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**DIAMOND EPITAXY AND DIAMONDLIKE COATINGS**

**FINAL REPORT**

**J. NARAYAN**

**June 10, 1993**

**U. S. ARMY RESEARCH OFFICE**

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**NORTH CAROLINA STATE UNIVERSITY**

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## 1. FOREWORD

Diamond has a number of unique and desirable properties for structural and electronic device applications. Diamond has the highest number density of atoms ( $1.77 \times 10^{23} \text{ cm}^{-3}$ ), which coupled with strong interatomic potentials (elastic constant =  $1.08 \times 10^{13} \text{ dyn cm}^{-2}$ ) leads to highest hardness. The thermal conductivity of type II-a diamond (20 W/cm.K at room temperature) is the highest of all known materials, about 5 times higher than the value for copper. The thermal coefficient of expansion is quite small ( $0.8 \times 10^{-6} \text{ K}^{-1}$  at 293 K). Attractive properties from the standpoint of electronic devices include radiation resistance, wide band gap (5.45 eV), low dielectric constant (5.5), high electron and hole mobilities ( $2200 \text{ cm}^{-2}/\text{V}\cdot\text{sec}$ ), large refractive index (2.42) and stability at high temperature ( $>500^\circ\text{C}$  in air). Because of high carrier saturation velocity, high breakdown voltage, relatively low dielectric constant, and high thermal conductivity, diamond is extremely attractive for high-frequency and high-power device applications including high-voltage optoelectronic switching devices and radiation resistant integrated circuits [1].

Diamond phase is metastable at normal pressure and temperature. Graphite to diamond transformation is associated with a change in enthalpy of  $1.872 \text{ KJ}\cdot\text{mol}^{-1}$  and an entropy change of  $-3.22 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ . The solid state transformation under thermodynamic equilibrium requires very high pressures and temperatures ( $>200 \text{ kbar}$  and  $>4000\text{K}$ ). However, nonequilibrium routes of chemical vapor deposition can be employed for synthesis of diamond [2,3]. Under this category, different methods of processing are employed, for example thermally assisted CVD (hot filament, hot flames,  $\text{CO}_2$  laser) and plasma assisted CVD (high frequency, microwave, DC discharge) [4-13].

We have mainly used the hot filament chemical vapor deposition (HFCVD) and laser-assisted HFCVD techniques for processing of diamond films. During the deposition process, any graphitic phase formed is etched away preferentially by atomic hydrogen formed in the presence of high temperature at the filament. The quality of the diamond films depends strongly on the efficiency of removal of graphite layers. Diamond films of p-type can be made by doping with boron by mixing diborane in the reactant gas consisting of appropriate proportions of methane and hydrogen. The formation of continuous, defect free diamond films, particularly for advanced electronic applications, requires detailed understanding of nucleation and growth of diamond phase, epitaxial growth processes, formation of defects, and nature of interface interactions between the film and the interface. To realize this ultimate goal in the field of diamond, we need an integrated effort including: (a) novel methods of synthesis and processing; (b) theory, modelling and simulation; and (c) atomic scale characterization of defects and interfaces. From the investigations on atomic structure of defects, it is possible to devise means to manipulate defect microstructures and minimize their harmful effects. As an example, electrically active dislocations and grain boundaries can be converted into electrically inactive defects. Thus, polycrystalline diamond films with electrically inactive dislocations and grain boundaries may offer hope for fabrication of advanced electronic devices. This report describes the progress made in the last three years under the existing grant.

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## 3. PROGRESS OF RESEARCH

### 3.1 Summary of Research on diamond and diamondlike films

During the three year period of the program, a significant progress has been made in synthesis and processing, and characterization and modelling of defects in diamond and diamondlike films [12-33]. Specific areas of research include: (1) Enhancement of nucleation and adhesion of diamond films on nondiamond substrates, (2) Laser patterning of diamond films on nondiamond substrates, (3) Novel methods of formation of diamond films on nondiamond substrates, (4) Characterization of diamond films : defects and grain boundaries, and (5) Laser Processing and characterization of diamondlike films. These

areas were addressed to enhance our understanding of nucleation and growth of thin films, adhesion and interfacial properties, epitaxial nature of diamond films on nondiamond substrates, selective deposition of diamond films, and novel methods for processing diamond-like films having improved physical and mechanical properties. A total of 20 refereed journal articles and 5 conference proceedings papers have been published, and a U. S Patent has been filed under the present contract.

### **3.2. Enhancement of nucleation and adhesion of diamond films on nondiamond substrates<sup>20</sup>.**

Deposition of diamond thin films on nondiamond substrates has been carried out by several researchers by a variety of chemical vapor deposition techniques such as hot filament CVD, plasma CVD etc.. The nondiamond substrates used for this purpose can be classified into two main categories: (i) strong carbide formers and (ii) substrates with no affinity for carbon. The latter substrates tend to have poor adhesion. Nucleation of diamond is generally difficult in both classes of substrates. In order to form continuous diamond films, it is necessary to understand the nucleation and growth phenomena. Adhesion of the diamond films is very important for practical applications. Adhesion is primarily determined by bonding characteristics and interfacial reactions between the film and the substrate. Atomically clean surface is essential for developing diamond films with good adhesion.

We have made preliminary investigations of the enhancement of nucleation and improvement of adhesion of diamond films deposited by hot filament CVD technique. In this method, the surface of a noncarbide forming substrate, in particular copper or stainless steel, was cleaned using laser pulses. A thin layer of carbon was deposited on the substrates by laser deposition and further melting of the underlying layer was carried out in-situ by laser pulses. Using a typical 25 nsec excimer laser, the melting and solidification cycle was completed in less than 100 nsec. The carbon film on the surface has been found to convert into fine microcrystalline particles of diamond. Residual carbon was blasted off the surface due to high thermal energy and stresses associated with the laser source. A similar method of enhancing nucleation was carried out by forming carbides on carbide forming substrates.

Adhesion of diamond films on nondiamond substrates is an important property that dictates the use of diamond coatings for varieties of applications. Our preliminary experiments illustrate that diamond particles can be embedded into the substrate with the laser surface treatment. After the initial HFCVD and before a continuous diamond thin film is formed, the specimen is irradiated with nanosecond laser pulse to melt a thin layer of underlying substrate. The wavelength and the laser parameters are chosen in such a way that there is minimum interaction between the photon beam and the diamond particles. As a result, the diamond particles are embedded into the molten layer of substrate and become integral part of the substrate. A few pulses were shown to be effective to accomplish this result, as shown in figure 1. Further deposition was continued to build thicker layers of diamond on the copper substrate. These preliminary experiments proved to be very useful in embedding diamond particles in copper matrix. Further investigations are needed in understanding the mechanisms of embedding the diamond into copper and also in developing alternate techniques for improvement in adhesion.

### **3.3. Laser patterning of diamond films on nondiamond substrates<sup>21</sup>, Patent (pending).**

Patterning of diamond film is an important consideration for microelectronic applications. We have made preliminary investigations of the effectiveness of laser patterning, its selectivity as well as simplicity of implementation. During these studies of laser patterning, we were also able to gain interesting insight into the nucleation characteristics of diamond. Silicon (strong carbide former) and copper (with no affinity to carbon) substrates have been employed for these experiments. These substrates were mechanically polished with diamond or alumina powders separately before laser annealing to achieve selectivity. These two pretreatments resulted in extensive scratches in both cases in the near surface regions. The pretreated specimens were selectively laser annealed before HFCVD. An illustrative example of laser patterning after HFCVD is shown in fig. 2. From these preliminary studies on deposition characteristics in the specimens treated with diamond and alumina powders, we established that the residual diamond seed crystals introduced during diamond abrasion play a central role in diamond nucleation and that the role of surface damage and microcracks is relatively insignificant. The diamondlike carbon deposited separately has also been found to be effective in aiding the nucleation of diamond phase.

### **3.4 Novel methods of formation of diamond films on nondiamond substrates<sup>22,34</sup>.**

Diamond nucleation on silicon was found to be very insignificant. However, as mentioned previously, abrading the substrate with diamond grit was found to be effective for nucleation enhancement wherein diamond particles provide additional nucleation sites during subsequent deposition. In other cases such as iron substrate or iron alloys or hastelloy, diamond nucleation was very low even with pre-abrasion treatment. In these cases the high mobility of carbon may be associated with lack of nucleation centers. Intermediate layers of c-BN are extremely useful because of the small lattice mismatch and compatible interatomic potentials with diamonds. Diamond deposition on Si (100) with c-BN has been carried out successfully and the diamond nucleation has been studied as a function of ambient hydrogen pressure and the substrate temperature. We have also carried out preliminary studies of diamond nucleation by deposition of an iron overlayer on <100> silicon substrate followed by thermal annealing and HFCVD of diamond. As shown in figure 3., some diamond nucleation is observed in virgin silicon crystal but not in the region where iron is deposited. Figure 4. shows the diamond films on the thermally annealed (700°C for 20 minutes) specimens. The nucleation density is found to be larger than in silicon. After continued thermal annealing for 40 minutes at the same temperature and deposition, diamond nucleation was found to be enhanced by an order of magnitude. Since the structure of FeSi<sub>2</sub> is a deformed CaF<sub>2</sub> type (silicon or diamond like), these localized regions having tetrahedral bonding provide favorable nucleation sites for diamond. These preliminary studies of enhancement of diamond nucleation on nondiamond substrates were found to be useful in other systems also. Further studies are needed on the epitaxial relation between silicides and diamond films, including characteristics of interfaces.

### 3.5. Characterization of diamond films: defects and grain boundaries<sup>14</sup>

We have used Stillinger-Weber and Tersoff potentials to calculate the atomic structures of  $\langle 011 \rangle$  tilt boundaries with  $S=1 + 2n^2$  ( $n=1,2,3,4$ ) in silicon, germanium and diamond lying in (111), (122), (133) and (144) planes with corresponding misorientation angles of  $70.53^\circ$ ,  $38.94^\circ$ ,  $26.53^\circ$ , and  $20.50^\circ$ , respectively. The calculated atomic positions are used to simulate atomic resolution TEM images as a function of specimen thickness and objective lens defocus. Both Stillinger-Weber and Tersoff potentials gave consistent values of grain boundary period, which were found to be in good agreement with coincidence site lattice periods. The boundaries with tilt angles  $q < 20.50^\circ$  can be represented by arrays of  $(a/2)\langle 110 \rangle\{001\}$  dislocations with no dangling bonds. High-resolution electron microscopy results on the atomic structures of  $S=3$ , fivefold twins, and  $S=9$  are discussed in the above paper. The high energy  $S=9$  boundary (second order twin) has been shown to split into two low energy  $S=3$  (first-order or primary twin) boundaries (Fig. 5). These boundaries consist of 5-7 ring structure with no dangling bonds, implying that  $\langle 110 \rangle$  textured films have low level of intrinsic electrical activity, thus may be suitable for certain device (LED) applications.

### 3.6 Laser Processing and properties of diamondlike films<sup>35,19</sup>

The laser deposition process manifests nonequilibrium features during deposition. Atomically, electronically and ionically excited species are quenched fast, leading to the formation of films in metastable states having superior properties. We have shown that the nonequilibrium features of laser ablation can result in deposition of hard diamondlike films. Furthermore, nonequilibrium features can be incorporated into laser ablated plasma by coupling capacitively stored energy to the laser ablated plume in synchronism with the laser pulse. Uniform depositions over a significantly large area are characteristic of this deposition technique. The unique features of this technique are: (1) low temperature deposition; (2) formation of hydrogen-free diamondlike films; and (3) ability to manipulate microstructure as a function of laser and substrate parameters. The amorphous and hard carbon films deposited by this method show improved optical properties as well as increased hardness when compared to films deposited by the conventional laser ablation method. These improvements result from an increase in the  $sp^3$  to  $sp^2$  ratio in the DLC films. The simplest scheme for laser ablation/ deposition of the DLC films is the direct ablation of a graphite target in a vacuum of about  $10^{-6}$  torr. The substrates were single crystal silicon mounted on a heater. The target was mostly a single crystal mineral graphite. The XeCl and KrF laser sources at a fluence of about  $5 \text{ Jcm}^{-2}$  were used. The growth rate of the film was 0.03 to 0.05 nm/pulse. Raman, FTIR and mechanical properties of diamondlike films were studied as a function of laser pulse energy density and substrate temperature. The figures 6 and 7 exhibit the Raman spectra of the laser plasma deposited samples deposited at various substrate temperature and in vacuum and hydrogen ambient respectively. The role of hydrogen in diamondlike films was also investigated as a function of laser and substrate parameters. The microhardness values for laser plasma deposition scheme in vacuum ambient are much higher than those of the conventional laser ablation technique and support the contention that an increase in  $sp^3$  bonds takes place with plasma excitation.

### 3.7 Summary of important results

Enhancement of nucleation and adhesion of diamond films on nondiamond substrates such as Cu, stainless steel, hastelloy, WC, BN, TiN and Si has been carried out by deposition of a thin layer of carbon and further melting the underlayer. The surface carbon layers were responsible for enhanced nucleation of diamond and improvement of adhesion by embedding. Laser patterning of diamond films on nondiamond substrates was achieved by mechanical polishing and selectively laser annealing before HFCVD to remove the nucleation sites. Diamond nucleation on <100> silicon was achieved by deposition of an iron overlayer followed by thermal annealing to form a silicide layer which is favorable for tetrahedral diamond bonding. Characterization of diamond films was carried out to determine the defect configurations such as dislocation, stacking faults, twins and grain boundaries. Computer modelling has been carried out to determine the energy associated with these defects. Formation of diamondlike carbon films by capacitively coupled laser ablation showed improved optical properties as well as increased hardness compared to the normal laser ablation. These improvements were found to result from an increase in  $sp^3$  to  $sp^2$  ration in DLC films.

## 4. TECHNOLOGY TRANSFER

For electronic device applications, major challenges facing diamond technology include: (a) formation of continuous diamond film on heterostructures; (b) control of point and microstructural defects; (c) doping with appropriate impurities, particularly, n-type; (d) contact metallurgy; and (e) etching and patterning. This proposal is devoted to the solutions of some of these problems. We have ongoing technology transfer with Kopin Corp. on laser patterning for electronic packaging and microelectronic devices and with Sandvik, Inc. on coating applications of polycrystalline diamond films.

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## 6. SCIENTIFIC PERSONNEL

The following students received the M. S degree:

1. M. Longo
2. G. Matera
3. V. Manoj

The following students received the Ph. D degree:

1. A. S. Nandedkar
2. A. Rengan

The following personnel were research associates:

1. Dr. S.M. Kanetkar
2. Dr. X. Chen
3. Dr. V. P. Godbole

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1. Laser patterning of diamond thin films
2. Novel methods for synthesizing diamond films

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## 9. FIGURE CAPTIONS

- Fig.1 Improvement in adhesion by interface melting and embedding of diamond crystallites as a junction of laser parameters: (a)  $2.0 \text{ Jcm}^{-2}$ , pulse: (b)  $E=2.0 \text{ Jcm}^{-2}$  20 pulses.
- Fig. 2 Laser patterning of diamond films: SEM micrographs, after laser annealing at  $3 \text{ Jcm}^{-2}$  and HFCVD at  $800^\circ\text{C}$  for 3 hours (ratio  $\text{CH}_4:\text{H}_2::1:100$ , pressure 20 Torr) showing patterns as a function of increasing magnification.
- Fig. 3 SEM micrographs of HFCVD diamond films: as deposited Fe-Si specimen.
- Fig. 4 SEM micrographs of HFCVD diamond films: diamond film on Fe-Si specimen, annealed at  $700^\circ\text{C}$  for 20 minutes.
- Fig. 5 Annealing of primary  $\Sigma=3$  twins by movement of  $a/6\langle 121 \rangle$  partials in the primary and conjugate planes. The formation of "defect free" regions is clearly shown in Figs. (a) and (b). Fig. 5(c) shows the bending of twins, which is indicated by an arrow.
- Fig. 6 Raman spectra of DLC films deposited by laser-plasma ablation of graphite in vacuum ambient at substrate temperatures: (a)  $25^\circ\text{C}$ ; (b)  $100^\circ\text{C}$ ; (c)  $200^\circ\text{C}$ ; (d)  $300^\circ\text{C}$ ; (e)  $400^\circ\text{C}$ ; (f)  $500^\circ\text{C}$ .
- Fig. 7 Raman spectra of DLC films deposited by laser-plasma ablation of graphite in hydrogen ambient at substrate temperatures: (a)  $100^\circ\text{C}$ ; (b)  $300^\circ\text{C}$ ; (c)  $500^\circ\text{C}$ ; (d)  $860^\circ\text{C}$ .

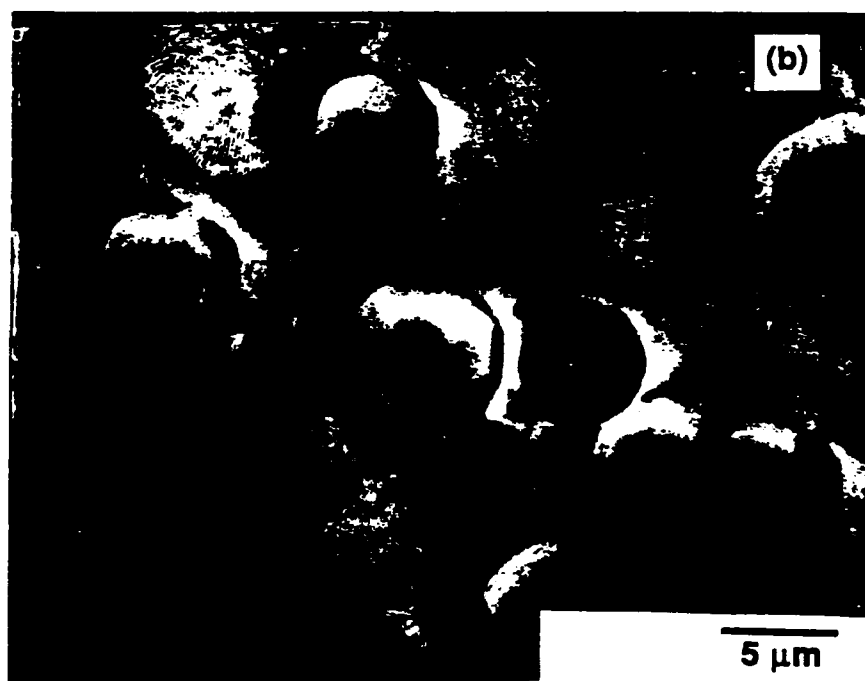
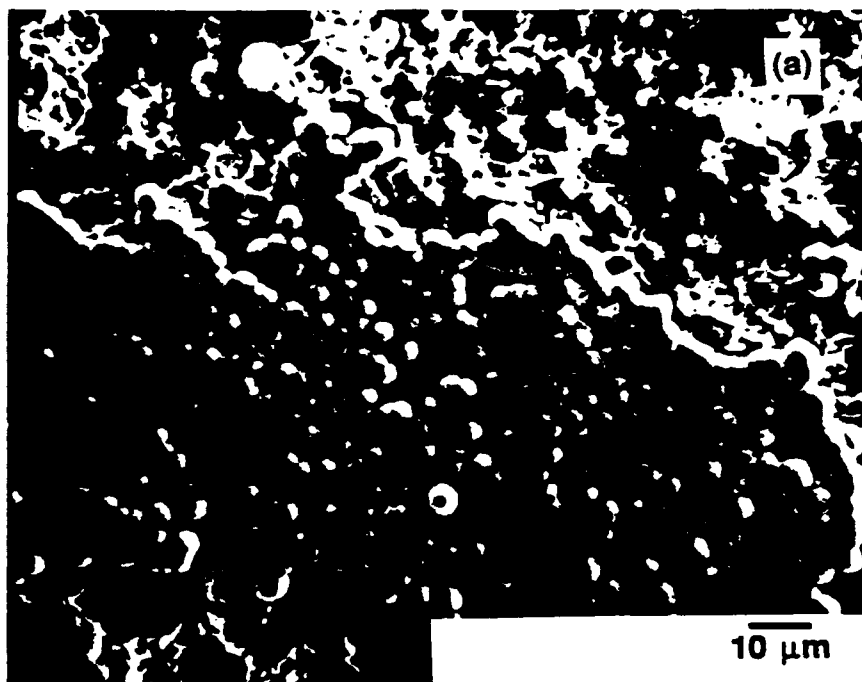


Figure 1

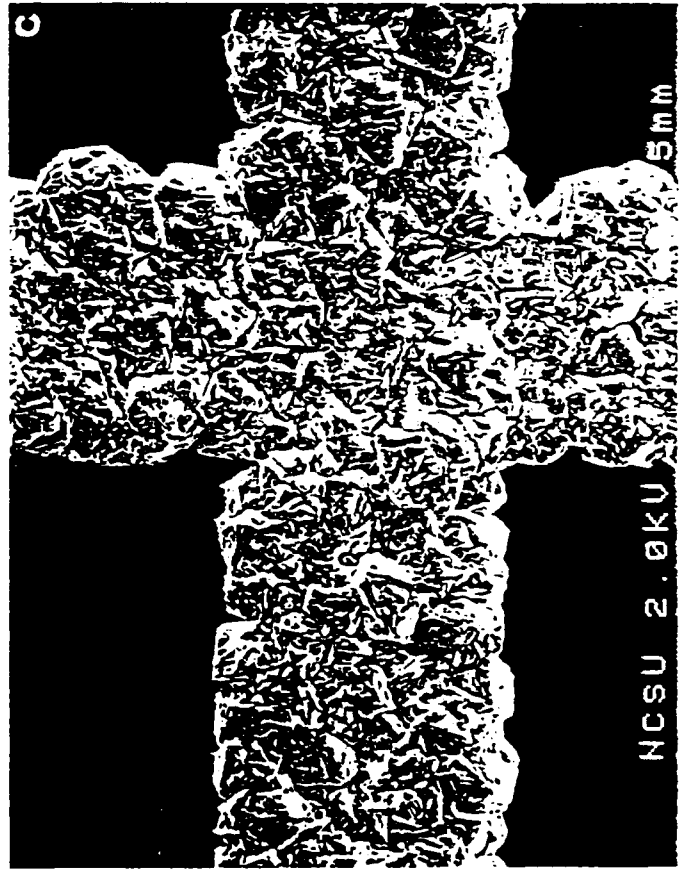
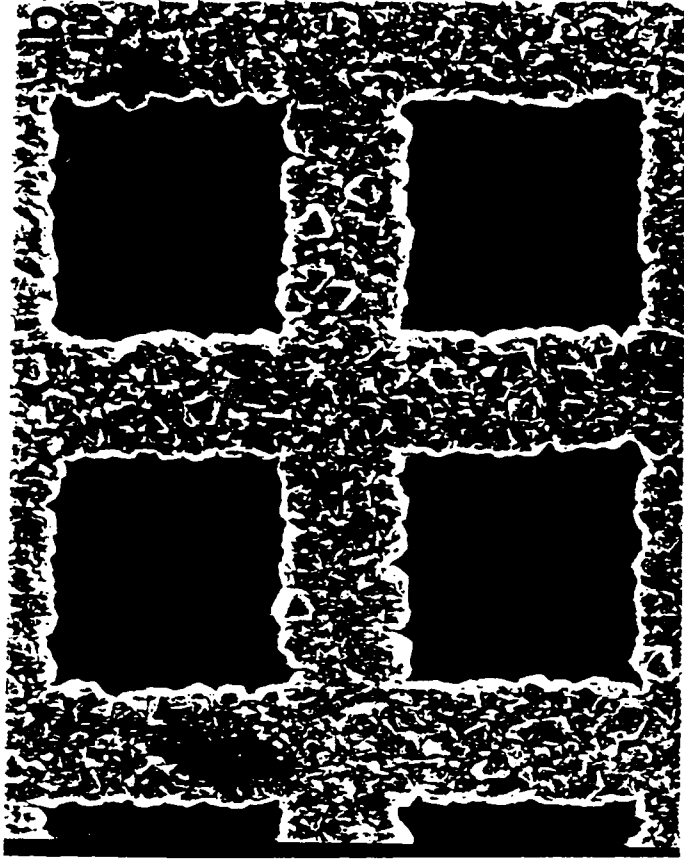
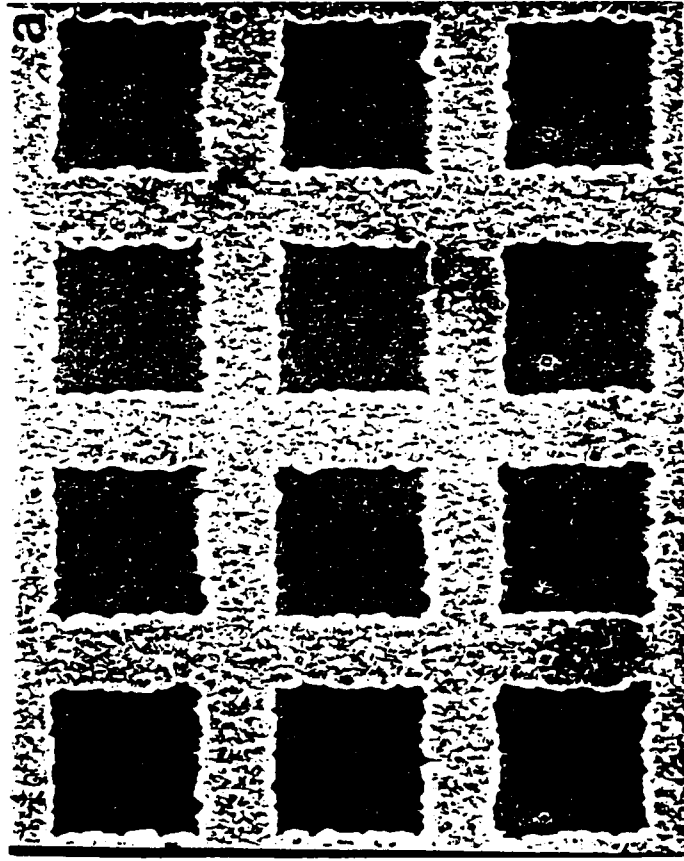


Figure 2

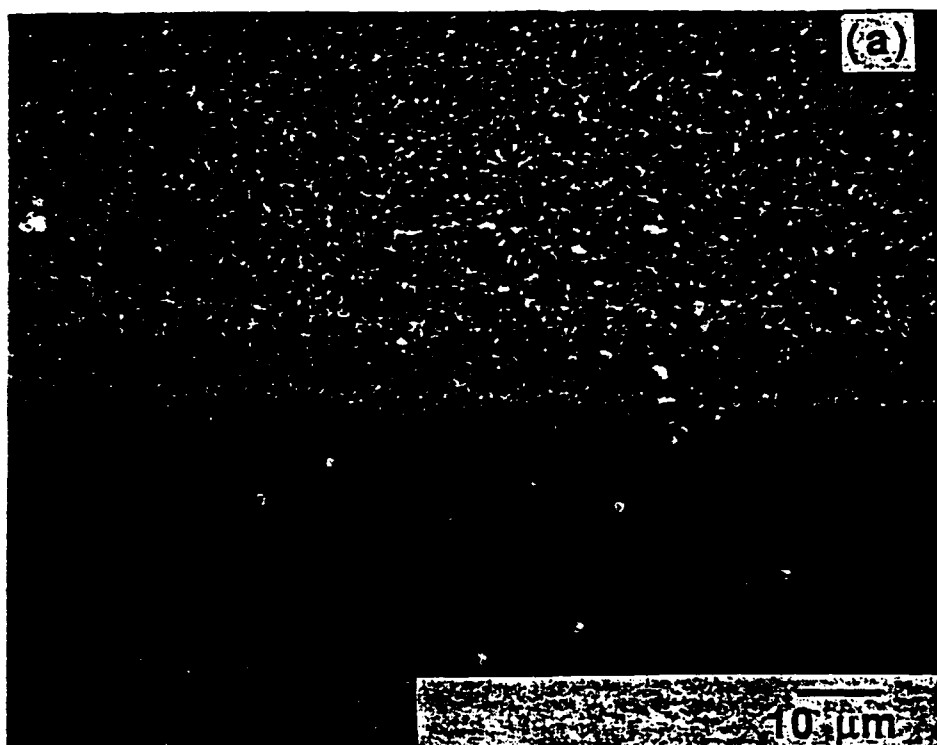


Figure 3

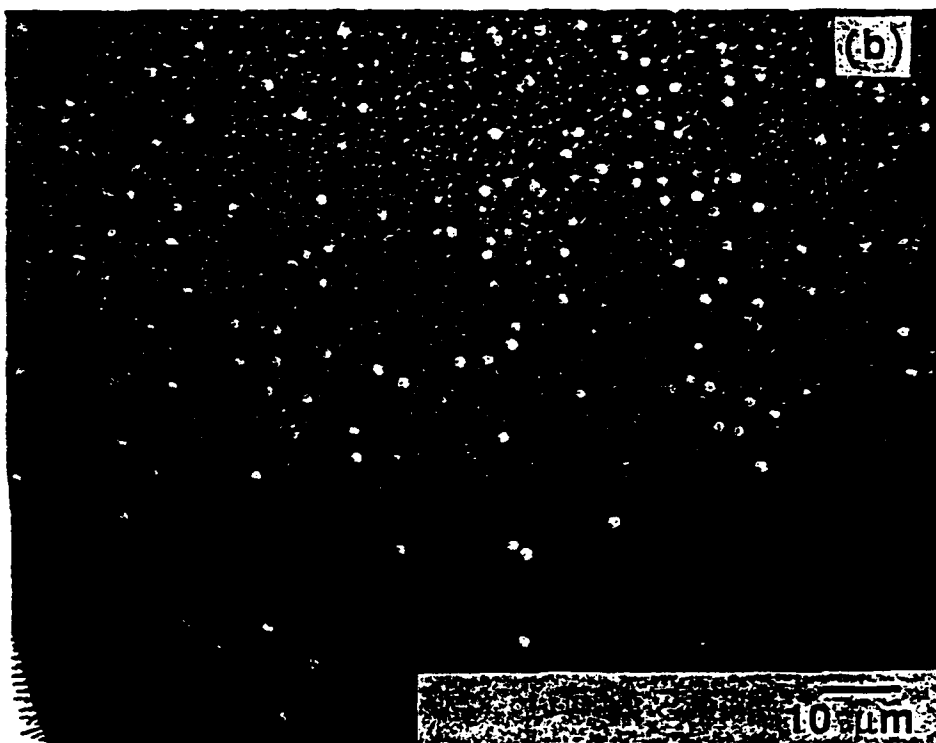


Figure 4



Figure 5(a)

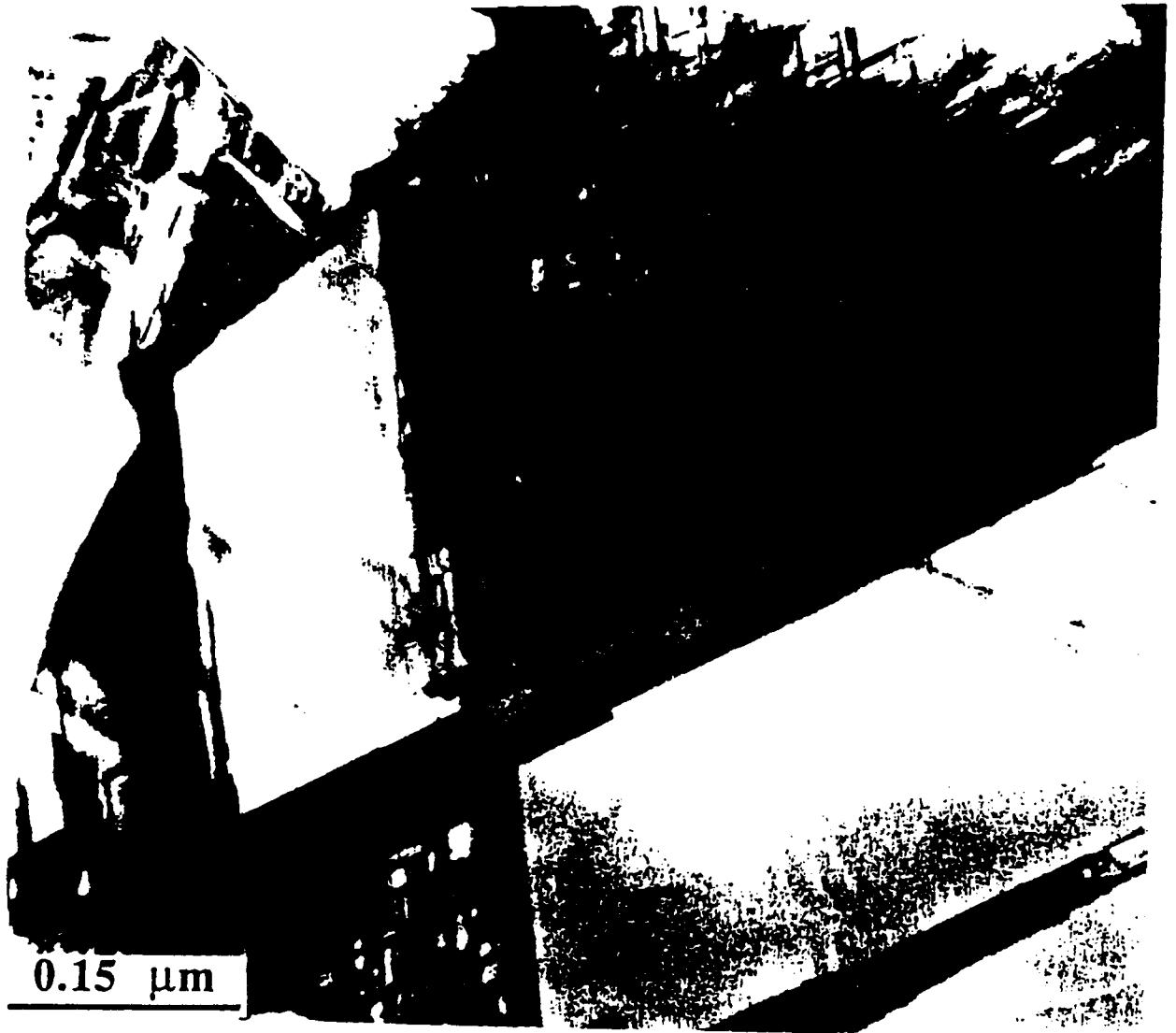


Figure 5(b)



Figure 5(c)

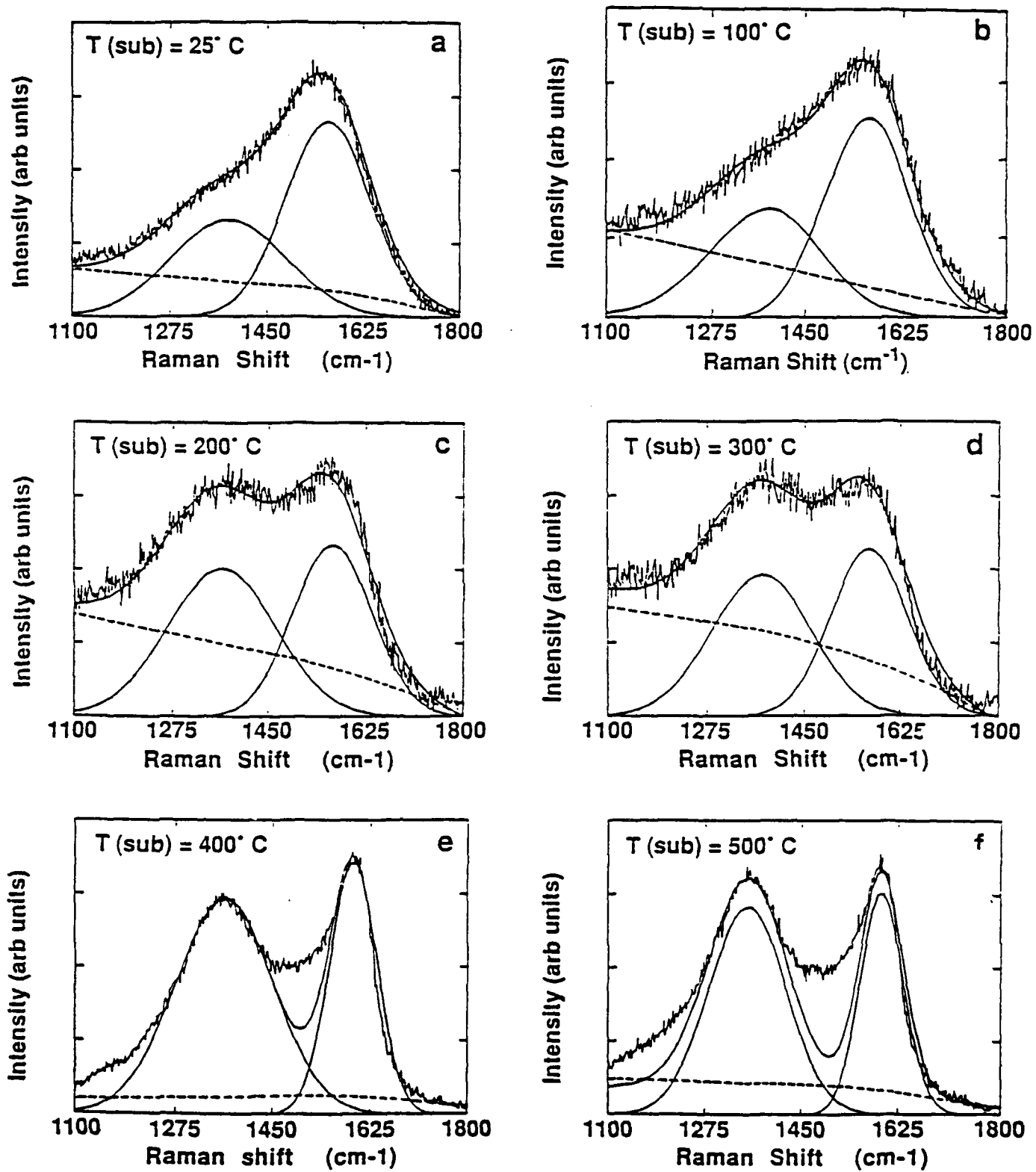


Figure 6

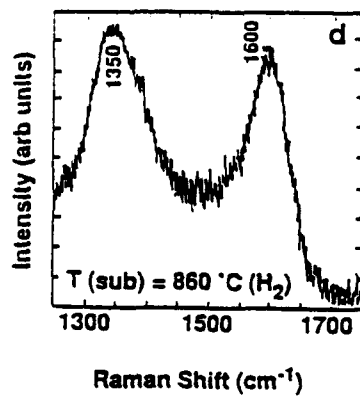
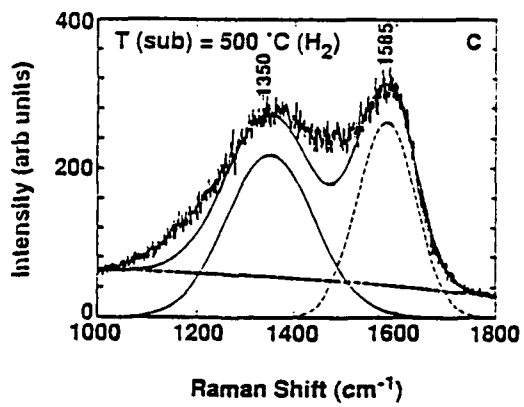
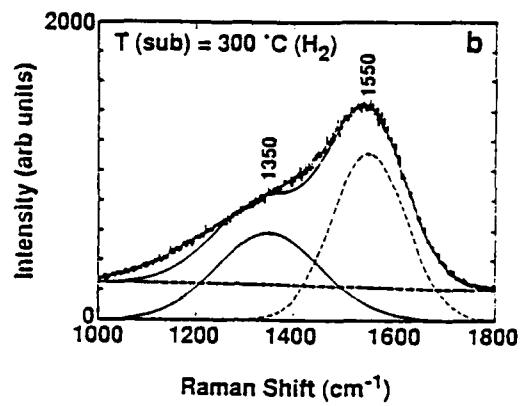
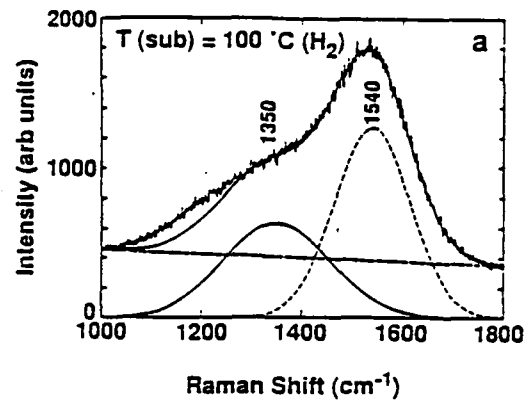


Figure 7