ACTA PHYSICA SINICA
Volume 2, Number 1 (Overseas Edition) January, 1993

GROWTH CHARACTERISTICS OF DIAMOND FILMS DEPOSITED ON Si AND W SUBSTRATES

ZHANG FANG-QING (张仿清), ZHANG WEN-JUN (张文军),
ZHANG YA-FEI (张亚菲), and CHEN GUANG-HUA (陈光华)
Department of Physics, Lanzhou University, Lanzhou 730001, China
GAO QIAO-JUN (高巧君)
Department of Physics, Peking University, Beijing 100871, China
JIANG XIANG-LIU (蒋翔六)
Beijing Institute of Science and Technology, Beijing 100044, China

(Received 17 January 1992)

Growth characteristics of diamond films synthesized by using a dc arc discharge plasma CVD were studied by means of XRD, SEM and reflection electron diffraction. The results showed that columnar growth of the diamond films was observed, the columns having an average diameter of about 15 μm, with sharp and regular base edges. Diamond grains grown on the substrate were initially of uniform polygons. An interfacial transition layer of polycrystalline SiC was observed between the diamond film and Si substrate. Diamond grains grown during the early-stage on W substrate were also uniform, and an interfacial transition layer of polycrystalline WC was observed between the diamond film and the substrate.

PACC: 6855; 6848; 6890; 8115H

I. INTRODUCTION

Diamond have many potential applications due to its exceptionally high hardness, thermal conductivity, electron saturated drift velocity, and hole and electron mobilities, as well as good chemical and thermal stability, and optical transmission[1]. In past years diamond films were synthesized on various substrates (such as natural diamond, Si, Mo, Ta, WC, SiC, SiO_2, Al_2O_3, etc.) by means of many kinds of chemical vapour deposition (CVD) methods, using hydrocarbon and hydrogen as reaction gases[2-4]. Deposition techniques have been developed rapidly. However, the nucleation and growth mechanisms have not been completely clarified yet. So it is very important to investigate the nucleation and growth process, morphology and structure of diamond films. In this work, diamond films are deposited on Si and W substrates by dc arc discharge CVD. The X-ray diffraction (XRD), scanning electron microscopy (SEM) and reflection electron diffraction (RED) are used to investigate the growth process and morphology characteristics of the films. Finally the experimental results will be discussed.

II. EXPERIMENTAL

The diamond films used in this work were prepared by dc arc discharge plasma CVD method. Both mixtures of CH_4+H_2 and of $C_2H_2+H_2$ were used as the reactant gas, and the percentages of CH_4 and C_2H_2 relative to H_2 were both 1%. The cathode and anode of the arc discharge were made from tungsten bars. The arc discharge voltage was 200 – 300 V, and the corresponding discharge current was 5 – 4 A. In the reaction chamber the pressure was kept at $(2.4-2.7)\times10^4$ Pa. The substrates were c-Si(100) wafers and W wafers or W tips, and substrate temperature was in the range of 800 – 1000 °C. Silicon and tungsten substrates were pretreated by abrasion with diamond powder. Since W tips were very thin (tens of micron to 100 μm), they were not pretreated. The growth rate was about 20 – 50 μm/h. Raman scattering, XRD and SEM were used to identify the samples, the results of which were reported elsewhere[5].

XRD, SEM and RED were also used to study the surface morphology and interfacial transition layer of the diamond film specimens.

III. RESULTS AND DISCUSSION

A. Si substrate

XRD measurements were carried out to study the interface between the diamond film and substrate. The diamond films were deposited on c-Si(100) wafers, using CH_4 as the carbon source, and the thickness of the film was about 100 μm. Experimental results for $\alpha=3°$, 5° and 7° are shown in Fig. 1 (curve *a*, *b*, *c* respectively), where α is the angle made by the incident X-ray and the sample surface. Information of the crystal structure and composition at various depths of the samples was obtained from the XRD patterns for various α[6]. The penetration depth for $\alpha=3°$ was estimated to be about 4 μm, that is to say, the results for $\alpha=3°$ represented the surface characteristics of the sample. The result for normal scanning ($\theta-2\theta$ scan) is also shown in Fig. 1(curve *d*). In the patterns for $\alpha=3°$, 5° and 7°, there were only diamond and tungsten carbide characteristic peaks. The reflection peaks of WC were due to the contamination of the tungsten bars. In the profiles for normal scanning, in addition to the reflection peaks of diamond and WC, there were also re-

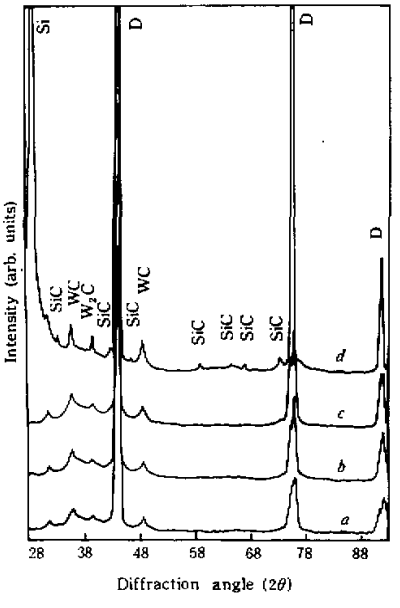

Fig. 1. XRD patterns obtained for different α (pattern *a*, $\alpha=3°$; pattern *b*, $\alpha=5°$; pattern *c*, $\alpha=7°$) and a $\theta-2\theta$ scanning (pattern *d*).

flection peaks of SiC and a strong characteristic peak of Si substrate. These results proved that there is a polycrystalline SiC layer between the diamond and the substrate.

The SEM morphologies of different films deposited on silicon, using CH_4 and H_2 as the gas source, are shown in Fig. 2. Figure 2(a) is a typical morphology of diamond film deposited for 1 h. Figures 2(b), 2(c) and 2(d) are the cross-section views of different samples deposited for 8 h. The diamond film was lifted-off from the substrate slightly at the position observed by SEM. The samples were titled slightly so as to observe the SEM morphologies of both the cross-section and interface layer of the films. As shown in the figures, diamond films grew as columns which stood in good order. Initial columns were separated by gaps

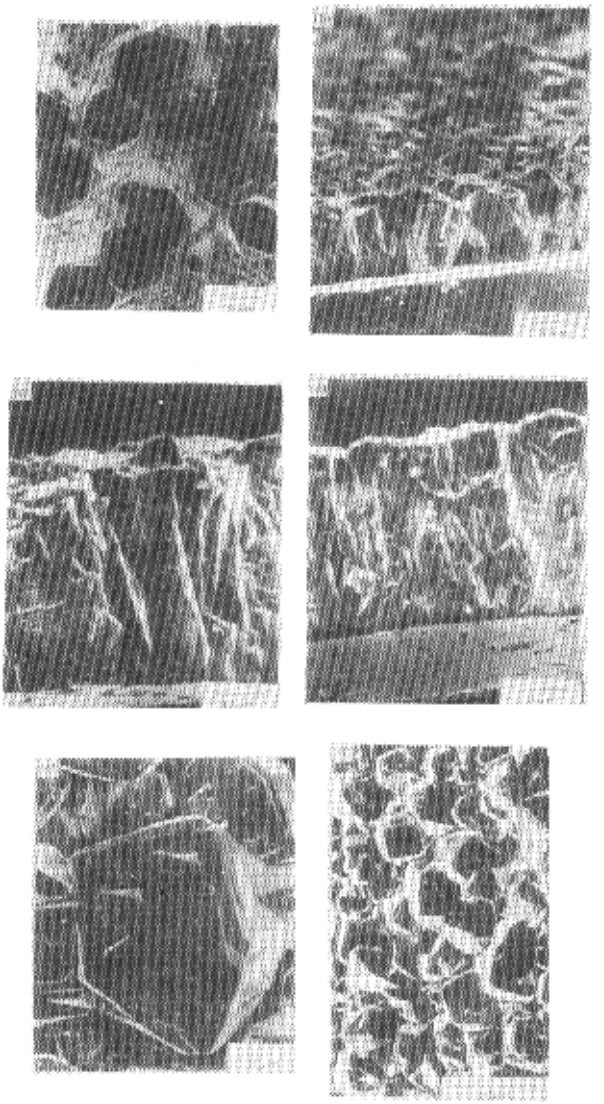

Fig. 2. SEM images of diamond films deposited on Si substrate, using CH_4 as a carbon source. (a) The surface morphology of diamond film deposited for 1 h; (b, c and d) the cross-section morphologies of diamond films deposited for 8 h; (e and f) the surface morphologues of diamond films deposited for 8 h.

and the maximum of the gaps could be tens of micron. There was a transition layer between the diamond film and Si substrate. At the beginning, nuclei were regular-shaped, the crystal grains were uniform, as can be seen in Fig. 2(b). Then, the secondary nucleation came about to form twinned particles and crystal facets, and these small particles were polymerized with the large crystals. Finally, polycrystalline grains of regular shapes were formed, as shown in Figs. 2(e) and 2(f), the (100) face being more prominent at the surface.

To study the composition of the transitional layer by RED, the Si substrate was etched in a mixture of nitric and HF acids at a moderate temperature only to remove the substrate and left the interface behind. It was observed that there existed strong SiC RED patterns, as shown in Fig. 3. It was proved that the transitional layer was SiC. The results of XRD and RED were similar to that of X-ray photoelectron spectrum (XPS)[7].

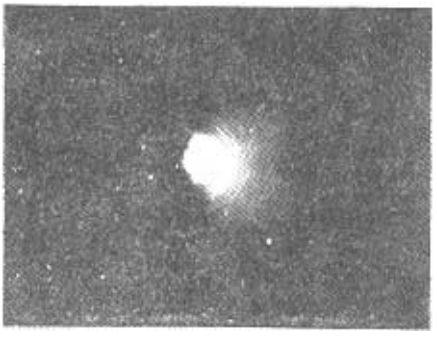

Fig. 3. SiC RED patterns for the interface between the diamond film and the silicon substrate.

To investigate the universality of the columnar growth, C_2H_2 and H_2 were also used as the gas source to deposit diamond films on c-Si (100) wafers, with the same experimental set-up and under the same experimental conditions as the above. The percentage of C_2H_2 relative to H_2 was also 1%. Deposition time was 6 h. Then the samples were broken for observing the SEM cross-section morphologies of diamond films. Similar SEM cross-section views to those of Figs. 2(b), 2(c) and 2(d) were obtained, as shown in Figs. 4(a) and 4(b). One can see from Fig. 4 that the diamond films also grow in columns which arrange

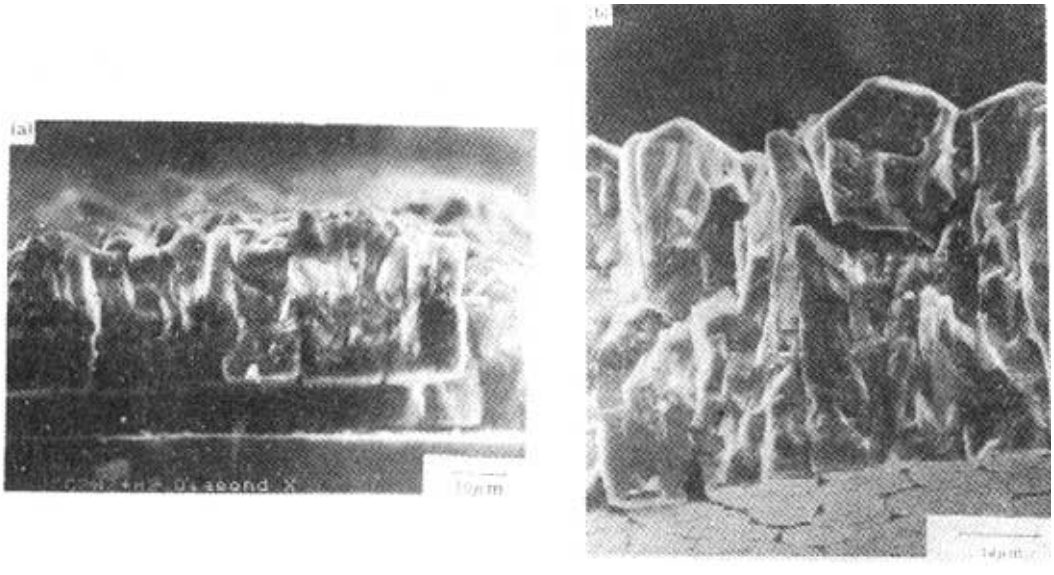

Fig. 4. SEM cross-section morphologies of diamond films deposited on Si substrate, using C_2H_2 as the carbon source.

in good order, and that at the beginning the nuclei are of regular shape and uniform. After the secondary nucleation occurred, small crystal grains, twinned crystals and the growth of large grains were also observed. In Fig. 4(b), it seems that some large regular crystal have fallen on the diamond film. Further investigations are needed to clarify this phenomenon.

The results stated above are very similar to those of the films grown by microwave plasma CVD(MPCVD)[8-10], though there are differences between the two methods, such as excitation mode, growth rate and grain size.

B. W substrate

The diamond films discussed in this paragraph were prepared on substrates of W wafer (15mm × 15mm) by dc arc discharge plasma CVD method, with reaction gases of CH_4 and H_2, in which the percentage of CH_4 relative to H_2 was 1%. The deposition time was 8 h. SEM was used to investigate the morphology of the surface of the films and the interface between the diamond film and W substrate. The results are shown in Fig. 5. One can see from the top surface of the diamond film that the diamond film is of a polycrystalline structure, in which most of the diamond particles are cubical polygons. The average diameter of the diamond particles is 5 μm, and the crystal facets are smooth. However, the SEM image of the interface between the diamond film and tungsten substrate shows that the size of the crystals is large (about 30 μm), and the density of nucleation is higher around the scratches on the substrate surface, and as a result the grains are small there.

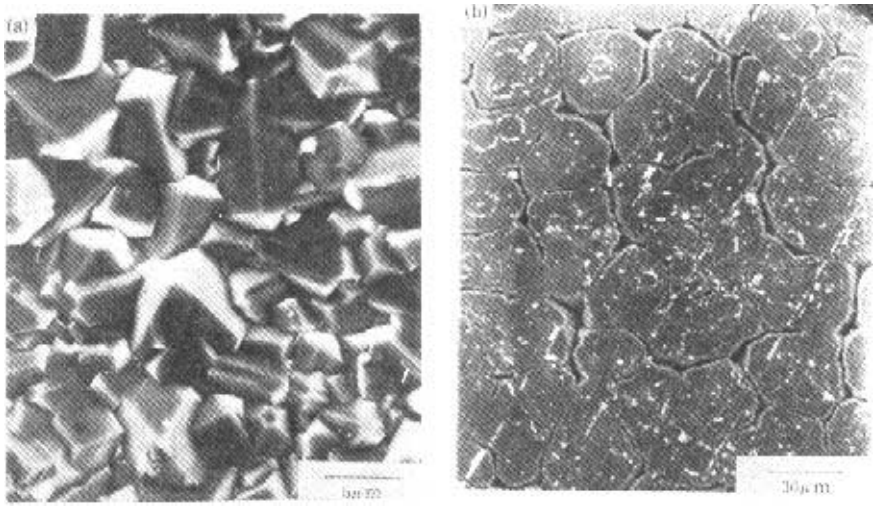

Fig. 5. (a) SEM surface morphology of the diamond films deposited on W substrates; (b) SEM morphology of the interface between the diamond film and the W substrate.

The θ-2θ scanning of X-ray diffraction was carried out to investigate the interface between the diamond and the tungsten substrate. The diffraction pattern is shown in Fig. 6. In addition to the reflection peaks of diamond, there are strong reflection peaks of WC and W substrate, showing that a polycrystalline layer of WC is formed as an interfacial transition layer.

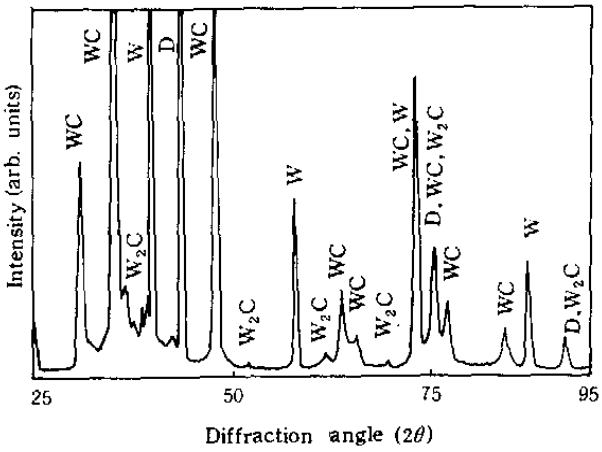

Fig. 6. The θ-2θ scanning XRD pattern of the diamond films deposited on W substrates.

To study the atomic images of ultrathin diamond films by field-ion microscopy (FIM), diamonds were deposited on very thin tungsten tips, with a deposition time of 20 – 30 min. The results of FIM have been published elsewhere[11]. SEM morphologies of diamonds on tips were also obtained, as shown in Figs. 7(a) and 7(b) in which single crystals of diamond in perfect structure can be clearly observed.

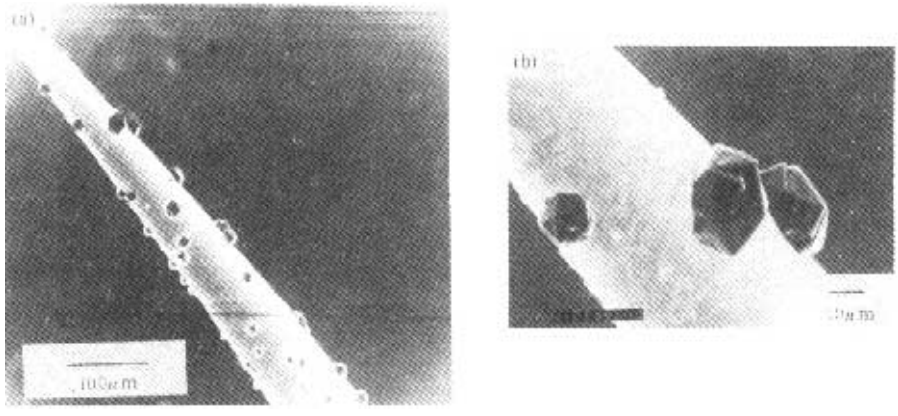

Fig. 7. SEM morphologies of diamond on W tips. (a) 250×; (b) 1030×.

Moreover, W tips could be adhered on the reflection mesa of the electron microscopy so that the incident electron beam made a suitable grazing angle with the surface of the sample, and RED images could be obtained, which are shown in Fig. 8.

In Fig. 8(a), there are both diffraction spots for single crystals of diamond and rings for polycrystalline WC interface. Experimental data are listed in Table 1. Calculating by using these data, one can see that the diffraction spots for diamond single crystals are related to the [111] zone axis. The diffraction pattern for another region of the same sample, spots for single crystal diamond and rings for polycrystalline WC are shown in Fig. 8(b), where the diffraction spots are related to [211] zone axis. Based on these results, we suggest that

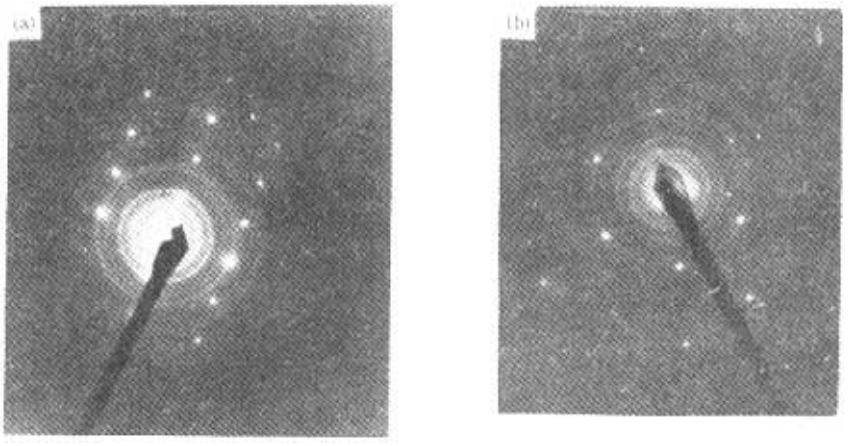

Fig. 8. RED images of diamond deposited on W tips.

during the growth course of diamond films, polycrystalline WC transition layers are formed at first, then single crystalline diamond grains are deposited on the WC layers, and finally they polymerize to form polycrystalline diamond films.

Table 1. Diffraction data corresponding to Fig. 8(a).

	Observed d(Å)	ASTM d(Å)	(hkl)
Spots for single	1.257	1.261	(220)
Crystalline diamond	0.726	0.728	(422)
Rings for polycrystalline WC	2.83	2.83	(001)
	2.516	2.51	(100)
	1.857	1.87	(101)
	1.410	1.421	(002)
	1.257	1.258	(200)
	1.22	1.233	(102)
	1.14	1.149	(201)
	0.88	0.905	(121)

IV. CONCLUSION

1. There is a polycrystalline interfacial transition layer between the diamond film and the Si substrate. Diamond grains grown on the substrate are initially uniform polygons. Diamond grains in the films will grow as columns with an average diameter of the column bases of about 15 μm. The edges of the column base are sharp and regular. The columns will generally grow upward during the entire thickness formation of the film. With the increase of the deposition time, the columns grow faint at the top of the film as a result of secondary nucleation and twinning.

2. Both CH_4 and C_2H_2 have been used as the carbon sources for the reactant gases, but similar results have been obtained.

3. The polycrystalline WC interfacial transition layers can be observed whether W wafers or W tips are used as substrates. Initially diamond particles grow uniformly on these two

kinds of substrates.

REFERENCES

[1] J. E. Field, Properties of Diamond (Academic Press, London, 1979).
[2] B. V. Spitsyn, L. L. Bouilov and B. V. Deryagin, *J. Cryst. Growth*, **56**(1981), 219.
[3] M. Kamo, Y. Sato, S. Matsumoto and N. Setaka, *J. Cryst. Growth*, **62**(1983), 62.
[4] K. Korihara, K. Sasaki, M. Kawarada and N. Koshino, *Appl. Phys. Lett.*, **56**(1988), 437.
[5] Fangqing Zhang, Yafei Zhang, Yinhu Yang, Guanghua Chen and Xiangliu Jiang, *Appl. Phys. Lett.*, **57**(14) (1990), 1467.
[6] Fangqing Zhang, Zhizhong Song, Jingqi Li, Guanghua Chen, Xiangliu Jiang and Qiuzi Cong, *Thin solid Films*, **199**(1991), 123.
[7] D. N. Belton, S. J. Harris, S. J. Schmeiq, A. M. Weiner and T. A. Perry, *Appl. Phys. Lett.*, **54**(1989), 416.
[8] Koji Kobashi, Kozo Nishimura, Yoshio Kawate and Takefumi Horiuchi, *Phys. Rev.*, **B38**(1988), 4067.
[9] B. E. Williams and J. T. Glass, *J. Mater. Res.*, **4**(1989), 373.
[10] D. J. Pickrell, W. Zhu, A. R. Badzian, R. E. Newnham and R. Messier, *J. Mater. Res.*, **6**(1991), 1264.
[11] Q. J. Gao, Z. X. Zhang, M. Lu, Y. Wang, P. Wang, Z. Y. Huang, Z. D. Lin, F. Q. Zhang, W. J. Zhang, Y. F. Zhang, G. H. Chen and X. L. Jiang, *Surface Science*, **246**(1991), 205.