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Filament-assisted growth of diamond films

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Filament-assisted pyrolytic growth of diamond films on (1 0 0) Si wafers was investigated in an attempt to grow quality layers for semiconductor applications. The work was carried out in hydrogen ambient under a reduced pressure condition of about 1 0 0 torr (133, 322 × 10^2 Pa). Using isopropanol and methanol as carbon source chemicals, the growth process and film properties were characterized as functions of reactant concentration, filament and substrate temperature, reaction pressure and the total gas flow rate. Diamond films of good quality were grown under condition of low source concentration and small flow rate. However, the growth rates were generally slow. The films were polycrystalline. The filament and substrate temperatures were fairly critical to the nucleation and growth processes. The substrate surface finishing from diamond paste polishing predominated the nucleation site and grain size of the deposits.

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1. Introduction

As a jewel, the value and meaning of a diamond crystal to a human heart in the modern world is unique. As a scientific material, diamond crystals possess superior properties which can be utilized for different purposes. Therefore, synthesis of diamond has been of interest to scientists and engineers for many years. However, it has proved difficult to produce diamonds of large grain size for commercialization thus far. In the recent years, because of technological advancement in material development, growth of polycrystalline diamond thin films on various kinds of substrate for engineering applications has shown good progress. Different techniques of diamond film synthesis have been developed, of which all appear to be effective for demonstrative purposes. Although for most industrial applications further developmental work is needed, the mechanism of diamond thin-film synthesis is better understood.

From a material quality point of view, all the synthesized diamond films are polycrystalline because they are deposited on foreign substrates in a contaminated ambient. The grain size generally varies in the range of less than 100 μm diameter depending on growth conditions. The impurity content also varies depending on the purity of the source chemicals and the apparatus. However, because of the nature of the process, the films always contain uncrystallized carbon atoms. In some severe cases, they may have inclusions of chunk graphite. More details of this aspect are discussed.

Carbon atoms crystallize into either a cubic or a hexagonal lattice with four nearest neighbouring atoms with sp^3 bonds as diamond. With three neighbouring atoms, they may also take the form of a layered structure with sp^2 bonds which is known as graphite. Because of the bonding nature, diamond crystals are extremely hard. Thus, synthesized diamond has become most useful as an abrasive material, though the grain sizes are very small. Diamond crystals are thermally very conductive and electrically very resistive. They are, therefore considered to have high potential for electronic packaging application. Because diamond has a wide band-gap energy of about 6 eV with high carrier mobility, it is also considered to be a good semiconductor material. Finally, because it is optically highly transparent, it has been considered for optoelectronic applications.

During the progress of recent development on diamond synthesis, investigations have mainly centred on the development of vapour-phase growth techniques at nonequilibrium conditions. The techniques include filament assisted chemical vapour deposition (CVD) [1–3], microwave plasma CVD [4–7], d.c. and r.f. plasma CVD [8, 9], ion-beam deposition [10] and laser-induced CVD [11], for example. While the new growth methods are developed, improvements in growth rates and film quality are obtained. In general, all the techniques require a substrate temperature of about 800 – 1000 °C and some means of pre-growth treatment of reactants to obtain sp^3 hybridized CH_3 radicals for deposition of diamond. Under the low-pressure conditions (less than 1 torr (133.322 Pa)) in hydrogen ambient, from pyrolysis of CH_4, C_2H_5OH, and CH_3OH of different concentrations, investigators could only obtain a low growth rate of a fraction of 1 μm h^{-1} [1]. On increasing the reaction pressure to about 100 torr by adding hydrogen, the growth rate can be increased to about 10 μm h^{-1} [6, 9, 12]. In addition, by adding an oxidizing reagent, such as O_2, CO_2, CO or H_2O, same investigators obtained higher growth rates, exceeding 10 μm h^{-1} [12]. However, much of the information was obtained from growth on metallic and ceramic substrates. Because of the nucleation and facet growth conditions, the interfacial property and morphology of the diamond films are generally very poor. As the growth rate of diamond films on foreign substrates can be made fast enough to be comparable with semiconductor epitaxial growth, it is justifiable to investigate diamond epitaxy on silicon as a semiconductor material. Therefore, this work was initiated in an attempt to improve the nucleation and growth conditions for diamond film deposition on silicon to obtain better interfacial and morphological characteristics for semiconductor application.

2. Experimental procedure

The investigation was carried out using filament-assisted chemical vapour deposition in a home-made reactor. Briefly, the reaction system consists of three sections of apparatus as shown in Fig. 1, which includes (a) a quartz reaction chamber with a resistance-heated pedestal and a tungsten filament which are separately connected to two different power supplies, (b) a gas manifold with mass flowmeters and flow tubes for control of the feeding rates of reactants, (c) a mechanical pump with gas scrubbers connected to the exhausting end. In this reactor the filament may be heated up to 2500 °C, while the temperature of the pedestal can be raised to 1200 °C. The reaction pressure may vary from 1 torr to 1 atm.

(1 0 0) and (1 1 1) oriented silicon wafers were the main substrates though molybdenum tungsten and Al_2O_3 were also tested as substrates in order to verify the growth conditions of diamond for comparison with literature information. CH_3OH and C_2H_5OH and hydrogen were the main reactants. In addition, toluene and other oxygen-containing hydrocarbons were also tested. To enhance nucleation conditions, the surface of the silicon substrates was polished using different grades of diamond paste. Of course, excessive cleaning, including degreasing by organic solvents, removal of native SiO_2 by dilute HF, and DI water rinsing to $> 10\ M\Omega$ was followed.

The crystalline quality was determined by Romma spectrum analysis and the morphology was studied by means of scanning electron microphotography.

3. Results and discussion

It is generally understood that the nucleation process in vapour-phase growth takes place at surface kinks and step edges of the atomic layers on the substrate surface where the mobile species of the reactants come to rest. For homogeneous growth, one would expect that growth by atomic layer expansion occurs under a supersaturation condition of nucleation. However, heterogeneous interfacial growth of the stable nuclei may occur in both upwards and horizontal directions depending on the nature of the reactants and substrates and the supersaturation conditions.

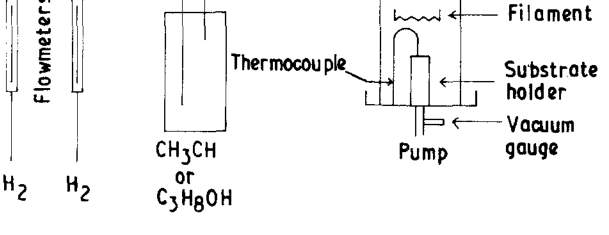


Figure 1 Schematic drawing of the CVD growth apparatus.

In filament-assisted pyrolytic growth of diamond on silicon, a heterogeneous growth process, it was found very difficult to induce nucleation on the normal electronic-grade single-crystalline silicon wafers, possibly because of the nature of the process which provides a very narrow range of spontaneous nucleation conditions, because filament excitation is not an effective means of ionizing the reactive species to give sp^3 bonds for nucleation of diamond crystallites. However, in the presence of diamond seeds under supersaturation conditions of reactants, both homogeneous growth and spontaneous nucleation would occur. Therefore, we expect to see nucleation and growth of particulate diamond films on silicon, if the substrate is polished using diamond paste which would leave crystallite seeds of diamond at the subsurface and scratches on the surface. In this work, we found no nucleation nor growth on silicon without surface treatment after 1 h of growth experiment. On tungsten carbide-polished silicon, nuclei formed by spontaneous nucleation along the scratches, but were not always diamond crystallites.

In order to grow polycrystalline diamond films on silicon by means of a filament-assisted pyrolytic process, it is necessary to pretreat the substrate to recondition the surface by diamond-paste polishing. Experiments were carried out using silicon substrates which were polished using different grades of diamond paste with particle sizes varying from 1–6 μm. The results indicate that diamond crystallites with well-developed facets and random orientation grew as if from the nuclei of spontaneous nucleation. The density of the crystallites ranged in 10–$10^2\ cm^{-2}$ depending on the process conditions. However, the growth process was not sensitive enough to differentiate any particle-size effect on the substrate surface treatment. The growth process was further characterized by experiments of extended growth time which result in polycrystalline diamond films of large grain size under various process conditions.

This work used oxygen-bearing hydrocarbons as reactants in an attempt to provide conditions for a reversible reaction in order to obtain growth of better quality crystals. After a few screening experiments of the reagents including alcohols and aromatic compounds, isopropanol and methanol were chosen for detailed study.

3.1. Isopropanol as a source chemical for diamond growth

3.1.1. Temperature effect on growth rate

Using isopropanol as a carbon source with the rest of the parameters fixed including the substrate temperature at 850 °C, we studied the filament temperature effect on growth rates. The results as shown in Fig. 2

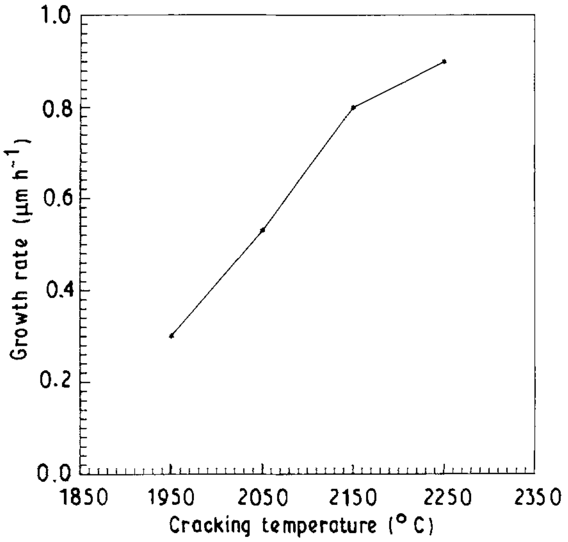


Figure 2 Growth rate versus filament temperature.

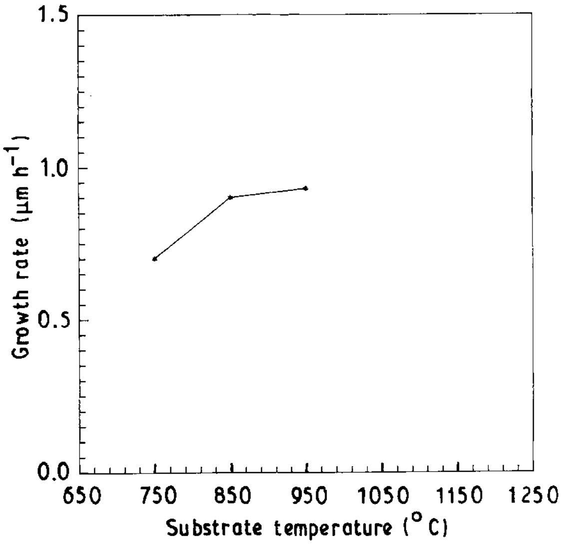


Figure 3 Growth rate versus substrate temperature.

indicate that the growth rate increases by a factor of more than 3 with the filament temperature in the range 1950–2250 °C. This means that a high cracking temperature is needed to increase the ionization rates of the radicals and hydrogen atoms for formation of the sp^3 bond that is required for diamond epitaxy. Because the trend of growth rate slows down at temperatures higher than 2200 °C, the filament temperature was fixed at 2200 °C for the rest of the work. Similarly, the substrate temperature was also experimentally determined. Fig. 3 shows a plot of growth rate against substrate temperature, which indicates that in the range 850–950 °C the growth rate was less sensitive to the substrate temperature. Thus, 850 °C was chosen as the sustrate temperature for investigation of other parameters in this work.

3.1.2. Temperature effect on growth quality

It is generally understood that the substrate temperature is the most influential factor on quality for vapour-phase growth, because on the substrate surface the condensing species require energy to diffuse to a stable position resulting in a crystal lattice of good perfection. In this work, samples which were grown at different substrate temperatures were subjected to Raman spectroscopic analysis. Fig. 4 shows the three sets of spectra, of which all have a high-intensity peak about 133 nm due to diamond lattice scattering, while the spectra of the samples grown at lower temperatures have an additional broad peak near 155 nm from the graphite content in the samples. The crystal quality can be characterized by comparing the relative intensities of the two peaks of a spectrum. It is obvious that growth under the supersaturation conditions at 750 °C produces a large percentage of graphite. As the substrate temperature increases, the intensity of the diamond peak also increases, while the graphite peak gradually diminishes. This indicates that under the experimental conditions for growth of better quality, a higher growth temperature is needed. Although the dectability of Raman spectroscopy on graphite in diamond is not known, in this series of experiments, growths at temperatures above 850°C contained mostly diamond.

Fig. 5 shows a series of scanning electron micrographs of the corresponding samples to show the morphology. They indicate very clearly that growths at 850 and 900°C result in strongly reflective surfaces of crystal facets, although they are not smooth and flat. This is typical of the nature of vapour phase growth of polycrystalline diamond films on silicon. On the other hand, the deposits at 750 °C have dull surfaces typical of particulate growth of two-phase globules of diamond and graphite.

3.1.3. Source concentration effect on growth

The source concentration rate is an important factor in vapour-phase growth, because it is directly related to the supersaturation condition for growth. In this work, when the temperature and pressure conditions are fixed, the effect of source concentration on growth are investigated. Fig. 6 shows the plot of growth rate

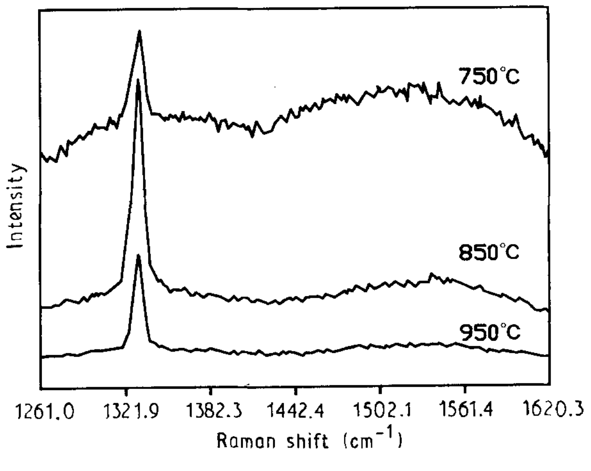
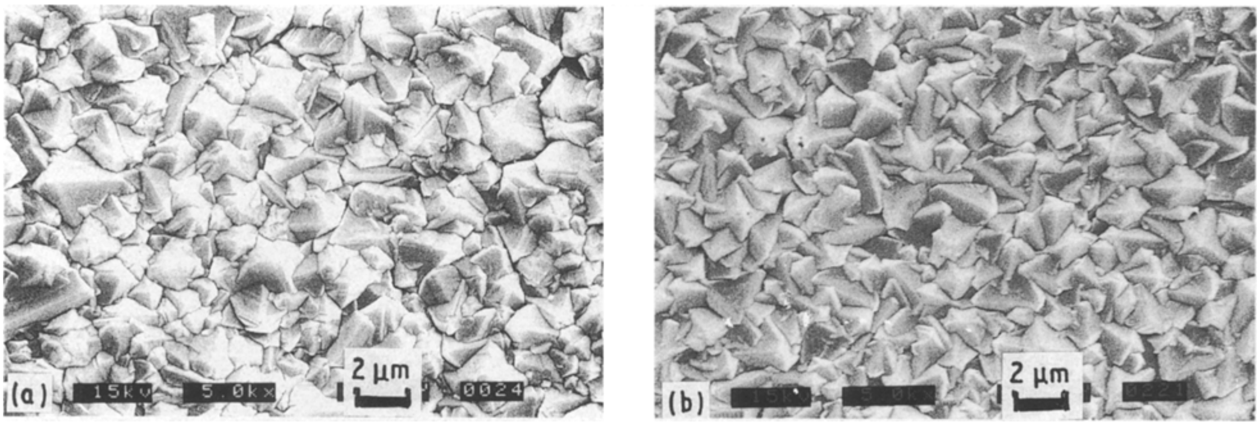


Figure 4 Raman shift spectra of samples grown at different temperatures.



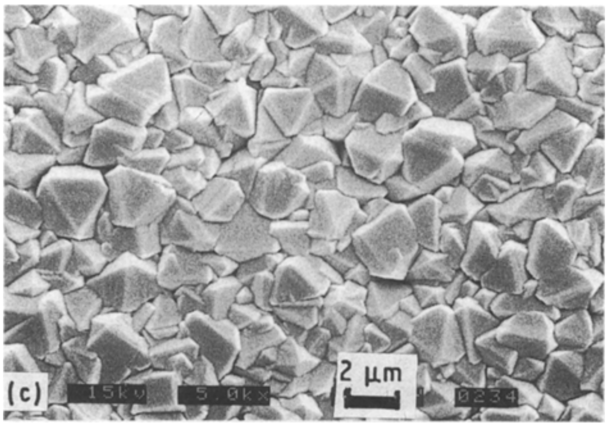


Figure 5 Scanning electron micrographs of samples grown at different temperatures. (a) 750 °C, (b) 850 °C, (c) 950 °C.

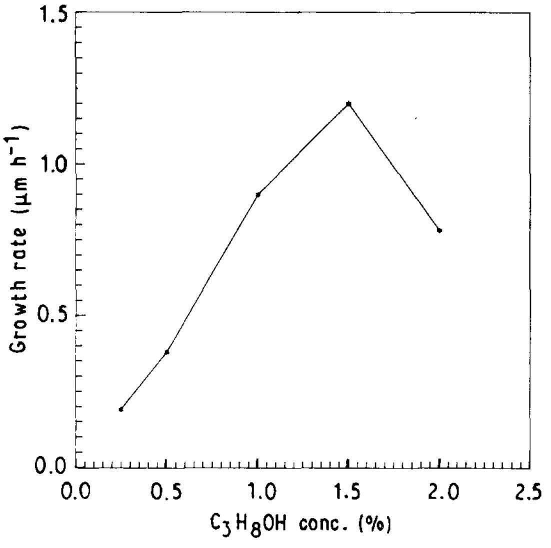


Figure 6 Growth rate versus isopropanol concentration.

against source concentration in terms of volume ratio of the source carrier to the total flow rate. The growth rate increases with the source concentration to a maximum of about 1.2 µm h^{-1} at 1.5% source concentration, because there are more ionized radicals available for growth of diamond. Then it decreases to about 0.8 µm h^{-1} at about 2.0% source concentration, which is probably due to the formation of graphite with a lower growth rate, because of the conditions of the reversible reaction.

The variation in growth quality with the source concentration was characterized by means of both Raman spectroscopy and SEM analysis. Fig. 7 shows 5 Raman spectra for the experiments with variable source concentrations from 0.25%– 2.0%. The results indicate that when the source concentration is 1.5% or higher, the graphite content in the film is significant. This conclusion agrees with the morphological analysis from the scanning electron micrographs, as shown in Fig. 8. Where the change in growth surface with source concentration is clearly seen: when the concentration is 1.0% or less, the growth surface consists of highly reflective facets of diamond crystals while it becomes dull due to globular growth of graphite and diamond when the concentration increases to 1.5% or more.

3.1.4. The effect of reaction pressure on growth rate and quality

The reaction pressure is related to the density of the source molecules on the substrate surface and the mass transfer coefficient, which are both supposed to play a role in vapour-phase deposition affecting growth rate and quality. In this work, experiments

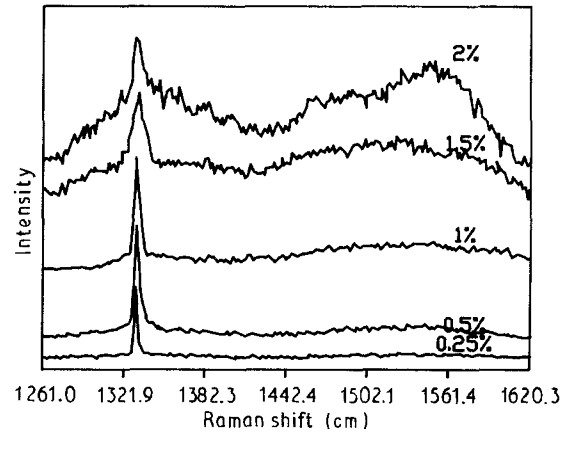


Figure 7 Raman shift spectra of samples grown with different isopropanol concentrations.

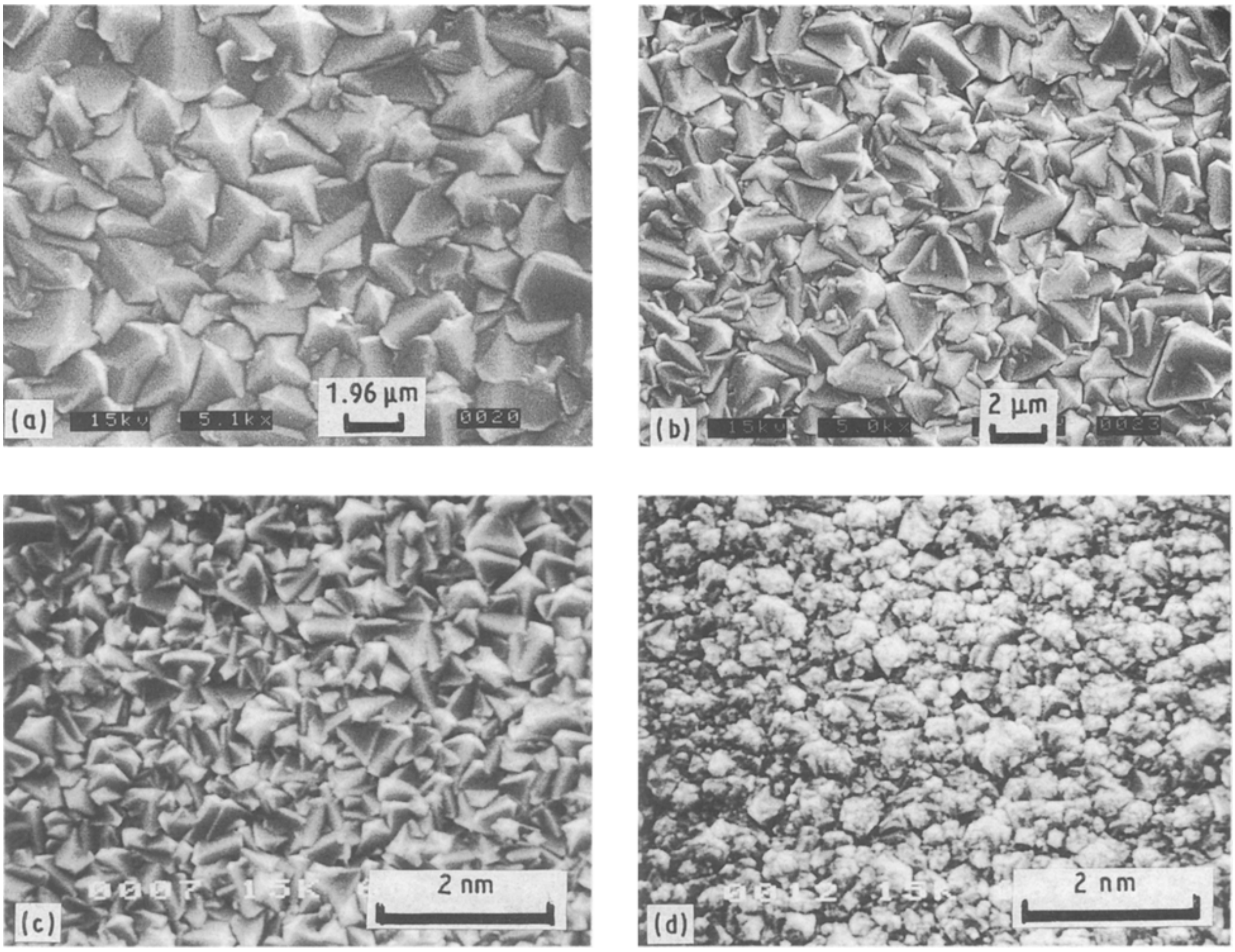


Figure 8 Scanning electron micrographs of samples grown with different isopropanol concentrations. (a) 0.25%, (b) 0.5%, (c) 1%, (d) 1.5%.

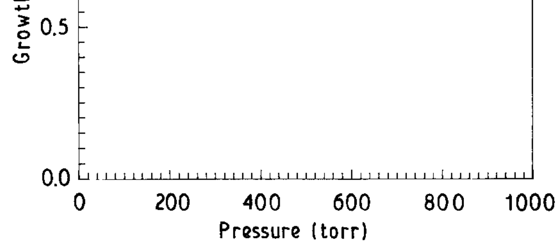


Figure 9 Growth rate versus reaction pressure.

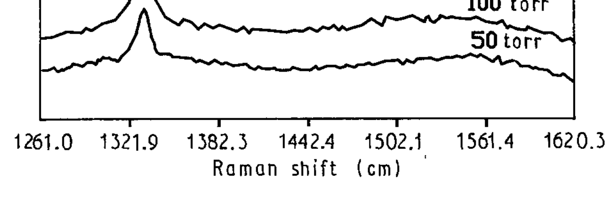


Figure 10 Raman shift spectra of samples grown under different reaction pressure.

were carried out with reaction pressures varying from 50–800 torr while the remaining parameters were fixed. The effect on growth rate is shown by the data plotted as a function of pressure in Fig. 9. In the lower pressure range, the growth rate increases with pressure, probably due to the mass-transfer mechanism controlling the rate of deposition, while in the higher pressure range, the growth rate increases very slowly with pressure, where the growth rate appears to be controlled by the surface reaction mechanism. The growth quality results in the form of Raman spectra are shown in Fig. 10. The results indicate that growths are free from graphite content when the reaction pressure is kept below 100 torr, but as the reaction pressure increases to 200 torr or higher, the graphite content in the diamond film becomes significant.

3.2. Methanol as a source chemical for comparison

3.2.1. Source concentration effect on growth rate and quality

It is obvious that the methanol molecule contains only one carbon which is different from that of isopropanol. The isopropanol molecule has a carbon to oxygen ratio of 3 : 1 while the methanol molecule has the ratio of 1. Although the detailed reaction may not be the same for optimum growth of epitaxial diamond, one would expect to use different concentrations of molar percentages of the carbon sources. That is, when methanol is used as a carbon source, a higher reactant concentration should be used for growth.

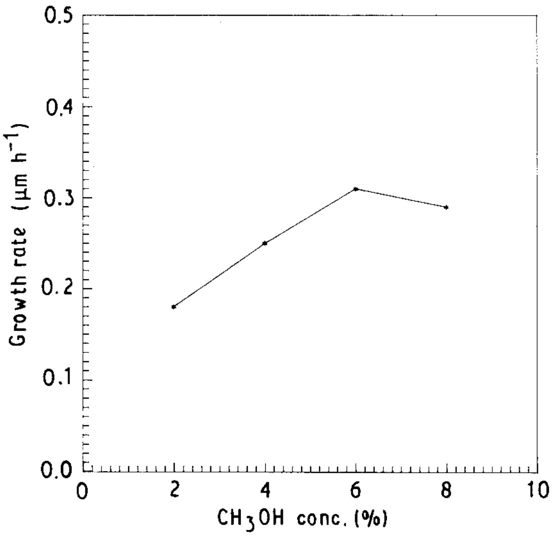


Figure 11 Growth rate versus methanol concentration.

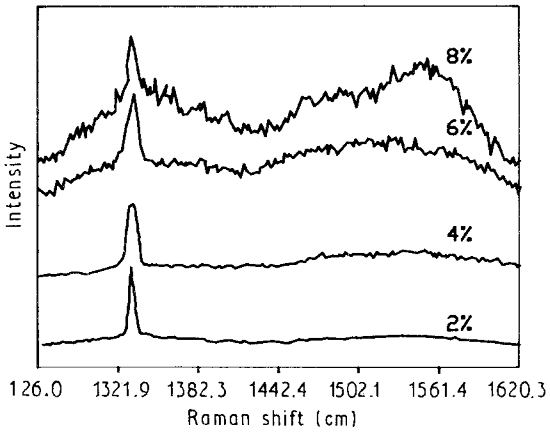


Figure 12 Raman shift spectra of samples grown with different methanol concentrations.

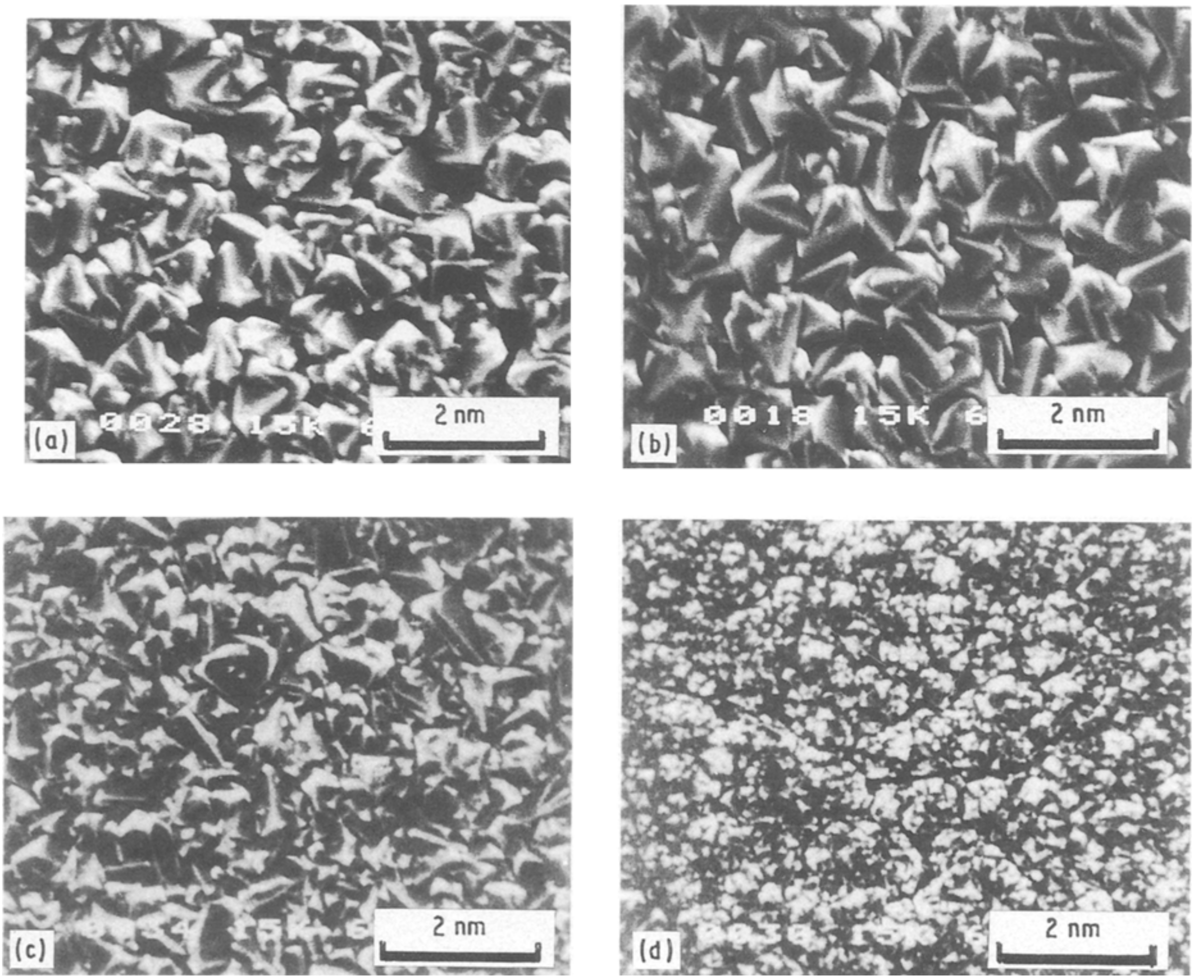


Figure 13 Scanning electron micrographs of samples grown with different methanol concentrations. (a) 2%, (b) 4%, (c) 6%, (d) 8%.

Here a series of experiments was carried out to investigate the effect of source concentration on growth rate and quality when methanol was used as the carbon source. Fig. 11 shows the results of growth rate versus methanol concentration in volume percentage of the carrier gases. In the lower concentration range, the growth rate increases with source concentration, as expected. After it reaches a maximum rate of 0.3 $\mu m\ h^{-1}$ at a concentration of 6%, it decreases probably due to the dominance of graphite deposition at higher source concentrations. Fig. 12 shows the Raman scatter spectra of the samples grown with different methanol concentrations. The results indicate clearly that the graphite content increases with source concentration, although all the samples appear to have some amount of graphite growth. Fig. 13 shows scanning electron micrographs of the corresponding samples which indicate that the morphological appearance agrees with the results of Raman spectroscopy analysis. Namely, diamond facet growth occurs for source concentrations less than 6%, while globular growth of the mixed phase of diamond and graphite takes place at source concentration of 8%.

In short, using methanol as the carbon source under the same temperature and pressure conditions, a much higher source concentration is required to grow epitaxial diamond with an appreciable growth rate. This is because methanol has a low carbon to oxygen ratio of 1. A higher concentration than isopropanol is required to provide the supersaturation conditions for nucleation and growth of diamond.

4. Conclusion

Filament-assisted pyrolytic growth of diamond films on silicon using methanol and isopropanol as source chemicals under reduced pressure conditions was investigated. The filament temperature, $T_f = 2250\,^\circ C$, substrate temperature, $T_s = 850\,^\circ C$, and reaction pressure, $P = 100$ torr, were found to constitute very favourable growth conditions. With the same source concentration of about 10^{-3} mol %, a growth rate of 1.2 $\mu m\ h^{-1}$ can be obtained from C_3H_5OH, while from CH_3OH the growth rate is about 0.2 $\mu m\ h^{-1}$ which is comparable with the literature data of growth rate from CH_4. The growth rate generally increases with source concentration. However, the quality rapidly deteriorates as the source concentration increases in both cases.

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