Available online at www.sciencedirect.com

SCIENCE DIRECT®

Diamond & Related Materials 14 (2005) 1753 – 1756

DIAMOND AND RELATED MATERIALS

www.elsevier.com/locate/diamond

The orientation effect of silicon grains on diamond deposition

Yin-Hao Su, Li Chang*, Hou-Guang Chen, Jhih-Kun Yan, Ting Chou

1001 Tahsueh Rd, Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 300, Taiwan

Received 4 April 2005; accepted 13 May 2005
Available online 25 October 2005

Abstract

Diamond deposition on mirror-polished polycrystalline silicon substrates which have grains in various orientations has been investigated using electron backscatter diffraction (EBSD) method with scanning electron microscopy (SEM). Diamond was deposited by microwave plasma chemical vapor deposition with application of a negative bias voltage on the substrate. The evidence from systematic SEM observations shows that silicon orientation determined by EBSD has a strong effect on diamond nucleation. In general, the diamond nucleation density on Si grains oriented close to <100> is the highest, while it is the lowest for those grains close to <111>, under the same experimental conditions for deposition. The same phenomena have been observed in the range of methane concentration from 2% to 4% in hydrogen.

Keywords: Plasma CVD; Diamond crystal; Nucleation; Bias growth

1. Introduction

Diamond nucleation in the chemical vapor deposition process plays an important role on film microstructures and heteroepitaxy on substrate [1–4]. Even though chemical vapor deposited (CVD) diamonds have been successfully produced for the past two decades, it is still not fully understood the nucleation behavior, particularly on the bias-enhanced nucleation (BEN), which is not only increasing the nucleation density without any mechanical pretreatment, but also an essential method for deposition of heteroepitaxial diamond films [5–14]. It is well known that the substrate has a critical effect on the nucleation of diamond. Though most of studies of diamond deposition have been carried out on Si substrate, there are rarely reports on systematic studies on the orientation effect of Si on BEN nucleation of diamond. One of the reasons is due to the problem of uneven distribution of diamond nuclei on the substrate [10–14]. Here, we have used mirror-polished polycrystalline silicon of micrometer-sized grains with various orientations as the substrate, which allowed us to deposit diamonds on different oriented Si grains under the same plasma CVD conditions. The result from scanning electron microscopy (SEM) with electron back-scatter diffraction (EBSD) shows that the orientation of Si from (100) to (111) does have a strong effect on diamond nucleation. Previous works have shown the orientation effect of Ni and Ni_3Al polycrystalline substrates on diamond nucleation [15,16].

2. Experimental conditions

Polycrystalline silicon ingots in a size of several centimeters were cut and polished to smoothness in mirror extent. To remove the surface damage on the Si, we further polished the sample with de-ionized water for 5 min, and with Syton(r) (colloidal silicas) for 1 min in the final step. Examination under optical microscope showed almost free of scratches on the surface. Atomic force microscopy measurements showed that surface roughness after polishing was less than 0.7 nm. X-ray diffraction showed no preferred orientations. SEM with EBSD was carried out in a JEOL 6350F scanning microscope equipped with an Oxford Instrument EBSD detector. The typical morphology of poly-Si surface obtained after 70° tilting of the specimen is shown in Fig. 1. It can be seen that the main characteristic feature exhibits a colony

---

* Corresponding author. Tel.: +886 3 5731615; fax: +886 3 5724727.
E-mail address: lichang@cc.nctu.edu.tw (L. Chang).

0925-9635/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2005.05.005

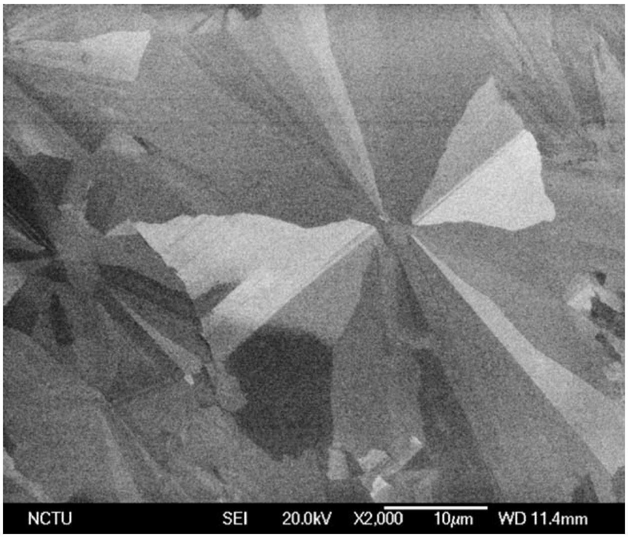

Fig. 1. SEM micrograph showing the surface morphology of the poly-Si substrate after polishing. Specimen tilted 70° for imaging for contrast enhancement due to backscattering of electrons.

with a shape of flower which consists of petal-like Si grains with various orientations in different contrast. The area of the colonies is 50–100 μm, and the petal-like grain size is in the range of several micrometers, which was much greater than the spatial resolution of EBSD (~0.1 μm) [17]. Thus, the grain orientation can be assessed under the same processing conditions without the necessity of consideration of the effect of uneven distribution within plasma.

Diamond deposition was carried out in an ASTeX type microwave plasma CVD reactor. A hydrogen plasma was applied for 15 min to increase the substrate temperature to 800 °C and to remove native oxide of Si. The deposition process consisted of bias and growth steps. The negative bias of −200 V was applied on the substrate for 30 min using a gas mixture of 2% CH_4 and H_2. For the growth stage, CH_4 concentration was reduced to 0.67% with bias turned off. The growth time was 30 min. In all stages, the microwave power and the pressure was maintained at 800 W and 20 torr.

3. Results and discussion

Fig. 2a shows the diamond deposition on a poly-Si substrate in large area view. An inhomogeneous distribution can be clearly seen in high-magnification SEM micrograph in Fig. 2b. On some of the Si grains, a high density of diamond crystallites forms, while there are only a few of diamonds seen on the rest grains. The crystallites on different Si grains have a similar size of 0.7 μm in average. The determined orientations of grains with low density of diamond shown in Fig. 3a is plotted on the stereographic triangle in Fig. 3b. Interestingly, for those three grains with lowest density (no. 1–6, 11–15, and 17–18) the orientations are close to [111], whereas the grains with a relatively low density of diamonds (no. 7–8 and 9–10) have orientations around the center of the triangle. Statistically, for the examination of Si grains with low density of diamonds (over 20 grains from different colonies) none of them have orientations close to [100] and [101]. In contrast, on the grains with high density of diamonds, the uncovered regions can still be probed by the electron beam for the acquisition of EBSD pattern after tilting the specimen about 70°. The hindrance of backscattering electrons from the diamond crystallites onto the detector was avoided by the careful selection of the proper regions. Such grains with high densities of diamonds have orientations more close to [100] as shown in Fig. 3c and d. Examination of more than 10 petal-like regions and from different samples shows the same behavior. For example, Fig. 3d and e show that Si grains with lower densities of diamonds are oriented near [101]. Therefore, it is suggested that the diamond nucleation density on Si grains is increased from (111), (110) to (100).

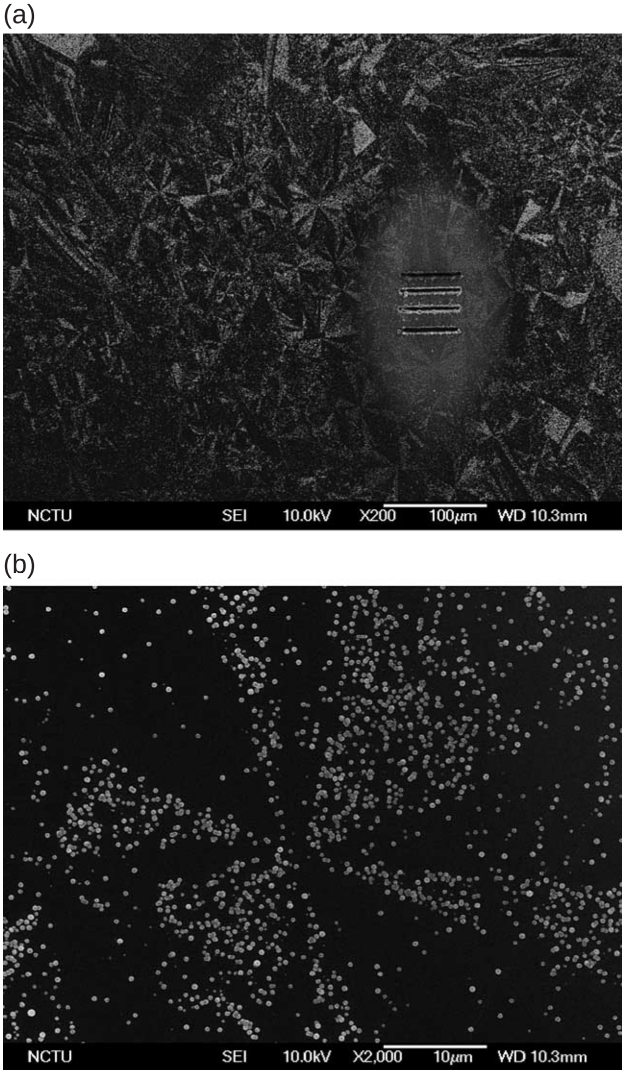

Fig. 2. SEM micrographs after diamond deposition showing (a) general morphology with laser marks for reference for EBSD pattern acquisition with accurate positioning of electron beam, and (b) on a petal-like region in high-magnification.

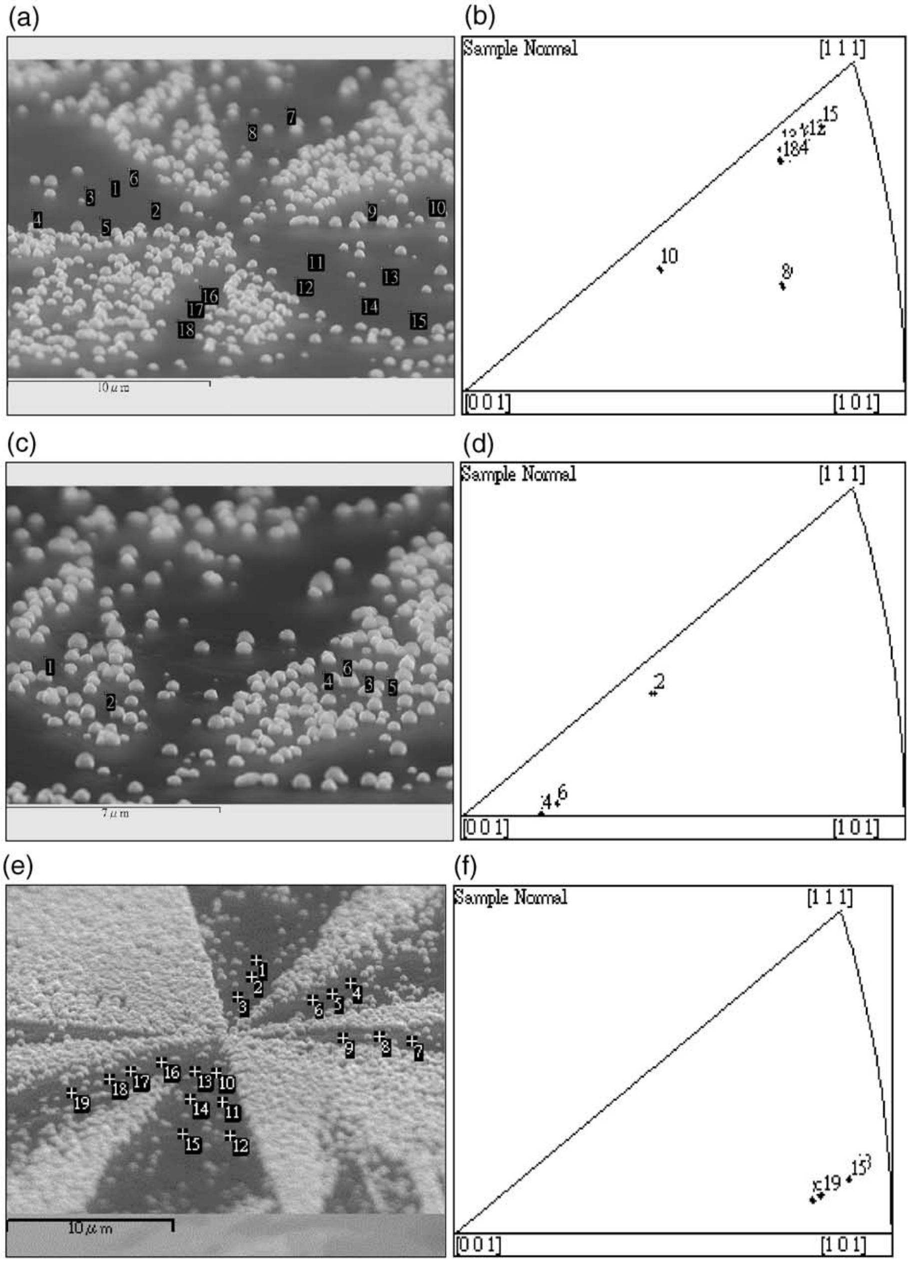

Fig. 3. (a) SEM micrograph showing diamond deposition in another area. The numbers showing the positions for EBSD, and (b) the orientations plotted in stereographic projection showing points 1–6 and 11–18 in (a) are close to [111]. (c) SEM micrograph of a different area showing the probed positions in the denser areas of diamond nuclei for orientation determination shown in (d), 1–2 close to [113] and 3–6 close to [001]. (e) from another sample showing the diamond distribution and (f) showing the orientations determined from Si grains with low density of diamonds.

To further confirm this result, we have done a number of precision experiments in which Si grains with orientations determined before diamond deposition could be positioned by using laser-marked reference points. After deposition, the same locations can be exactly tracked back in SEM observations to examine whether the grains have been covered or not by diamonds. This allows us to ensure the orientation of the grain on which diamond has been deposited. Fig. 4a shows the SEM micrograph of the substrate surface superimposed with the Si orientation map before diamond deposition, Fig. 4b shows diamond crystallites deposited on the same corresponding regions, and Fig. 4c exhibits the corresponding orientation in color in a stereographic triangle. It is clearly shown that diamond nucleation mainly occurs on Si grains close to [001] orientation where the density of deposited diamonds is the highest, while almost none on those near [111], and a few diamond particles on those close to [101]. This is supported by the results from Fig. 3.

With increase of methane concentration to 4% CH_4 and growth time in deposition, a continuous diamond film will

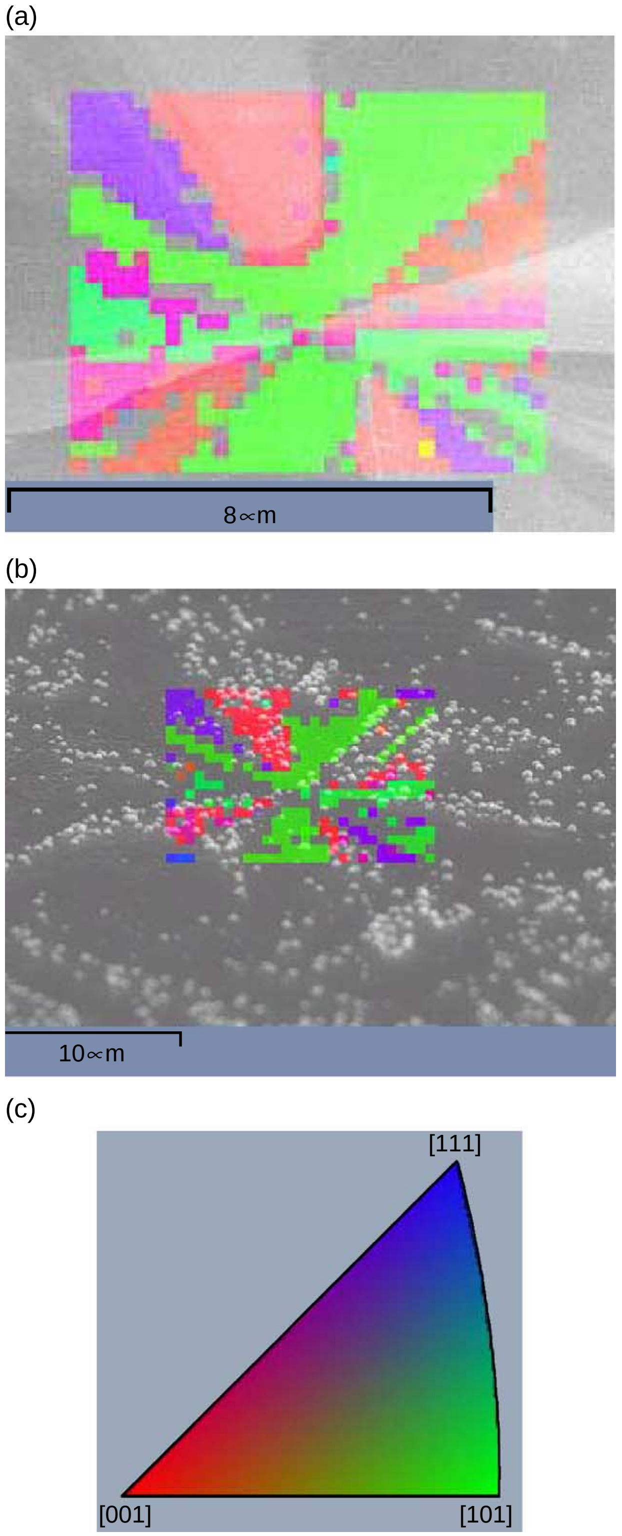

Fig. 4. (a) SEM micrograph superimposed with colored orientation map before diamond deposition. (b) The same area after diamond deposition. (c) stereographic projection triangle within which the orientations is shown by different colors. Blue [111], red [001], and green [101].

eventually be formed all over the substrate surface whatever the Si grain orientation is. However, it is found that the time for formation of a continuous diamond film on Si (111) grains is longest. Furthermore, we notice that the diamond particles have a similar size on differently oriented Si grains. Hence, the nucleation on Si is likely a kinetic process in the BEN stage. This suggests that the energy barrier might be lowered on [001] oriented Si grains. The barrier height could depend on adsorption of carbon radicals, their diffusion, and the surface free energy, which are influenced by the surface structure of Si. The surface structure of Si is quite different between (111) and (001) faces, and their vicinal surfaces are more complex because of steps and kinks. Also, one cannot exclude the possibility of the etching effect of hydrogen plasma on different oriented Si grains.

In summary, the orientation effect of Si on diamond nucleation has been systematically investigated by using EBSD on poly-Si substrates. Generally, the rate of nucleation on Si decreases in the order of Si (100)>(110)>(111).

Acknowledgements

This work was supported by National Science Council, Taiwan, R.O.C. under contract of NSC 93-2216-E-009-014. The travel ship of L.C. is supported by Chunghwa Picture Tubes, LTD, Taiwan. The Si ingots were kindly provided by Sino American Silicon Products Inc.

References

[1] John C. Angus, Cliff Hayman, Science 241 (1988) 913.
[2] J.C. Angus, A. Argoitia, R. Gat, Z. Li, M. Sunkara, L. Wang, Y. Wang, Phil. Trans. R. Soc. Lond., A 342 (1993) 195.
[3] J.E. Butler, R. Woodin, Phil. Trans. R. Soc. Lond., A 342 (1993) 209.
[4] F.G. Celii, J.E. Butler, Annu. Rev. Phys. Chem. 42 (1991) 643.
[5] S. Yugo, T. Kanai, T. Kimura, T. Muto, Appl. Phys. Lett. 59 (1991) 417.
[6] S. Yugo, T. Kimura, T. Kanai, Diamond Relat. Mater. 2 (1992) 328.
[7] B.R. Stoner, G.H. Ma, S.D. Wolter, J.T. Glass, Phys. Rev., B 45 (1992) 11067.
[8] X. Jiang, C.P. Klages, R. Zachai, M. Hartweg, H.J. Füsser, Appl. Phys. Lett. 62 (1993) 3438.
[9] W. Kulisch, L. Achermann, B. Sobisch, Phys. Status Solidi, A Appl. Res. 154 (1996) 155.
[10] K.H. Thurer, M. Schreck, B. Stritzker, Phys. Rev., B 57 (1998) 15454.
[11] S. Barrat, S. Saada, I. Dieguez, E. Bauer-Grosse, J. Appl. Phys. 84 (1998) 1870.
[12] I.-H. Choi, S. Barrat, E. Bauer-Grosse, Diamond Relat. Mater. 12 (2003) 361.
[13] R. Stöckel, K. Janischowsky, S. Rohmfeld, J. Ristein, M. Hundhausen, L. Ley, Diamond Relat. Mater. 5 (1996) 321.
[14] C.J. Chen, L. Chang, T.S. Lin, F.R. Chen, J. Mater. Res. 10 (1995) 3041.
[15] J.M. Huh, D.Y. Yoon, Diamond Relat. Mater. 9 (2000) 1475.
[16] H.G. Chen, L. Chang, Diamond Relat. Mater. 14 (2000) 183.
[17] F.J. Humphreys, J. Mater. Sci. 36 (2001).