

COMPARISON OF HIGH ELECTRICAL QUALITY CVD DIAMOND AND NATURAL SINGLE-CRYSTAL IIA DIAMOND

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INTRODUCTION

Diamond has long been regarded as a promising semiconductor for electronic applications. Among its strengths are¹: highly mobile electrons and holes, a high dielectric breakdown strength, and superior resistance to radiation damage. These characteristics have been seen in the highest quality natural IIA diamonds and similar properties approaching or exceeding those of natural diamond have been measured in synthetic diamond films. In this paper, we compare the electronic properties of natural IIA diamonds with those of the best diamond films examined to date.

EXPERIMENTAL SETUP

At present, one striking difference between the two forms of diamond is the polycrystallinity of the synthetic material. With the exception of homoepitaxial films, which will not be discussed here, all synthetic diamond films deposited from the gas phase have been polycrystalline, with grain size varying from hundreds of angstroms to hundreds of microns. The samples discussed here are intrinsic diamond films that have not been intentionally doped. Such films are well suited for use as ionizing radiation detectors. Their high intrinsic resistivity ($>10^{12} \Omega\text{-cm}$) means low leakage currents and high signal-to-noise ratios when ionizing radiation is absorbed. The films were deposited either by microwave plasma CVD or DC arc jet. Further description of the deposition can be found elsewhere.²

To study the properties of intrinsic diamond, two techniques were used: photoconductivity (PC) and particle-induced conductivity (PIC). Both techniques rely on creation of free electrons and holes by absorption of radiation. Measurement of the current arising when these free carriers drift under an electric field allows the mean free drift distance or collection distance d to be measured. This distance is related to the carrier mobility μ and lifetime τ by the relation:

$$d = \mu\tau E,$$

where E is the applied electric field. With PC, the transient decay from a single photon pulse can also be measured, which allows both the carrier mobility and lifetime to be measured separately. The PC response of natural IIA diamonds using this technique is fairly well understood and has been described earlier.^{3,4} Comparisons between PC and

PIC applied to a natural IIa diamond can be found elsewhere.⁵ In this paper, we compare results from the latest polycrystalline diamond films with typical natural IIa diamonds.

The transient PC measurements were conducted using 3 to 5 ps pulses of 6.1 eV photons produced by a dye laser pumped by a mode-locked Nd:YAG excited the free carriers.⁶ The recording system had a time resolution of approximately 60 ps. For the PIC measurements, a ⁹⁰Sr source was also used, producing electrons with a β -spectrum up to an endpoint of 2.28 MeV.⁷ Above an energy of ~1 MeV these electrons are minimum ionizing, allowing the energy loss to be known precisely. A typical 10 μ Curie source can produce rates of up to 10^4 Hz. In this case, the total charge is collected and no attempts are made to measure the time-resolved signal. It should be noted that neither measurement, as conducted, distinguishes the separate electron and hole contributions to the current, and that the mobility and drift distance are actually weighted sums of the two components.

For the PC measurements, electrical contacts to the samples was 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 was the active region which was probed with a uniform illumination of laser light. A second geometry used for the PIC measurements involved the same contact metals, but applied to opposite sides of the sample. The β -electrons passed through one contact, into the sample, and out through the other contact, thus, probing the entire thickness of the sample. This was in contrast to the PC measurement, where the light was absorbed in less than 2 μ m, so only a small fraction near the surface of the sample was examined.

RESULTS

Comparison of PIC and PC at room temperature

Both PC and PIC has confirmed that many of the latest polycrystalline samples have collection distances comparable to natural IIa diamonds. An interesting observation, however, is that a gradient in material quality exists through the thickness of the films. A series of films deposited by DC arc-jet were examined using both PC and PIC. These films varied in deposition conditions and in thickness and had varying degrees of film quality. Nevertheless, by comparing the PC and PIC measurements, the material near the growth surface can be compared to the material throughout the entire thickness of the sample.

In all cases, the collection distance at the growth surface was roughly *twice* the distance measured through the entire thickness of the sample. Figure 1 illustrates this relationship. The collection distance measured by PC is compared to that measured by PIC, both taken at an applied electric field of 10 kV/cm. While the overall films varied in quality, as reflected by the different collection distances, the relation is similar between d in the bulk and at the surface.

Further evidence to support the gradient in properties came from measuring the collection distance in a series of microwave CVD films, grown under similar conditions, but to different thicknesses. Using PC to measure d at the growth surface, the improvement was roughly linear with thickness. On the substrate surface d was near zero. Further discussion of this data can be found elsewhere.²

Temperature dependence, as measured with PC

In natural IIa diamonds, the mobility at low fields (200 V/cm) and low densities ($\leq 10^{16} \text{ cm}^{-3}$) varies as $T^{-3/2}$, indicative of phonon-scattering limited transport.⁸ See Fig. 2. Similar measurements performed on a polycrystalline film deposited by microwave plasma CVD indicated that the mobility at room temperature was around $2500 \text{ cm}^2/\text{V-s}$, comparable to that of IIa diamond. However, the mobility was rather insensitive to temperature, unlike the case of natural diamond.

In the polycrystalline film, the lifetime at low fields also appeared independent of temperature, but at higher fields showed a slow increase with temperature. At 10 kV/cm, τ could be described by a fit: $\tau = 103 + 0.070 T^{1.2}$, for $100 \text{ K} \leq T \leq 370 \text{ K}$. This is in contrast to the IIa case, where τ was fit to the equation: $\tau = 295 + 1.27 \times 10^{-4} T^{2.6}$, for $200 \text{ V/cm} \leq E \leq 5 \text{ kV/cm}$. A temperature dependence of $T^{2.5}$ was seen in germanium and attributed to capture of carriers at dislocations.⁹

Films with high mobilities and long lifetimes

Among the films that have been examined by PC are samples with lifetimes exceeding a nanosecond. Fig. 4 shows the mobility and decay times for such a sample, taken at a low-field (200 V/cm). The closed symbols represent the mobility (left axis) and the open symbols the decay time (right axis). Data from a natural IIa diamond are represented as squares. Data from the polycrystalline sample are represented as triangles. Again, because of electron-hole scattering, the mobility drops off in both samples as the excitation density exceeds 10^{16} cm^{-3} . This is the same effect that causes the decay times to increase for densities $> 10^{16} \text{ cm}^{-3}$. The lifetime for these samples can be taken to be the value at the lowest densities (approximately 300 ps for the IIa, ~1 ns for the synthetic diamond). The collection distance for this particular sample was around 40 μm at an applied field of 10 kV/cm.

The latest samples produced by DC arc jet exhibit collection distances, for a given field, in excess of those of the best natural IIa diamonds. Using PIC, the collection distance in one sample was measured to be around 45 μm at 10 kV/cm, compared to 35 to 40 μm in the best IIa samples for the same field.¹⁰ This sample may exhibit even higher collection distances using PC measurements, which will be done shortly. (See Fig. 1 and related results above.)

DISCUSSION

Polycrystalline diamond films with electronic transport properties exceeding those of the best natural diamonds have been produced. Both microwave and DC arc jet methods are capable of producing such high quality films. In all polycrystalline films examined to date, the material quality improves with thickness, as evidenced by the collection distances measured by PC and PIC. Similar gradients in material quality have been reported in diamond films grown by combustion flame, examined by cathodoluminescence,¹¹ and in microwave grown films, examined using thermal conductivity.¹² In polycrystalline silicon, a gradient in mobility has also been reported.¹³ It is not known whether the improvement saturates with thickness. Films examined to date (up to ~500 μm thickness) have not shown any saturation effects. The improvements correlate with increased grain size, but it is not clear whether the grain boundaries or some other defect is the limiting factor. Whatever the defect is, its density appears to decrease with

thickness, and the trend is observed in diamond films deposited by a variety of techniques.

While room temperature results for the mobility and lifetime are similar between the microwave CVD films and natural diamonds, the temperature dependence differs significantly. The polycrystalline films are rather insensitive to temperature. This suggests the mobility may be limited by a neutral defect. The lifetime is only weakly temperature dependent, and only at higher electric fields. Similar measurements are planned for the DC arc-jet samples.

Lifetimes as high as 1 nanosecond have been achieved in the latest arc-jet films. This exceeds the lifetime in natural diamonds, which is sample dependent, but is usually between 100 and 600 ps. This is a promising result. Further improvements in film quality should yield even longer lifetimes. Such material would be useful for radiation detectors, where the longer lifetime would lead to higher sensitivity.

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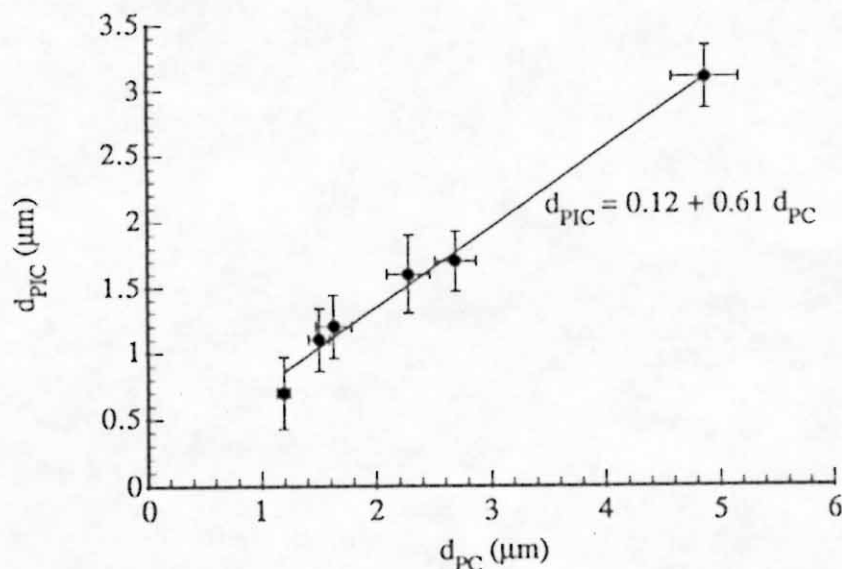


Figure 1. Collection distance measured using particle-induced conductivity vs. photoconductivity. The material at the growth surface has approximately twice the collection distance as that measured throughout the thickness of the sample. This is suggestive of a near linear gradient in material as a function of thickness.

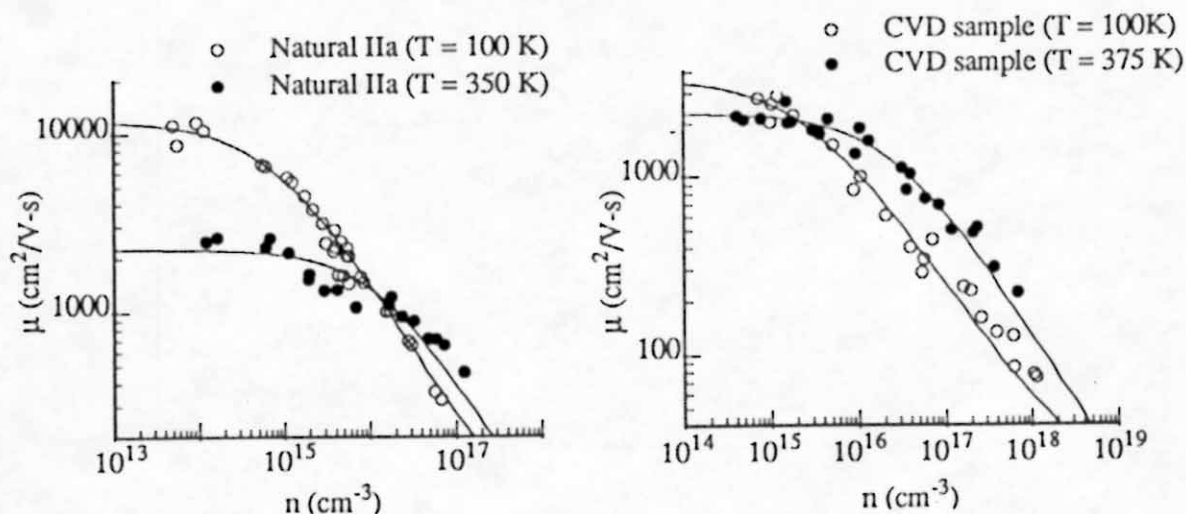


Figure 2. The mobility in a natural diamond and a CVD film. In natural diamond, the mobility goes approximately as $T^{-3/2}$ at low densities, indicative of phonon scattering. In the CVD sample, the mobility at low densities was rather insensitive to the temperature. In both samples, at higher densities, the mobility is dominated by electron-hole scattering. The curves are calculated using a term for electron-hole scattering and a term independent of density.

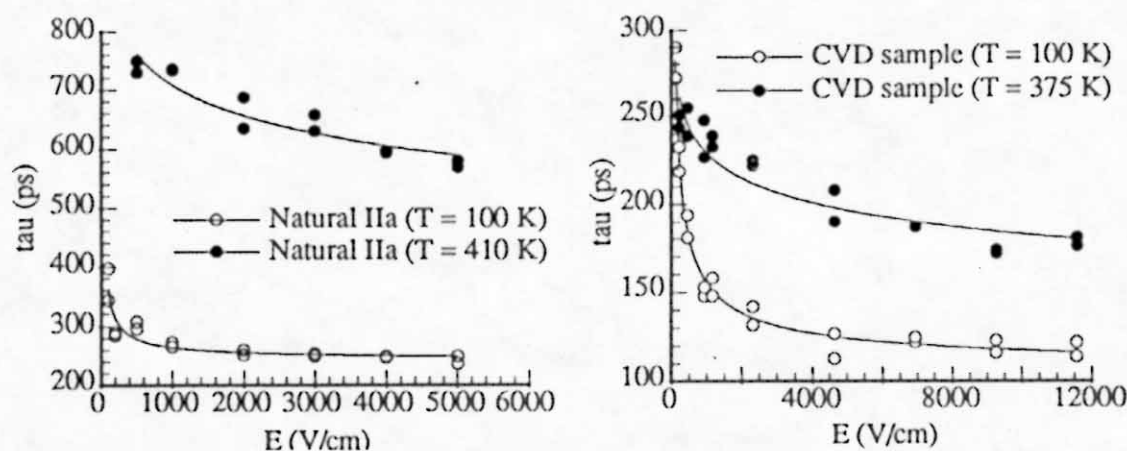


Figure 3. The lifetime in a natural diamond and a CVD film. In natural diamond, the lifetime increases with temperature at all fields, roughly as $c_1 + c_2 T^{2.6}$, where $c_1 + c_2$ are constants. In the CVD sample, the lifetime at low fields is a constant, but at high fields, varied as roughly $c_1 + c_2 T^{1.2}$. The curves are fits to guide the eye.

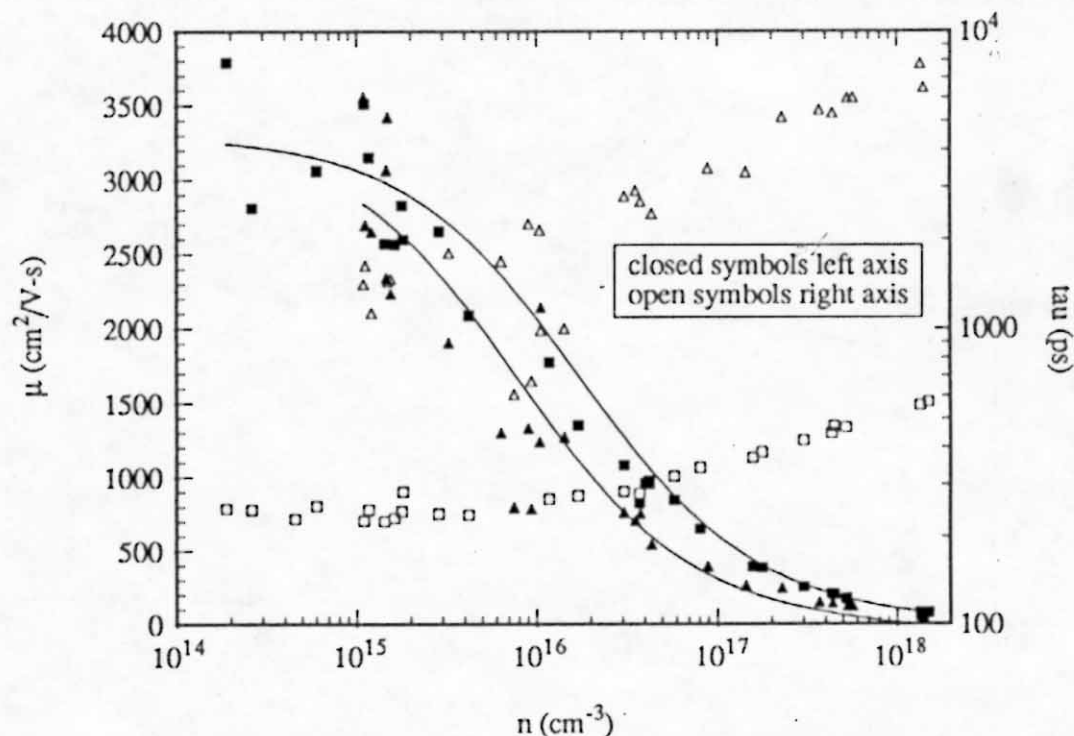


Figure 4. Among the latest films produced by DC arc jet are samples with mobilities comparable to those of natural diamond, but with much longer lifetimes. The dark symbols represent mobility and the open symbols the decay times, with the rectangles representing the natural diamond and the triangles the synthetic sample. Lifetimes as high as a nanosecond have been measured in synthetic diamond.