Novel Techniques for Selective Diamond Growth on Various Substrates

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There is a need for selective diamond growth in microelectronic and tool industries. This research was directed towards novel approaches in the selective diamond growth on non-diamond substrates. Diamond film was selectively deposited on the copper substrate by laser-hydrocarbon liquid (benzene C_6H_6) interaction at room temperature which was used as seed for subsequent growth of diamond by the hot filament chemical vapor deposition (HFCVD). Diamond was also selectively grown on the gold patterned alumina substrate by manipulating HFCVD processing conditions. Diamond was selectively grown on the patterned silicon wafer (without having any scratches).

Keywords
laser-liquid interaction, nano crystalline diamond film, patterning

1. Introduction

DIAMOND has many desirable properties for advanced microelectronics and coating applications, including (1) high hardness; (2) high thermal conductivity; (3) resistance to heat, acidic environments, and radiation; (4) excellent electrical insulating properties and control of conductivity by doping; (5) small dielectric constants; (6) large hole mobility; and (7) a large band gap (Table 1). Because of its superior properties, diamond holds promise for use in high-performance electronic devices and many other defense applications. In fact, the electrical properties of diamond films and metal/diamond contacts and the possible fabrication of test devices such as thermistors, light-emitting elements, and field-effect transistors are currently under active investigation. Diamond thin films can be grown by various chemical vapor deposition (CVD) techniques, including hot filament CVD (Ref 1, 2), thermal plasma CVD (Ref 3), microwave plasma CVD (Ref 4), and radiofrequency plasma (Ref 5).

A number of significant problems must be resolved before diamond films can be fully exploited. Techniques need to be developed for epitaxial diamond film growth, selective continuous thin-film growth, and mask materials that do not dissolve rapidly under an atomic hydrogen atmosphere. The nucleation density of diamond is dependent on surface conditions, such as the presence of scratches, diamond seeds, and so on. The growth morphology of diamond is dependent on deposition parameters—for example, gas composition, substrate temperature, and gas flow dynamics.

Novel techniques have been developed to grow diamond selectively on nondiamond substrates, including copper, gold-

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Table 1 Comparison of the properties of semiconductor materials

Property	Diamond	β-SiC	GaAs	Silicon
Lattice constant, Å	3.567	4.358	5.65	5.430
Thermal expansion, $\times10^{-6}$/°C	1.1	4.7	5.9	2.6
Density, g/cm^3	3.515	3.216	...	2.328
Melting point, °C	4,000	2,540	1,238	1,420
Band gap, eV	5.45	3.0	1.43	1.1
Saturated electron velocity, $\times10^7$ cm/s	2.7	2.5	1.0	1.0
Electron	2,200	400	8,500	1,500
Hole	1,600	50	400	600
Breakdown, $\times10^5$V/cm	100	40	60	3
Dielectric constant	5.5	9.7	12.5	11.8
Resistivity, Ω · cm	10^{13}	150	10^8	10^3
Thermal conductivity, W/(cm · K)	20	5	0.46	1.5
Absorption edge, μm	0.2	0.4	...	1.4
Refractive index	2.42	2.65	3.4	3.5
Hardness, kg/mm^2	10,000	3,500	600	1,000
Johnson figure of merit, $\times10^{23}$ WΩ/s^2	73,856	10,240	62.5	9.0
Keyes figure of merit $\times10^2$ W/(cm · s · °C)	444	90.3	6.3	13.8

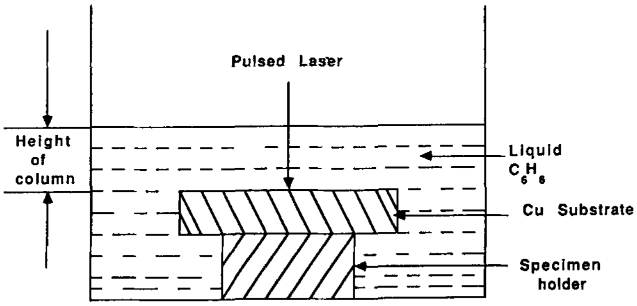


Fig. 1 Schematic of laser-mediated processing of a diamond thin film

patterned alumina, and silicon wafers. These techniques and the influence of the above-mentioned parameters are described in this paper.

2. Copper Substrate

Single-crystal (100) and polycrystalline copper specimens were immersed in liquid benzene (C_6H_6) (Fig. 1) and irradiated with high-power laser pulses from an Excimer laser (λ = 308 mm, $\tau = 30 \times 10^{-9}$ s, E = 1 to 4 J/cm^2). The liquid benzene layer

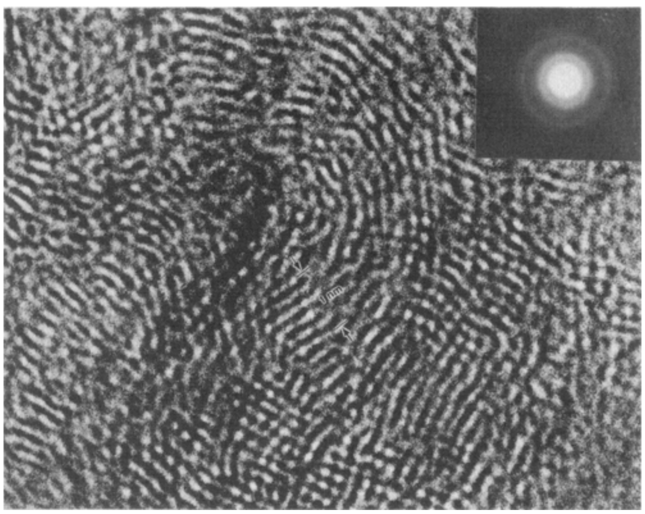


Fig. 2 HRTEM micrograph from the nanocrystalline region, showing carbon atoms with cubic patterns. The corresponding selected-area electron diffraction pattern is shown in the inset.

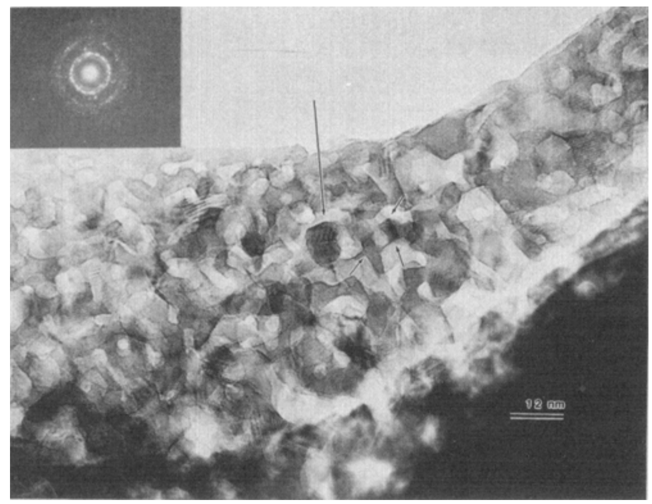
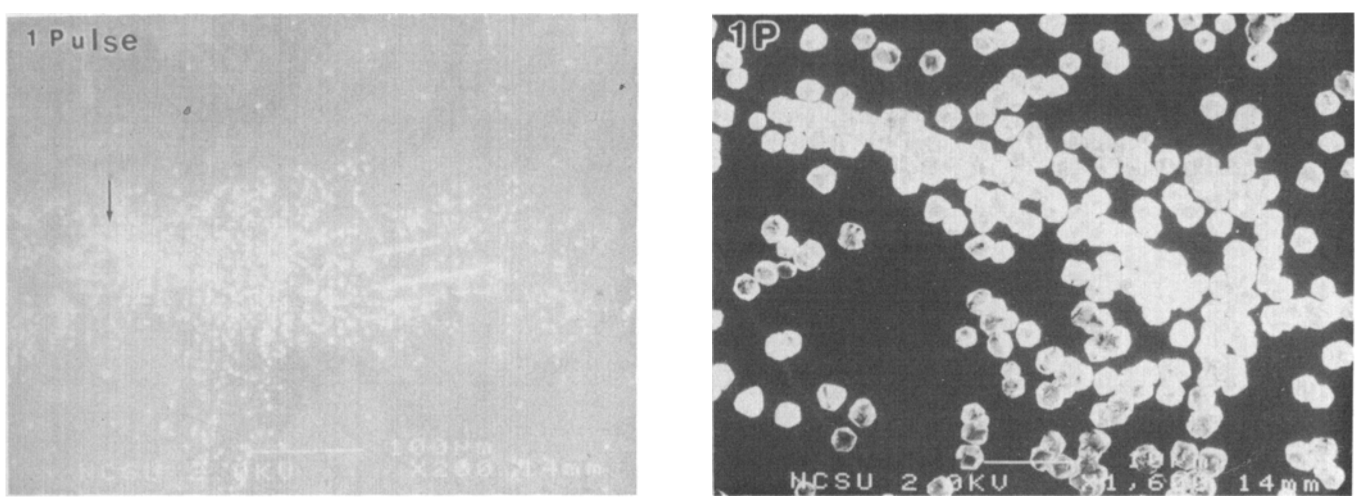
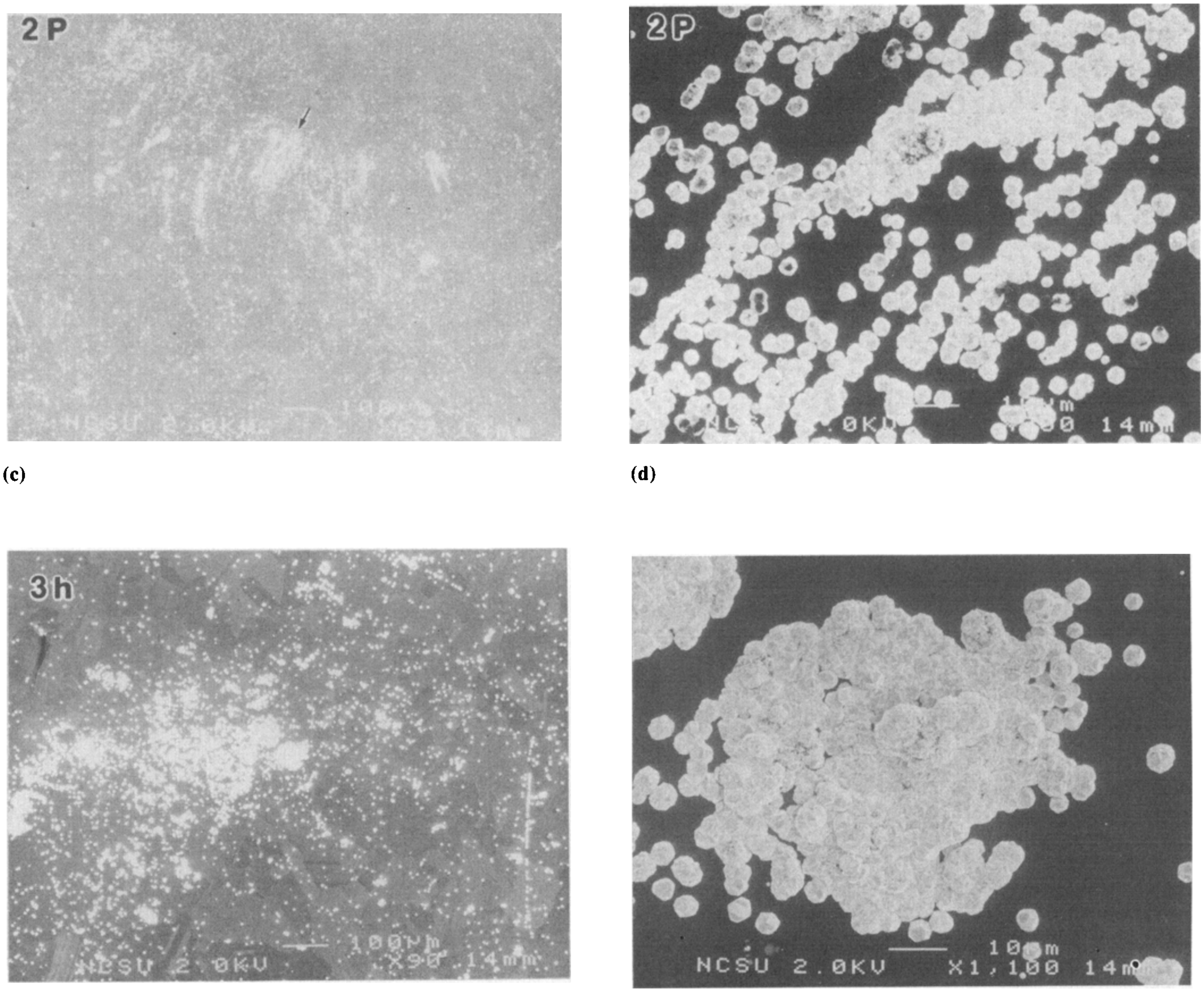


Fig. 3 HRTEM micrograph of a diamond thin film grown with a laser energy of 3 J/cm^2 and ten pulses. The corresponding diffraction pattern is shown in the inset.



(a) (b)

Fig. 4 SEM micrographs of laser-treated samples after diamond deposition by the HFCVD process at 800 °C for 3 h, showing selective growth and high density of diamond as a function of laser pulse at a laser energy 3.7 J/cm^2. (a) One pulse. (b) Higher-magnification view of the region indicated by the arrow in (a). (c) Two pulses. (d) Higher-magnification view of the region indicated by the arrow in (c). (e) Four pulses. (f) Higher-magnification view of the region indicated by the arrow in (e) (continued)



(c) (d)

(e) (f)

Fig. 4 (cont.) SEM micrographs of laser-treated samples after diamond deposition by the HFCVD process at 800 °C for 3 h, showing selective growth and high density of diamond as a function of laser pulse at a laser energy 3.7 J/cm^2. (a) One pulse. (b) Higher-magnification view of the region indicated by the arrow in (a). (c) Two pulses. (d) Higher-magnification view of the region indicated by the arrow in (c). (e) Four pulses. (f) Higher-magnification view of the region indicated by the arrow in (e)

Table 2 ***d*-Spacing (in Å) of diffracting rings in polycrystalline diamond thin film**

Number of rings	Measured *d*-spacing	3*C*-cubic diamond	2H-hexagonal diamond	6*H*-hexagonal diamond
1	2.06	2.06(111)	2.06	2.06
2	1.89	1.77(200)	1.92	1.93
3	1.52	...	1.50	...
4	1.30	...	...	1.37
5	1.27	1.26(220)	1.26	1.26
6	1.20	...	1.17	1.16
7	1.04	...	1.07	1.07
8	0.97	...	1.055	1.06

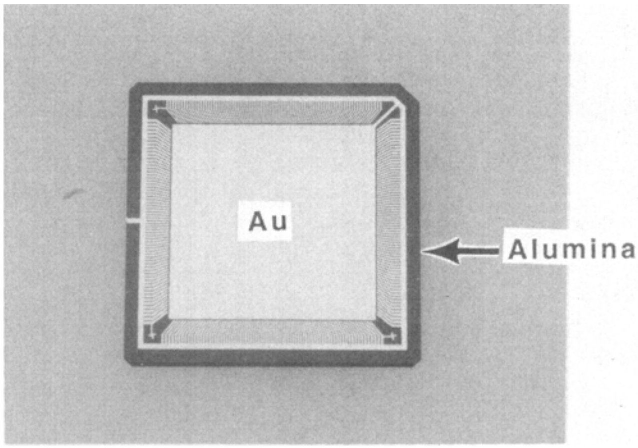
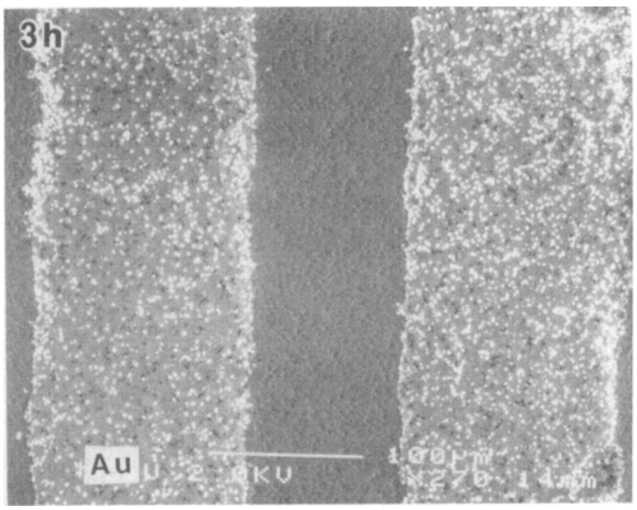


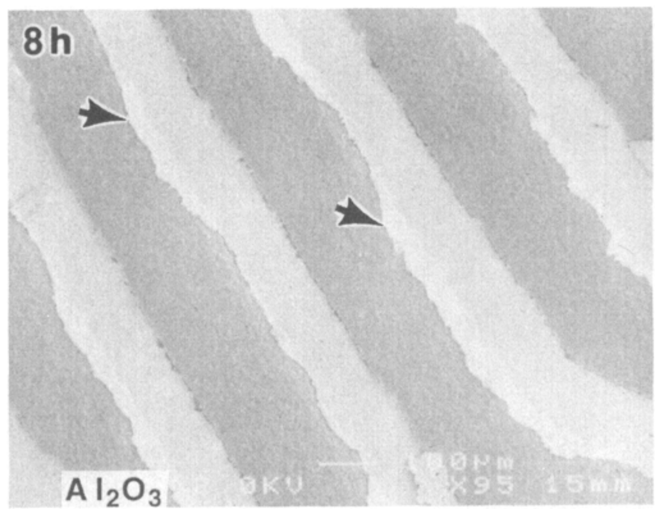
Fig. 5 Gold-patterned alumina substrate (1 by 1 by 0.2 cm)

above the specimens was approximately 3 mm, and the copper specimens were typically 10 by 10 mm. A high-resolution transmission electron microscopy (HRTEM) micrograph of the thin film grown on the copper substrate as a result of pulsed laser irradiation (E = 3 J/cm^2 and five pulses) is shown in Fig. 2. The corresponding selected-area electron diffraction pattern (inset) shows the ring patterns representative of a face-centered cubic polycrystalline material. The characteristics of (111) and (220) rings were indicative of the presence of diamond cubic tetrahedra in the film (Ref 6).

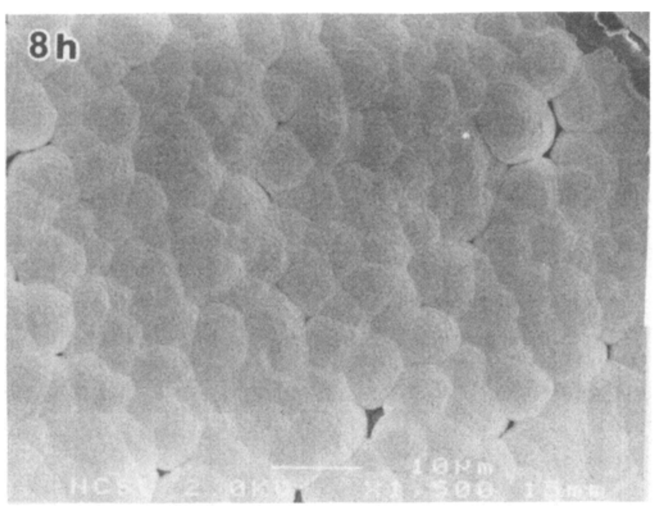
Figure 3 shows an HRTEM micrograph of the diamond thin film grown with a laser energy of 3 J/cm^2 and ten pulses. Again, the corresponding diffraction pattern is shown as an inset. The measured interplanar spacing of the diffracted spots is given in Table 2, which compares the d-spacings with reported values for diamond, lonsdaleite (2H-hexagonal diamond), and 6H-



(a)



(b)



(c)

Fig. 6 SEM micrographs showing the selective growth of faceted diamond crystallites on a gold substrate using the HFCVD process. (a) Growth time, 3 h; T_s, 815 °C; methane, 1.5%. (b) Growth time, 8 h; T_s, 815 °C; methane, 1.5%. (c) Higher-magnification view of (b) showing spherical diamond crystallites

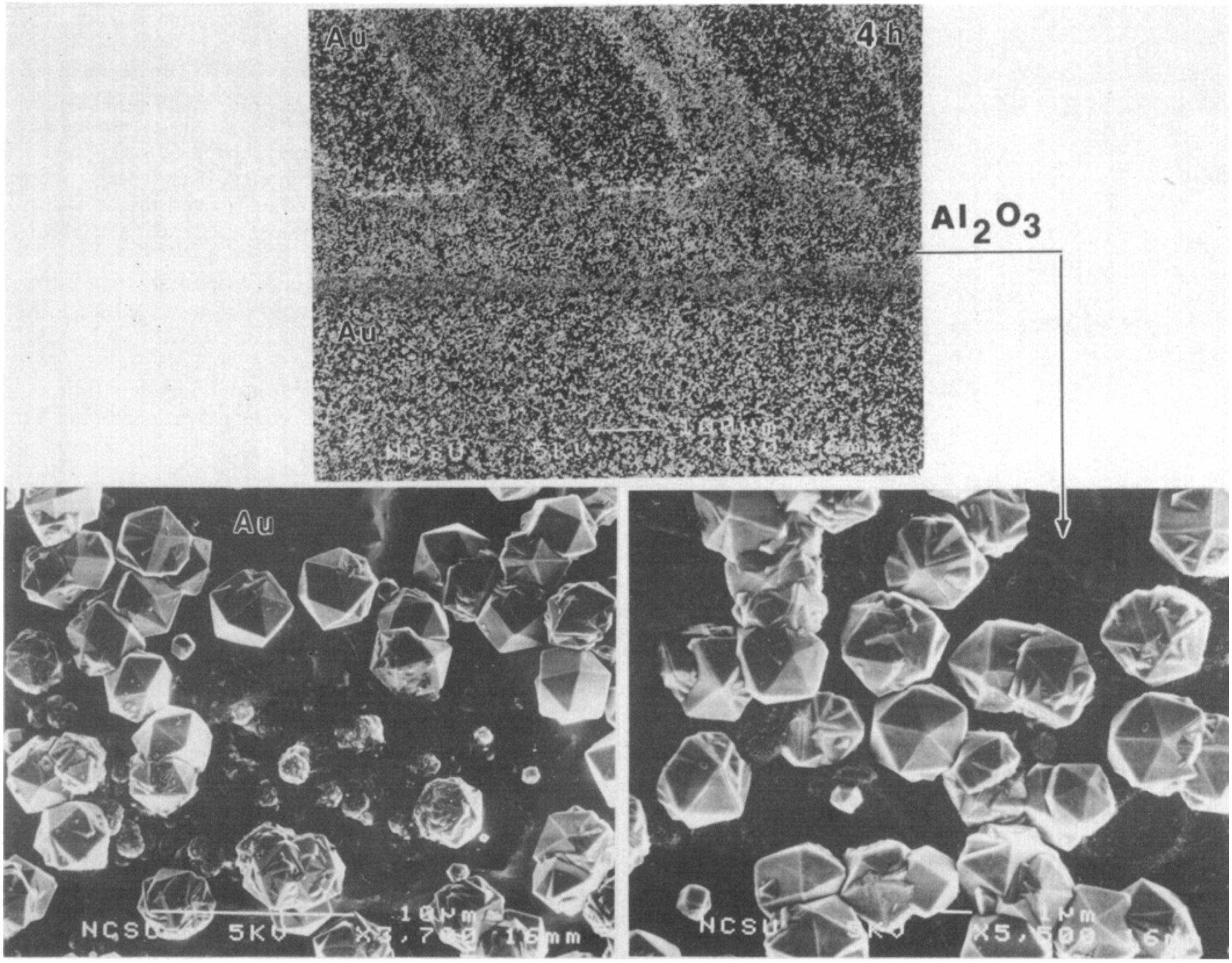


Fig. 7 SEM micrographs showing the selective growth of faceted diamond crystallites on gold surfaces using the HFCVD process. The crystallites were grown at a T_S of 850 °C for 4 h. (a) View showing the outlines of the gold surfaces on the alumina substrate. (b) Higher-magnification view of the diamond crystallites on a gold surface. (c) Higher-magnification view of the diamond crystallites on an alumina surface

hexagonal diamond. The synthesis of a diamond thin film from a liquid hydrocarbon such as benzene by laser/liquid/solid interaction is an innovative technique. Details of this research work have been published in Ref 6.

To determine whether the diamond produced by a laser/solid interaction process acts as a seed for diamond growth, the laser-treated copper specimens were subjected to a hot-filament chemical vapor deposition (HFCVD) process. A tungsten filament, at a temperature of about 1950 °C as measured by an optical pyrometer, was positioned approximately 8 mm above the substrate. A premixed gas flow of $CH_4 + H_2$ was directed onto the substrate through an orifice above the filament source. The gas flow was measured by a flowmeter in terms of standard cubic centimeters per minute, and gas flow was controlled by a mass flow controller. The system was continuously pumped during deposition by a mechanical vacuum pump to maintain a constant pressure of 20 torr. The substrate temperature (T_s) varied from 775 to 935 °C during deposition, the methane in the gas mixture of $CH_4 + H_2$ varied from 1.0 to 2.0%, and the deposition time varied from 3 to 8 h. Figure 4 presents scanning electron microscopy (SEM) micrographs showing a high density of diamond crystallites in the laser-irradiated area as a function of laser pulses (i.e., at a laser energy of 3.7 J/cm^2 and one, two, or four pulses). In certain areas, the density of diamond was significantly higher and appeared as a continuous diamond film. As the number of laser pulses increased from one to four, the density of diamond crystallites also increased. At four pulses, an almost continuous film (about 40 to 50 μm) was achieved. The diamond crystallites appeared to be faceted, with an average size of about 2 to 3 μm. These results indicate that the laser interaction produced fine diamond particles that acted as seeds for further growth of diamond.

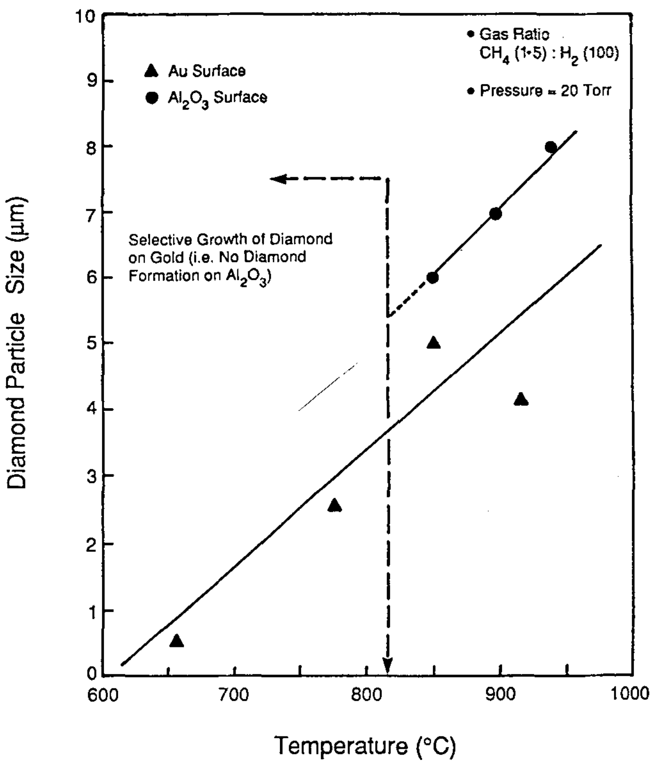


Fig. 8 Diamond crystallite size as a function of temperature for gold and alumina

3. Gold-Patterned Alumina Substrate

Gold-patterned alumina substrates (Fig. 5) are used extensively in the computer industry. The gold liner serves as an interconnector and thermal conductor to extract the heat generated during computer operation. The thermal conductivity of diamond is about five times greater than that of gold; therefore, applying diamond coatings on such materials should improve thermal conductivity.

A section of gold-patterned alumina substrate (1 by 1 by 0.2 cm) was used as a specimen in the present study. Diamond was selectively grown on the specimen by the HFCVD process. Figures 6(a) to (b) are SEM micrographs showing the growth of diamond crystallites on the gold surface at a deposition temperature of 815 °C for up to 8 h. The coverage of diamond crystallites was determined to be about 20%. Diamond growth was not observed on the alumina substrate at this temperature. The diamond crystallites were faceted, with an average size of 2.5 µm.

Continued growth at this temperature for 8 h produced a continuous diamond thin film only on the gold surface, with negligible growth on the alumina substrate (selective deposition). Overgrowth of diamond crystallites on gold was also observed (see arrows in Fig. 6b). During the extended growth, the growth morphology of diamond changed from faceted crystallites to spherical particles (Fig. 6c). It is important to note that selective growth of diamond was observed only up to a deposition temperature of 815 °C. At a higher deposition temperature of 850 °C (for 4 h), the selectivity of diamond growth was destroyed and about 20% of the alumina substrate was covered with a diamond film. In addition, the coverage of diamond on the gold surface was dramatically increased to about 95%, with a crystallite size of about 5 µm (Fig. 7)

The size of the crystallites and the extent of diamond coverage were dependent on the substrate temperature, which ranged from 775 to 915 °C. Diamond coverage on the gold surface increased as a function of increasing substrate temperature: from 20% at 775 °C to about 90% at 850 °C to almost 100% at 915 °C. Similarly, diamond coverage on alumina was found to be negligible up to a temperature of approximately 815 °C. It then increased as a function of increasing substrate temperature to nearly 95% at a deposition temperature of 915 °C. Average diamond size was also found to increase linearly as a function of temperature (Fig. 8). Thus, a temperature range was established for selective growth of diamond on a gold surface with limited growth on the alumina substrate.

4. Silicon Substrate

Various techniques have been employed to grow continuous diamond thin films on silicon substrates, including reactive-ion etching, amorphous-silicon masking, and a photolithographic method (Ref 7). These processes use diamond seeds for the selective growth of diamond and involve various time-consuming and costly steps. The present effort undertook to selectively grow diamond on a silicon substrate without using diamond seeds and simply monitoring the process parameters.

Square patterns (ranging in size from 2 to 100 µm) were made on the silicon substrate by standard etching procedures (Ref 7, 8). The depth of the square patterns was kept constant at about 0.5 µm. The HFCVD process was employed to grow diamond selectively in these wells at a CH_4:H_2 gas ratio of 1:100.

Selective diamond growth was observed in these square patterns (Fig. 9). The 5 and 10 µm square patterns appeared to created favorable conditions for selective growth. However, the average size of the diamond within the patterned region was about 50% larger than the diamond grown on the flat, unpatterned surface. The morphology of diamond inside the square pattern appeared to be cubo-ocathedron. As the concentration of methane was increased from 1.0 to 1.5% in the gas mixture, the density and growth rate of diamond were also increased on the silicon substrate (Fig. 10), but selective growth of diamond was destroyed.

It is important to mention here that it generally is difficult to grow diamond on silicon substrates without surface preparation. The density of diamond grown on silicon is reported to be increased by scratching the surface with diamond paste (Ref 8). During polishing, it is assumed that the diamond particles present in the paste become embedded in the silicon surface and act as seeds for the growth of diamond crystallites. In the present investigation, no diamond paste was used or scratched on the silicon substrate. It is evident that the presence of the square

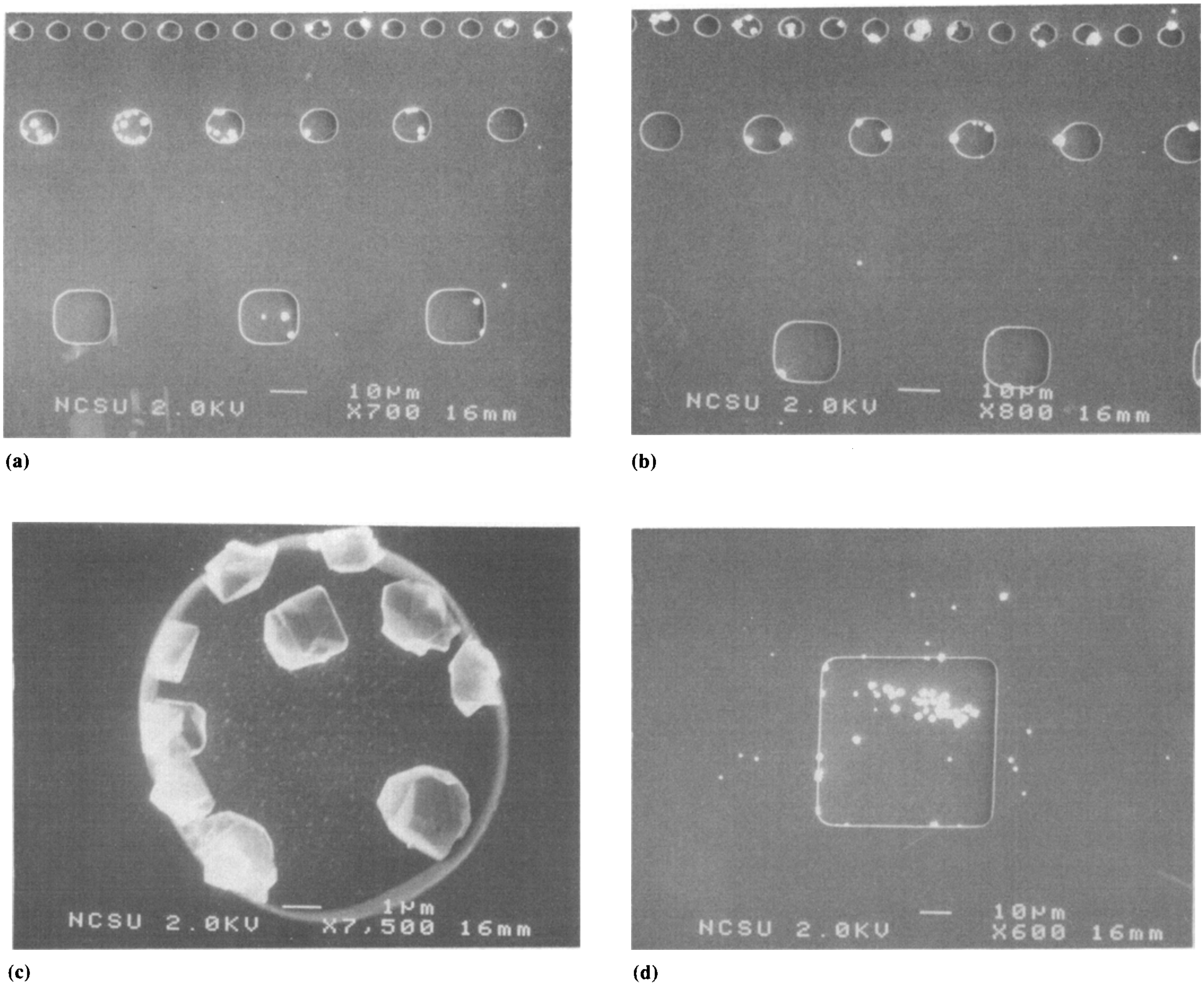


Fig. 9 SEM micrographs showing the selective growth of diamond within the wells of a silicon substrate. The diamonds were grown with a methane concentration of 1.0%.

patterns was the only factor that contributed to the increase in the growth density of diamond crystallites.

5. Conclusions

Diamond was synthesized on a copper substrate from liquid benzene in air by laser/liquid/solid interaction. These diamonds then acted as seeds for the subsequent growth of CVD diamond. Diamond was found to grow selectively on a gold surface at a relatively lower temperature (<800 °C) than on an alumina surface. Diamond was selectively grown on a silicon substrate with square patterns (2 to 5 µm) that favored the nucleation and growth of diamond within 0.5 µm deep wells.

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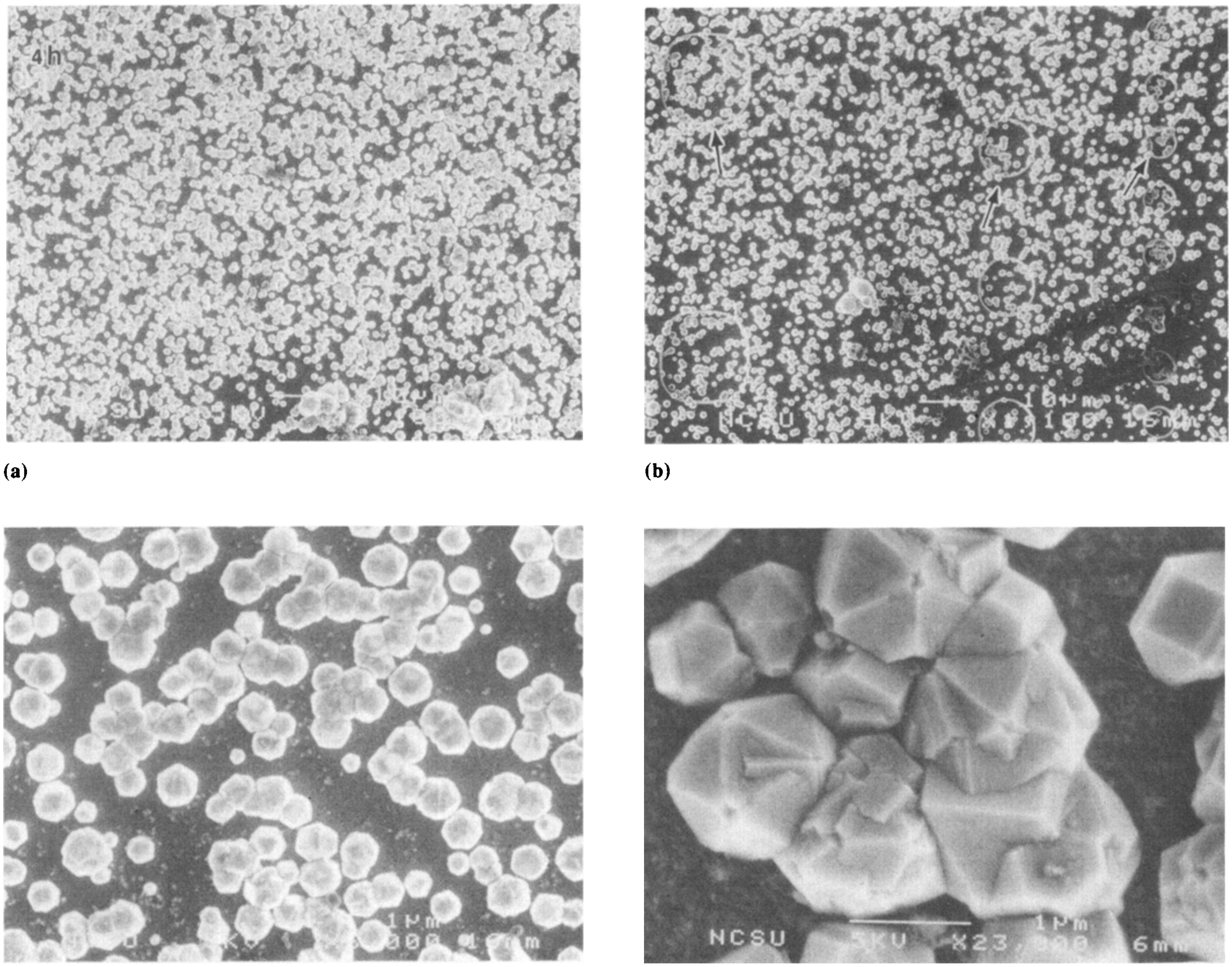

(a) (b) (c) (d)

Fig. 10 SEM micrographs showing the high density of diamond growth on a silicon substrate, resulting from the use of a methane concentration of 1.5%. Arrows in (b) indicate location of diamond growth in the wells.

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