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Microstructures of diamond films deposited on (1 0 0) silicon wafer by microwave plasma-enhanced chemical vapour deposition

JUNG HO JE, G.Y. LEE*
Department of Materials Science and Engineering, Pohang Institute of Science and Technology, PO Box 125, Pohang, Kyungbuk, Korea

Diamond films were deposited on (1 0 0) silicon wafer by microwave plasma-enhanced chemical vapour deposition. The microstructural changes of the diamond films were studied in relation to the pre-treatment of the silicon substrate, the methane concentration and the substrate temperature. The ultrasonic method for the pre-treatment of the silicon substrate increased the nucleation density, resulting in the deposition of small diamond particles. The surface morphology changed from the close-packed (1 1 1) to the (1 0 0) plane with increase in the methane concentration due to the decreased adatom mobility. The morphology also changed from (1 1 1) to (1 0 0) planes with substrate temperature, due to the effect of the increased chemical species. The change in the crystallinity with deposition time was also investigated.

1. Introduction

Diamond has potential applications in many fields due to its excellent and unique properties. Moreover, a diamond coating chemically bonded to inexpensive non-diamond surfaces at low costs would open up a much wider range of applications [1]. This potential has prompted an acceleration in the research based on the low-pressure deposition of diamond from the vapour phase, by many researchers. However, the deposition mechanism of diamond film is still unclear.

There are many technological problems in diamond coating from the vapour phase at low pressure: a poor adhesion, high substrate temperatures, difficulties of growing single-crystal film and in controlling the surface morphology of the film, etc. In order to solve such problems, much work is underway, largely focusing on the influences of the deposition parameters on diamond growth, especially the morphology and the crystallinity of the diamond film.

In this study, the effects of some deposition parameters were investigated on the growth of diamond film by microwave plasma-enhanced chemical vapour deposition (MPCVD). The microstructural changes of the diamond films were studied in relation to the pre-treatment of the silicon substrate, the methane concentration and the substrate temperature. The change in the crystallinity was also investigated with deposition time.

2. Experimental procedure

The reaction chamber of the MPCVD system consists of a vertically mounted quartz tube, 3.8 cm o.d. and 76 cm long, which confines the plasma as shown in Fig. 1. The reaction gases, methane and hydrogen, flow through the gas inlet at the top of the reaction chamber. Also located at the top of the reactor is a glass viewport used to observe the progress of the deposition and to measure the substrate temperature with an optical pyrometer. Because of the interference of the plasma, the substrate temperature was calibrated by a thermocouple (type K). The (1 0 0) silicon wafer substrate was heated only by interaction with the microwave power and the plasma; no external heating was used. The flow rates of the gases were controlled by the mass flow controllers (MFC), and the pressure of the reaction chamber was monitored using a capacitance manometer and controlled with a micro-metering valve.

The reaction conditions were: methane concentration, 0.5–5.0 vol%; hydrogen concentration, remainder; total flow rate, 100 standard $\mathrm{cm^3\,min^{-1}}$; total pressure, 30 torr; microwave power, 330–460 W; substrate temperature, 780–910 °C; deposition time, 1–10 h.

Pre-treatment of the silicon wafer substrate was done by three different methods: (1) the mechanical vibration method (the substrate was mechanically vi-

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* *Present address*: Hyundai Electronics, Semiconductor Research and Development Laboratories, San 136-1, Ami-ri, Bubal-eub, Ichon-kun Kyoungki-do, 467-860, Korea.

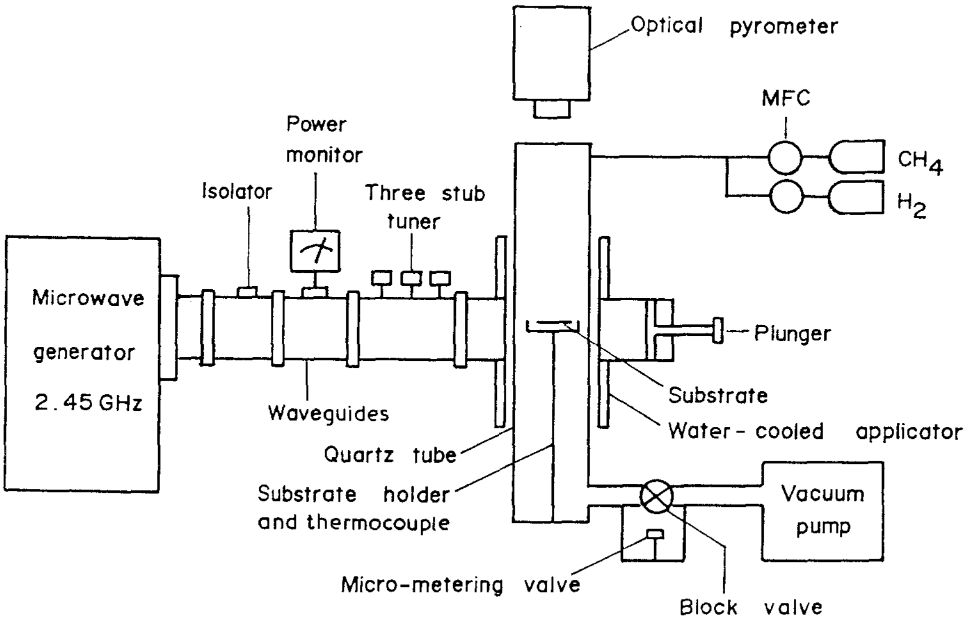

Figure 1 Schematic diagram of the microwave plasma-assisted CVD system.

brated in SiC powder), (2) the polishing method (the substrate was polished with 1 μm diamond paste), and (3) the ultrasonic method (the substrate was ultrasonically vibrated in acetone solution dispersed with 1 μm diamond powder). All silicon substrates were ultrasonically cleaned in acetone before deposition.

The microstructure of the deposited film was observed by scanning electron microscopy, and the crystal structure of the film was investigated by X-ray diffraction analysis. A Raman spectroscope was also used for the identification of diamond and non-diamond phases.

3. Results and discussion

3.1. Effects of pre-treatment of the substrate

Fig. 2 shows the surfaces of silicon substrates pretreated by the three different methods. Among the substrates pre-treated by the mechanical vibration method, the substrate treated with the SiC powder, no. 80 (177 μm), was severely deformed locally on the surface (Fig. 2a), while the fine powder of SiC, no. 200 (74 μm), did not effectively give rise to flaws (Fig. 2b). Scratches were found on the substrate polished with 1 μm diamond paste (Fig. 2c), and the substrate pretreated by the ultrasonic method showed uniform defects (Fig. 2d).

Fig. 3 shows the morphologies of the films deposited on these substrates. The deposits were prepared at 1.0% methane concentration, and a substrate temperature of 910 °C, with a microwave power of 460 W, for a deposition time of 10 h. In the substrate pretreated with the SiC powder 80, (1 0 0) planes of diamond were observed on the surface of ball-like particles which seemed to be amorphous (Fig. 3a). However, with the finer SiC powder 200, no discernible crystalline particles of diamond could be observed (Fig. 3b). The X-ray diffraction pattern for this film also showed no crystalline phase. Meanwhile, crystalline diamond films could be deposited on substrates pre-treated by the polishing and ultrasonic methods with diamond powder (Fig. 3c, d). On the substrate polished with 1 μm diamond paste, large diamond particles were deposited and (1 0 0) planes were dominant on the surface, but the ultrasonic method caused the deposition of (1 1 1) plane-dominated diamond particles of small size. The difference in the particle

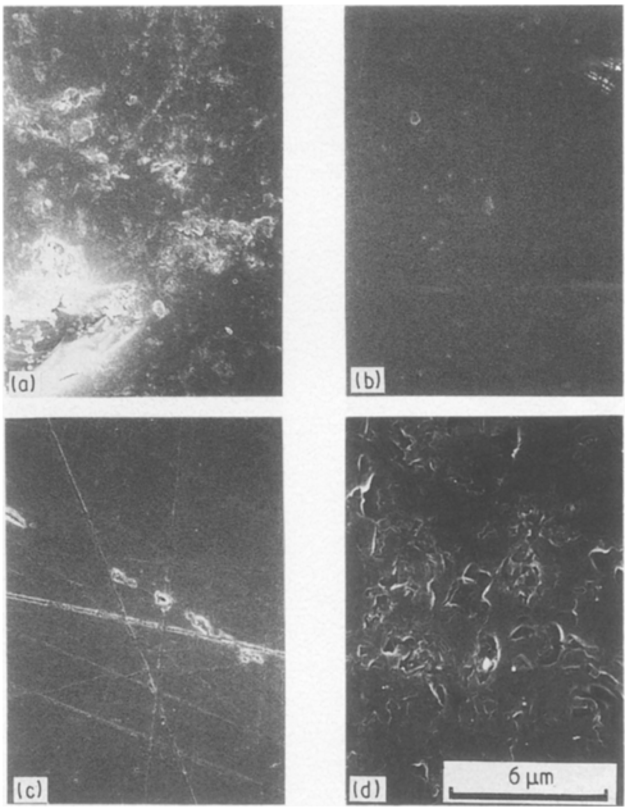

Figure 2 Scanning electron micrographs of the pre-treated Si (1 0 0) n-type wafers: (a) mechanically vibrated with 80 SiC powder, (b) mechanically vibrated with 200 SiC powder, (c) polished with 1 μm diamond paste, (d) ultrasonically vibrated in acetone dispersed with 1 μm diamond powder.

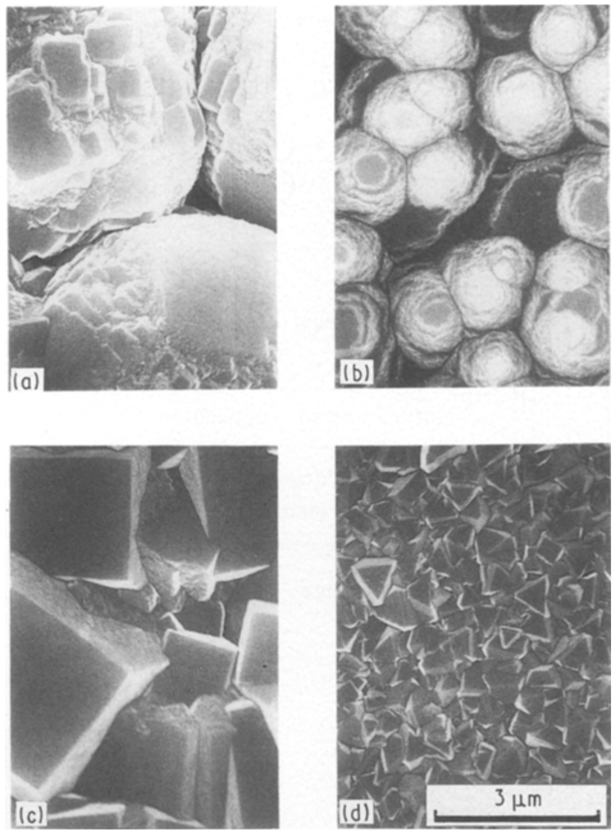

Figure 3 Scanning electron micrographs of the diamond films deposited on the silicon substrates pre-treated by the methods described in Fig. 2.

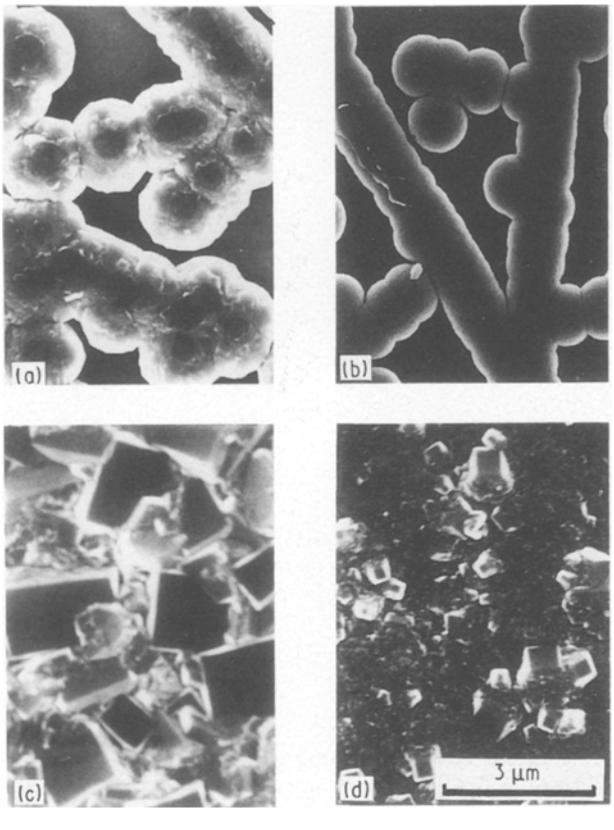

Figure 4 Scanning electron micrographs of the deposits on the silicon substrates pre-treated by the polishing method (a, b) and (c, d) the ultrasonical vibration method at (a, c) 4% and (b, d) 5% methane concentration (Substrate temperature 910 °C, deposition time 10 h).

sizes on both substrates seems to be due to the difference in the nucleation density on the substrate surfaces in the early stage.

From these results, it is suggested that the material used for the pretreatment of the substrate affects the crystallinity and the nucleation density of the deposits and that even for the same pre-treated material, the pretreatment method influences the nucleation density. The ultrasonic method induced many more surface defects and a higher nucleation density, resulting in the deposition of small diamond particles.

Fig. 4 shows the microstructures of films deposited at a higher methane concentration on substrates pre-treated by the polishing and ultrasonic methods with diamond powder. An amorphous phase was deposited on the substrate pre-treated by the polishing method with 4% and 5% methane (Fig. 4a, b). Meanwhile by the ultrasonic method, diamond phase could be deposited even at 5% methane concentration (Fig. 4d). Fig. 5 shows Raman spectra for the diamond films deposited at 1% and 4% methane concentrations for the substrates pre-treated by the ultrasonic method. Both films show the Raman shift for diamond at $1332\ \mathrm{cm}^{-1}$. For the films deposited at 4% methane concentration, a broad band around $1500\ \mathrm{cm}^{-1}$ is also observed in addition to the Raman shift for diamond at $1332\ \mathrm{cm}^{-1}$. It is considered that the ultrasonic method enhances the nucleation of diamond phase on the substrate very effectively, even at high methane concentrations.

3.2. Effects of the methane concentration

For the silicon substrates pre-treated by the ultrasonic method, the morphological change in the diamond films was studied with methane concentration. Fig. 6 shows the microstructures of the deposited films prepared at various methane concentrations at a substrate temperature of 910 °C for 10 h. As the methane concentration increased, the crystallinity of the film deteriorated. Up to 2% methane, the surfaces of the deposits were mainly covered with (1 1 1) plane triangles, while square (1 0 0) planes began to be dominant from 3% methane. That is, the crystal plane on the surface of the deposit changed from (1 1 1) to (1 0 0) with increasing methane concentration. As the methane concentration increased further, the density of particles having (1 0 0) planes on the surface began to decrease. Thus the nucleation density of crystalline diamond in the initial stage of the deposition, decreased. The change in the crystalline surface from (1 1 1) to (1 0 0) and the deterioration of the crystallinity with methane concentration have been frequently reported [2–4].

The formation of thin film does not always occur under thermodynamic conditions and the orientation of the deposit is mainly determined by kinetic factors. With a high substrate temperature, a low deposition rate and low concentration of chemical species, the adsorbed particles have enough time to move on the surface very easily and to diffuse to energetically favourable positions. That is, the adsorbed particles would be arranged with an orientation having the

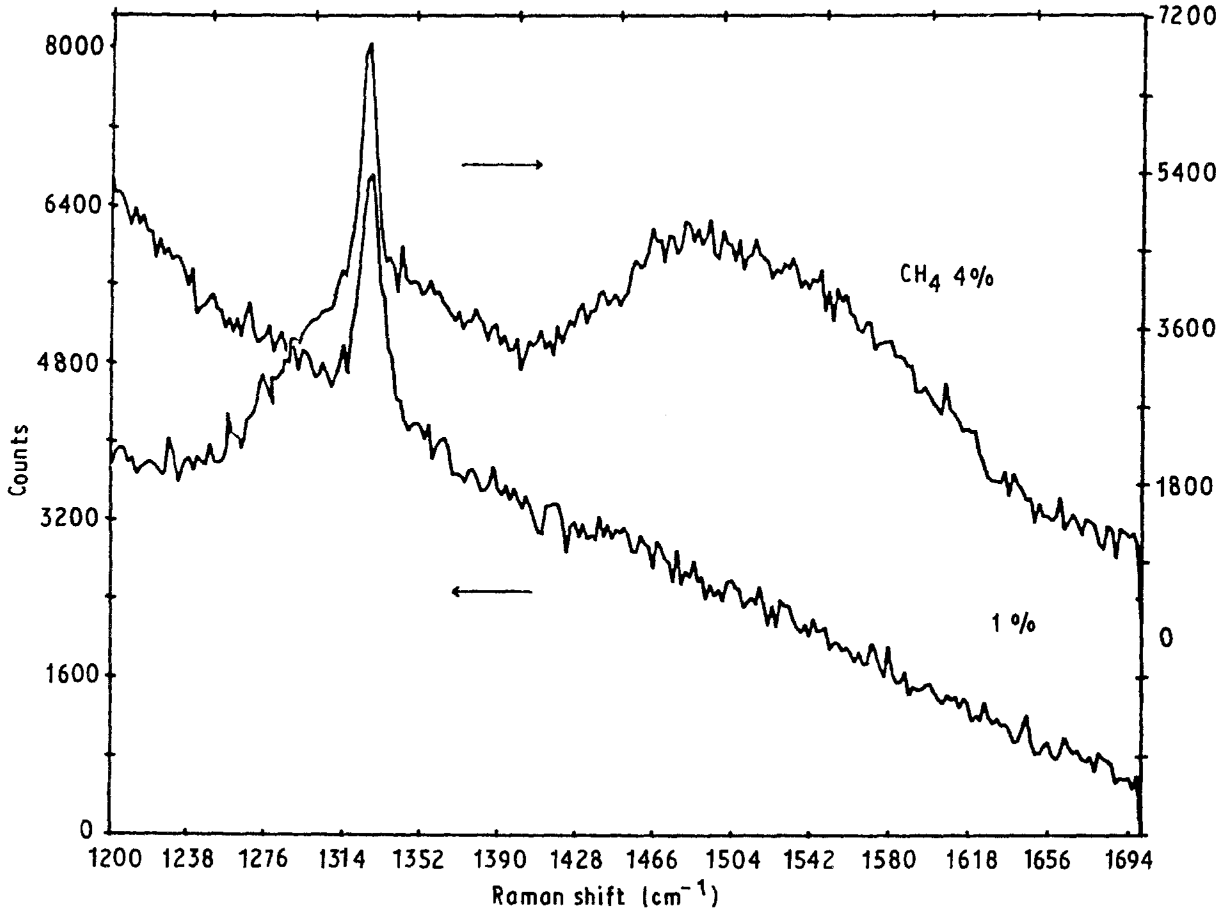

Figure 5 Raman spectra of the diamond films deposited on Si(1 0 0) substrates at 1% and 4% methane concentration. The substrates were ultrasonically vibrated with 1 μm diamond paste in acetone.

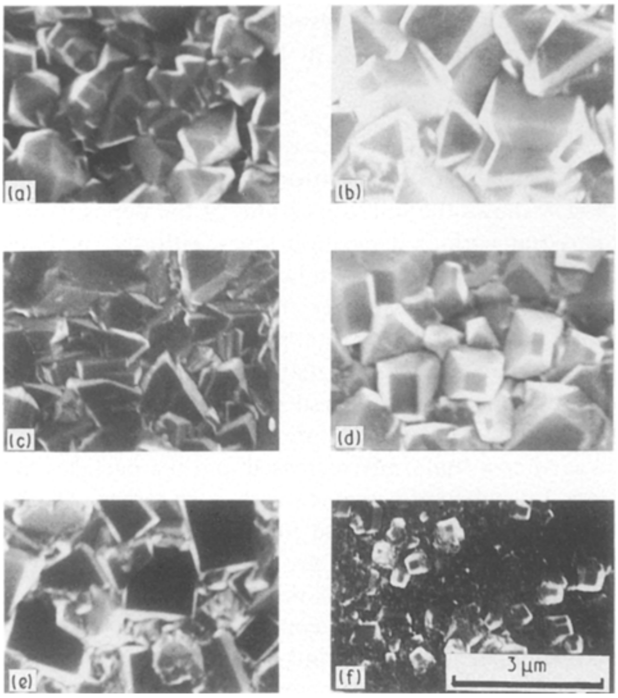

Figure 6 Scanning electron micrographs of the diamond films deposited on the silicon substrates at a substrate temperature of 910 °C for methane concentrations of (a) 0.5%, (b) 1.0%, (c) 2.0%, (d) 3.0%, (e) 4.0%, and (f) 5.0%.

energetically favourable plane, e.g. (1 1 1) plane [5]. Meanwhile at low substrate temperature, high deposition rate and high concentration of chemical species, the adsorbed atoms or molecules do not have enough time to move to the energetically favourable position and would be arranged with a less dense plane, e.g. (1 0 0). It is considered that the increase in methane concentration provides the increase in the source of supply of hydrocarbon in this MPCVD system, and this induces the increase in the activated chemical species for the diamond deposition. Therefore, it is believed that this high concentration of chemical species causes the change of the surface plane from the close-packed (1 1 1) to the (1 0 0) plane.

In Fig. 3c and d, the difference in the morphologies of the films, i.e. (1 0 0) and (1 1 1) planes, with the same deposition conditions except for the substrate pre-treatment, seems to be related to the nucleation density. The relative chemical species arriving on the growing particles are believed to be high when the nucleation density is low. Therefore, it is considered that the polishing method giving rise to a low nucleation density caused the morphology of the (1 0 0) planes on the surface, and this low nucleation density could also induce large diamond particles.

In general, it has been reported that at a high methane concentration above 1%, diamond films of high quality are not well deposited and the transition concentration from (1 1 1) to (1 0 0) planes on the surface of the film is also not high, $\lesssim 1\%$ methane [2,3]. These seem to be related to the method of substrate pre-treatment. The pre-treated condition of the substrate critically decides the crystallinity of the nuclei, and effective pre-treatments of the substrates are able to enhance the crystallinity of the nuclei.

Therefore, it is believed that effective pre-treatment of the substrate by the ultrasonic method used in this study could increase the transition concentration from (1 1 1) to (1 0 0) surface morphologies. The crystallinity of the nuclei also seems to play an important role in the determination of the microstructure and the crystallinity of the films.

3.3. Effects of substrate temperature

Fig. 7 shows the microstructures of diamond films deposited at various substrate temperatures: 780, 845, and 910 °C with the applied microwave powers, 330, 400 and 460 W, respectively. At this time, the methane concentration was 4%, total flow rate 100 standard $cm^3\,min^{-1}$, total pressure 30 torr, and deposition time 10 h. As the substrate temperature increased, the area of the amorphous phase existing between the growing particles increased, and the surface of the growing diamond particles was gradually changed from (1 1 1) to (1 0 0) planes.

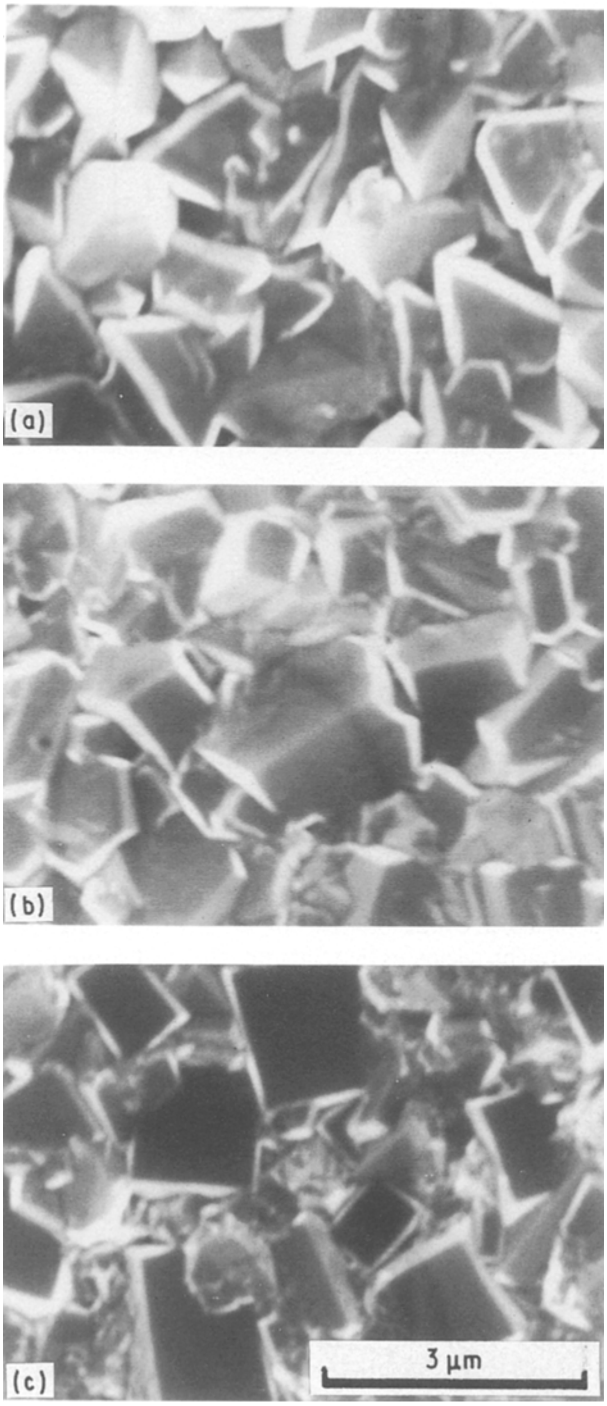

Figure 7 Scanning electron micrographs of the diamond films deposited on the silicon substrates at 4% methane concentration for substrate temperatures of (a) 780 °C, (b) 845 °C, and (c) 910 °C.

It was reported that the morphologies of the deposited films changed from (1 1 1) to (1 0 0) by Badzian [4] and Spitsyn *et al.* [6], but from (1 0 0) to (1 1 1) by Haubner and Lux [7] with substrate temperature. The increase in the substrate temperature is able to cause two effects which conflict with each other. One is to promote the decomposition of methane, and thus an increase of chemical species. This would make the surface morphologies transform from (1 1 1) to (1 0 0) planes as does an increase in the methane concentration. The other effect is to increase the atomic mobility on the substrate surface and thus promote the change of the surface morphology from (1 0 0) to (1 1 1) planes. In fact, the change in the surface morphology would be very sensitively dependent upon the pre-treatment conditions of the substrate. In this study, it is considered that the surface morphology was changed from (1 1 1) to (1 0 0) planes, because the effects of the increase of chemical species are greater than the effects of the atomic mobility with the substrate temperature, because an increase in the substrate temperature produces an increase in the plasma intensity. As the temperature increased further, the crystallinity of the film deteriorated. This results from the promotion of higher chemical species at higher substrate temperatures.

3.4. Effects of deposition time

Fig. 8 shows the microstructures of the deposits prepared at various deposition times with 4% methane concentration, 845 °C substrate temperature with 400 W microwave power, 100 standard $cm^3\,min^{-1}$ total flow rate, 30 torr total pressure. After deposition for 1 h, cubo-octahedral diamond particles grew separately on the surface and some particles had twin structures. After deposition for 3 h, the particle size was almost uniformly increased and the particles began to come into contact with each other. As the deposition time increased further, the substrate was further covered with the growing particles, and completely covered at 10 h. It was found that there was a facetless phase on the contact boundary between growing particles. This kind of phase, which seems to be amorphous, would increase with the area of the contact boundaries. This was proved by the Raman spectra as shown in Fig. 9. The film deposited for 3 h showed only the Raman shift for diamond at $1332\,cm^{-1}$, but the film deposited for 10 h showed a broad band around $1500\,cm^{-1}$ corresponding to an amorphous phase in addition to the Raman shift for diamond at $1332\,cm^{-1}$. Therefore, it is believed that deterioration of the crystallinity of the diamond film with deposition time results from the amorphous phase formed at the contact boundaries between growing particles.

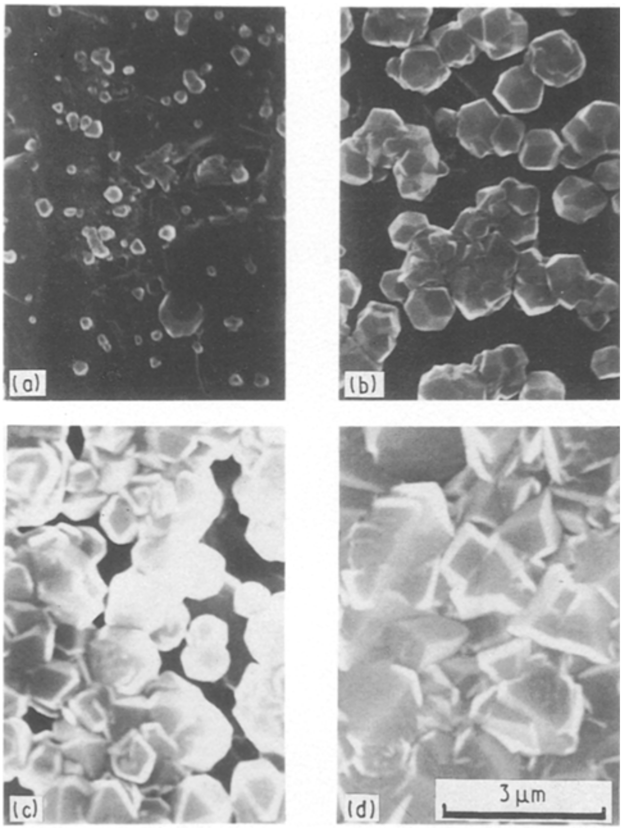

Figure 8 Scanning electron micrographs of the diamond deposits on the silicon substrates at 4% methane concentration and a substrate temperature of 845 °C after (a) 1 h, (b) 3 h, (c) 5 h, and (d) 10 h.

4. Conclusion

The material used for the pre-treatment of the substrate affects the crystallinity and the nucleation density of the deposits and, even for the same pre-treated material, the pre-treatment method influences the nucleation density. The ultrasonic method caused many more surface defects and a higher nucleation density, resulting in the deposition of small diamond particles.

An increase in methane concentration induces an increase in activated chemical species for the diamond deposition, and this high concentration of chemical species causes the change of the surface plane from the close-packed (1 1 1) to the (1 0 0) plane, due to the decreased adatom mobility.

The increase in substrate temperature could cause two competing effects on the change of film morphology. The surface morphology would be very sensitively dependent upon the pre-treatment condition of the substrate. The surface morphology was changed from (1 1 1) to (1 0 0) planes because the effects of the increase of chemical species are greater than the effects of atomic mobility with substrate temperature.

The deterioration of the crystallinity of the diamond film with the deposition time results from the amorphous phase formed at the contact boundaries between growing diamond particles.

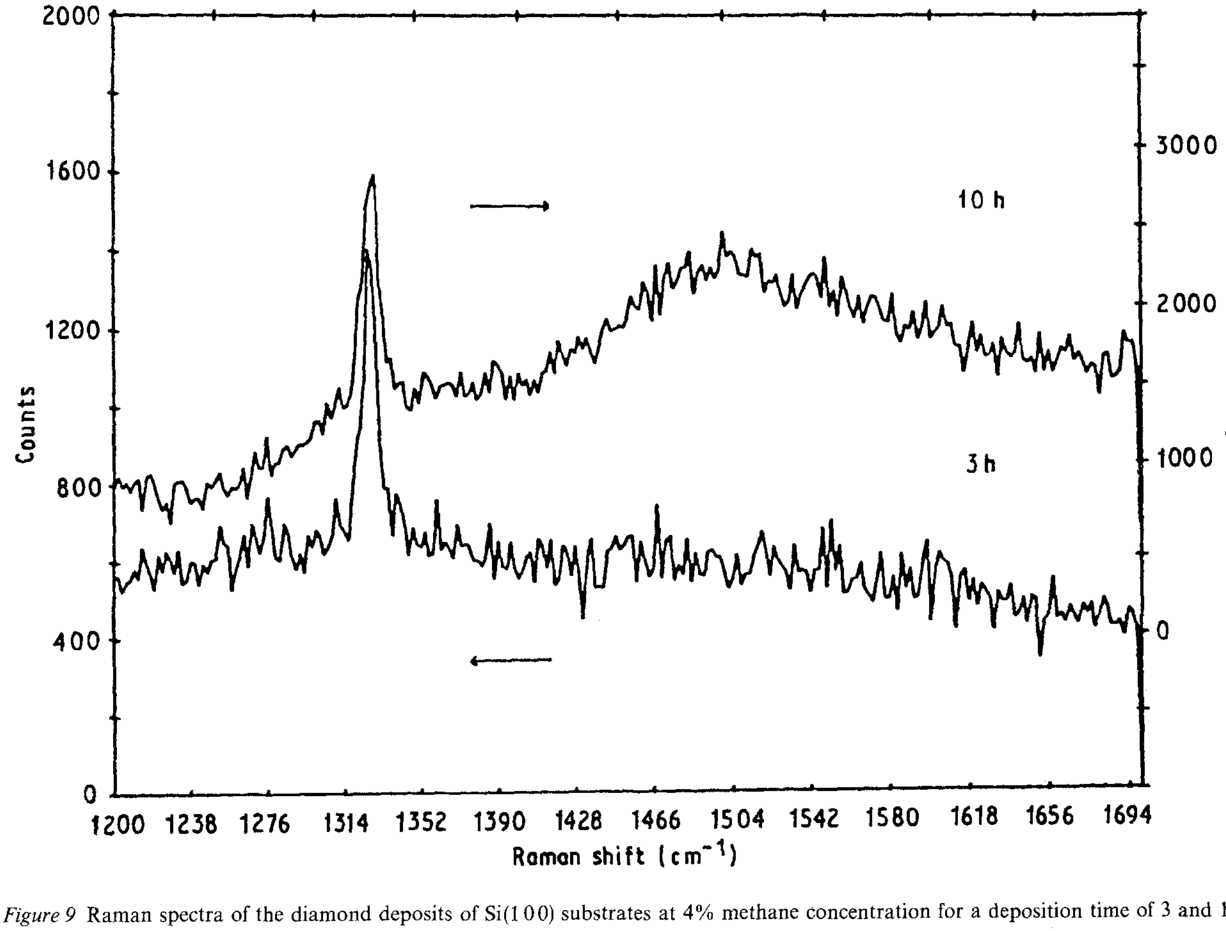

Figure 9 Raman spectra of the diamond deposits of Si(1 0 0) substrates at 4% methane concentration for a deposition time of 3 and 10 h.

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