ELECTRICAL PROPERTIES OF HIGH QUALITY DIAMOND FILMS

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Abstract

Significant improvements have been made over the last year in the quality of chemical vapor deposited (CVD) diamond films. In particular, efforts have been made to improve the mobilities and lifetimes of free carriers. Values as high as 4000 cm^2/V-s have been measured for the combined electron and hole mobilities in the best polycrystalline diamond, which is comparable to that of the best single-crystal IIa diamonds. Comparable carrier lifetimes have also been observed, ranging from 150 ps to 1 ns in CVD diamond, compared with 100 to 600 ps in natural IIa diamonds.

The films were produced by microwave-assisted chemical vapor deposition (CVD), and both polycrystalline and epitaxial films were studied. The carrier mobility and lifetime were measured using transient photoconductivity as a function of electric field and excitation density. Both velocity saturation and electron-hole scattering were observed in the CVD films, similar to behavior measured in natural diamonds. The drift distance at an electric field of 10 kV/cm was as high as 15 μm. The improved properties are most likely due to lowered defect densities. Comparable results between epitaxial and polycrystalline films suggest that structural defects may not be the limitation. The improved quality is a significant step toward the production of electronic devices made of diamond, in particular diamond detectors for ionizing radiation. Already CVD diamond has been used to detect ultraviolet light, x-rays, and high energy charged particles.

Introduction

The development of diamond for electronic applications continues to progress rapidly. Recent improvements in the quality of diamond films produced by chemical vapor deposition (CVD) have been dramatic. Despite being polycrystalline, the best films now exhibit properties comparable to those of single-crystal type IIa natural diamonds. This is extremely promising for those diamond applications which utilize intrinsic diamond, such as ionizing radiation detectors.

The films to be discussed here were deposited by microwave-assisted chemical vapor deposition (CVD). Further details of the growth process are presented elsewhere.[1] In this paper, we will summarize the electrical properties of these films. Three different sets of films will be discussed to illustrate the significant progress in improving the quality of the material. The three sets will be referred to as A, B, and C films throughout this paper. All were deposited on silicon substrates, which were subsequently etched away to leave free-standing diamond films. The A films were the first microwave films grown for electronic properties and were a significant improvement over films deposited by a DC-enhanced plasma. These samples were less than 10 μm thick, with average grain sizes around 1 μm. The results of this set have been described earlier[2] and will be discussed only briefly here. Further iterations to optimize the material have produced sets B and C, with the C films possessing many properties similar to single-crystal natural IIa diamonds. Raman spectroscopy of the C films indicate that the material contains little to no detectable non-diamond bonded carbon. The best polycrystalline sample (from set C) had a FWHM of around 3.3 cm^{-1}, compared to 2.4 cm^{-1} for a single-crystal IIa natural diamond and 5.8 cm^{-1} for the first A films.

The electrical properties were studied using transient photoconductivity (PC),[2] where a known quantity of carriers is excited by light and the change in conductivity is measured. The magnitude of the signal provides a measure of the mobility (μ), and the decay of the signal is a measure of the free carrier lifetime (τ). For certain applications, such as detectors designed for high sensitivity, the average drift distance (d) of these carriers is also a relevant quantity, and this quantity can also be extracted by this technique. The measurement, as conducted, however, does not distinguish the separate electron and hole contributions to the current, and the mobility and drift distance are actually weighted sums of the two components. The PC response of natural IIa diamonds using this technique is fairly well understood and has been described earlier.[3,4] Comparisons between a natural diamond and the films will be presented in this paper.

Electrical contacts to the CVD samples were made by sputtering a 1 mm wide line of titanium, followed by gold, on the diamond surface with a gap of 1 mm in the line. The gap area is the active region that is probed with a uniform illumination of light. These structures were checked for linear current-voltage characteristics in the dark. Intrinsic photoconductivity was induced with a 5 ps pulse of 6.1 eV photons from an ultraviolet laser system. The penetration depth of the photons at this energy is less than 2 μm, and thus this measurement only probes a small fraction of the film. The transient decay of the PC was measured with a system-limited resolution of 50 ps.

Results

In the earlier work, the "A" microwave films exhibited mobilities around 50 cm^2/V-s and lifetimes less than 50 ps. The average drift distance of the carriers, defined as the product $\mu\tau E$, where E is the electric field, was less than 0.1 μm. These films were 3 and 6 μm thick, with average grain sizes around 1 μm. The ratio of the drift distance to the grain size suggested that the grain boundaries were not a significant limitation to the transport, but rather the transport was limited by intragranular defects.

Since that study, a series of microwave films have been produced with gradual improvements in the electrical response. An intermediate series of material ("B" films) was produced by optimizing thermal properties. Further improvements have culminated in the latest set of films (set "C"), which have properties comparable to natural IIa diamonds. Table 1 compares the photoconductivity mobilities and lifetimes measured in these series of films.

The largest improvements have been seen in the mobility of the carriers. The lifetimes have also been increased, although the change has not been as dramatic. Fig. 1 shows the measured mobility as a function of excited carrier density. The mobility decreases with density because of increased scattering between the electron and hole ensembles. Data for a type IIa natural diamond is also shown, as are data for films A and B. At low densities, in all cases, the mobility appears to saturate and become independent of the carrier density. For the best samples, the low-density mobility is limited by acoustic phonon scattering. This is supported by temperature dependent measurements in natural IIa diamond, which showed that the mobility decreased as $\sim T^{-3/2.5}$ The values for the mobility at low excitation densities for Film C and the natural diamond ($\sim$4000 cm^2/V-s at $\leq 10^{15}$ cm^{-3}) are higher those reported in the past for either electrons or holes alone. Because PC measures a weighted sum of both electron and hole motion, these values suggest that both electrons and holes are highly mobile.

Decay times of the transient are a measure of the lifetime of the free carriers. In Film A, these times were short (< 50 ps) and independent of the excitation density.[2] For Films B and C, as a function of excitation density, the decay times increase, as shown in Fig. 2. The increase in decay times begins at around 10^{16} cm^{-3}, where the mobility begins to decrease (Fig. 1). This change in mobility is what causes the increase in decay times; i.e., a non-constant mobility during the decay tends to lengthen the pulse. This is again similar to behavior seen in natural IIa diamonds. At low excitation densities, the decay time is a true measure of the lifetime, and it can be seen that both films B and C have shorter lifetimes than the IIa diamond (< 100 ps vs. 300 ps).

The data shown in Figs. 1 and 2 were taken at low electric fields (200 V/cm). Figs. 3 and 4 show how the mobility and decay times are a function of the electric field for Film C and a natural diamond. The data shown in these figures was taken at relatively low excitation densities, around 10^{16} cm^{-3}. Velocity saturation causes the mobility to decrease at higher fields, as shown in Fig. 3 in both Film C and the natural diamond. The corresponding velocity at a field of 10 kV/cm has not saturated and is around 1.7 x 10^7 cm/s in the natural diamond and 1.4 x 10^7 cm/s in Film C and

around 4×10^6 cm/s for Film B. The error associated with the mobility and velocity is about 30%. The decay times as a function of electric field are shown in Fig. 4. The rapid decrease as a function of field is unexplained, but appears to approach a constant for fields greater than 2000 V/cm. Again, for a given condition, the times are shorter for Film C, and shorter still for Film B.

Discussion

The data shown in Figs. 1-4 for the films were taken from the growth surface. There appears to be a significant difference in the properties of the material between the growth and substrate surfaces. Fig. 5 shows the mobility from the two surfaces of a 360 μm thick sample (Film B). On the growth side, the mobility is a factor of 50 larger at low densities. The lifetimes (not shown) are a factor of 2 to 3 longer on the growth side. The poor response of the substrate side may be due to the existence of an interfacial layer, which may be a carbide or some form of non-diamond bonded carbon. No well defined grains can be seen on this surface, whereas the growth surface shows clear, distinct grains. It is not clear whether the material improves continuously with thickness, or whether the material is of good quality throughout, except at the interfacial region, where it is particularly poor.

PC measurements were also performed on a series of B films grown under similar conditions, but to different thicknesses. Fig. 6 shows how the mobility (open circles) at ~10^{16} cm^{-3} and the decay times (closed diamonds) at ~10^{18} cm^{-3} both increased with thickness. This is consistent with recent thermal conductivity measurements performed on a similar set of such films, in which the thermal conductivity increased with thickness of the film.[6] Scanning electron micrographs of the surface showed that the grain size increased with thickness, which suggests that the larger the grains, the higher the quality of the diamond making up the grains. In the case of the thermal conductivity, an average over the entire thickness of the films was measured. With the PC, the shallow penetration depth of the light ensures that only the outermost few microns are probed.

For a given growth condition, generally the grain size increases as the thickness of the film increases. The highest quality material generally appears to be on the growth side. Graham and Ravi recently reported cathodoluminescence measurements on large single crystallites of diamond deposited by the combustion flame technique.[7] The intensity of the CL increased as the probe was moved from the substrate side to the growth side. The authors suggested that this may be interpretted as a decreasing density of dislocations with thickness. This supports our observation that the diamond improves in electrical properties with thickness.

In the development of applications such as a sweepout radiation detector, an important parameter is the drift distance of the free carriers. It is simply the product of the mobility, the lifetime, and the electric field. Shown in Fig. 7 are drift distances as a function of the applied field for Films B, C, and the natural diamond. In Film A (not shown), the distance never exceeded 0.1 μm. At a field of 10 kV/cm, in Film B, this distance is around 2 μm, and in film C, the distance is between 15 and 20 μm. In natural diamond, the distance is almost 30 μm. It is desirable to

maximize this distance, which would increase the sensitivity of a radiation detector made of diamond. It appears that the mobility may be near the limit set by acoustic phonon scattering, and further improvements in the drift distance may only be possible by increasing the lifetime.

Film C shows many similarities to the natural diamond sample, despite being polycrystalline. The main property that has been improved throughout the development has been the carrier mobility. The lifetime, which has increased as well, but not as dramatically, presently accounts for the somewhat lower drift distances seen in Fig. 7, when compared with the natural IIa diamond. It appears to be a more difficult property to improve upon. Even in natural diamond, the lifetime is short, ranging from 100 to 600 picoseconds, depending on the sample. It is not clear whether the lifetimes are limited by the same mechanisms in the two types of diamond, and whether the mechanism is related to impurities or structural defects. PC measurements performed on undoped and lightly doped epitaxial samples suggest that the introduction of impurities (the dopants) significantly lowers the mobilities and the lifetimes.[8] Explanations are being explored which account for this and the observation that properties also improve with thickness. With a better understanding of the limiting mechanisms, it is possible that lifetimes in CVD diamond may exceed that of natural diamonds and that the electrical properties can be tailored to specific applications.

Acknowledgment

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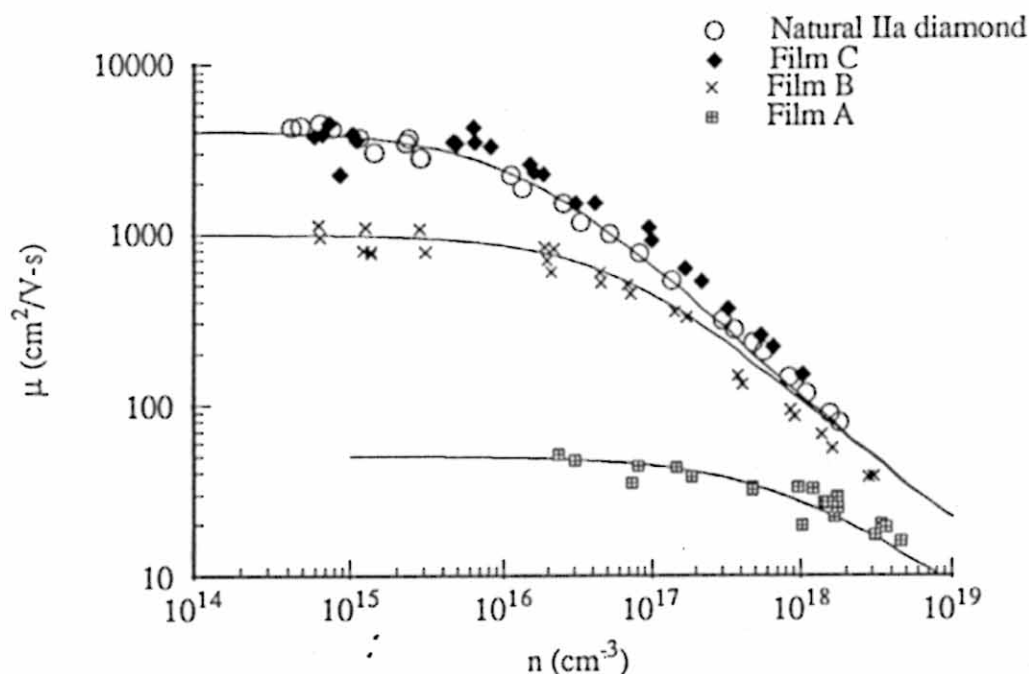
Fig. 1. Mobility measured with intrinsic photoconductivity for films A, B, and C, and a natural IIa diamond. The mobility falls off at high densities due to electron-hole scattering. The solid lines are calculated mobilities based on electron-hole scattering.
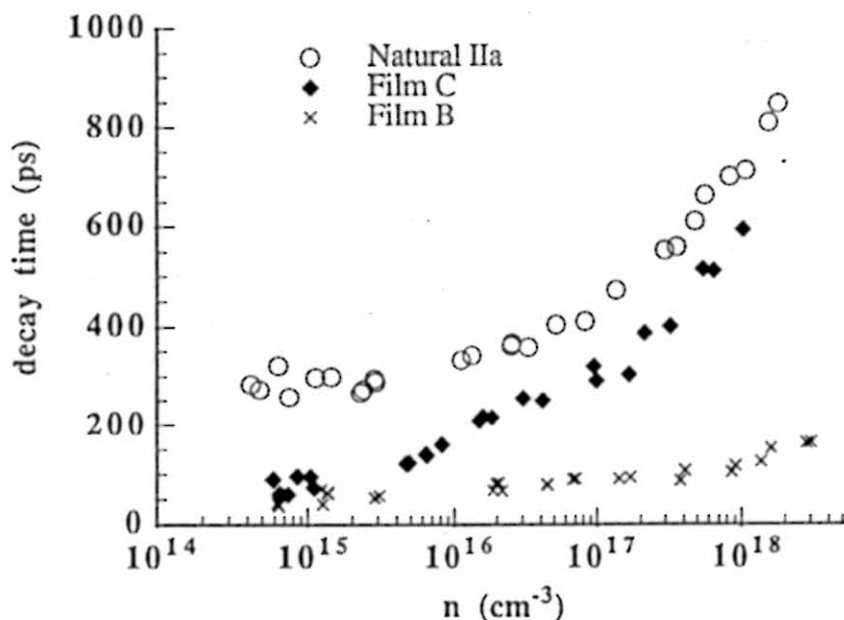

Fig. 2. Decay times increase as a function of excitation density in both the natural IIa diamond and the films Band C. The increase is due to change in mobility as a function of density (Fig. 1).
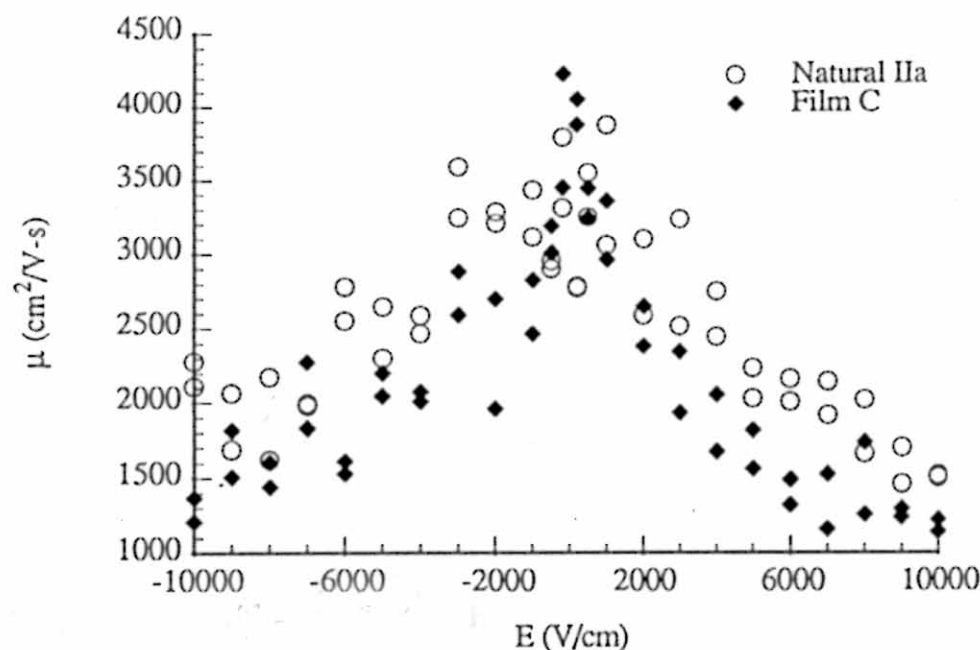
Fig. 3 The photoconductivity mobility for a natural IIa diamond and Films B and C. The decrease is due to velocity saturation with field.
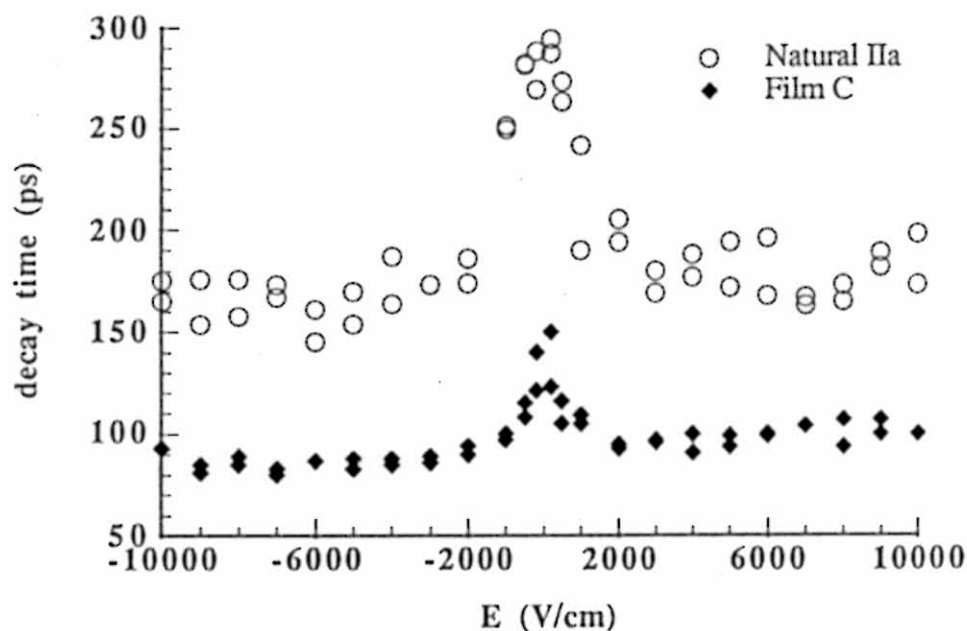

Fig 4. Measured decay times as a function of the applied field. The excitation density was around 10^{16} cm^{-3}. The change in decay times as a function of field is unexplained.
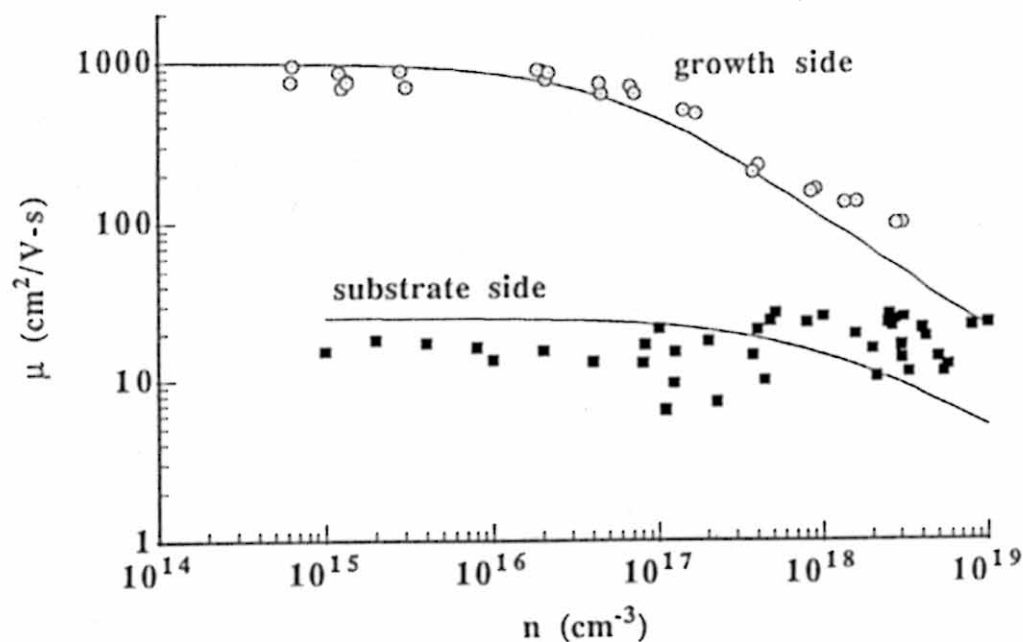
Fig. 5. Comparison of the mobility of carriers excited on the growth side and on the substrate side of Film B. At low exciation densities, the difference is a factor of 50.
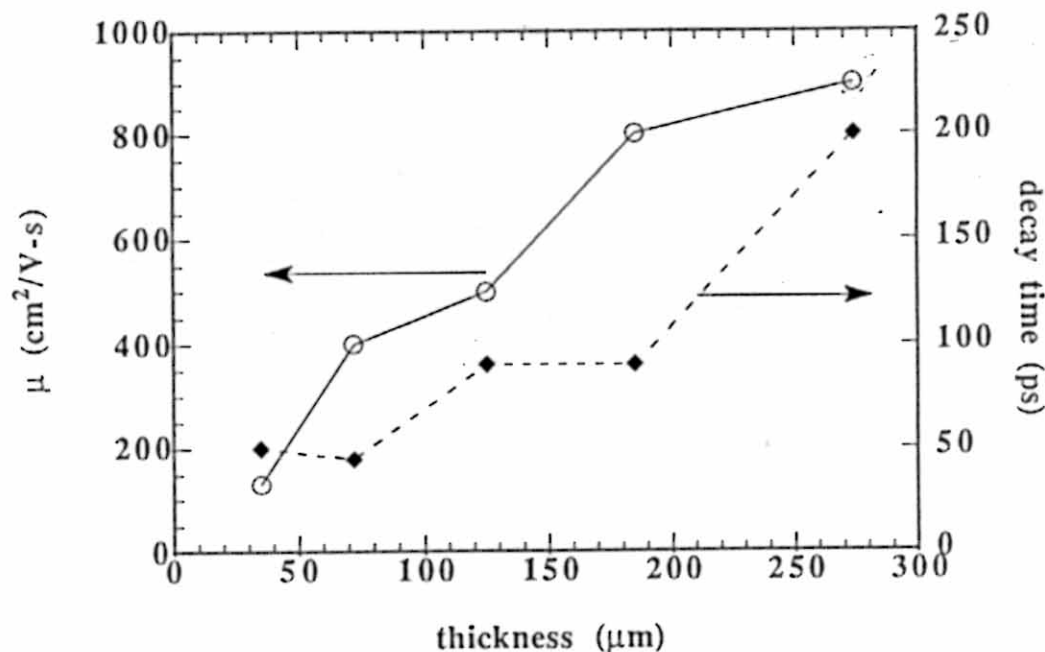

Fig. 6. Mobility at low densities ($\sim 10^{16}$ cm^{-3}) (open circles) and decay time at 10^{18} cm^{-3} (closed diamonds) increased in a series of films grown under similar conditions, but to different thicknesses.
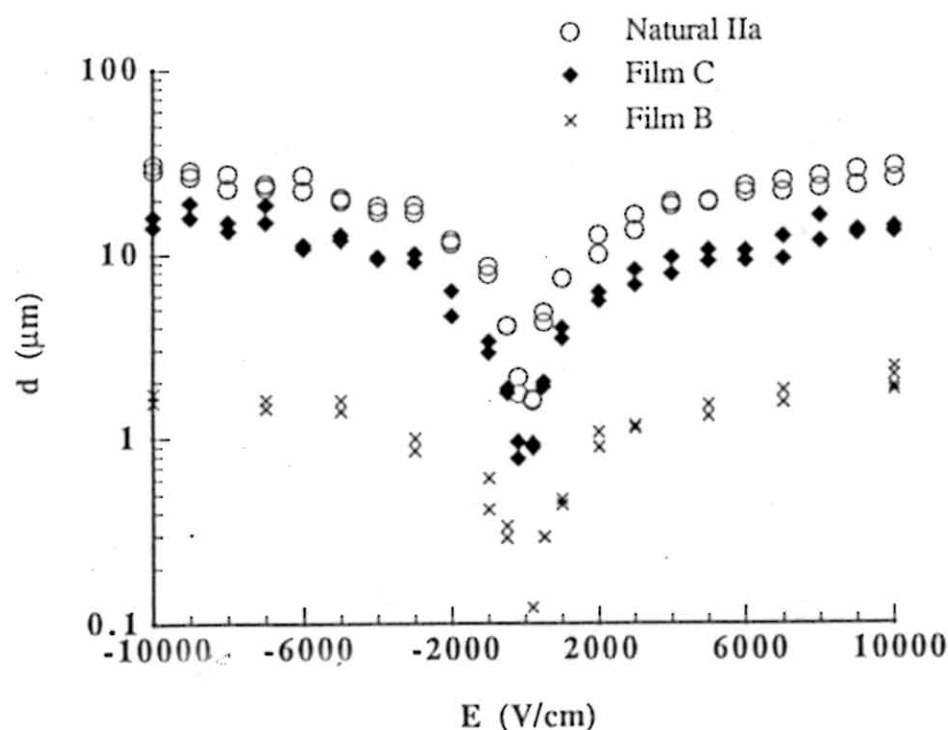
Fig. 7. Drift distance in Films B and C, and natural diamond. Film C approaches the performance of the natural diamond, with the difference due to shorter lifetimes in the film.

	μ (cm^2/V-s) (@10^{15} cm^{-3}, 200 V/cm)	lifetime (ps) (@10^{15} cm^{-3}, 200 V/cm)	d (μm) (@10^{15} cm^{-3}, 10 kV/cm)
Natural IIa single-crystal	4000	300	30
C	4000	100	20
B	1000	50 - 60	2
A	50	< 50	< 0.1

Table 1. Properties of Best Samples of Each Set