Diamond & Related Materials 18 (2009) 124–127

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Growth and characterization of diamond films on TiN/Si(100) by microwave plasma chemical vapor deposition

Wei-Chun Chen, Wei-Lin Wang, Rajanish N. Tiwari, Li Chang *

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

ARTICLE INFO

Available online 30 October 2008

Keywords:
Diamond film
Nitrides
Chemical vapor deposition
Interface characterization
Morphology

ABSTRACT

Polycrystalline diamond films were deposited on silicon (100) substrate by microwave plasma chemical vapor disposition (MPCVD) using ~300 nm thick <001> textured titanium nitride (TiN) films as buffer layer which were prepared by radio-frequency reactive sputtering. The diamond/TiN films were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy. The results show that no apparent change can be observed for the <100> oriented TiN buffer layers after MPCVD even with a negative bias voltage applied onto the substrates.

1. Introduction

The growth of a polycrystalline diamond film had been deposited often on Si because of the availability and inexpensive nature of silicon single crystal wafers. There were some studies using carbon nitride, AlN, TiN, TiC, GaN, and WC [1–4] as buffer layer for deposition of diamond on Si substrate. Results indicated that the use of these buffer layers were effective in enhancing the nucleation density of diamond.

Titanium nitride (TiN) is a common material used in semiconductor devices, for example, as a barrier layer between silicon and metal in integrated circuit device fabrication. Its lattice parameter (4.24 A) lies between diamond (3.56 A) and Si (5.43 A) and therefore it can be used as a domain lattice-matched template between Si and diamond [5]. The benefit of TiN as a buffer layer include low diffusion for carbon [6], high thermal stability, chemical stability, good adherence to silicon, and a compatible thermal expansion coefficient with silicon. Though diamond deposition on Si has intensively studied in the past two decades, there are only a few reports of diamond deposition on TiN [4,7–9]. Previous studies of diamond deposition on TiN layer show that it has substantially improved the diamond nucleation rate with a high density [4,7,8].

Chalker et al. [9] in the study of nucleation and growth of diamond on TiN buffer layer using hot-filament chemical vapor deposition (CVD) showed that TiN surface is chemically stable under diamond–CVD reactions at high temperatures. In this paper, we report growth of diamond on TiN which has been sputtered on silicon substrate using microwave plasma CVD. Also, we evaluate the stability of TiN after bias-enhanced nucleation (BEN) pretreatment in a microwave plasma chemical vapor deposition (MPCVD). It has been known that BEN often results in damage on Si. Here we demonstrate that TiN as buffer layer is effective to protect Si surface from plasma etching.

2. Experimental

Diamond films were grown in a 2.45 GHz/1.5 KW ASTeX-type microwave plasma chemical vapor deposition reactor. Titanium nitride films in 300 nm thickness as buffer layer were prepared on smooth Si (100) substrates by radio-frequency (RF) reactive sputtering of a Ti target prior to diamond deposition. Before the experiment, the Si substrates were ultrasonically cleaned in baths of acetone, isopropanol and DI water for 20 min. Si substrates were then etched in 2% HF for 1 min to remove native oxide on Si before sputtering. The sputtering condition was as follows: N_2/Ar flow ratio of 0.1, RF power 200 W, base pressure ~1×10^{-6} Torr, and substrate temperature ~700 °C. After TiN film sputtering, a 10 mm×5 mm TiN/Si substrate was placed on a molybdenum holder in the MPCVD reactor. The reactant gas for diamond deposition was a mixture of methane and hydrogen. Before the diamond deposition process, the TiN layer was treated in a mixture gas of 2% methane and hydrogen for carburization, followed by BEN pretreatment using a dome-shaped Mo anode at 100 V for 90 s [10]. After the BEN step, the Mo anode was removed for further diamond growth. During the MPCVD, the substrate temperature was approximately 750–800 °C and the pressure was kept constant. The detailed experimental conditions of the diamond film deposition were listed in Table 1.

The crystallinity of the films was examined by X-ray diffraction (XRD) analysis using a Siemens D5000 diffractometer with Cu-Kα radiation of 1.54 Å. For Raman measurements, 100 mW power of an argon ion laser with 488 nm emission wavelength was used as an excitation source at room temperature. In addition, the surface and cross-section morphologies of the films were analyzed using a field-

* 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 © 2008 Published by Elsevier B.V.
doi:10.1016/j.diamond.2008.10.018

Table 1
Experimental parameters for diamond film deposition

Conditions of diamond films deposition	
Pressure	20–40 Torr
Flow rate	300 sccm
Microwave power	800 W
Bias voltage	−100 V
CH_4 in H_2	1.6–2%
Deposition time	180 min

emission scanning electron microscope (Hitachi S-4300 FE-SEM) and a transmission electron microscope (TEM, Philips Tecnai 20).

3. Results and discussion

X-ray diffraction scan measurements were carried out on a series of 300 nm thick TiN films deposited on Si (100) substrate at 700 °C for N_2/Ar flow rate of the ratio of 0.1. Fig. 1 shows a typical θ–2θ scan XRD pattern of the TiN layers grown on Si(100) substrates. Only TiN reflections were detected along with Si substrate reflections, suggesting that no reactions occur between the film and substrate during sputtering. From the intensity ratio of (200), (111) and (220) reflections, it can be shown that the TiN films have (200) preferred orientation. Fig. 2 shows a typical XRD pattern from a sample after diamond deposition at 20 Torr. The results also show that no apparent change can be observed for the <100> oriented TiN buffer layers after MPCVD of diamond, implying that TiN remains stable during deposition even with a negative bias voltage applied onto the substrate. It is also noticed that no TiC peaks can be detected in the XRD patterns, implying that TiN has not been carburized to form carbide. Because there is no change on the positions of the TiN peaks, it is likely that the carbon solution in TiN is negligible in MPCVD. Also the Raman spectrum from the sample in Fig. 3 clearly shows the diamond peak at 1332 cm^{-1} with non-diamond phases at D-band (1350 cm^{-1}) and G-band (round 1520 cm^{-1}). There are also two peaks at 1140 cm^{-1} and 1480 cm^{-1} which have been attributed to the trans-polyacetylene segments in the grain boundaries of nanocrystalline diamonds and other defects and nondiamond phases [11–15]. The appearance of these two peaks suggests that the diamond films deposited on TiN using the MPCVD experimental conditions may contain defects, surface structures, amorphous material, or any other nondiamond material in nanocrystalline diamonds.

Fig. 4(a) and (b) shows SEM micrographs of the sample after carburization step and BEN for 90 s, respectively. As shown in Fig. 4(a), the TiN surface remains to be relatively uniform and smooth after carburization. Also, the TiN surface is seen to be crack free after carburization which had been cooled from 800 °C. After the BEN step, 20–50 nm sized diamond crystallites of a density of 3×10^9 cm^{-2} had nucleated on the TiN. To understand the stability of TiN in the microwave plasma, the TiN films were also treated with hydrogen plasma without methane. Fig. 4(c) and (d) shows a TiN film before and after hydrogen plasma treatment, respectively. It is seen that the TiN film is still continuous without any delamination from the substrate, and its thickness of 300 nm remains almost unchanged, implying that TiN is thermally and chemically stable in the microwave plasma. The result is in agreement with the report of Contreras etc. [6]. Also, the TiN surfaces are seen to be crack free after all the plasma treatments, indicating that the TiN layers were capable of standing the thermal stresses produced after cooling from high temperature in the experiments. Fig. 4e) shows the surface morphology of a diamond film on TiN after 3 h growth. In addition to grains of smaller size (<50 nm) which are probably due to secondary nucleation, it is seen that there are a number of large diamond grains in square-like shape with flat surface. The 2 μm thick diamond film is continuous as shown in the inset of Fig. 4(e).

Fig. 5 exhibits a cross-sectional TEM micrograph with the corresponding selected-area diffraction (SAD) pattern of a diamond film deposited with 20 Torr for 3 h. The TiN film is in good contact with diamond and Si. The interface between diamond and TiN is seen to be sharp without interlayer, indicating that no reactions occur between

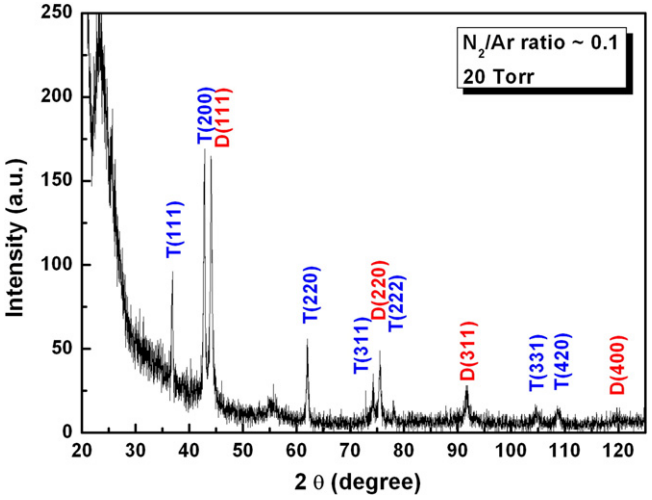


Fig. 2. θ–2θ XRD pattern of diamond film deposited on TiN layer with gas pressure of 20 Torr.

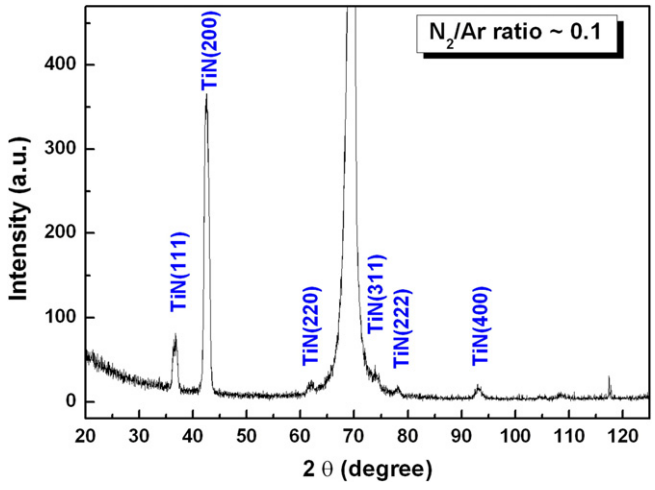


Fig. 1. XRD pattern of a sputtered TiN film.

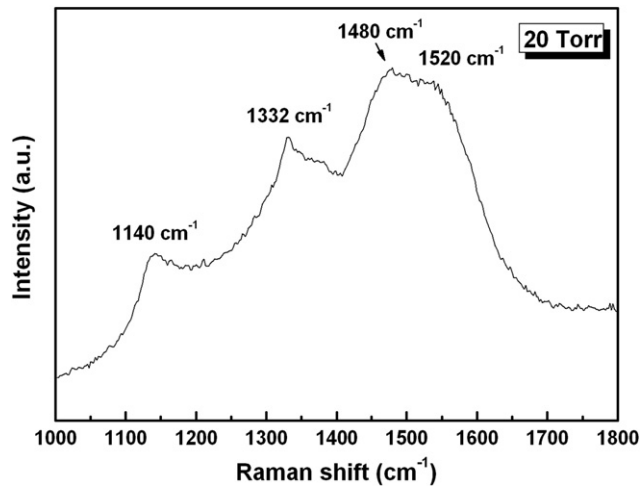
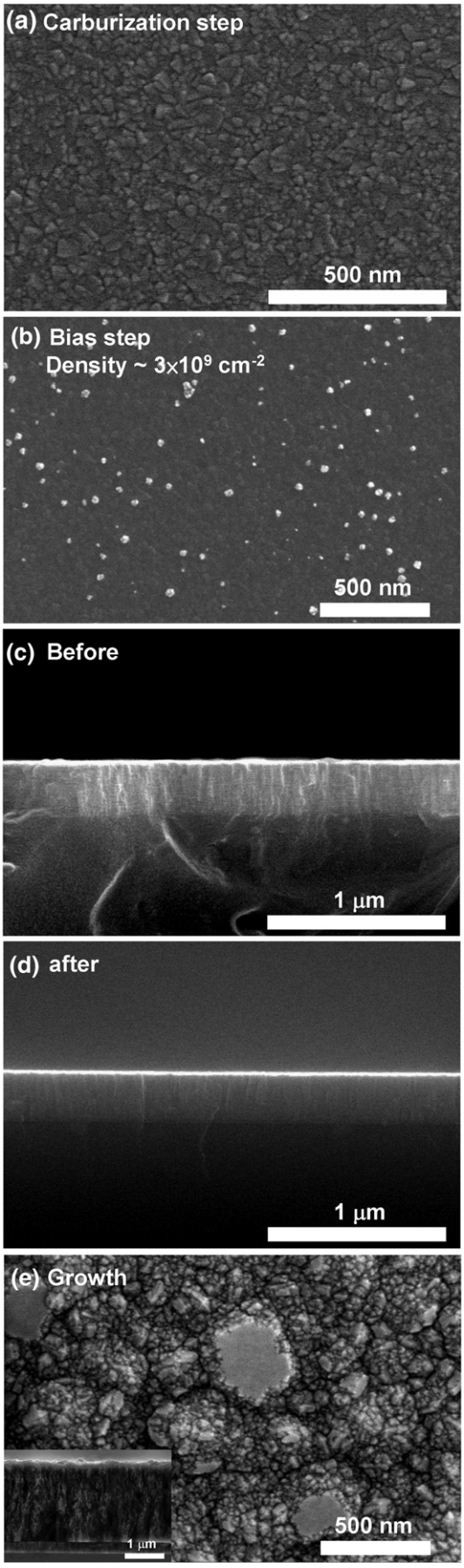


Fig. 3. Raman spectrum of diamond film deposited on TiN.



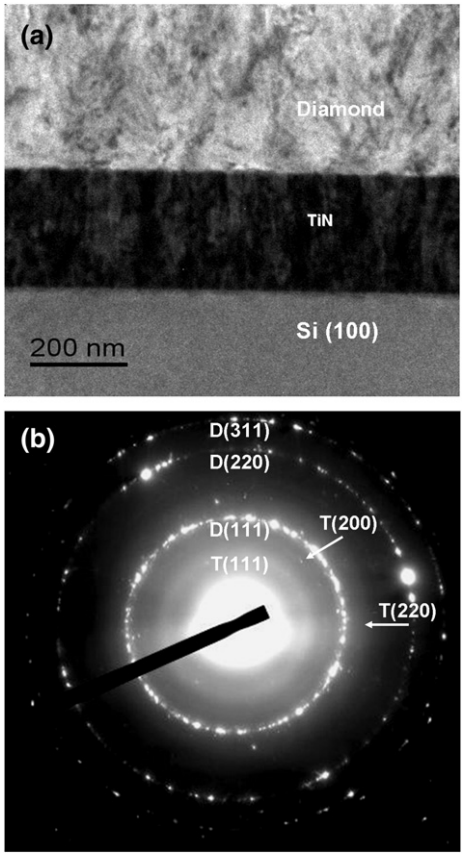


Fig. 5. (a) Cross-sectional TEM image and (b) the corresponding SAD pattern from diamond film deposited at 20 Torr for 3 h.

them. Therefore, it confirms that TiN is stable in the whole microwave plasma processing from carburization and BEN to growth. The SAD pattern only consists of diamond and TiN reflections. Individual diffraction spots can be identified as TiN reflections, while the rings are corresponding to diamond, indicating that it is a polycrystalline diamond film with fine grains.

4. Conclusion

In summary, diamond films have been deposited at 20 Torr on (100) textured TiN buffer layer sputtered on Si substrate. The nucleation density of diamond can reach 3×10^9 cm^{-2} with bias-enhanced nucleation pretreatment. X-ray diffraction and electron microscopy results show that no apparent change on microstructure and thickness occurs for the <100> oriented TiN layers after microwave plasma chemical deposition of diamond with bias-enhanced nucleation pretreatment.

Acknowledgements

This work was supported by National Science Council, Taiwan, R.O.C. under contracts of NSC96-2622-E-009-002-CC3 and NSC96-2622-E-009-002-CC3.

Fig. 4. SEM of surface morphology after (a) The carbonized step and (b) BEN for 20 Torr. (c) and (d) Cross-sectional SEM images of TiN layer before and after H plasma treatment, respectively. (e) SEM image showing surface morphology of a diamond film after growth at 20 Torr for 3 h.

References

[1] Y. Otsuka, S. Suzuki, S. Shikama, T. Maki, T. Kobayashi, Jpn. J. Appl. Phys. 34 (1995) L551.
[2] M.Y. Liao, X.M. Meng, X.T. Zhou, J.Q. Hu, Z.G. Wang, J. Cryst. Growth 236 (2002) 85.
[3] J. Isberg, J. Hammersberg, E. Johansson, T. Wikstrom, D.J. Twitechen, A.J. Whitechead, S.E. Coe, G.A. Scarsbrook, Science 297 (2002) 1670.
[4] A. Kumar, Q. You, J.S. Kapat, A. Mangiaracina, A. Catletge, Y. Vohra, Thin Solid Films 308 (1997) 209.
[5] Q.J. Chen, L.X. Wang, Z. Zhang, J. Yang, Z.D. Lin, Appl. Phys. Lett. 68 (1996) 176.
[6] O. Contreras, G.A. Hirata, M. Avalos-Borja, Appl. Surf. Sci. 58 (2000) 236.
[7] J.J. Lee, W.S. Yang, J.H. Je, J. Mater. Res. 3 (1997) 657.
[8] W. Kulisch, C. Popov, V. Vorlicek, P.N. Gibson, G. Favaro, Thin Solid Films 515 (2006) 1005.
[9] P.R. Chalker, C. Johnston, S. Romani, C.F. Ayres, I.M. Buckley-Golder, Diamond Relat. Mater. 3 (1994) 393–397.
[10] J.K. Yan, L. Chang, Thin Solid Films 498 (2006) 230.
[11] R. Pfeiffer, H. Kuzmany, P. Knoll, S. Bokova, N. Salk, B. Gunther, Diamond Relat. Mater. 12 (2003) 268.
[12] R. Pfeiffer, H. Kuzmany, P. Knoll, S. Bokova, N. Salk, B. Gunther, Diamond Relat. Mater. 12 (2003) 268.
[13] S. Prawer, K.W. Nugent, D.N. Jamieson, J.O. Orwa, L.A. Bursill, J.L. Peng, Chem. Phys. Lett. 332 (2000) 93.
[14] A.C. Ferrari, J. Robertson, Phys. Rev., B 63 (2001) 121405.
[15] J. Filik, J.N. Harvey, N.L. Allan, P.W. May, J.E.P. Dahl, S. Liu, R.M.K. Carlson, Phys. Rev., B 74 (2006) 035423.