

# Polycrystalline CVD Diamond Films with High Electrical Mobility

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Advances in the deposition process have led to dramatic improvements in the electronic properties of polycrystalline diamond films produced by chemical vapor deposition (CVD). It is now possible to produce CVD diamond with properties approaching those of IIa natural diamonds. The combined electron-hole mobility, as measured by transient photoconductivity at low carrier density, is 4000 square centimeters per volt per second at an electric field of 200 volts per centimeter and is comparable to that of the best single-crystal IIa natural diamonds. Carrier lifetimes measured under the same conditions are 150 picoseconds for the CVD diamond and 300 picoseconds for single-crystal diamond. The collection distance at a field of 10 kilovolts per centimeter is 15 micrometers for the CVD diamond as compared to 30 micrometers for natural diamonds. The electrical qualities appear to correlate with the width of the diamond Raman peak. Also, although the collection distance at the highest fields in the films nearly equals the average grain size, there is no evidence of deleterious grain boundary effects.

Because of its large bandgap, high electron and hole saturation velocities, high mobilities, high breakdown strength, and high radiation hardness, diamond has been proposed for a wide variety of electronic applications, particularly those involving extreme conditions (1-4). Some research in this area has focused on prototype systems based on natural or homoepitaxial single-crystal diamond (5-9). However, polycrystalline CVD diamond films, which can be grown over large areas on nondiamond substrates such as silicon, represent an alternate medium for research and development of both active and passive diamond electronic applications (10).

To date, the electronic performance of CVD diamond films has been inferior to that of the highest quality single-crystal natural IIa diamond. Polycrystalline CVD diamond films with combined electron and hole mobilities of  $50 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and lifetimes of 50 ps have been reported (11). Further development of diamond films for applications that require high thermal conductivity resulted in material with mobilities of  $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and lifetimes of 100 ps (12). In this report we describe polycrystalline diamond films that have combined electron and hole mobilities of  $4000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and carrier lifetimes of 150 ps, properties that approach those of the best IIa diamonds. We compare measurements of the combined mobility, drift velocity, lifetime, and collection distance to those of other CVD films and to natural

diamond. Such high-quality CVD polycrystalline diamond, because of its manufacturing flexibility and low cost, may make it possible to develop diamond devices that otherwise would have been too expensive or impractical with single-crystal diamond.

The polycrystalline diamond films were grown on silicon substrates in a microwave (13) CVD plasma reactor that used methane, carbon monoxide (14), and hydrogen gases. The important growth parameters were systematically varied to determine the process for growth of high-quality diamond. These parameters include microwave power, pressure, gas mixture, and growth temperature. Raman spectroscopy was used as a first step in determining the success of a particular process. Scanning electron micrographs were used to study the surface morphology and to measure the grain size of the films. The ultimate tests of the process were the mobility and lifetime of the free carriers measured with transient photoconductivity (PC) (11).

With transient PC, one measures the mobility ( $\mu$ ), the lifetime ( $\tau$ ), and the average collection distance ( $d$ ) of free carriers by following the changing current associated with the absorption of light. The free carriers are intrinsically excited by a 5-ps pulse of 6.1-eV photons. The absorption depth at this energy is less than 2  $\mu\text{m}$ . Electrical contacts to the samples are made by sputtering a 1-mm-wide line of titanium and gold. A gap in the line defines the active region of the test structure. The current-voltage relation in the dark is linear for these structures. After the absorption of the light pulse, the transient decay of the PC is measured with a high-speed measurement system that has a resolution of 50 ps. This technique has been used on natural IIa diamonds (15, 16) and

on earlier sets of diamond films (11, 12).

To illustrate the dramatic improvement, we will discuss three sets of diamond films. Films grown in mid-1990 to late 1991 will be labeled film A; films grown in late 1991, which were developed for use in thermal management, will be labeled film B (12, 17); and the most recent films, grown specifically for electronic applications, will be labeled film C. The process conditions for these three film types are shown in Table 1. The improvement in electrical behavior from film A to film C correlates with increased grain size, higher growth temperatures, and improved purity of the diamond films.

Raman spectroscopy is one of the most commonly used techniques for characterizing diamond films because of its high sensitivity to various phases of carbon bonding. Spectra from all three CVD diamond films were recorded. All of the CVD films display the characteristic diamond peak at  $1332 \text{ cm}^{-1}$ . Film C has the narrowest diamond peak with a full width at half maximum (FWHM) of  $3.3 \text{ cm}^{-1}$  compared to about  $2.4 \text{ cm}^{-1}$  for a IIa diamond. The FWHMs for the three films are listed in Table 2. The amount of non-diamond-bonded carbon that would contribute a broad peak at  $1550 \text{ cm}^{-1}$  is negligible in all three films.

A representative scanning electron micrograph of film C is shown in Fig. 1. We determined the average grain size by counting the number of grains in a region, dividing the area of the region by the number of grains, and taking the square root. Film C has average grain sizes of 14 to 16  $\mu\text{m}$ , film B 10 to 12  $\mu\text{m}$ , and film A 3 to 6  $\mu\text{m}$ . The grain size is dependent on the process chemistry, the growth temperature, and the thickness of the film. If the process causes continuous renucleation, the resultant grain size is generally smaller. Owing to the competitive growth of the columnar grains, the grain size increases with thickness (18). The difference in grain size between film A and the other films is due mostly to thickness; temperature and chemistry account for the dif-

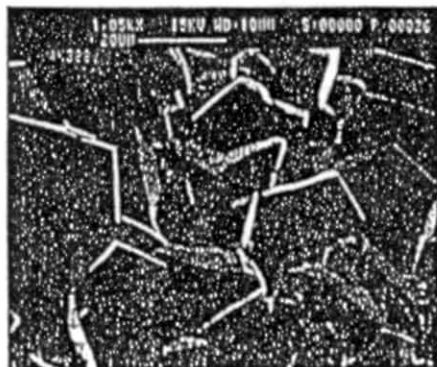


Fig. 1. Scanning electron micrograph of the morphology and grain size of high electrical quality CVD diamond (film C).

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ferences observed between film B and film C.

The mobility was measured as a function of excited carrier density for the three sets of CVD diamond films and a IIa diamond (Fig. 2). The carrier density is calculated from the amount of absorbed energy, the volume of excitation, and the photon energy. The mobility decreases with density because of increased scattering between the electron and hole populations (15). At low densities, in all cases, the mobility saturates and becomes independent of the carrier density. Temperature-dependent measurements in IIa diamond have shown that the mobility scales as  $\sim T^{-3/2}$  (15), indicating that the mobility is limited mainly by acoustic phonon scattering. These values for the mobility at low excitation densities ( $\sim 4000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at  $n \leq 10^{15} \text{ cm}^{-3}$ ) at an applied electric field of  $200 \text{ V cm}^{-1}$  are higher than those reported in the past for either electrons or holes alone (8). However, PC measures a weighted sum of both electron and hole motion, and thus these values suggest that both electrons and holes contribute to the current flow.

Decay times of the transient are a measure of the lifetime of the free carriers. In film A, these times were short ( $< 50 \text{ ps}$ ) and

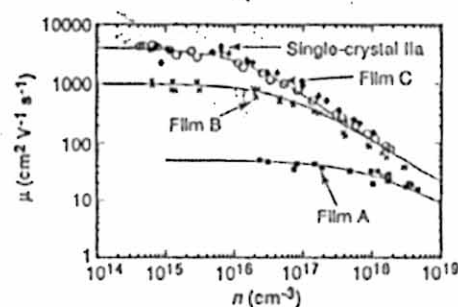


Fig. 2. Mobility measured with intrinsic PC for films A, B, and C and a IIa diamond. The mobility falls off at high densities as a result of electron-hole scattering. The solid lines are calculated mobilities based on electron-hole scattering.

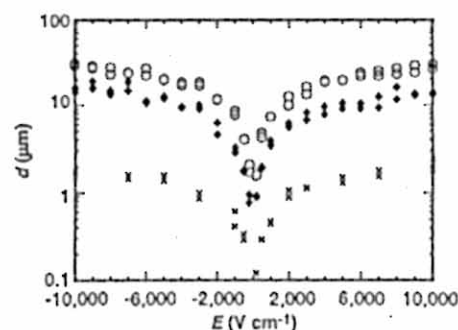


Fig. 3. Collection distance as a function of electric field for films B (x) and C (♦) and a IIa diamond (O). The collection distance of film C approaches that of the IIa diamond with the difference in performance due to shorter lifetimes in the CVD film.

independent of the excitation density (11). For films B and C the decay times at low excitation density have values of 50 and 150 ps, respectively. In IIa diamonds the decay time varies from 100 to 400 ps, depending on the sample. For the IIa diamond discussed here the decay time is 300 ps at low excitation densities. The decay times for all films and natural diamond examined to date show a rapid decrease as the electric field increases and approaches a constant for fields greater than  $2000 \text{ V cm}^{-1}$ . This finding is unexplained at present.

In the development of applications such as radiation detectors, another important parameter is the collection distance  $d$  of the free carriers. This distance determines the sensitivity of the detector. Recent Monte Carlo work (3) indicates that a prototype multilayer sampling calorimeter detector would require a minimum collection distance of  $25 \mu\text{m}$ . Typical operating electric fields for such detectors would be  $30$  to  $40 \text{ kV cm}^{-1}$ . A plot of the collection distance versus electric field for films B and C and the natural diamond is shown in Fig. 3. In film A (not shown) the distance never exceeded  $0.1 \mu\text{m}$ . At a field of  $10 \text{ kV cm}^{-1}$ , which was the limit of the PC system, this distance was  $2 \mu\text{m}$  in film B. At the same field, in film C the distance is between  $15$  and  $20 \mu\text{m}$ , whereas in natural diamond the distance is almost  $30 \mu\text{m}$ . These results indicate that films of quality equal to type C are suitable for detectors, particularly if operated at higher fields.

Throughout the development process the carrier mobility in CVD films has been continuously improved. Film C has a combined mobility equal to that of IIa diamond ( $4000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at low carrier density). The lifetime  $\tau$ , although improved as well, has not shown so dramatic an increase and presently accounts for the lower collection distances shown in Fig. 3. At present, it is

about half that of the IIa diamond ( $150 \text{ ps}$  versus  $300 \text{ ps}$ ). The much shorter lifetimes found in lower mobility CVD films can be attributed to trapping at a variety of defects known to be present in low-quality films: dislocations, stacking faults, impurities, and twins. It is possible that the longer carrier lifetime found in film C compared to earlier CVD films is the result of a lower density of defects but that the overall defect density is still somewhat higher than that in IIa natural diamonds.

Examination of the Raman spectra of CVD films used here and in previous studies (11) reveals a relation between the Raman spectrum and the electrical properties. Films with narrower Raman line shapes and low  $sp^2/sp^3$  ratios (as measured by the peak at about  $1500 \text{ cm}^{-1}$ ) tend to have larger combined mobilities and thus a larger collection distance. Although the mobilities of film C and the IIa diamond are identical, the diamond phonon FWHM is still somewhat larger in the CVD film than in the IIa diamond ( $3.3 \text{ cm}^{-1}$  versus  $2.4 \text{ cm}^{-1}$ ). A relatively narrow diamond linewidth appears to be a necessary but not sufficient condition for a high-mobility CVD film, and in high-mobility films carrier lifetime is inversely related to the Raman linewidth.

In CVD films, the linewidth has been linked to the phonon domain size (19, 20) and to inhomogeneous stress distributions (20). The rough relation between Raman FWHM and electrical properties suggests that the linewidth may be related to the defect density. The Raman linewidth in CVD diamond is determined, as it is in single-crystal material, by the lifetime of the optical phonon created in the Raman process, and it is possible that the symmetry constraints of this process ( $\Delta k = 0$ ) may be relaxed at the defects, leading to shorter optical phonon lifetimes in CVD material and broader line shapes.

Table 1. Microwave deposition parameters.

Sample	Substrate temperature (°C)	Pressure (torr)	Microwave power (W)	Microwave frequency (GHz)	Methane concentration (%)
Film A	650	50	1000	2.45	0.1
Film B	700	90	1900	2.45	3.0
Film C	950	100	1900	2.45	1.0

Table 2. Summary of the electrical and Raman results for the IIa diamond and films A, B, and C.

Sample	Mobility ( $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ) at $200 \text{ V cm}^{-1}$	Lifetime (ps) at $200 \text{ V cm}^{-1}$	Collection distance $d$ ( $\mu\text{m}$ ) at $10 \text{ kV cm}^{-1}$	Raman FWHM ( $\text{cm}^{-1}$ )
IIa	4000	300	30	2.4
Film A	50	50	$< 0.1$	7.1
Film B	1000	100	2	4.8
Film C	4000	150	15	3.3

Because the average grain size of the polycrystalline CVD diamond films is comparable to the charge collection distance measured in these films, a large percentage of the charge carriers must be influenced by the grain boundaries. However, combined electron and hole mobilities for the CVD films are comparable to those measured in IIa diamonds and the dependence of the mobility and lifetime is also similar. This indicates that the mobility is not adversely affected by the grain boundaries in polycrystalline diamond films. This unexpected result along with the recent improvements in the electrical transport properties are encouraging findings in the development of diamond electronic devices. Fast, radiation-hard detectors for ionizing radiation may be among the first of such devices.

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