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Processing and Properties of CVD Diamond for Thermal Management

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One of the many remarkable properties of diamond is its thermal conductivity, about five times that of copper and the highest of all known materials. The high thermal conductivity in combination with the relative ease of diamond film growth by chemical vapor deposition process makes the material suitable for many applications such as thermal management in high power electronic circuits. For thermal managements applications, various processing steps are needed for the diamond films, such as the metallization for reliable solder bonding, metallurgical processes for planarizing of the faceted growth surface and removal of fine-grained diamond regions with poor thermal conductivity. This paper will review the properties and processing of diamond films for thermal management applications.

Key words: Chemical vapor deposition (CVD) process, diamond film, planarization, solder bonding, thermal management

INTRODUCTION

The synthesis and applications of diamond films by chemical vapor deposition (CVD) have received increasing attention in recent years. Interest in diamond is driven by its extreme properties, as it is harder than any known solid, has the highest elastic modulus, highest atomic density, highest Debye temperature, highest acoustic velocity, and highest thermal conductivity at room temperature. In addition, it is chemically inert, has a very low frictional coefficient and thermal expansion coefficient, and is highly transparent from the ultraviolet to the infrared. Diamond is a wide band-gap semiconductor that may be useful at high temperatures or high voltages. These remarkable properties in combination with the ease of diamond growth as films at relatively moderate conditions have made the material desirable for many potential applications, such as heat spreaders, optical windows, x-ray lithography, low-friction or wear-resistant surface coatings, cutting tool coatings, and active electronic device elements.

The basic physical properties of diamond are listed in Table I. Some of the fascinating properties of diamond have been known for many centuries. However, it was not known until the French chemist, Antoine Lavoisier's diamond-burning experiment in 1772 to produce CO_2 that diamond is made up of carbon. It was not until the 1950s that artificial diamond was first made at General Electric by using a high-pressure, high-temperature technique, and not until the 1980s that a chemical vapor deposition technique was discovered and improved to synthesize high-quality, wide-area films without using high pressure. Diamond and related materials have begun to be an integral part of modern technology, and the knowledge on synthesis, properties, and applications of man-made diamond continues to increase at a rapid pace.

Since graphite, not diamond, is the stable phase at room temperature and ambient pressure, the synthesis of diamond structure from less dense graphite requires special processing conditions such as very high pressure and temperature (e.g., 60,000 atmospheres and 1200°C).[1] In spite of many advantages, the high pressure process has some limitations. The limited yield strength of the synthesis cell materials in the high-pressure, high-temperature environment limits the maximum size of man-made diamond. In addition, the required use of liquid metal catalysts during the synthesis often causes undesirable trapping of the metals as impurities or inclusions thus deteriorating the properties of diamond.

An alternative diamond growth processing based on chemical vapor deposition technique[2,3] does not require the use of high pressure. Therefore, there is no

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Table I. Some Physical Properties of Diamond

Density (g/cm^3)	3.515
Molar Density (g-atom/cm^3)	0.293
Specific Heat at 300K (Joule/g)	6.195
Debye Temperature (K)	1860
Thermal Conductivity (W/cm-K)	22
Acoustic Velocity (cm/s)	1.8×10^6
Hardness (GPa)	90
Bulk Elastic Modulus (N/m^2)	5.9×10^{11}
Compressibility (cm^2/Kg)	1.7×10^{-7}
Thermal Exp. Coeff. At 293K (K^{-1})	0.8×10^{-6}
Refractive Index at 590 nm	2.42
Dielectric Constant	5.7

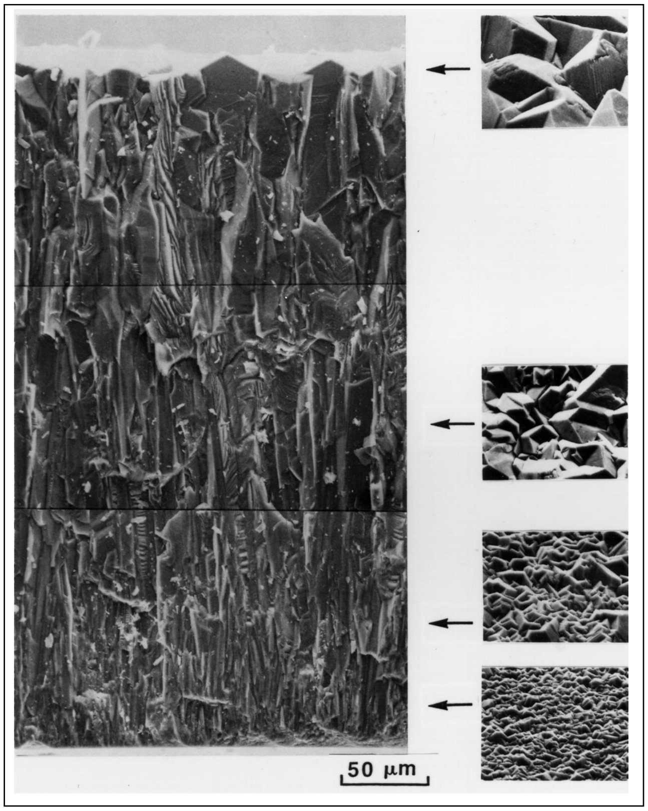

Fig. 1. Cross-sectional SEM micrograph (fracture surface) showing the dependence of grain size on the height of CVD diamond film above the substrate.

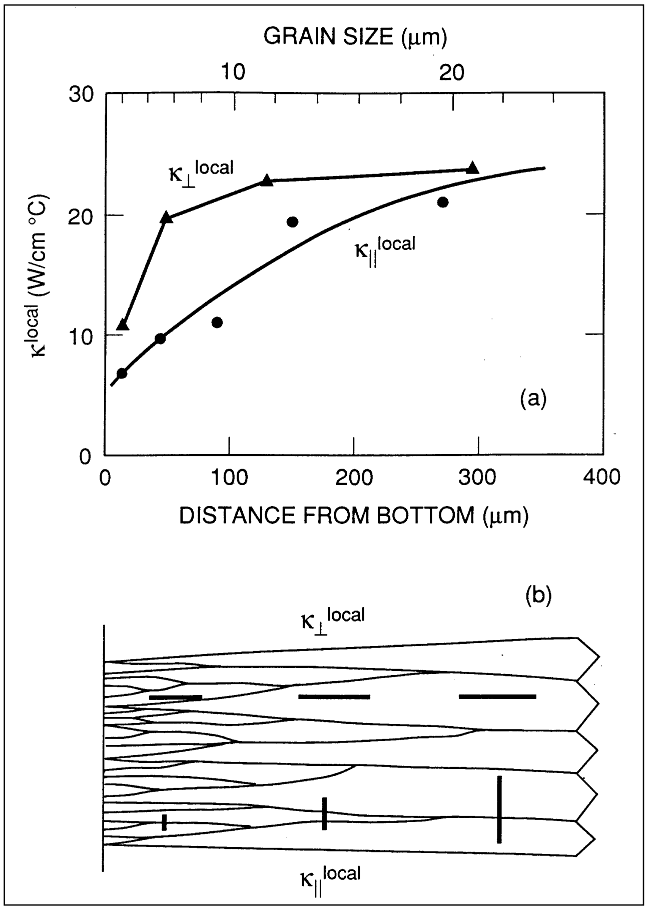

Fig. 2. (a) Local thermal conductivity vs height (distance from the bottom), and (b) schematic illustration of the nonuniform, anisotropic microstructure in CVD diamond films.

inherent limitation in the size of the synthesized diamond other than by the growth kinetics, and a large-area deposition of diamond films is possible. The CVD synthesis processing also produces high-purity diamond free of metal inclusions.

The CVD deposition of diamond films is based on the decomposition of hydrocarbon gas (such as CH_4) and subsequent nucleation and growth of diamond and graphite on a substrate. The simultaneous presence of atomic hydrogen etches away the graphite component thus enabling the formation of pure diamond. Several different CVD methods for diamond synthesis, depending mostly on different ways of generating the atomic hydrogen component, have been developed during the past decade or so. These methods include hot filament process, oxyacetylene torch flame method, microwave plasma CVD, DC plasma, RF plasma, and DC plasma jet CVD.

As high-power electronic circuits and devices are packaged to progressively higher densities, synthetic diamond films are being considered as efficient heat spreaders for the prevention of thermal damage. In this article, the properties and metallurgical processing of diamond films for thermal management applications will be reviewed.

THERMAL CONDUCTIVITY BEHAVIOR OF CVD DIAMOND

With a thermal conductivity (K) ~22 watts/cm·K (and even higher if made isotopically pure), diamond films[4] are the best materials for efficient thermal management, e.g., as a heat spreader for high power electronic and optoelectronic devices,[5,6] microwave diodes, laser diodes, GaAs power transistors, etc. The practical speed of high performance computers is not necessarily limited by the inherent switching speed of the transistors within the IC circuits but by the length of the interconnecting signal lines, the density and length of which are thermally limited. The low dielectric constant of diamond is also an important factor for some thermal management applications. Good diamond adhesion to the active devices and other substrates using suitable metallization layers and solder materials is desirable. Accommodation of thermal expansion mismatch between diamond and other component materials or substrates is another parameter that needs to be considered in the thermal management assembly.

CVD diamond films tend to exhibit anisotropic thermal conductivity behavior with the perpendicular conductivity being much higher than the in-plane conductivity. This is due to the microstructurally anisotropic nature of the diamond films.[4] CVD diamond grows on substrates by random nucleation followed by competitive growth during which nuclei oriented with the fastest growth direction (e.g., <110> under certain processing conditions) outgrow the less favorably oriented grains. As a result, CVD films often exhibit a columnar grain structure with a very fine-grained region near the film-substrate interface and a large-grained faceted region near the top surface as shown in Fig. 1. As the grain boundary regions in diamond generally scatter phonons more than the grain interior, the columnar microstructure exhibits anisotropic as well as thickness-dependent thermal conduction behavior as illustrated in Fig. 2. For heat spreader design and applications, it is desirable to keep this nonuniform thermal conduction in mind, e.g., by considering a removal of the fine-grained, low K region or having the large-grained, high K region face the heat-generating device.

THINNING AND POLISHING OF DIAMOND

Nearly all applications of CVD diamond films including thermal management require, geometrically flat, well-polished diamond surfaces. Because of the more commonly observed columnar growth during the CVD process, diamond films tend to exhibit a roughly cone-shaped grain structure with a very fine-grained region near the bottom (against the substrate, typically Si) and large-grained faceted regions near the top surface. The fine-grained region exhibits much inferior thermal conductivity because of the increased phonon scattering by grain boundaries themselves and possible impurities segregated at the boundaries. The rough growth facets are undesirable as many diamond applications require flat surfaces. For these reasons, it is desirable to remove both the top and bottom part of the CVD diamond films.

Because of the extreme hardness of diamond, mechanical polishing or thinning of diamond is time consuming and costly. Polishing by reaction with oxygen ions or gas tends to cause excessive grain boundary etching and pitting in diamond films. Other techniques, such as laser ablation, argon ion-beam irradiation, hot metal lapping, and electrical discharge have been reported. It would be desirable to have a fast and convenient thinning technique simultaneously applicable to a large number of diamond films avoiding the polishing of individual films.

It has been found in recent years that massive thinning and shaping of diamond films can be accomplished by relatively simple techniques based on diffusional removal of carbon into metal foils either by using solid state reaction[7,8] or by interaction with molten rare earth metals.[9–12]

Shown in Fig. 3 is the well-known iron-carbon binary phase diagram.[13] Utilizing the high solubility of carbon in Fe near or above 900°C, diffusional thinning of CVD diamond films was accomplished.[7] Free-standing (~220 μm thick) diamond films were sandwiched between iron foils (~250 μm thick) and heat treated under weight at 900°C for 48 h in an argon gas atmosphere.

Shown in Fig. 4 are scanning electron microscopy (SEM) cross-sectional views of the diamond film before and after the thinning heat treatment. As is evident from the figure, an extensive thinning of the film (from ~220 to ~120 μm thickness) has been attained. As the thinning process takes place on both surfaces of the diamond film shown in Fig. 4a, both the fine-grained bottom region and most of the rough facets on the top surface have been eliminated after the heat treatment as shown in Fig. 4b. The removal of the growth facets is further illustrated in SEM micrographs of Fig. 5, which was taken at an inclined angle to show both the top surface and the fracture surface. The top surface of the thinned sample, Fig. 5b, is relatively smooth with only occasional and

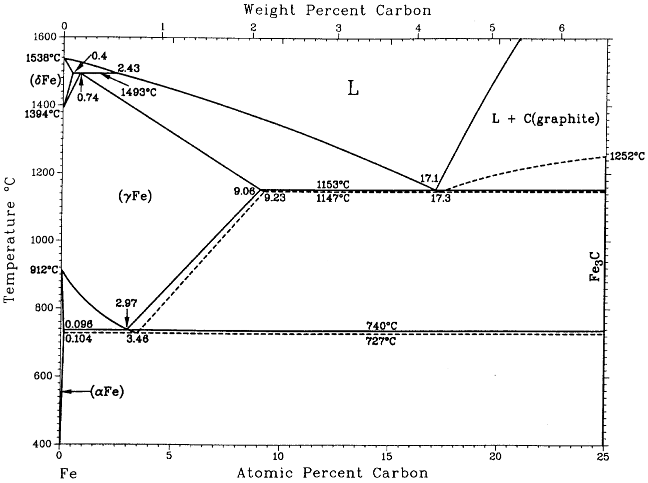

Fig. 3. Fe-C binary phase diagram.[13]

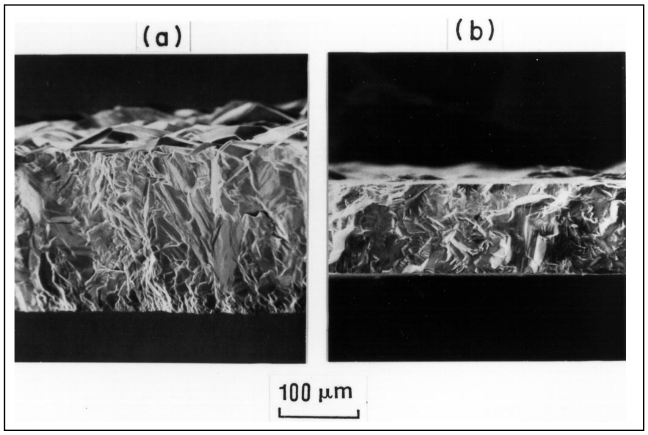

Fig. 4. Cross-sectional SEM photograph of the CVD diamond film (a) before and (b) after diffusional thinning with Fe.

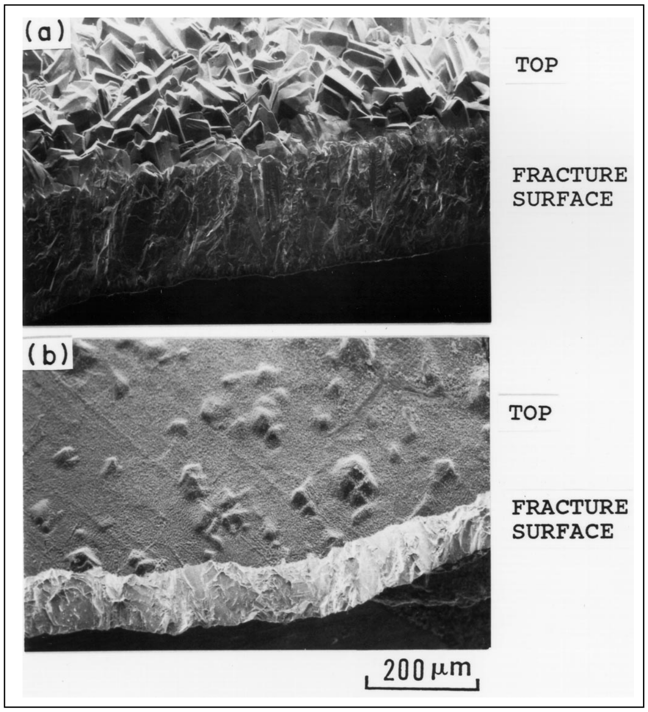

Fig. 5. SEM microstructures of the diamond film at an inclined angle (a) before and (b) after etching with Fe.

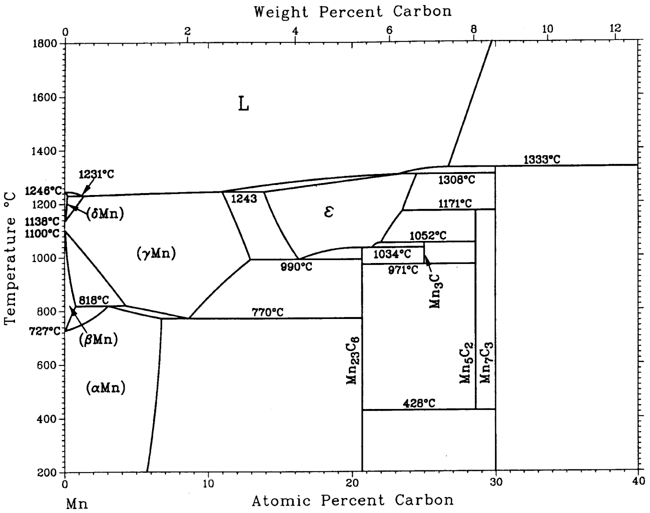

Fig. 6. Mn-C binary phase diagram.[14]

partial remnants of the growth facets present. The extensive thinning of the diamond film is again evident from the fracture surface shown in Fig. 5b. Some mechanical fine polishing is needed after the thinning process to obtain flat surfaces for thermal management applications.

A similar diamond-etching behavior is observed with manganese.[8] The Mn-C phase diagram,[14] Fig. 6, shows a higher solubility of carbon in Mn than in Fe at ~900°C. SEM micrographs of Fig. 7 illustrate the efficient diamond thinning characteristics of Mn powder pressed on CVD diamond surface and heat treated at 900°C for 48 h.

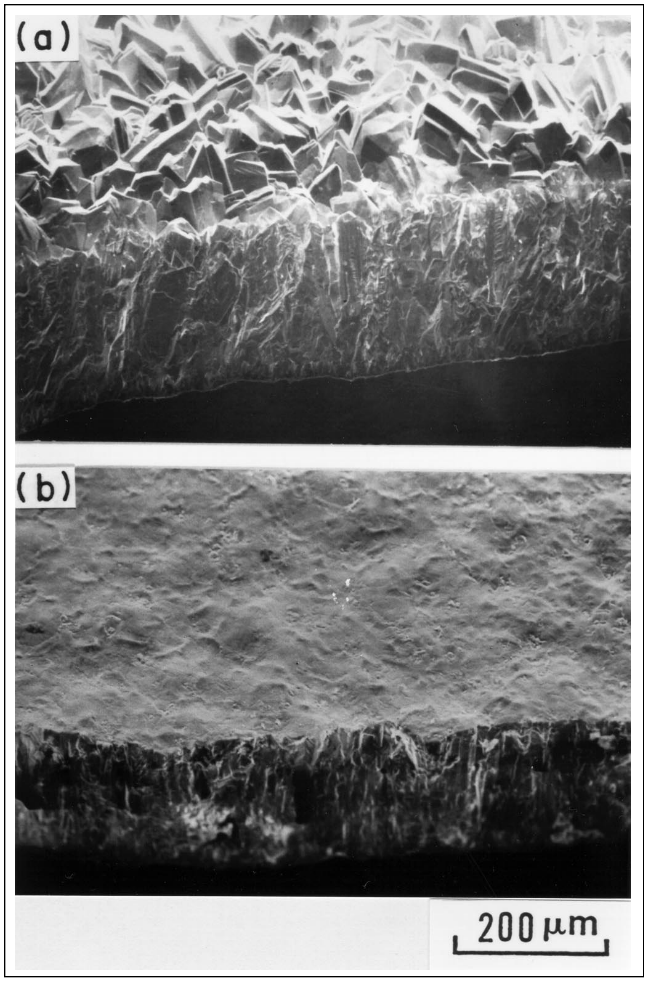

Fig. 7. SEM images of CVD diamond film (a) before and (b) after etching with Mn powder.

Even higher solubility of carbon (and faster etching of diamond) is obtained with molten rare earth metals[9] such as Ce or La. The Ce-C phase diagram,[15] Fig. 8, indicates a very high solubility of carbon in molten cerium, about 25 atomic % at ~900°C. Since the diamond-etching material is now in the liquid form with an excellent wettability, there is no need to apply a substantial pressure to ensure the contact between the diamond and the etchant metal sheet. A much higher kinetics of diamond etching is also expected because of the fast diffusion of carbon in the molten metals (Ce, La) as compared to the solid metals (Fe, Mn).

Shown in Fig. 9 are the cross-sectional SEM micrographs of the CVD diamond before and after the Ce etching. The diamond film was sandwiched between two Ce sheets and heated to above the melting point of Ce (~798°C) to 920°C and held for 4 h. Much of the diamond etching occurs during the first several minutes of the interaction with the molten metal. The diamond thinning effect as well as the surface smoothing effect are evident.

The use of alloy etchants such as the low-cost mischmetal[11] (an impure rare-earth metal mixture containing La, Ce, Pr, etc.) or rare earth/transition metal alloys with lower melting temperature eutectic[12] (e.g., La-Ni, Ce-Cu, etc.) has also been demonstrated. A very fast diamond etch rate in excess of 50 μm per min in thickness reduction has been accomplished using molten mischmetal.[11]

BONDING OF DIAMOND

Thermal management applications of diamond require a close-contact attachment of the diamond heat spreader onto the device to be cooled. Various mounting techniques such as mechanical clamping, solder bonding, brazing, or adhesive bonding can be used. Diamond surfaces at atmospheric conditions are often covered by chemisorbed species such as oxygen, hydrogen, or hydroxyl groups, or by physisorbed layer of water or organic materials. Adhesion of solid materials in the presence of such layers results in weak, van der Waals type bonding with poor wetting and adhesion. For strong bonding of solid materials to diamond surface, chemical or covalent type carbon-metal bonding interactions at the interface is desirable.

Strong carbide forming elements such as Ti, Zr, V, Nb, Ta, Cr, Si generally provide reliable metal-diamond bonding. These elements also exhibit a strong affinity to oxygen, thus they are capable of removing chemisorbed or physisorbed oxygen and other species from the diamond surfaces. However, oxidized surfaces of these metals can induce poor wetting and reduced bond strength during subsequent bonding processing such as soldering or brazing. A common practice to overcome this problem is to cover the reactive metal surface with a protective inert metal such as Au, Ag, Pt, Cu, Sn. An alternative approach is to alloy the soldering or brazing material with a small amount (typically less than several per cent) of the carbide forming elements, which enhances the adhesion at the diamond-metal interface. Since the use of minimal amount of bond materials is desirable to minimize thermal impedance, the interface layers or bonding materials are often prepared by thin film deposition methods, e.g., by sputtering.

An exemplary metallization for solder bonding of CVD diamond for thermal management in laser diode devices[16] uses a three-layer configuration of Ti/Pt/Au. The titanium layer provides bonding to diamond, the platinum layer is for diffusion barrier and the gold overcoat serves as a protective layer to minimize Pt-solder reactions and also as a bond layer to the Au-Sn eutectic solder. The thicknesses of sputter-deposited metallization layers on diamond are, for example, 100 nm Ti, 200 nm Pt, 500 nm Au, and 2.5 μm total of 80%Au-20%Sn eutectic solder layer (either as multiple alternating layers of Sn and Au or as a single alloy layer). The solder bonding of the laser diode onto the diamond heat spreader is carried out by rapid thermal annealing, e.g., at 300–350°C for several seconds.

SUMMARY

One of the remarkable properties of diamond is its high thermal conductivity, about five times that of copper. The high thermal conductivity in combination with the relative ease of diamond film growth by CVD makes the material suitable for efficient thermal management in electronic device packaging. With the recent trend toward higher and higher device packaging densities, the unique thermal conduction property of diamond can be exploited to enable efficient designs of high-density, high-power electronic devices. Recent design studies on three-dimensional multilayer (40 layers) packaging using diamond substrates (each with a 4 × 4 × 0.040 inch dimension with metallized via holes) indicate that as much as 20 kilowatts of power dissipation is feasible.[17] Opportunities exist for further improvement in metallurgical processing techniques such as diamond thinning and polishing, in bonding materials, properties and interfacial reactions, as well as for efficient thermal management applications for various present and future electronic devices.

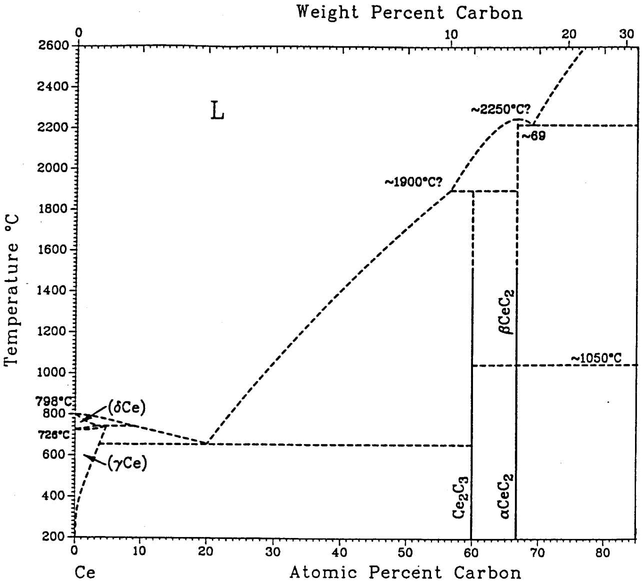

Fig. 8. Ce-C binary phase diagram.[15]

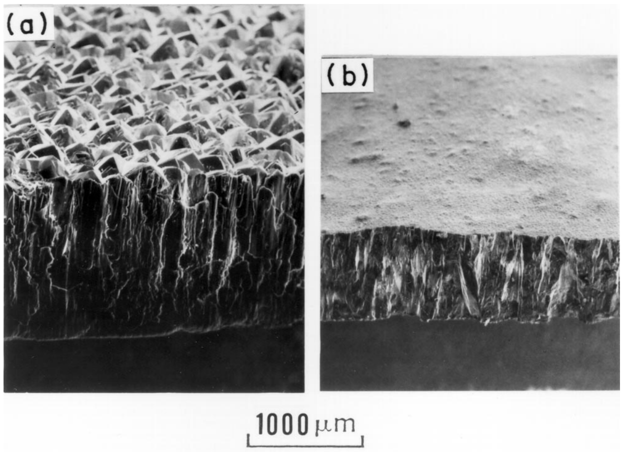

Fig. 9. SEM micrographs of the CVD diamond (a) before and (b) after etching with molten Ce.

REFERENCES

1. F.P. Bundy, H.T. Hall, H.M. Strong and R.J. Wentorf, *Nature*

176, 51 (1955).

2. J.C. Angus, H.A. Will and W.S. Stanko, *J. Appl. Phys*. 39, 2915 (1968).
3. B.V. Spitsyn, L.L. Bouilov and B.V. Deryagin, *J. Cryst. Growth* 52, 219 (1981).
4. J.E. Graebner, S. Jin, G.W. Kammlott, J.A. Herb and C.F. Gardinier, *Nature* 359, 401 (1992).
5. M. Seal, *The Properties of Natural and Synthetic Diamond*, ed. J.E. Field, (New York: Academic Press, New York, 1992), Ch. 16, p. 607.
6. M.N. Yoder, *Diamond and Diamond-like Films and Coatings*, ed. R.E. Clausing et al., (New York: Plenum Press, 1991, p. 1.
7. S. Jin, J.E. Graebner, G.W. Kammlott, T.H. Tiefel, S.C. Kosinski, L. Chen and R.A. Fastnacht, *Appl. Phys. Lett*. 60, 1948 (1992).
8. S. Jin, J.E. Graebner, T.H. Tiefel, G.W. Kammlott and G.J. Zydzik, *Diamond and Related Materials* 1, 949 (1992).
9. S. Jin, J.E. Graebner, M. McCormack, T.H. Tiefel, A. Katz and W.C. Dautremont-Smith, *Nature* 362, 822 (1993).
10. S. Jin, L.H. Chen, J.E. Graebner, M. McCormack and M. Reiss, *Appl. Phys. Lett*. 63, 622 (1983).
11. S. Jin, W. Zhu and J.E. Graebner, *Applications of Diamond Films and Related Materials*, ed. A. Feldman, et al., (Gaithersburg, MD: NIST Special Publication 885, 1995), p. 209.
12. M. McCormack, S. Jin, J.E. Graebner, T.H. Tiefel and G.W. Kammlott, *Diamond and Related Materials* 3, 254 (1994).
13. *Binary Alloy Phase Diagrams*, ed, T.B. Massalski, 2nd Ed., (Metals Park, OH: ASM International, 1991), p. 843.
14. *Binary Alloy Phase Diagrams*, ed. T.B. Massalski, 2nd Ed., (Metals Park, OH: ASM International, 1991), p. 860.
15. *Binary Alloy Phase Diagrams*, ed. T.B. Massalski, 2nd Ed., (Metals Park, OH: ASM International, 1991), p. 834.
16. A. Katz, K.W. Wang, F.A. Baiocchi, W.C. Dautremont-Smith, E. Lane, H.S. Luftman, R.R. Varma and H. Curnan, *Mater. Chemistry and Phys.* 33, 281 (1993).
17. R. Schaefer, R. Eden and T. Moravec, Norton Diamond (private communication).