

2-377-3

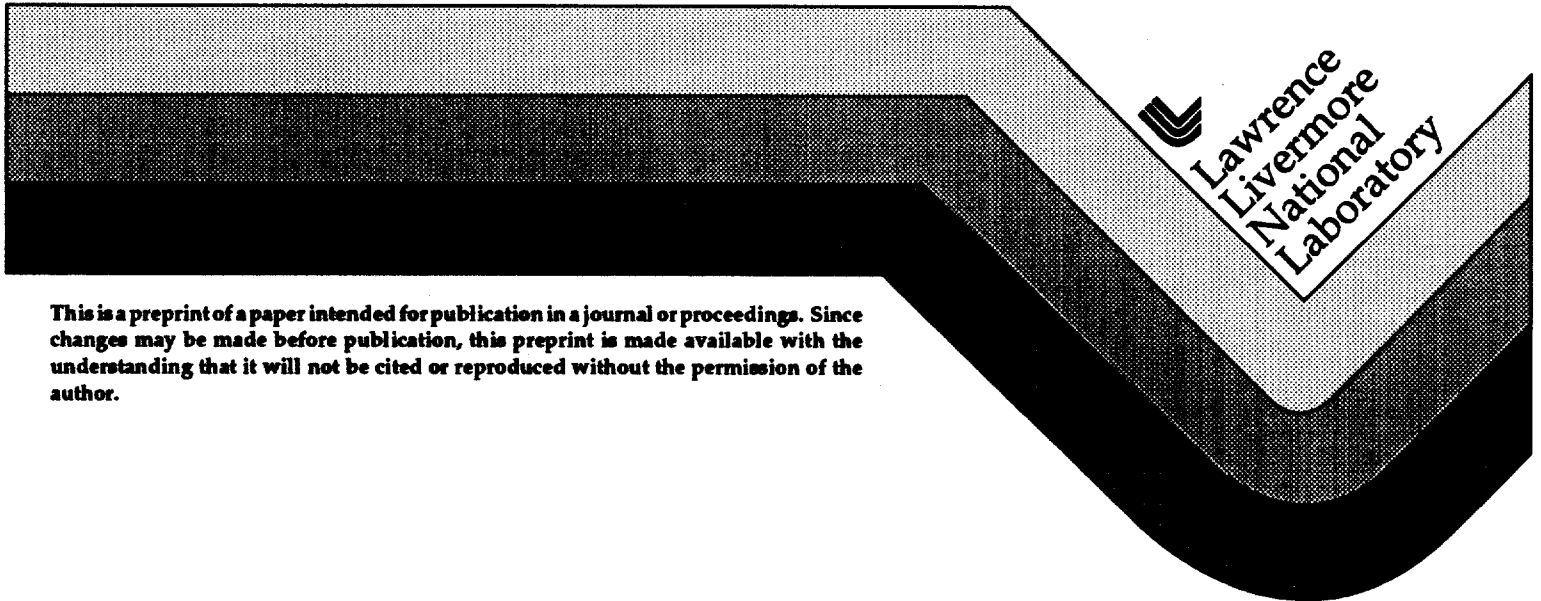
UCRL-JC-127288 Pt 2  
PREPRINT

# Diamond Radiation Detectors II. CVD Diamond Development for Radiation Detectors

Don R. Kania

This paper was prepared for submittal to the  
Proceedings of the International Summer School of Physics  
"Enrico Fermi"  
Bologna, Italy  
July 30-August 2, 1996

May 16, 1997



This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

## Diamond radiation detectors

### II. - CVD diamond development for radiation detectors

D. R. KANIA

*Advanced Microtechnology Program, Lawrence Livermore National Laboratory  
Livermore, CA 94551*

#### 1. - Introduction

Interest in radiation detectors has supplied some of the impetus for improving the electronic properties of CVD diamond. In the present discussion, we will restrict our attention to polycrystalline CVD material. We will focus on the evolution of these materials over the past decade and the correlation of detector performance with other properties of the material.

#### 2. - Collection distance measurements

Two techniques are used to measure the detector figure-of-merit,  $d$ . One is transient photoconductivity (PC) and the other is charge collection measurements using  $^{90}\text{Sr}$  or other penetrating, high-energy radiation. PC measurements employ a sample with a gap, typically 1 mm, in a transmission line structure. The gap is illuminated by a  $< 10$  ps pulse of UV laser light with a photon energy 6.11 eV which is above the bandgap of diamond. This radiation penetrates about  $2\ \mu\text{m}$  into the material. The resulting current pulse is recorded on a high-speed oscilloscope. The decay of the pulse is related to the carrier lifetime,  $\tau$ , and the integral of the current pulse is the collected charge,  $q$ . This is a surface measurement of the material characteristics, typically the applied electric field is perpendicular to the growth direction (see fig. 1).

The collection distance is also measured using high-energy electrons from a  $^{90}\text{Sr}$  radiation which emits 2.3 MeV particles or electrons from a storage ring with energies above 0.5 GeV. These are called minimum ionizing particles (MIP). These measurements are referred to as charged-particle induced conductivity (CPIC) tests. This method employs the measurement of the collected charge. The energy deposition rate in the charge track left by a MIP is well determined and can be considered to be

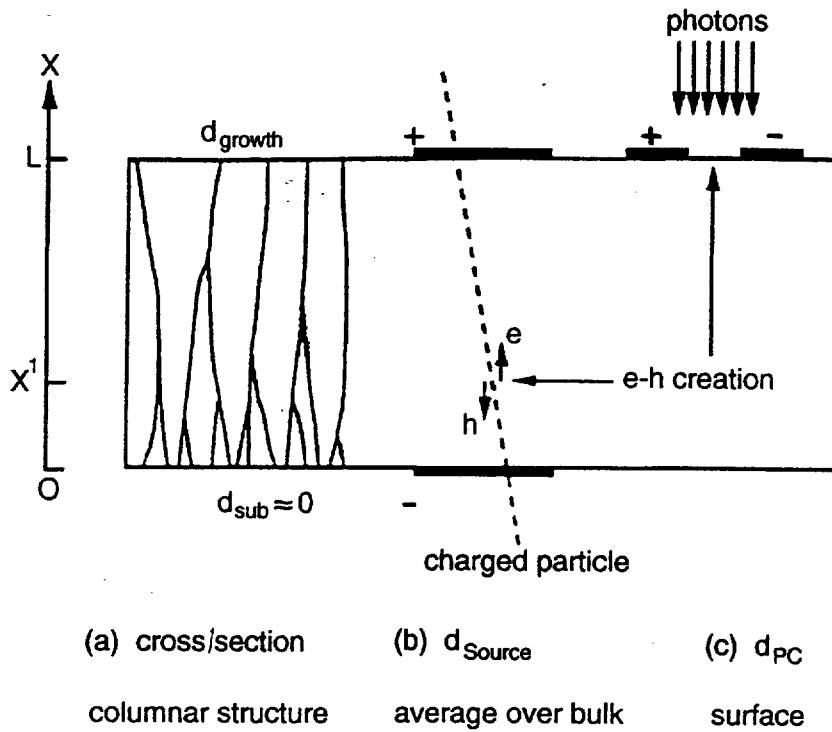


Fig. 1. - A cross-section of a PC and CPIC radiation detectors on CVD diamond.

uniform through the thickness of the material. The particle leaves 36 electron-hole pairs per micrometer, creating a track density of  $10^{13}$  pairs/cm<sup>3</sup>. The collection distance can be easily calculated from this measurement. These are vertical devices. The electric field and the particle path are parallel to the growth direction.

In an isotropic sample, such as a geologic IIa diamond, the PC and CPIC measurements should agree on the measurement of  $d$ . Tests were under performed which verified this result. Therefore, it has been established that in the absence of any material anisotropy the collection distance through the bulk of a diamond sample is the same as that of the surface [1].

### 3. - Detector fabrication

Before any metalization is applied the diamond surface must be cleaned. Chemical cleaning is usually performed, although excellent results are obtained with *in situ* sputter cleaning. A typical procedure is to degrease the sample with an acetone bath in a ultrasonic cleaner followed by boiling in a chromic-acid and sulfuric-acid bath. The sample is rinsed in a boiling mixture of  $NH_4OH$  and  $H_2O_2$ . A final rinse is

performed in deionized water. This procedure terminates the surface of the diamond in oxygen [2].

All of the detectors discussed in this lecture use multilayer metal contacts on the diamond surface. Typically, titanium is first deposited to form a carbide sticking layer. Sputtering is the preferred approach, the large incident kinetic energy provides sufficient energy for carbide formation to take place [3]. If the contacts are evaporated a post-deposition thermal anneal is required. Platinum may be deposited as a diffusion barrier and then thick gold for contact to the external electric circuit. This approach will result in ohmic contacts to the diamond, resulting in linear  $IV$  characteristics and minimum polarization of the detector. The contacts can be removed by boiling the sample in hot  $H_2SO_4$  or other strong oxidizing agents.

In summary, as shown in fig. 1, two different detector geometries are used in our tests. The PC measurements interrogate the surface of the sample. The CPIC measurements integrate over the path of the particle from the growth surface to the substrate. As illustrated, as the CVD material grows the crystallite size increases with increasing thickness.

#### 4. - The evolution of CVD diamond for detectors

Over the past several years we have studied a large number of CVD samples. In this section we will touch on the highlights of this development. As the CVD diamond growth community matured in the 1980's and early 90's, so did the quality of the material. Table I summarizes the evolution of polycrystalline CVD diamond during this period.

The earliest measurements on submicrometer thickness, DC plasma CVD samples were of very poor quality. The Raman spectrum indicated the presence of significant non-diamond bonded carbon along with a low resistivity of  $10^4 \Omega \text{ cm}$  and large optical absorption. This material was unsuitable for detectors and exhibited microsecond lifetime, persistent photoconductive signal with picosecond pulse excitation. These persistent signals were associated with the non-diamond bonded carbon content of the

TABLE I. - *Evolution of the properties of polycrystalline CVD diamond.*

Date	$d (\mu\text{m}) @ 10^4 \text{ V/cm}$
$10^9 \text{ BC}$ (geologic IIa)	20 to 50
DC plasma (1989)	$10^{-3}$
microwave (1990)	$10^{-1}$
microwave (1991)	2.5
microwave (1992)	20

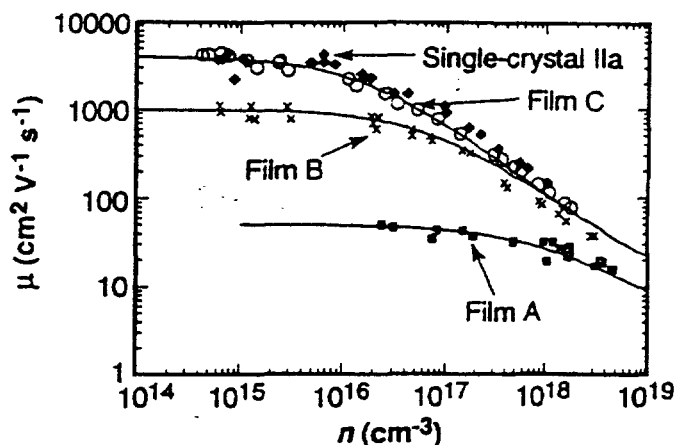


Fig. 2. - Mobility measured with PC: A(1990), B(1991) and C(1992). The mobility falls off at high density as a result of electron-hole scattering. The solid lines are calculated mobilities using electron-hole scattering theory.

films. As this material was eliminated in the growth, the collection distance increased, the resistivity increased and the persistent conductivity disappeared.

In 1990, higher-quality films approximately  $5\mu\text{m}$  thick produced by microwave CVD were tested. The non-diamond component was reduced dramatically, the resistivity was  $>10^8\Omega\text{cm}$  resulting in a collection distance of  $0.1\mu\text{m}$ . A critical development used to increase the resistivity was the use of a post-growth anneal step to drive off a conducting hydrogen from the diamond [4].

It was discovered that the Raman spectra were an excellent guide in developing detector material as it was for other material properties being developed at the same time. The goal was to eliminate any evidence of a non-diamond component and reduce the width of the  $1332\text{cm}^{-1}$  Raman peak, characteristic of diamond bonding. Additional correlations were noted with the optical clarity, UV absorption coefficient and film resistivity.

The continued optimization of the microwave grown films lead to a collection distance increase to  $2.5\mu\text{m}$  in 1991 and  $20\mu\text{m}$  in 1992. The latter result was very significant because the collection distance of polycrystalline diamond entered the range spanned by geologic IIa diamonds. In particular, the mobility of these films equaled that of the best geologic IIa diamonds. Figure 2 shows these data, the mobility of the films measured with PC. The mobility falls at high density as a result of electron-hole scattering. This work was reported by Plano *et al.* [5] in 1993. Three samples were grown with 2.45 GHz microwave excitation. The growth conditions are summarized in table II and the material characteristics in table III.

The trends are clear in the improvements in the diamond with growth conditions. Higher power, pressure and substrate temperature contribute to the quality. The

TABLE II. - *Microwave CVD deposition parameters.*

Sample	$T_{\text{substrate}}$ (°C)	$P$ (Torr)	Power (W)	CH <sub>4</sub> (%)	Grain size ( $\mu\text{m}$ )
1990	650	50	1000	0.1	4
1991	700	90	1900	3.0	11
1992	950	100	1900	1.0	15

TABLE III. - *Summary of the material properties.*

Sample	Mobility (electron and hole, $\text{cm}^2 \text{V/s}$ )	Lifetime (ps)	$d$ ( $\mu\text{m}$ )	Raman <sub>FWHM</sub> ( $\text{cm}^{-1}$ )
1990	50	50	< 0.1	7.1
1991	1000	100	2	4.8
1992	4000	150	15	3.3

correlation with the Raman FWHM and grain size is quite obvious. The collection distance as a function of electric field is shown in fig. 3.

The lifetime of the best material was the limiting factor in the collection distance. As noted in the previous lecture, nitrogen is a significant factor in determining the

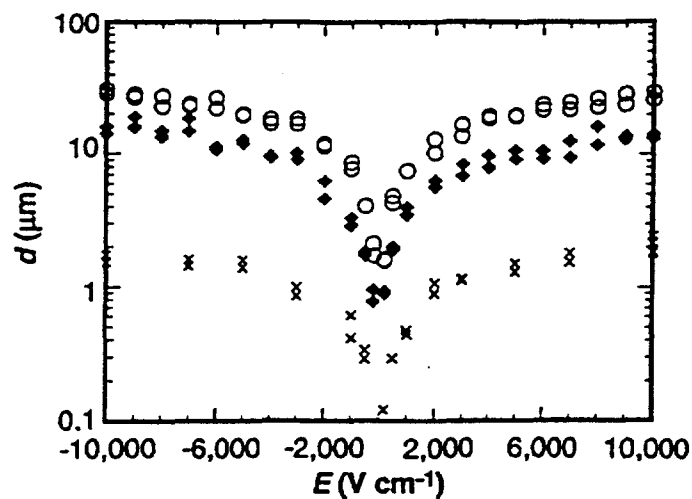


Fig. 3. - Collection distance as a function electric field: 1991 (x), 1992 (◆) and geologic IIa (○).

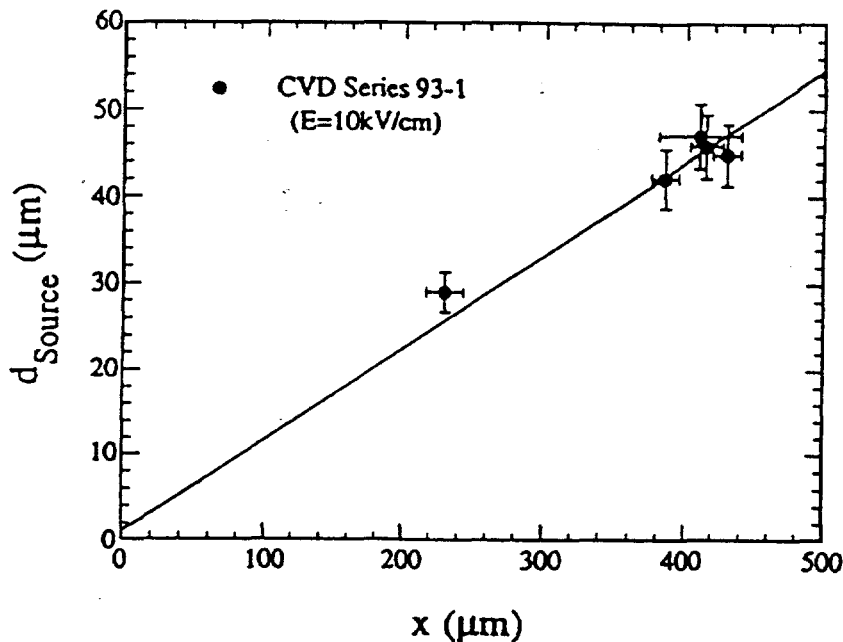


Fig. 4. - Collection distance as a function of film thickness showing a gradient in the material properties.

lifetime in geologic diamond. A SIMS analysis was performed on high-quality samples to determine the density of nitrogen and other elements. The results indicated that there was significantly less nitrogen in the CVD material than was in a geologic IIa by about a factor of 3 and no other impurities of significance were observed. Nitrogen was not limiting the lifetime. In addition, temperature-dependent conductivity measurements to 1000 °C were performed on these samples. The electrical conductivity of the CVD samples is an order of magnitude smaller than a geologic IIa, perhaps indicating higher purity.

With the advent of high-quality diamond films CPIC measurements became more common using CVD diamond detectors. A comparison of the collection distance measured with CPIC and PC revealed a factor of two difference between the two measurements on every sample. The PC measurements were consistently larger. This indicated that, like the thermal conductivity of CVD films [6], there exists a gradient in material properties in the films. This was first identified in the very same microwave CVD films used by Graebner *et al.* in ref. [6]. It has also been identified in DC arcjet grown films (see fig. 4). It was also noted that  $d$  never exceeded the grain size of the material. Again in analogy to the thermal/conductivity measurements, grain boundaries or the region near the grain boundaries are the probable location of the structural, not impurity, defects in the CVD intragrain material.

1-0



Author please, note that Prof. Tucciarone asked to give a clear definition either in the main text or in the caption of normalized growth rate, ?

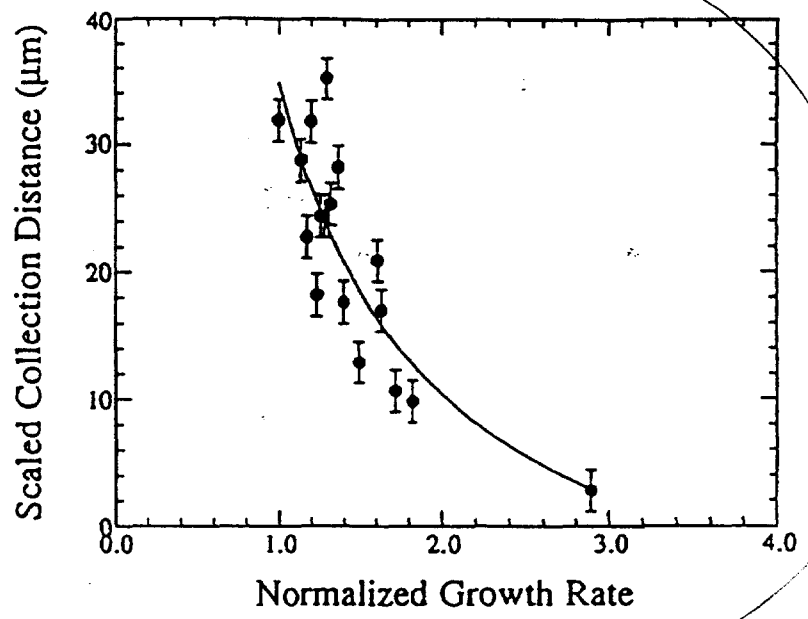


Fig. 5. - Collection distance as a function of normalized growth rate.

The gradient of the collection distance along the growth direction was mapped by measuring the collection distance profile. Two approaches were used. One approach used thick diamond samples cut from the same wafer which were tinned from the substrate side. Another set of samples was generated by varying the growth time at constant growth conditions to vary the sample thickness. Analysis of CPIC measurements and PC measurements on these samples uncovered a linear change in  $d$  as a function of thickness. This was true in the microwave and DC arcjet samples (see fig. 4).

The existence of a linear gradient in the CVD diamond reveals a strategy for producing improved particle detectors, remove material from the substrate side. This will increase the average properties of a CVD diamond sample.

Another observation was made at this time, high-quality films grow at reduced growth rate. Many applications required thick films, this stimulated an interest in a higher growth rate process, DC arcjet. After significant process optimization which was analogous to the development of microwave CVD films, the collection distance was improved to  $50\mu\text{m}$  in films several hundred micrometers thick. A clear correlation persisted between the collection distance and the growth rate (see fig. 5). The work of Zhao[7] showed several other distinct correlations of collection distance with the crystal lattice parameter, Raman FWHM, X-ray diffraction peak width and film transparency (see fig. 6). The clear trend in all of the correlation analysis is to push the diamond growth to lower stress and large grained films.

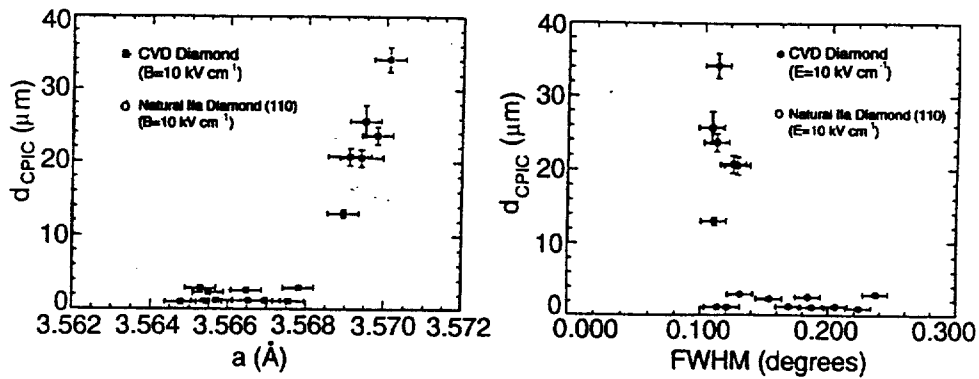


Fig. 6. - Collection distance as a function of lattice parameter and X-ray diffraction FWHM.

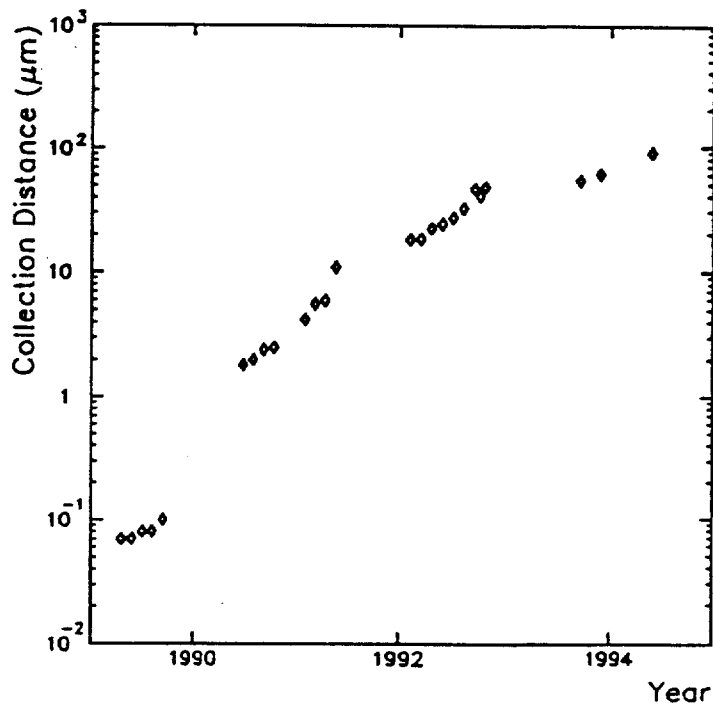


Fig. 7. - A summary of the development of detector quality CVD diamond.

Development has continued on the growth chemistry. This work has resulted in films with a collection distance in excess  $100\ \mu\text{m}$ . A summary of the development of detector grade CVD diamond is shown in fig. 7.

## 5. - Conclusion

Diamond CVD growth has made great strides in the past several years. High-purity, high-mobility diamond samples have been grown. In analogy to thermal properties, a gradient exists in the detector properties which improves from the substrate to the growth surface. Although it has not been established with certainty, grain boundaries or the defective region around grain boundaries limit the carrier transport in diamond. Collection distances of  $> 100 \mu\text{m}$  are achievable. This work suggests a growth strategy which emphasizes the growth of material with large grains in as thin a material as possible.

## REFERENCES

- [1] PAN L. S. *et al.*, *J. Appl. Phys.*, 74 (1993) 1086.
- [2] MORI Y., KAWARADA H. and HIRAKI A., *Appl. Phys. Lett.*, 58 (1991) 940.
- [3] NISHIMURA K. *et al.*, *MRS Symposium* 162 (1990) 341. /x
- [4] LANDSTRASS M. and RAVI K. V., *Appl. Phys. Lett.*, 55 (1989) 1391.
- [5] PLANO M. A. *et al.*, *Science*, 260 (1993) 1310.
- [6] GRAEBNER J. E. *et al.*, *Nature*, 359 (1992) 401.
- [7] ZHAO S., *Characterization of the Electrical Properties of Polycrystalline Diamond Films*, Ph. D. Thesis, Ohio State University, 1994.

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract no. W-7405-Eng-48.

---

*Technical Information Department • Lawrence Livermore National Laboratory*  
*University of California • Livermore, California 94551*

