JOURNAL OF SOLID STATE CHEMISTRY 91, 47–56 (1991)

Nucleation and Growth of Diamond on Si, Cu, and Au Substrates

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Received August 8, 1990; in revised form October 23, 1990

A hot tungsten filament reactor was used to deposit diamond films on silicon, copper, and gold substrates. Diamond can be readily nucleated on all three substrates, but the nucleation density is greatly enhanced by prescratching with 0.25-μm diamond paste. Visual examination of photomicrographs of diamond crystallites formed on prescratched silicon substrates indicates that no new nuclei are formed between 1 and 2 hr of deposition. However, new nuclei are formed throughout this period when the substrate is copper or gold. Deposited diamond films adhered to silicon substrates, but could be readily removed from copper and gold substrates. © 1991 Academic Press, Inc.

Introduction

Recently, there has been considerable interest in the synthesis of diamond thin films. The unique properties of diamond, e.g., hardness, optical transparency, thermal conductivity, and chemical inertness have motivated this work. Diamond films have been prepared by microwave plasma chemical vapor deposition (*1*), induction thermal plasma chemical vapor deposition (*2, 3*), electron-assisted chemical vapor deposition (*4*), ion beam deposition (*5, 6*), dc arc discharge plasma chemical vapor deposition (*7–9*), and finally, hot filament deposition (*10*). All the products studied showed properties similar, to some extent, to those of natural diamond. In all of the techniques a hydrocarbon, e.g., methane, and hydrogen are dissociated to produce atomic hydrogen and hydrocarbon radicals. The importance of atomic hydrogen in the formation of diamond has been discussed by Janssen *et al.* (*11*). The films described in this paper were made by hot filament-assisted chemical vapor deposition, which is an inexpensive and easy method to use for the preparation of diamond films.

In the preparation of diamond films, the density of nucleation can be increased by prescratching the substrate surface with diamond particles. (*12*). The scratching process with diamond powder has been used to achieve complete film coverage of the substrate when the rate of deposition is low. However, where a high growth rate method is used, e.g., dc arc (*7–9*), such pretreatment is unnecessary. High rate processes result in films which are rough and are composed of large grains. There-

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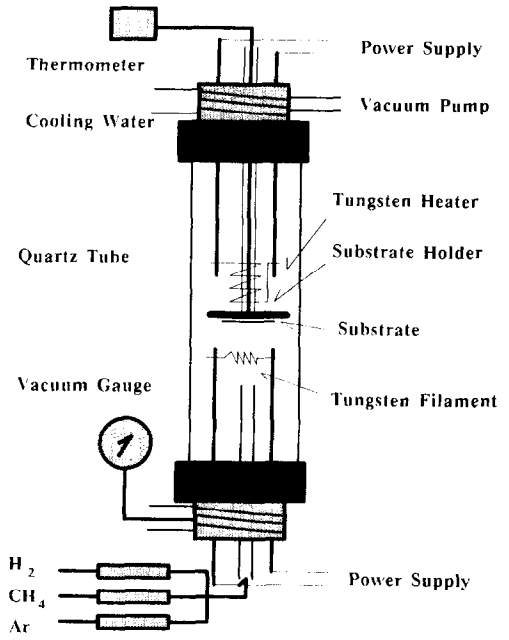

FIG. 1. Hot filament chemical vapor deposition (HFCVD) diamond growth system.

fore, the first concern of this study was to focus on the effect of diamond particle size used in the prescratch treatment of the substrate on the nucleation and growth of diamond films on various substrates.

Badzian *et al.* (*12*) indicated that a buffer layer of β-SiC or other carbides was necessary to improve adhesion of diamond on various substrates. This study will compare the nucleation, growth, and adhesion of diamond on silicon, where a buffer layer exists, with its growth on copper and gold, which do not form carbides.

Experimental

Reactor design. The apparatus for diamond deposition is shown in Fig. 1. The inner diameter of the reactor chamber was approximately 46 mm and its length was 42 cm. The silica substrate holder was centered in the reactor and the substrate was held downstream, above the filament, by four silica fingers. The distance between the substrate and the filament can be easily adjusted, and this was essential for preparing uniform films. A closely wound basket of 0.020-in. tungsten wire (no. 12070, E. F. Fullam, Inc., Latham, NY) was used as the precursor filament. A tungsten coil wound from 0.020-in. wire was positioned around the substrate holder above the substrate and served as a heater. The temperature of the substrate can be readily raised by increasing the voltage applied to this heater. The temperature of the precursor filament was measured with an optical pyrometer to within 5% accuracy, and the temperature of the substrate was determined by means of a thermocouple which was kept in contact with the substrate holder as shown in Fig. 1. The temperature at the substrate surface can be higher than that measured by the thermocouple as a result of radiation from the filament. Before a deposition experiment was made, the tungsten filament was first converted to tungsten carbide by heating at 2000(100)°C for 10 hr in a CH_4/H_2 (0.5 : 99.5) atmosphere and a pressure of 30 Torr.

Preparation of films. Substrates 1 cm^2 × 0.05 cm were cut from (100) wafers of silicon single crystal (Brookville Electronics, p-type) having a resistivity of .02 Ω-cm. These silicon substrates were cleaned by the procedure described by Fournier *et al.* (*13*) and received no further treatment. Copper and gold substrates were cut from 99.9% pure foil and the thicknesses of the 1-cm^2 substrates were 0.05 cm and 0.03 cm, respectively. The copper and gold substrates were polished flat with a Buehler minimet polisher using 600 grit silicon carbide sandpaper followed by aqueous slurries of 1 and 0.05 μm γ-Al_2O_3 on Texmet polishing cloth 40-7602 (Buehler). The final step was to place these substrates in an ultrasonic cleaner.

The copper and gold substrates were di-

TABLE I
CONDITIONS FOR DEPOSITION OF DIAMOND FILMS

Filament temperature	2000(100)°C
Substrate temperature	870(20)°C
Pressure	30 Torr
Ratio methane/hydrogen	0.5/99.5
Hydrogen/methane flow rate	30 sccm
Distance of substrate from filament	8 mm
Duration of deposition	1–6 hr

vided into two categories, those which were used as such after cleaning and those which were prescratched with diamond paste according to the following procedure. The treatment was performed by grinding the substrate for 15 min in the Minimet polisher with either 3- or .25-μm diamond paste on Texmet polishing cloth 40-7602 (Buehler). The substrate was then cleaned ultrasonically with acetone, methanol, and distilled water. In order to study the effects of scratching on diamond nucleation, several of the prescratched gold substrates were annealed in vacuum at 850°C for 4 hr and compared with unannealed substrates. The silicon substrates were divided into three categories: unscratched, scratched with diamond paste by the procedure described above, and scratched with 0.05-μm γ-Al_2O_3 by an analogous procedure. This last category was used to study the nucleation of diamond as a function of the prescratch material. Methane (Airco, Grade 2) and hydrogen (Matheson 99.999) were used as the gas sources. The conditions for the deposition of all the diamond films reported in this paper are given in Table I.

Characterization of products. X-ray diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high-intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). The patterns were taken from $12° < 2\theta < 100°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in./hr. Raman spectroscopy was recorded at room temperature in backscattering geometry using a SPEX 1403 Spectrometer. The 514.5-nm line was used for excitation. Electron microscopy studies were made with a JEOL-JSM-840F Microscope. It was operated at 1 kV to minimize the buildup of charge on the surface of the diamond films. Reflection electron diffraction patterns were collected with an RCA EMU-3 microscope operating at 100 KeV.

Results and Discussion

In order to prepare diamond films using a hot tungsten filament reactor, it is necessary to convert the tungsten to tungsten carbide. Unless this is done, the voltage to the heater cannot be adequately controlled. The conversion was carried out under the exact conditions used for film deposition (Table I). This process took about 10 hr and X-ray analysis of the filament indicated the formation of W_2C, WC, and WC_x.

Diamond can be readily nucleated on Si, Cu, and Au substrates without prescratching of the surface of the substrate with diamond particles (*12, 14*). However, the density of nucleation is very low. A high nucleation density can be achieved by scratching the substrates with 0.25-μm diamond particles. In this study, continuous films have been grown on Si, Cu, and Au substrates within 4 hr when they have been prescratched. Figs. 2a–2c show SEM images of films grown on these substrates under the conditions given in Table I. Microscopic examination showed trianglular crystallite surfaces characteristic of (111) faces. This is confirmed by X-ray diffraction data. All reflections can be indexed as belonging to cubic diamond and the intensity of the (111) reflection was greatly enhanced. The formation of diamond has also been confirmed by Raman spectroscopy, as shown in Fig. 3. The Raman spectra from natural diamond (*15*) is composed of one narrow peak at 1332 cm^{-1}. It can be seen from Fig. 3a that, in addition to the sharp

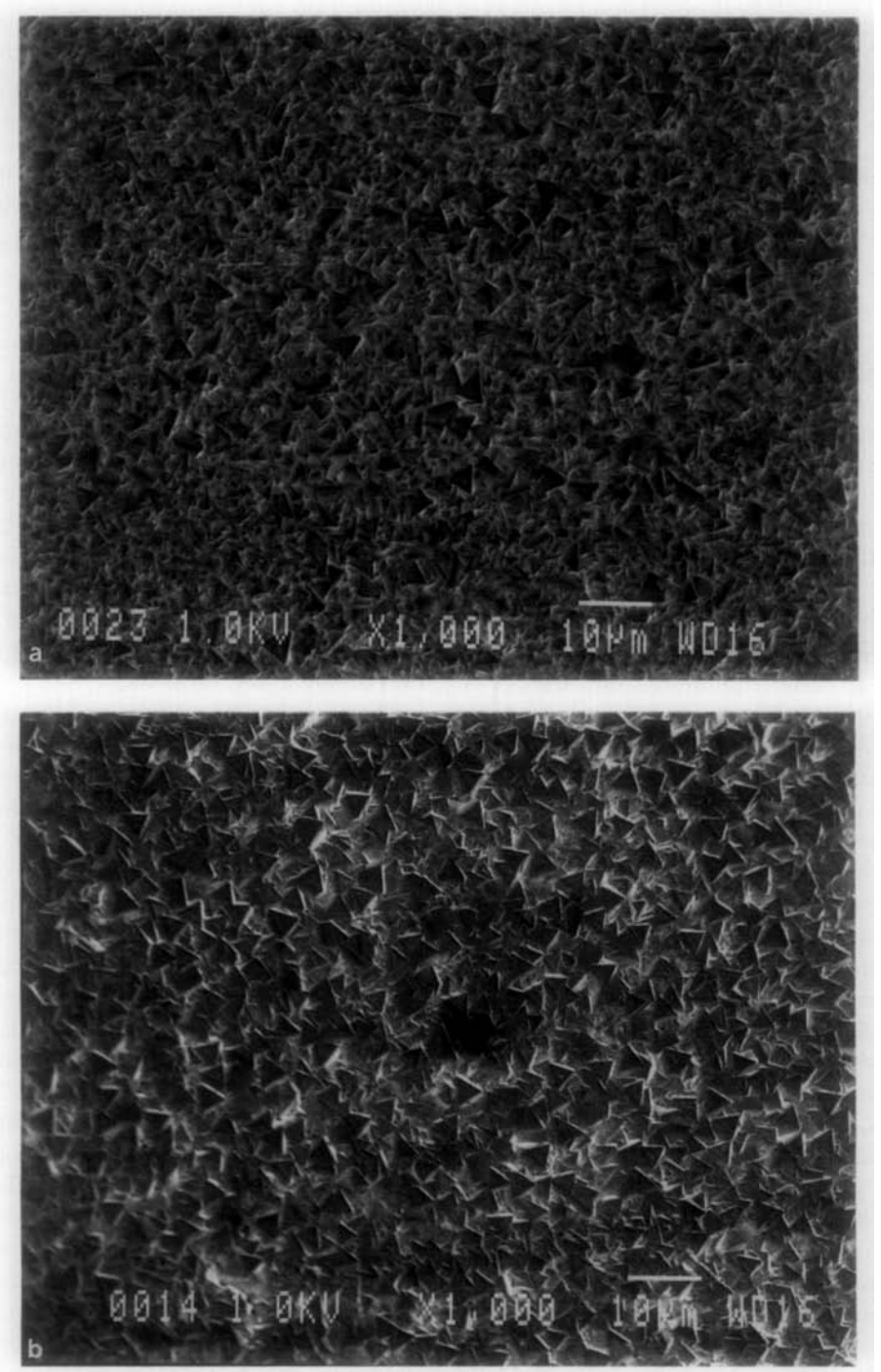

FIG. 2. Diamond films after 4 hr growth on prescratched substrates of (a) Si, (b) Cu, and (c) Au, (d) intersection view on Si.

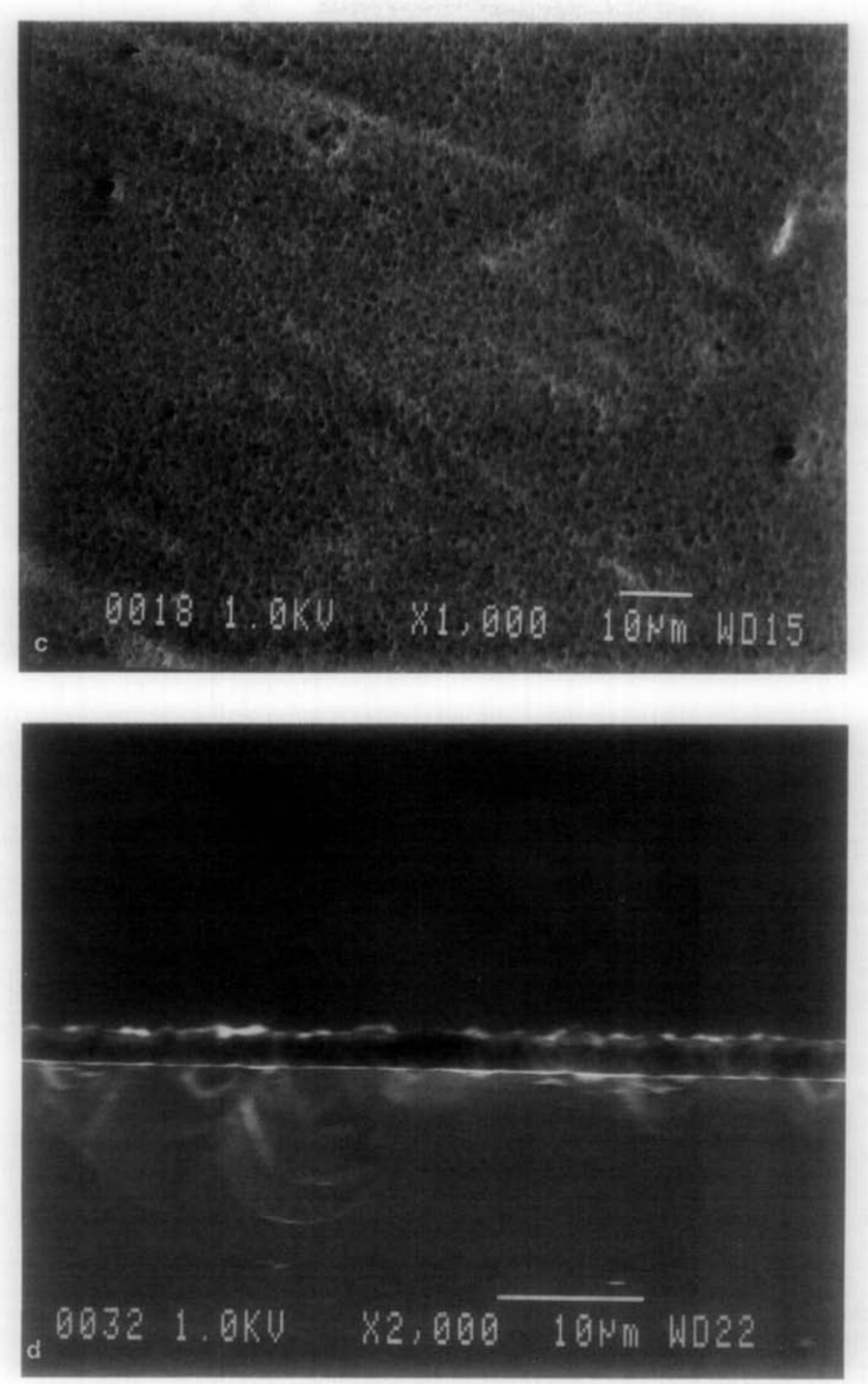

FIG. 2—*Continued*

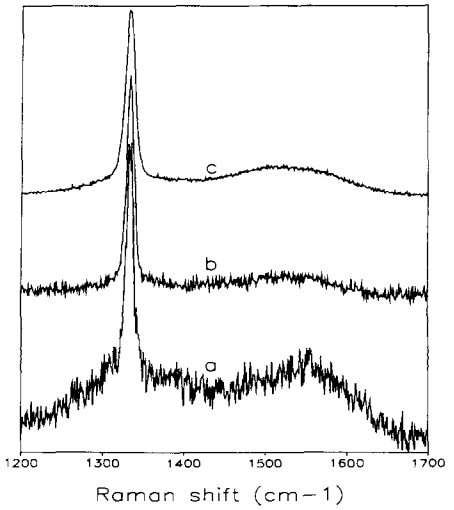

FIG. 3. Raman spectra of diamond films after 4 hr growth on prescratched substrates of (a) Si, (b) Au, and (c) Cu.

peak at 1333 cm^{-1}, there is a weak broad peak at approximately 1550 cm^{-1} for films deposited on silicon. This has been attributed to the existence of graphite-like nondiamond phases containing sp^2-bonded carbon atoms (*16, 17*).

It can be seen from Fig. 3 that the magnitude of the band at 1550 cm^{-1} is dependent on the substrate used. There is little evidence for the formation of such an amorphous graphite-like phase when films are deposited on copper and gold substrates (Figs. 3b and 3c). However, films produced on silicon substrates show clearly the formation of a Raman peak at 1550 cm^{-1} (Fig. 3a).

The density of nucleation of diamond on silicon substrates is dependent on the nature of the prescratch treatment. Table II compares the density of nucleation on an unscratched silicon substrate with those scratched by 0.05-μm γ-Al_2O_3 as well as by 3 and 0.25-μm diamond particles. These densities were obtained by multiplying the number of nuclei in a square centimeter of the photomicrograph by the appropriate scale factor. It can be seen that the density of nucleation remained unchanged by scratching the surface of the virgin substrate with γ-Al_2O_3. However, on scratching the surface with diamond particles, there was a marked increase in diamond nucleation. The deposition of a 3-μm thick diamond film (Fig. 2d) on a silicon substrate scratched with 0.25-μm particles took only 4 hr. The intersection view shown in Fig. 2d shows both the uniformity and the complete coverage of the film. However, complete coverage was not achieved after 4 hr when the substrate was treated with 3-μm particles. Only substrates prescratched with diamond showed any increase in deposition, and prescratching with the smaller particle gave greater film coverage.

Visual examination of photomicrographs taken of diamond crystallites which were formed on prescratched silicon substrates (3-μm diamond particles were used) indicates that no new nuclei are formed between 1 and 2 hr of deposition time. Figure 4 indicates that there is continued growth of the nuclei which initially formed on the scratched substrate. For substrates prescratched with 0.25-μm diamond particles, the larger number of nuclei which were apparent at the end of 1 hr gave almost complete coverage after 2 hr. However, new nuclei continue to form throughout this period when the substrate is Cu or Au.

TABLE II

THE EFFECT OF SCRATCHING ON THE DENSITY OF DIAMOND NUCLEATION ON SILICON

Treatment	Density of nucleation after 1 hr
Virgin surface	1×10^5
Scratched with 0.05-μm γ-Al_2O_3	1×10^5
Scratched with 3-μm diamond	1×10^7
Scratched with 0.25-μm diamond	1×10^8

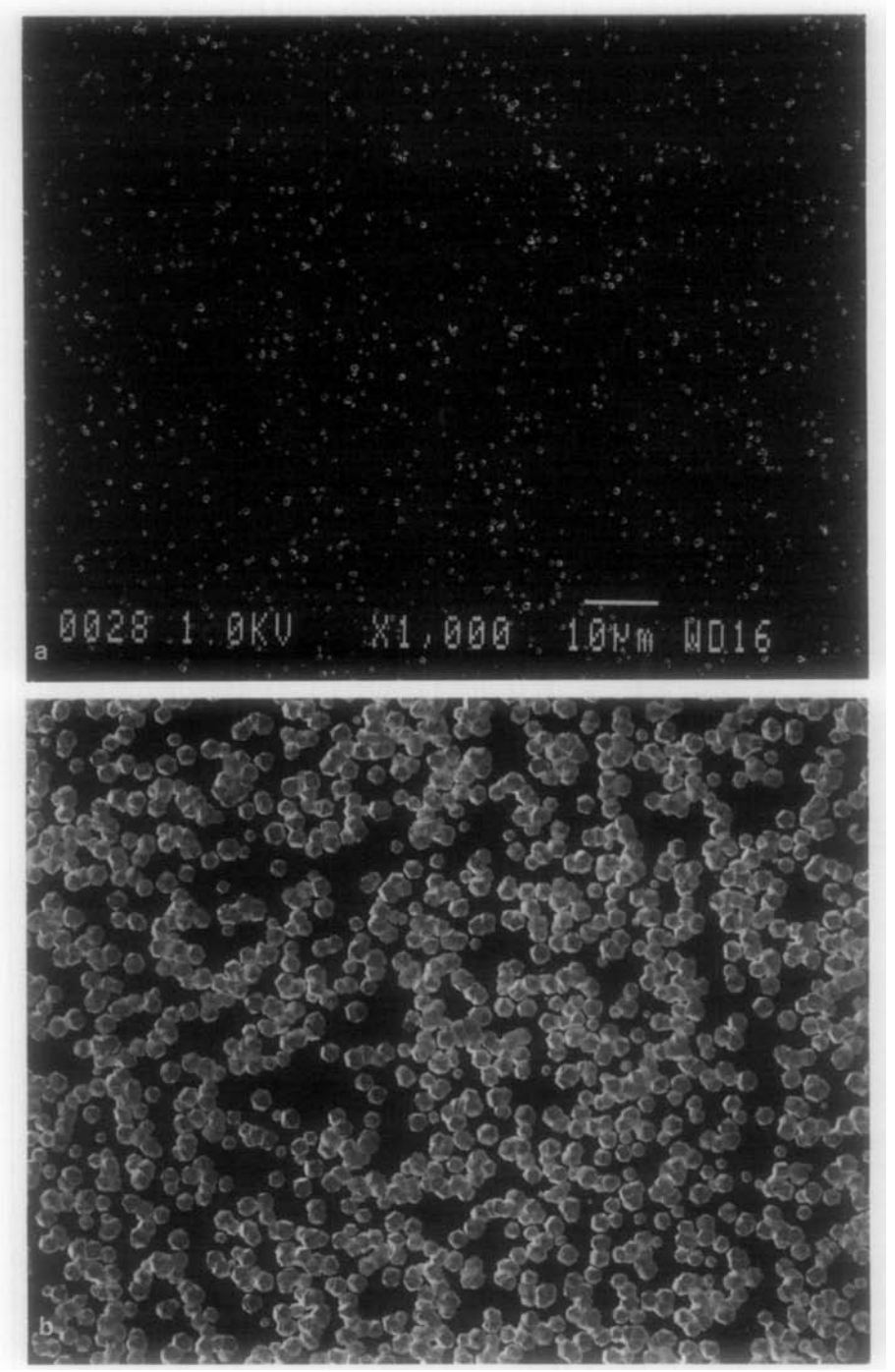

FIG. 4. Diamonds on prescratched Si (a) after 1 hr growth, and (b) after 2 hr growth. The magnifications are the same in both pictures.

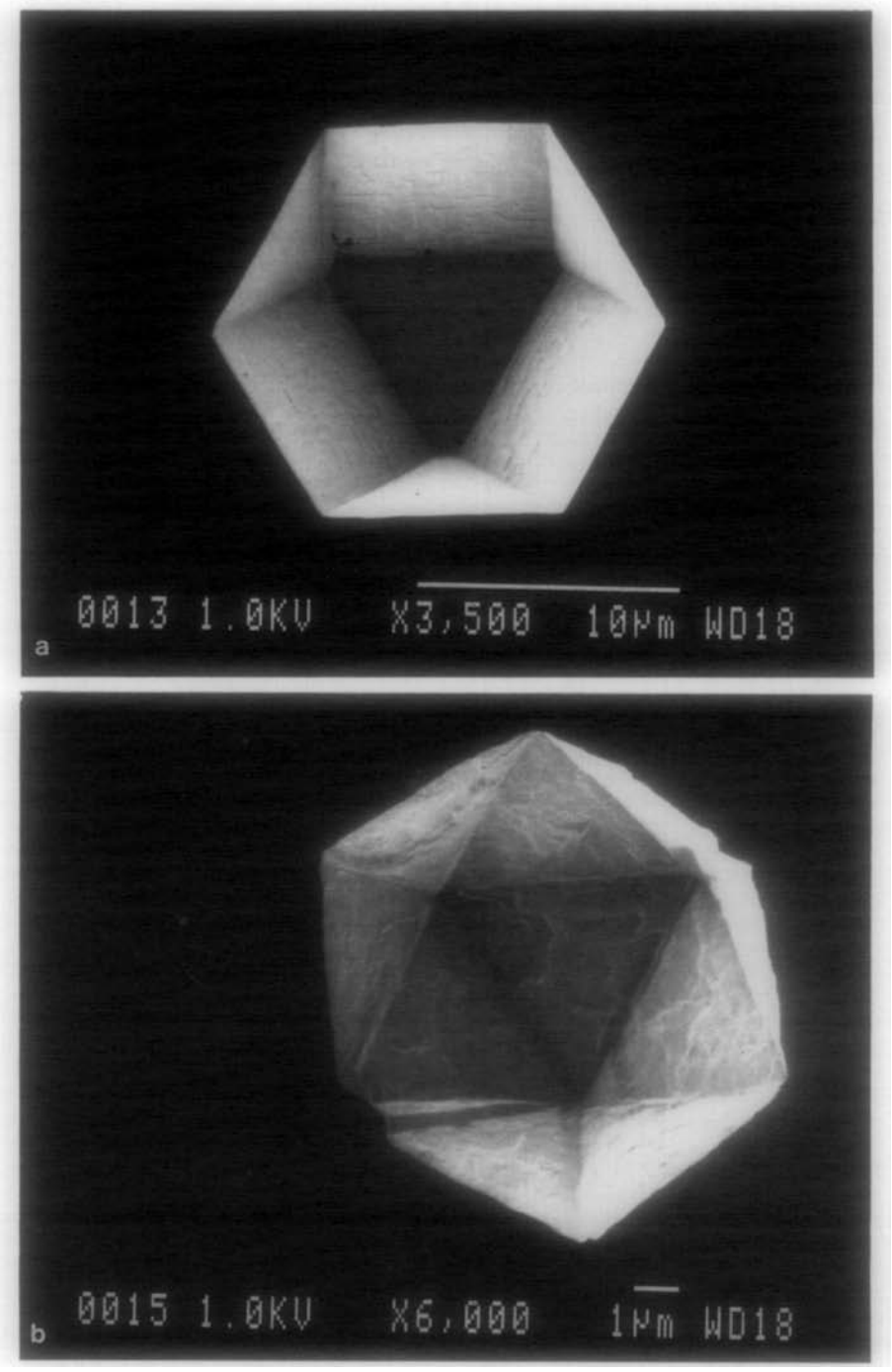

FIG. 5. (a) Octahedral and (b) "icosahedral" diamond particles after 6 hr growth on unscratched Au substrates.

The formation of continuous films on diamond-scratched substrates of Cu and Au indicates that carbide formation is not necessary to initiate nucleation sites for diamond. Neither copper nor gold are reported to form stable carbides. To further demonstrate that the treatment of the substrate surface plays a most important role for diamond nucleation, films were deposited under the conditions given in Table I for 4 hr on prescratched gold substrates, one of which had been annealed at 850°C. The unannealed prescratched substrate was ultrasonically cleaned and examined by means of electron diffraction; there was no evidence for the presence of diamond particles. Raman spectrascopic studies of diamond films grown for 4 hr on such substrates showed little evidence of the 1550-cm^{-1} band attributed to graphite-like sp^2 bonds (Fig. 3b). But Raman spectra obtained from 4 hr diamond films growth on the annealed substrate showed apparent formation of this additional phase. Whereas annealing of the prescratched gold substrate did not appreciably reduce the nucleation density, it did influence the formation of secondary phases.

The adhesion of diamond films to silicon substrates is undoubtedly due to strong bonding via a carbide intermediate. Moreover, the adhesion of films to Cu and Au substrates is poor and this is consistent with their inability to form carbide phases. Films prepared under the conditions given in Table I on these substrates were readily peeled off after the growth process.

Finally, large single diamond crystallites were obtained on an unscratched gold substrate after 6 hr of growth under the conditions given in Table I. Both octahedra and icosahedra crystallites are formed (Fig. 5). The formation of these crystallites is consistent with crystal growth theory (*18*) which predicts three-dimensional particle growth where there is little particle–substrate interaction. Williams *et al.* (*19*) studied multiply twinned crystallites formed by five tetrahedra sharing a common edge and showed that the 7.5° misfit present in such crystallites is accommodated at twin boundaries. Such misfits appear to be present in the "icosahedron" shown in Fig. 5b.

Conclusions

Diamond films have been deposited on silicon, copper, and gold substrates using a hot tungsten filament reactor. Diamond could be readily nucleated on all three substrate materials without prescratching with diamond particles, but the density of nucleation was low. It was shown that a high nucleation density could be achieved by scratching the substrates with fine diamond particles prior to film deposition. It was also shown that intermediate carbide formation is probably responsible for the good adherence of diamond films to silicon substrates.

Acknowledgments

This research was partially supported by the Office of Naval Research and by the GTE Laboratories, Incorporated, Waltham, Massachusetts. The authors also wish to acknowledge the help of K. Ostericher at GTE Laboratories, Incorporated for analyzing the substrate by electron diffraction and to M. Mello at Brown University for his assistance with the electron microscopy studies.

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