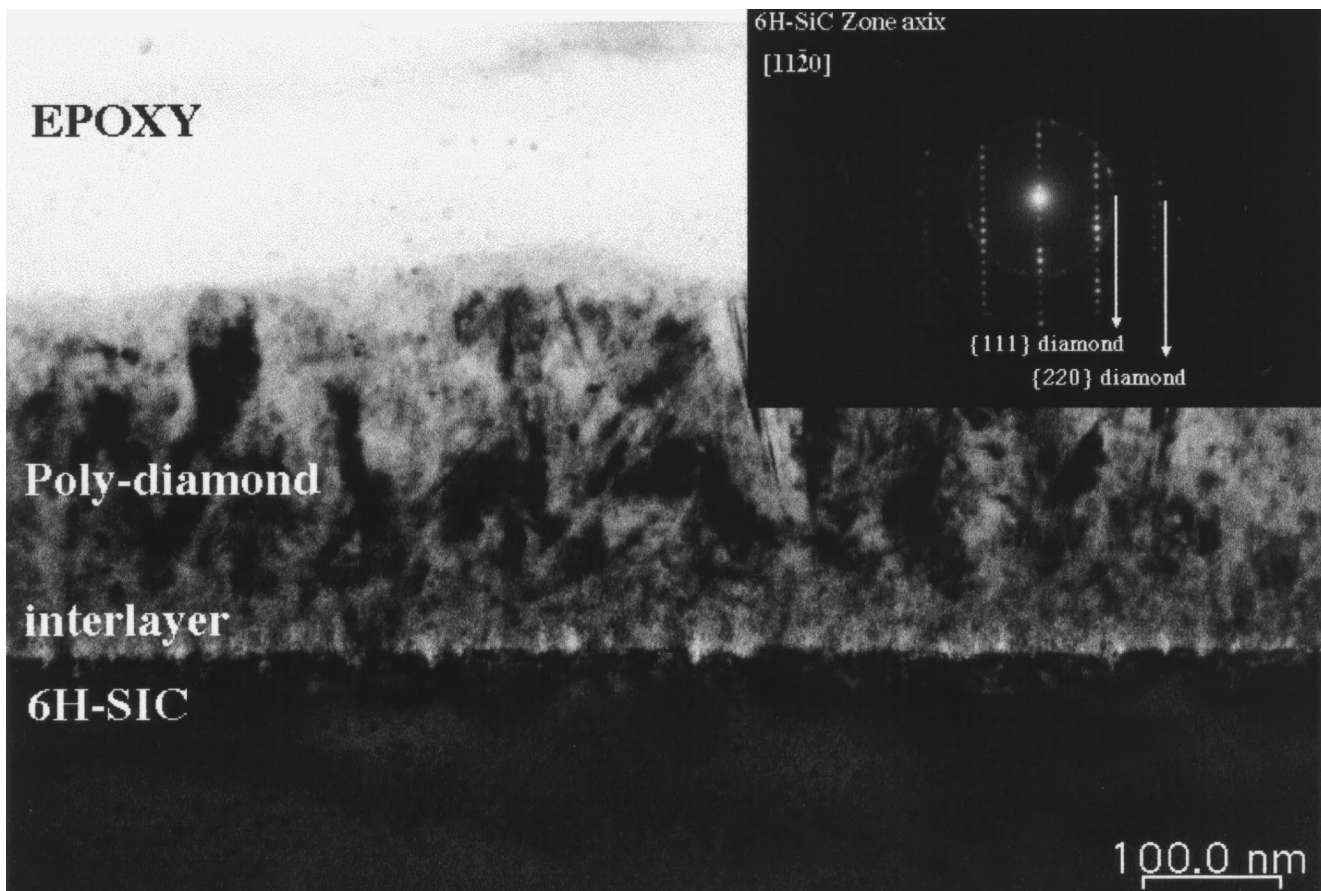


Fig. 3. TEM micrograph showing the microstructure of diamond deposited with 5% CH<sub>4</sub>. The SAD pattern is given in the inset.

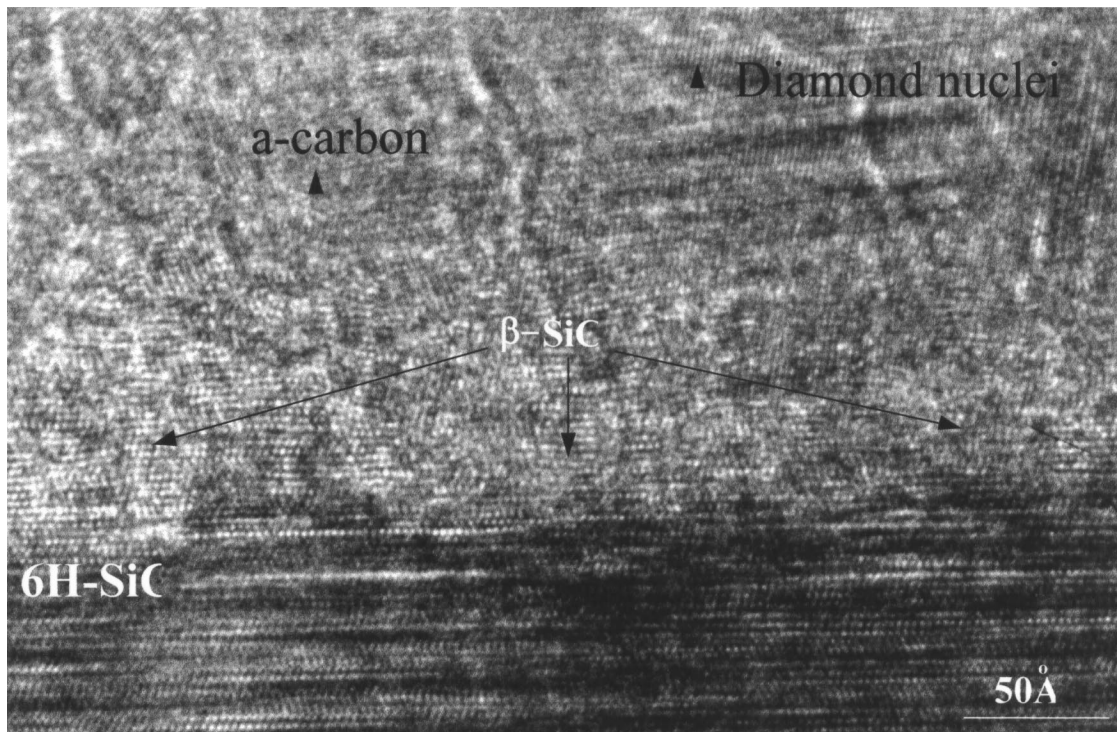


Fig. 4. HRTEM micrograph showing the interfacial region between diamond and 6H-SiC. Specimen deposited with 5% CH<sub>4</sub>.

ogy with a size in the range 200–300 nm as shown in Fig. 5. This roughly corresponds to a nucleation density of  $10^9 \text{ cm}^{-2}$ . Most of diamond grains exhibit an orientation of {111} planes parallel to 6H-SiC {0001} basal planes, as shown by the SAD pattern in the inset of Fig. 5. Fig. 6 is an HRTEM image taken from the center of a grain shown in Fig. 5 where the nucleation occurred. It reveals that no amorphous interlayer exists between diamond and the 6H-SiC substrate. Heteroepitaxial diamond in direct contact with 6H-SiC can be clearly seen in Fig. 6. Also, it is noted that the interface between diamond and the 6H-SiC substrate is smooth. However, defects of twin and stacking faults are observed within diamond grains close to the interface, resulting in loss of epitaxy. Fig. 7 shows the microstructure deposited with the 4% CH<sub>4</sub> condition. The grain size is about 100–150 nm. Diamond grains are less oriented than those grown in 4.5% CH<sub>4</sub> as shown by the spotty rings in the SAD pattern. However, some diamond grains can be epitaxially oriented with the underlying 6H-SiC substrate. A typical HRTEM image is shown in Fig. 8. As Fig. 6, it also shows no amorphous interlayer formed between diamond and the 6H-SiC substrate.

The epitaxial orientation of diamond in 4.5% CH<sub>4</sub> can be attributed to the lower nucleation density and the direct nucleation on substrate. The nucleation density achieved in 10% CH<sub>4</sub> is an order of magnitude higher than in 4.5% CH<sub>4</sub>. The rate of nucleation and growth is relatively invariant with the CH<sub>4</sub> concentration as the thickness of all specimens is about 200 nm. The

β-SiC formation may be due to the rearrangement of the 6H-SiC surface. Kawarad et al. reported that a layer of β-SiC formed before epitaxial diamond nucleation in their study of diamond deposition on β-SiC [6]. Yamamoto et al. found that the β-SiC layer was etched off during the negative bias treatments [10]. In the present work, higher carbon concentration results in amorphous carbon formation initially, followed by higher density of diamond nucleation. Therefore, it is reasonable that the β-SiC formed should have no significant influence on the subsequent nucleation of diamond. It is amorphous carbon resulting in the randomly oriented diamond grains. Without an amorphous carbon interlayer, diamond epitaxial growth can proceed with diamond {111} close packed planes parallel to the 6H-SiC {0001} basal plane, even though the lattice mismatch is high. For {111} β-SiC substrates, similar behavior would be expected. In our previous study of diamond nucleation on 6H-SiC with 2% CH<sub>4</sub> deposition [7], diamond was less oriented than that with 4% CH<sub>4</sub> deposition. The fact that no β-SiC is observed in CH<sub>4</sub> concentrations less than 5% implies that the plasma with strong ion impingement from bias causes no reconstruction of the 6H-SiC surface. At the moment, it is not known why diamond orientation varies with CH<sub>4</sub> concentration. With less CH<sub>4</sub>, the bias effect seems to be incapable of modifying the 6H-SiC surface. It is speculated that surface diffusion and more H<sub>2</sub> could stabilize the nuclei at low carbon concentration.

Heteroepitaxial diamond on an Si substrate can be

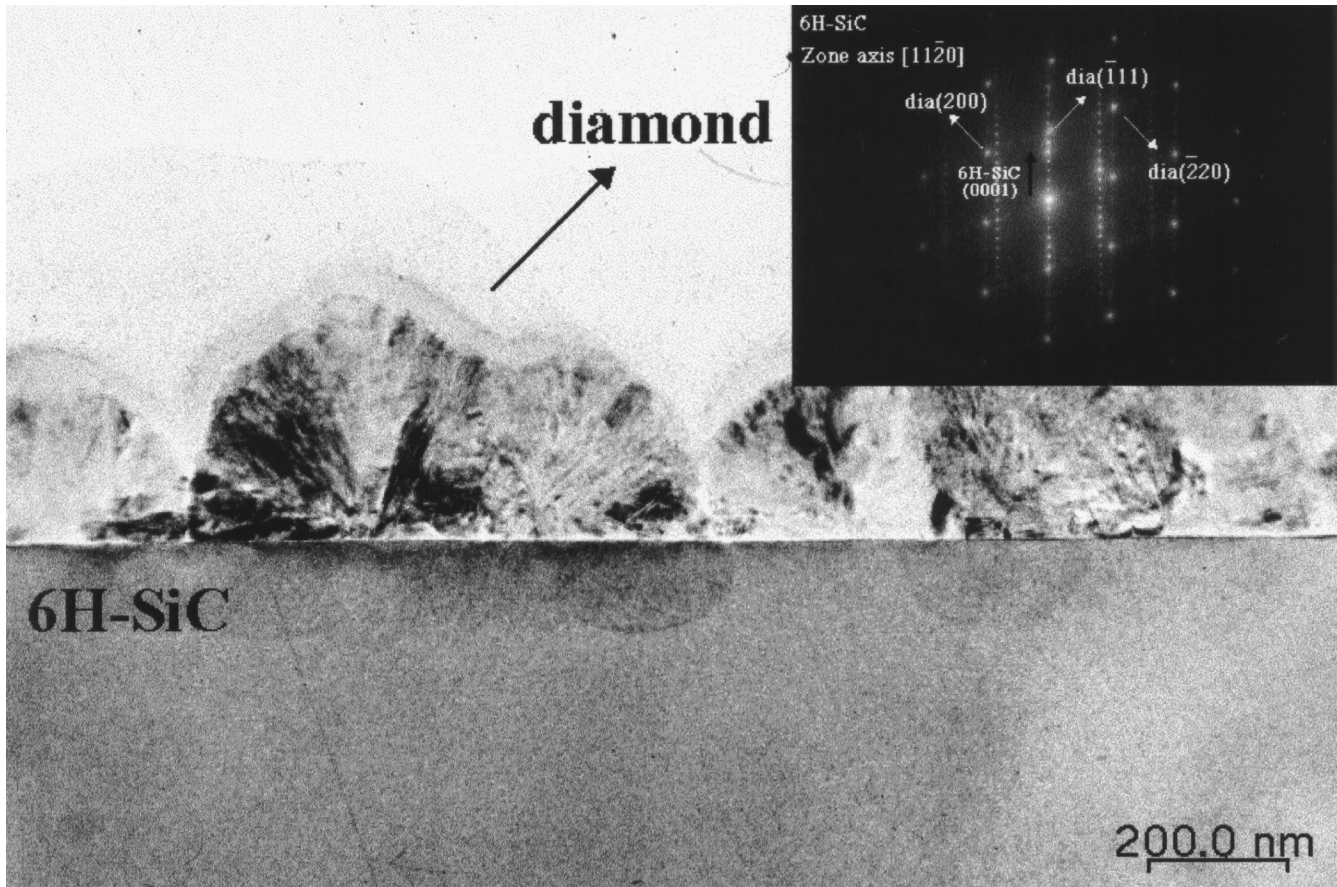


Fig. 5. TEM micrograph showing the microstructure of diamond deposited with 4.5%  $\text{CH}_4$ . The SAD pattern is given in the inset.

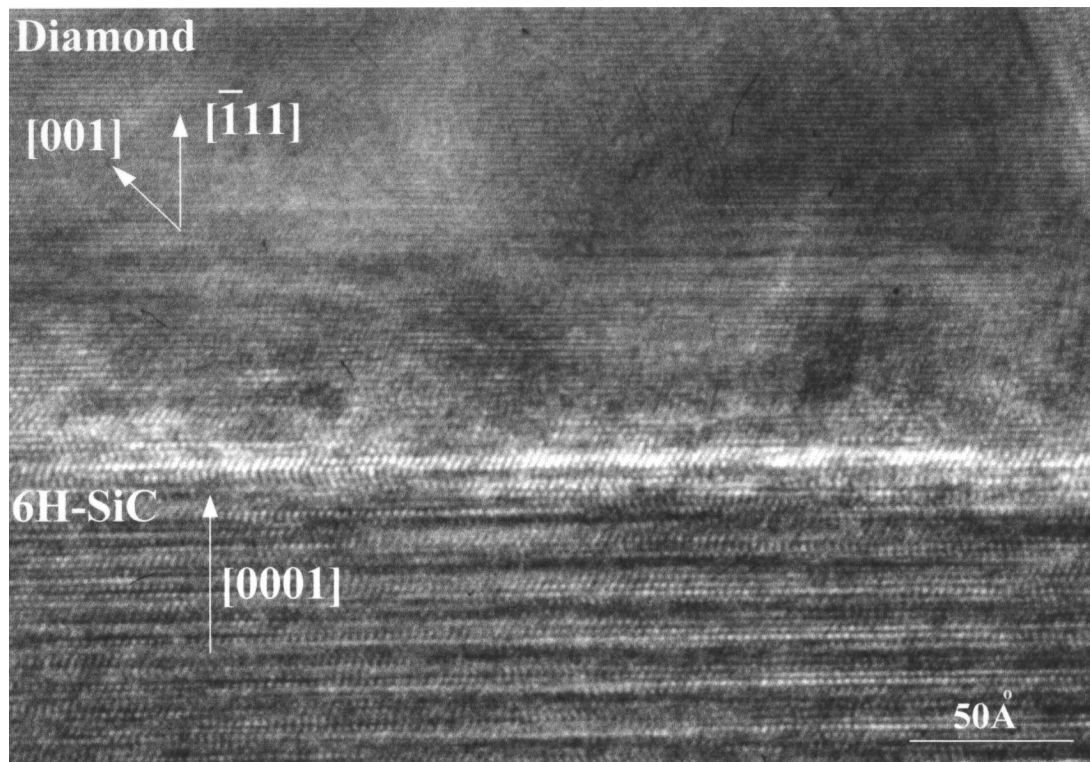


Fig. 6. HRTEM micrograph showing the interfacial region between diamond and 6H-SiC. Specimen deposited with 4.5%  $\text{CH}_4$ .

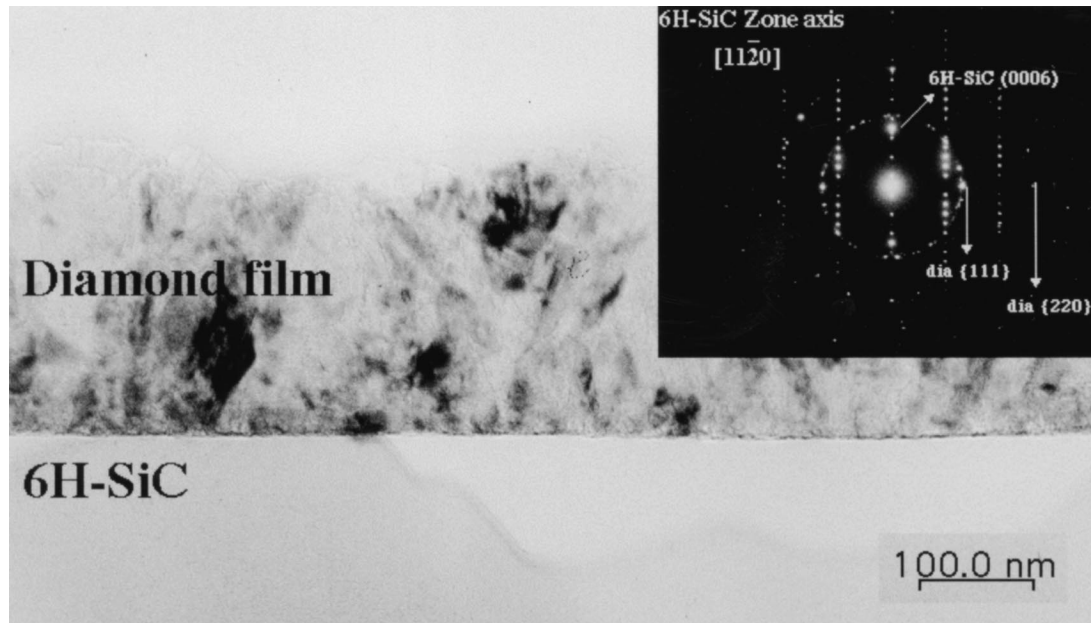


Fig. 7. TEM micrograph showing the microstructure of diamond deposited with 4% CH<sub>4</sub>. The SAD pattern is given in the inset.

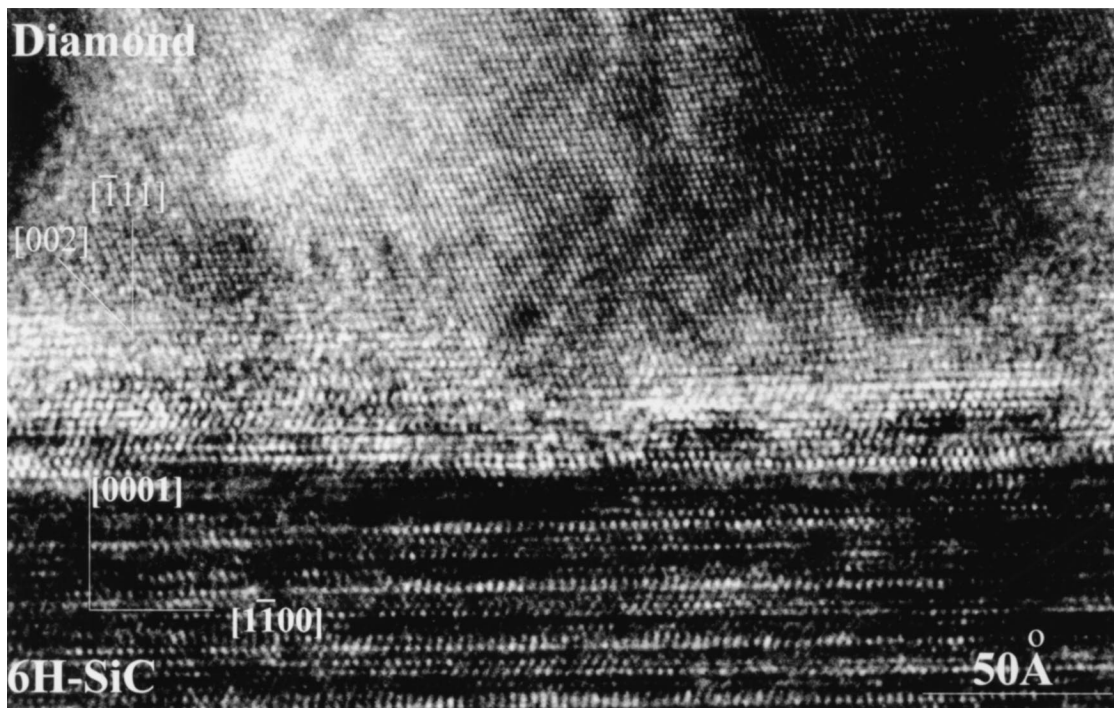


Fig. 8. HRTEM micrograph showing the interfacial region between diamond and 6H-SiC. Specimen deposited with 4% CH<sub>4</sub>.

deposited directly or through an SiC interlayer. Though the SiC interlayer can be in epitaxy with Si, the slight misorientation of SiC often results in diamond not oriented with the underlayer. Therefore, it is favorable for diamond to nucleate directly on the substrate to obtain good quality heteroepitaxial diamond.

Many variables may affect heteroepitaxial growth of diamond on 6H-SiC. The present investigation shows that

the CH<sub>4</sub> concentration has a strong effect on the epitaxial condition. Low concentration of CH<sub>4</sub> is favorable for heteroepitaxial growth. To improve the quality of diamond films, further studies on the effects of bias voltage and bias time are needed. Also, the surface type of 6H-SiC can have different influences on heteroepitaxial growth. It has been shown that diamond grown on carbon surfaces has better quality than that grown on Si surfaces [9].

#### 4. Conclusion

Deposition of diamond on a 6H-SiC single crystal substrate has been done with bias-enhanced nucleation pretreatment in a MPCVD reactor. Diamond films with  $\langle 111 \rangle$  texture were obtained with  $\text{CH}_4$  below 5% in  $\text{H}_2$ . Heteroepitaxial diamond is found in those films. The orientation relationship is  $[110]\text{diamond} // [11\bar{2}0]6\text{H-SiC}$  and  $\{111\}\text{diamond} // \{0001\}6\text{H-SiC}$ . With higher  $\text{CH}_4$  concentration, formation of an amorphous carbon interlayer before diamond deposition results in randomly oriented polycrystalline diamond films.

#### Acknowledgements

This work was supported by the National Science Council, Taiwan, ROC, under contract NSC 88-2216-E-009-019. We also thanks the Materials

Research Laboratories of the Industrial Technology Research Institute for providing the MPCVD facility.

#### References

- [1] X. Jiang, C.-P. Klages, *Diamond Relat. Mater.* 2 (1992) 698.
- [2] B.R. Stoner, J.T. Glass, *Appl. Phys. Lett.* 60 (1992) 698.
- [3] B.R. Stoner, G.H.M. Ma, S.D. Wolter, J.T. Glass, *Phys. Rev. B* 45 (1992) 11 067.
- [4] H. Maeda, M. Irie, T. Hino, K. Kusakabe, S. Morooka, *J. Mater. Res.* 10 (1995) 158.
- [5] W. Kulisch, L. Ackermann, B. Sobisch, *Phys. Stat. Sol. A* 154 (1996) 155.
- [6] H. Kawarada, C. Wild, N. Herres, R. Locher, P. Koidl, H. Nagasawa, *J. Appl. Phys.* 81 (1997) 3490.
- [7] L. Chang, T.S. Lin, J.L. Chen, F.R. Chen, *Appl. Phys. Lett.* 62 (1993) 344.
- [8] T. Suzuki, M. Yagi, K. Shibuki, *Appl. Phys. Lett.* 64 (1994) 557.
- [9] X. Li, Y. Hayashi, S. Lilov, S. Nishino, *Jpn. J. Appl. Phys.* 36 (1997) L1370.
- [10] T. Yamamoto, T. Maki, T. Kobayashi, *Appl. Surf. Sci.* 117/118 (1997) 582.