Diamond and Related Materials 11 (2002) 509–512

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

Diamond deposition on Si (111) and carbon face 6H–SiC (0001) substrates by positively biased pretreatment

Te-Fu Chang*, Li Chang

Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan 300, ROC

Abstract

The growth of textured diamond films on Si (111) and carbon face 6H–SiC (0001) has been achieved by positive bias-enhanced-nucleation in microwave plasma chemical vapor deposition. A bias voltage of +100 to +300 V, 3% CH_4 concentration in bias step, and 0.33% CH_4 concentration in growth step were used to synthesize diamond films on Si and carbon face 6H–SiC. Highly oriented diamond films were observed by scanning electron microscopy and X-ray diffraction patterns. Cross-sectional transmission electron microscopy showed that the interface between diamond and Si substrate was smooth, while it was rough between diamond and SiC. It also showed that diamond films were directly grown on both substrates. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diamond films; CVD; 6H–SiC; Bias

1. Introduction

Diamond, which has many excellent properties, such as wide band gap, high thermal conductivity and high hole mobility, is a promising semiconductor material for high temperature and high power electronic devices. For the purpose of electronic usage of diamond films, it is necessary to synthesize heteroepitaxial diamond films via diamond growth techniques. Microwave plasma chemical vapor deposition (MPCVD) coupled with a bias enhanced nucleation (BEN) method is one of the many important techniques used to obtain heteroepitaxial diamond films without any mechanical pre-treatment. The BEN method can significantly increase the nucleation density of diamond which is necessary for heteroepitaxial growth of diamond. Jiang and Klages first reported [001]-oriented diamond films epitaxially grown on Si(001) by applying negative BEN [1]. Since then, the negative BEN method in MPCVD has been widely used by many researchers to obtain heteroepitaxial diamond films on various substrates [1–6]. On a Si(111) substrate, Yugo et al. [7] and Schreck et al. [8] reported that heteroepitaxial diamonds can also be grown by applying a negative bias in MPCVD. However, no report has shown that diamond grows on a Si(111) substrate by positive d.c. bias pre-treatment. Positive BEN, which applies positive voltage to a substrate, can also increase the nucleation density of diamond in MPCVD [9]. Therefore, it is promising that a positive bias could provide another method of obtaining heteroepitaxial diamond films.

It has often been observed that a β-SiC interlayer forms between diamond and Si. Stoner et al. reported the formation of an interfacial layer of β-SiC and amorphous carbon on Si during negative bias treatment [2]. Stoner and Glass also demonstrated that locally epitaxial diamond films could be successfully obtained on β-SiC [3]. Due to the structural similarity of β-SiC(111) and 6H–SiC(0001), it is possible to form a heteroepitaxial diamond films on 6H–SiC(0001). Previous work by Chang et al. reported that heteroepitaxial diamond nucleation on Si face 6H–SiC is possible by negative biasing [10,11]. Li et al. also reported that textured diamond films could be successfully grown on 6H–SiC in hot-filament CVD [12,13]. Under positive bias conditions, diamond growth on both of the substrates has not been reported. Hence, it is of interest to deposit diamond on a 6H–SiC substrate for comparison with the results on Si. Here, we have demonstrated that textured diamond films could grow on Si(111) and the

*Corresponding author. Tel.: +886-3-5712121, ext.55373; fax: +886-3-5724727.

E-mail address: u8718513@cc.nctu.edu.tw (T.-F. Chang).

PII: S0925-9635(01)00672-0

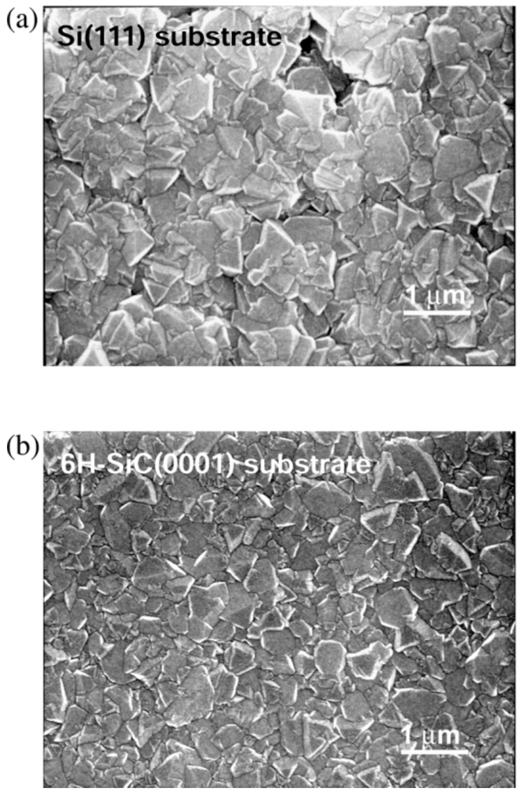

Fig. 1. SEM images showing (111) textured diamond films grown on (a) Si (111) and (b) carbon face 6H–SiC (0001) substrates deposited for 2.5 h growth. Bias voltage of +300 V.

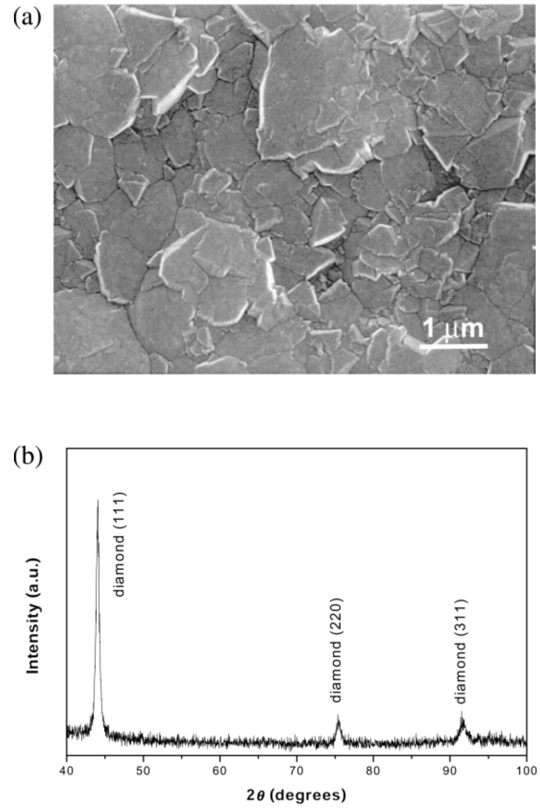

Fig. 2. (a) SEM images and (b) XRD pattern showing ⟨111⟩ texture of diamond film deposited with positive biasing at +200 V on Si (111) substrate for 20 h growth.

carbon face 6H–SiC(0001) substrates by positive BEN in MPCVD.

2. Experimental details

Commercially available carbon face 6H–SiC(0001) and Si(111) were selected as the substrates. Si wafers were used of the grade used for IC production. The carbon face 6H–SiC(0001) wafer, which was 1.5 inches in diameter, used for optical-electronic devices, was provided by Sterling Semi-Conductor Co. Ltd. Both substrates were received with a mirror-like polished surface. The sample size of carbon face 6H–SiC was then prepared as 3×10 mm by cutting and the size of the p-type Si (111) sample was 10 mm^2. The substrates were dipped in HF for 1 min to remove oxides, and ultrasonically cleaned with acetone for 5 min to remove contamination, followed by ultrasonically cleaning in de-ionized water before inserting into the MPCVD reactor. A tubular MPCVD reactor made of quartz, 50 mm in diameter, was used to deposit diamond. After reactant gases (mixture of CH_4 and H_2) flowed into the quartz tube, a 2.45-GHz microwave with 500 W power was input to excite the plasma, and the pressure was fixed at 20 torr. The substrates were put on a 2-cm Mo holder acting as an anode and grounded during positive d.c. bias pre-treatment while a counter electrode made of a 2-cm diameter Mo disk was negatively biased. The distance between the two electrodes was 3 mm in the bias step and 5 mm in the growth step. The corresponding applied bias voltage on the substrate was in the range of +100 to +300 V. CH_4 concentrations during the bias step were 3% and the biasing period was fixed for 20 min. After biasing, all samples received the same growth conditions with a CH_4 concentration of 0.33% for 2.5–20 h with the bias switched off.

3. Results and discussion

The methane concentrations of 3% in bias step and 0.33% in growth step were chosen to obtain textured (111) diamond films. Bias voltage in the range +100 V to +300 V was applied during the bias pre-treatment period. After 2.5 h growth, no continuous diamond film was formed with +100 V bias. SEM micrograph in Fig. 1a shows the morphology of a diamond film grown on Si (111) substrate for 2.5 h with biasing at +300 V. It is clearly seen that the diamond surface exhibits strong (111) facets in triangle shape, indicating that the diamond has a (111) texture. The nucleation density estimated from SEM images is approximately 1.3×10^9

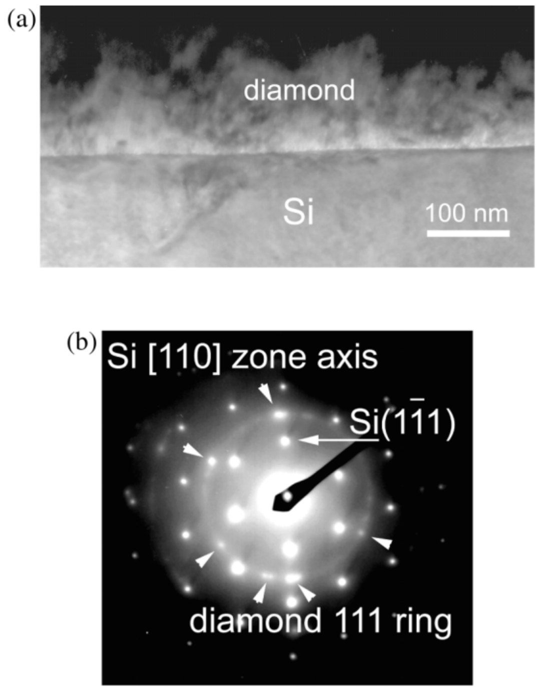

Fig. 3. (a) Cross-sectional TEM micrograph showing diamond deposition on Si (111) substrate with biasing pretreatment at +200 V. (b) The corresponding selected area electron diffraction pattern.

cm^{-2}. No significant difference can be observed from diamond films deposited on Si substrates with biasing at +200 V, which also reveals a highly oriented (111) surface. This implies that diamond nucleation is enhanced if the bias voltage is applied above a threshold value, similar to the cases with negative bias. Fig. 1b shows diamond grown on the carbon face of 6H–SiC(0001) for 2.5 h with biasing at +300 V. The diamond film also has a similar morphology of (111) texture to that on Si. Compared with Fig. 1a, diamond grains on the carbon face of 6H–SiC are relatively smaller than on Si. The nucleation density estimated from Fig. 1b is 1.5×10^{9} cm^{-2}, slightly higher than on Si. The SEM image and X-ray diffraction (XRD) pattern of a diamond film grown on Si substrate for 20 h with biasing at +200 V are shown in Fig. 2a,b, respectively. The texture of the diamond film is improved over that with shorter growth periods, as shown in Fig. 1a. The strong (111) peak of diamond can be seen in the XRD pattern, indicating that the diamond film has (111) preferred orientation.

The TEM micrograph in Fig. 3a shows the interfacial region between diamond and Si from a sample deposited with bias voltage of +200 V. The interface between diamond and Si is relatively smooth, suggesting that the etching on the Si surface is, if any, insignificant during bias step. In Fig. 3b, in a selected-area diffraction (SAD) pattern, only the diamond (111) ring can be seen in addition to Si diffraction spots, implying that the formation of a SiC crystalline interlayer was absent in our films. On the diamond (111) ring, strong diffraction spots are also seen around Si (111) spots, suggesting that there may be a significant number of diamond particles oriented in [111] directions. The oriented diamond nuclei may then develop a (111) texture. Detailed examination of interface in TEM image shows that diamond is directly grown on Si (111) over the whole area. This is different from the result of diamond deposition on Si (001) in which an amorphous carbon interlayer was formed during the positive bias stage [14]. The reason is currently not known until further studies are carried out.

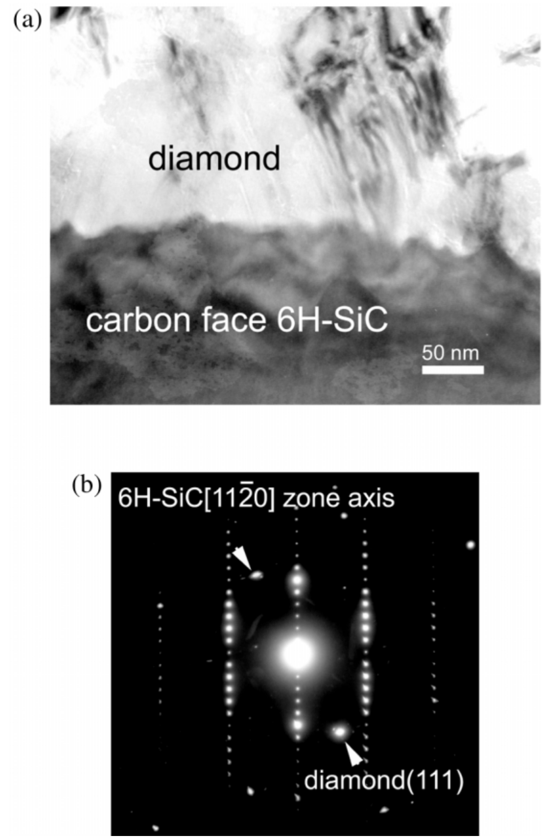

Fig. 4. (a) Cross-sectional TEM micrograph of diamond deposited with positive biasing at +200 V on carbon face 6H–SiC (0001) substrate. (b) The corresponding selected area electron diffraction pattern.

The TEM micrograph in Fig. 4a shows diamond growth on carbon face 6H–SiC (0001) with a bias voltage of +200 V. The diamond/SiC interface is very rough compared with the diamond/Si interface. The roughness is most likely caused by the poor conductivity of SiC, so that electron bombardment on the substrate would result in a charged effect. The corresponding SAD pattern in Fig. 4b shows strong diamond (111) spots, implying that a certain fraction of diamond grains may have oriented in parallel. Also, TEM shows that diamond is directly grown on carbon face 6H–SiC without any interlayer formation with positive BEN. Although the diamond/SiC interface is rough, the development of (111) texture of diamond is not affected in the growth stage as shown in Fig. 1b.

4. Conclusion

In conclusion, (111) oriented diamond films can be deposited on Si (111) and carbon face 6H–SiC (0001) by applying a positive bias voltage to the substrates in the nucleation stage. It is shown that the interface between diamond and Si (111) was smooth under positive bias conditions, while the interface of diamond with the carbon face of 6H–SiC (0001) was rough. The direct growth of the diamond films on both substrates without any interlayer was observed.

Acknowledgments

This work was supported by National Science Council, Taiwan, ROC under contract no. NSC 89-2216-E-009-033.

References

[1] X. Jiang, C.P. Klages, Diamond Relat. Mater. 2 (1993) 1112.
[2] B.R. Stoner, J.T. Glass, Appl. Phys. Lett. 60 (1992) 698.
[3] B.R. Stoner, G.-H.M. Ma, S.D. Wolter, et al., Diamond Relat. Mater. 2 (1993) 142.
[4] B.R. Stoner, S.R. Sahaida, J.P. Bade, J. Mater. Res. 8 (1993) 1334.
[5] C.J. Chen, L. Chang, T.S. Lin, F.R. Chen, J. Mater. Res. 10 (1995) 3041.
[6] R. Stockel, M. Stammler, K. Janischowsky, L. Ley, J. Appl. Phys. 83 (1998) 5433.
[7] M. Schreck, R. Hessmer, S. Geier, B. Rauschenbach, B. Strizker, Diamond Relat. Mater. 3 (1994) 510.
[8] S. Yugo, N. Nakamura, T. Kimura, Diamond Relat. Mater. 7 (1998) 1017.
[9] M. Katoh, M. Aoki, H. Kawarada, Jpn. J. Appl. Phys. 33 (1997) L196.
[10] L. Chang, T.S. Lin, J.L. Chen, Appl. Phys. Lett. 62 (1993) 3444.
[11] L. Chang, J.E. Yan, F.R. Chen, J.J. Kai, Diamond Relat. Mater. 9 (2000) 283.
[12] X. Li, Y. Hayashi, S. Lilov, S. Nishino, Jpn. J. Appl. Phys. 10B (1997) L1370.
[13] X. Li, T. Shirafuji, Y. Hayashi, S. Lilov, S. Nishino, Jpn. J. Appl. Phys. 36 (1997) 6295.
[14] T.F. Chang, L. Chang, J. Mater. Res. (submitted).