High-quality diamond grown by chemical-vapor deposition: Improved collection efficiency in α-particle detection

Marco Marinelli, E. Milani,[a] A. Paoletti, A. Tucciarone, and G. Verona Rinati
INFM–Dipartimento di Scienze e Tecnologie Fisiche ed Energetiche, Università di Roma ''Tor Vergata,'' I-00133 Roma, Italy

M. Angelone and M. Pillon
Associazione EURATOM–ENEA sulla Fusione, I-00044 Frascati, Roma, Italy

Diamond films were grown on silicon by microwave chemical-vapor deposition using a CH_4-H_2 gas mixture. The crystalline quality of the films was assessed through their α-particle detection performance, a property highly sensitive to film quality, by using a 5.5 MeV ^{241}Am source. A maximum collection efficiency η of 70%, 50% being the average value, was obtained in a 115-μm-thick sample after β-particle irradiation (''priming effect''). Unprimed efficiency $\eta=50\%$ maximum, 30% average, was also obtained on other samples. The dependence of the efficiency and the resolving power on the external electric field was studied as well. The results are interpreted by means of a Monte Carlo analysis of the α-particle detection process. It is concluded that, in the priming process, a saturation occurs of deep defects limiting the as-grown detector performance, and charge collection distance is only limited by grain boundaries located close to the substrate side. Therefore, there is indication that further improvement can be reasonably obtained by increasing film thickness. © 1999 American Institute of Physics. [S0003-6951(99)02846-6]

Synthetic diamond films grown by chemical-vapor deposition (CVD) have a great potential for applications in several fields, due to the many (mechanical, optical, electronic, etc.) exceptional properties of diamond.[1,2] However, their polycrystalline nature and the relatively high concentration of structural defects still represent a severe limitation for many applications. This is why the performance of several diamond-based devices currently under investigation[3–5] is strongly influenced by the growth and operating conditions.

A particularly important and high-quality demanding application of diamond films is nuclear particle detection.[6,7] The high-energy gap of diamond results in a very low number of free carriers, leading to extremely low-leakage currents. Moreover, the radiation hardness and the high-temperature operation capability of such devices is strongly increased with respect to silicon-based detectors, a crucial feature in view of the operation of next-generation particle accelerators.[8]

The main parameters assessing the quality of CVD diamond films to be used as particle detectors are the charge collection distance (CCD) and the efficiency, defined as follows. When an electron–hole pair is created by an ionizing particle in a parallel-plate detector of thickness (i.e., electrode spacing) L, it induces[9,10] in the external circuit a charge $q_c=ex/L$, x being the total distance the electron and hole move apart. The CCD is the average drift distance and is given by

$$\delta=(\mu_e+\mu_h)\tau E, \tag{1}$$

where μ_e, μ_h are the electron and hole mobilities, respectively, τ is the mobility weighted lifetime of electrons and

holes, and E is the applied electric field. The efficiency is the ratio of the collected charge Q_c to the total charge Q_0 generated by the ionizing particle

$$\eta=Q_c/Q_0. \tag{2}$$

The link between η and δ can be deduced from the Hecht theory:[11]

$$\eta=\frac{\delta}{L}\left[1-\frac{\delta}{4G}(1-e^{-2G/\delta})(1+e^{2(G-L)/\delta})\right], \tag{3}$$

G being the penetration depth in L of the particles to be detected [for Eq. (3) we assumed $\mu_e=\mu_h$ in Eq. 1 and uniform generation of charge over G]. The lifetime τ, and therefore δ and η, are limited by the presence of trapping defects (impurities and/or grain boundaries), so that the collection efficiency is strongly correlated with crystal quality.

In CVD diamond particle detectors a crucial role is played by their thickness. Due to the columnar nature of CVD diamond growth, the crystal quality is much worse close to the substrate interface than at the growth surface. In particular, the CCD has been found to increase with film thickness.[12,13] CCDs up to about 250 μm have been reported[14] in millimeter-thick synthetic diamond *after removing* about half of the sample thickness from the poor-quality substrate side. This result was obtained for ^{90}Sr β particles and in the so-called ''primed'' state of the detectors (i.e., an improved response condition obtained by β-particle priming irradiation to fill traps). Nevertheless, it should be pointed out that this very high CCD corresponds to a charge collection efficiency $\eta\cong20\%$ only and is, furthermore, *much lower than the film thickness L*, thus indicating a relatively limited extension in depth of the defect-free surface layer. Similarly, ^{241}Am α-particle spectra of CVD diamond detectors also showed relatively low values of η.[15]

a)Electronic mail: milani@ing.uniroma2.it

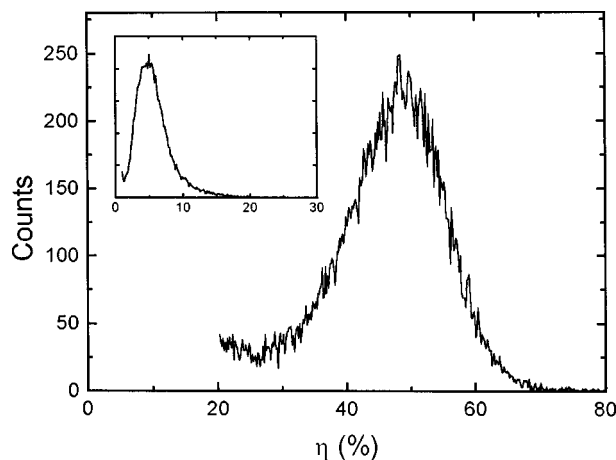Appl. Phys. Lett., Vol. 75, No. 20, 15 November 1999

Marinelli *et al.*   3217

FIG. 1. α-particle response spectra of the detector in the primed (full figure) and unprimed (inset) state. The collected charge is normalized by the generated charge to give the efficiency η.

FIG. 2. Behavior of the mean efficiency η (triangles) and the resolution R = FWHM/η (dots) of our detector (in a partially primed state) vs applied electric field.

In this letter, we report on high-quality CVD diamond films and their application as particle detectors with approximately 70% maximum collection efficiency and average value $\langle \eta \rangle \cong 50\%$: the corresponding CCD values go beyond the film thickness (about 250 and 120 μm, respectively, in an 115-μm-thick sample) and are obtained *without* any removal of diamond from the substrate side. (Note that, by assumption, electron and hole mean-free paths are 1/2 the CCD values.) The dependence of the collection efficiency and of the resolving power on the external electric field was also studied. In addition, evidence is presented from Monte Carlo simulations strongly supporting some current assumptions on the priming mechanism.

CVD diamond films were deposited in a microwave tubular reactor on silicon substrates.[16,17] A 1% $CH_4 - H_2$ gas mixture was used during the deposition process, while the substrate temperature was fixed at $T_s = 750 \, °C$. A 0.7 μm/h growth rate was estimated through a cross-section scanning electron microscope image of the films. Careful optimization of both the reactor geometry and the plasma energy density was necessary before the achievement of the best results.

Diamond-based detector prototypes were then built from the above samples. As the top electrode, a circular Au contact about 7 mm^2 size and 100 nm thick was thermally evaporated on the sample growth surface, while Ag paste was used as the silicon backing contact. The detector response to 5.5 MeV α particles was studied by using a ^{241}Am source. The irradiation was carried out through a pinhole, in the direction normal to the sample surface. The detector output was connected through a charge preamplifier and a shaping amplifier with a 2 μs shaping time to a multichannel analyzer.

It is well known[14] that CVD diamond detectors must be preirradiated with ionizing radiation (e.g., β particles) in order to achieve the highest detection efficiencies. This priming effect is qualitatively explained through a neutralization of trapping defects by irradiation. Before measuring efficiency with α particles, we therefore, irradiated our films with ^{90}Sr β particles for 60 h.

Figure 1 shows the α-particle detection efficiency of our sample in the primed state for an applied electric field E
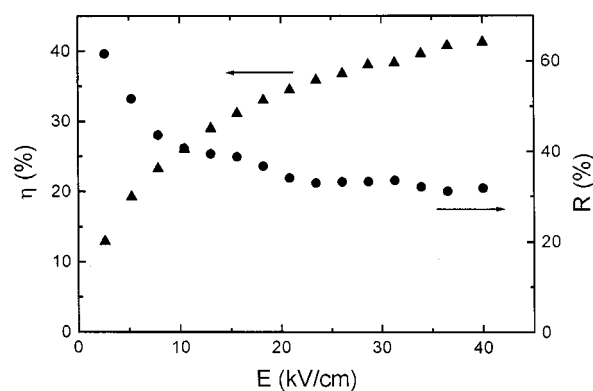
=40 kV/cm. The horizontal scale, i.e., the Q_0 value in Eq. (2), is obtained through calibration with a 100% efficiency silicon detector. It can be seen that the response extends up to a maximum efficiency of about 70%, with a very high-average value of about 50%. It must be stressed that the thickness of our sample is relatively low (115 μm) and that the whole sample has been utilized, without removing the lower-quality layer close to the substrate. The results, therefore, indicate that efficiencies very close to 100% might be achieved in CVD diamond detectors with a careful control of the deposition process, thus strongly reducing the performance gap with silicon-based devices. The reported maximum and average efficiencies correspond [Eq. (3)] to $\delta \cong 250$ μm and $\delta \cong 120$ μm, respectively. In other samples of lower thickness the unprimed efficiency reached $\eta = 50\%$ maximum, with 30% average value, corresponding to $\delta = 27$ μm and $\delta = 13$ μm, respectively in a 35-μm-thick film.

We also checked that all the α particles are actually detected. To this purpose, the ^{241}Am α source used was absolutely calibrated and the expected count rate was determined by means of a Monte Carlo calculation of the solid-angle factor for the source-to-detector geometry used. It was found that all the α particles which reach the detector are counted in the peak area.

It is well known that the response of particle detectors increases with the applied electric field. However, the increase in collection efficiency is accompanied by a widening of the peak, so that higher applied electric fields do not necessarily lead to better resolved spectra. In Fig. 2 we report the field dependence of both $\langle \eta \rangle$ and the ratio $R = W/\langle \eta \rangle$ between the full width at half maximum (FWHM) W and the mean value $\langle \eta \rangle$ of the response peak, showing that although $\langle \eta \rangle$ is, as expected, monotonically increasing with field, R substantially levels off for fields higher than about 20 kV/cm.

In view of the fundamental importance of the priming effect in the realization of high-efficiency CVD diamond particle detectors, we also tried to get some insight on some current assumptions on the priming mechanism in terms of deactivation of deep traps in the diamond gap. One sees from the α-particle response curves of our film reported in Fig. 1, in both the primed and unprimed (inset) state, that priming changes not only the position of the peak, but also its *shape*, from a right-asymmetric (positive skewness) to a left-
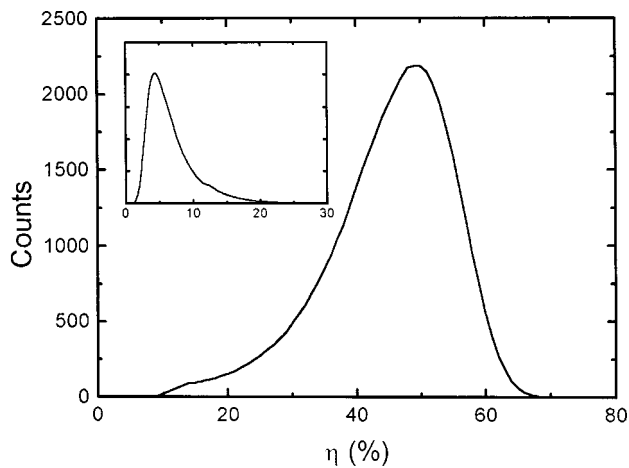
FIG. 3. Monte Carlo simulation of the α-particle response curves of our detector in the primed (full figure) and unprimed (inset) state.

asymmetric (negative skewness) one. In fact, there are basically two factors limiting the response of CVD diamond particle detectors; namely, in-grain defects and grain boundaries, the latter being not randomly distributed but strongly increasing in concentration towards the substrate side of the sample due to the columnar nature of CVD diamond growth. Only the former ones are expected to be deactivated by priming. This picture is strongly supported by a Monte Carlo simulation we developed for CVD diamond α-particle detection. We simply modeled in-grain defects by a homogeneous distribution of random trapping centers and grain boundaries by a density distribution $D(x)=A \exp [-x/b]$, where x is the distance from the diamond–substrate interface normalized to the thickness of the sample, and A, b are parameters. By using the α penetration depth in diamond $G \cong 15~\mu m$, we obtained the simulated response curves shown in Fig. 3, where the unprimed case was obtained by including *both* in-grain defects and grain boundaries, and the primed case by including *only* grain boundaries, with the same distribution utilized in the former curve. In particular, the curves in Fig. 3 are obtained using $A=75~\mu m^{-1}$ and $b=0.08$, while the average drift length due to in-grain defects (left curve) is about $6~\mu m$. These values correspond to a very low concentration of grain boundaries except close to the substrate interface, where a highly defective layer exists. This scenario is in agreement with that expected from the columnar growth of CVD diamond for samples with high-crystalline quality. In spite of the obvious crudeness of the model, the resulting curves reproduce very well the ones measured. The negative skewness appears, therefore, to be characteristic of high-crystalline quality samples where in-grain defects are substantially inactivated and grain boundaries limiting the response in the primed state are substantially located only close to the diamond–silicon interface, leading to high values of $\langle \eta \rangle$. It has to be stressed that, while the unprimed curve can be reproduced using in-grain defects only, the particular asymmetry of the primed curve strictly requires the particular shape of the grain-boundary distribution.

Because our films are almost free of grain boundaries for most of their thickness, increasing the thickness and removing the highly defective interface layer could reasonably lead to extremely high collection distances.

In conclusion, we have shown that very high-particle detection efficiencies can be reached in high-quality CVD diamond films, the priming effect being essential to improve performance. In-grain defects are not limiting the response of our primed films. The efficiency is only limited by grain boundaries close to the diamond–silicon interface, reaching values compatible with charge carrier mean-free paths close to the surface–interface distance; thus, charge collection distances appear subject to further improvement by increasing film thickness and/or removing the substrate interface layer. These results are supported by Monte Carlo simulations giving quantitative account of the transition observed from positive to negative skewness in the response curves during the priming process.

[1] *The Properties of Diamond,* edited by J. C. Field (Academic, London, 1979).
[2] *The Physics of Diamond,* edited by A. Paoletti and A. Tucciarone (IOS, Amsterdam, 1997).
[3] H. Kawarada, C. Wild, N. Herres, P. Koidl, Y. Mizuochi, A. Hokazono, and H. Nagasawa, Appl. Phys. Lett. **72**, 1878 (1998).
[4] T. Ito, M. Nishimura and A. Hatta, Appl. Phys. Lett. **73**, 3739 (1998).
[5] R. D. McKeag, S. S. M. Chan, and R. B. Jackman, Appl. Phys. Lett. **67**, 2117 (1995).
[6] L. S. Pan, S. Han, D. R. Kania, S. Zhao, K. K. Gan, H. Kagan, R. Kass, R. Malchow, F. Morrow, W. F. Palmer, C. White, S. K. Kim, F. Sannes, S. Schnetzer, R. Stone, G. B. Thomson, Y. Sugimoto, A. Fry, S. Kanda, S. Olsen, M. Franklin, J. W. Ager III, and P. Pianetta, J. Appl. Phys. **74**, 1086 (1993).
[7] F. Borchelt *et al.*, Nucl. Instrum. Methods Phys. Res. A **354**, 318 (1995).
[8] C. Bauer, I. Baumann, C. Colledani, J. Conway, P. Delpierre, F. Djama, W. Dulinsky, A. Fallou, K. K. Gan, R. S. Gilmore, E. Grigoriev, G. Hallewell, S. Han, T. Hessing, K. Honscheid, J. Hrubec, D. Husson, R. James, H. Kagan, D. Kania, R. Kass, K. T. Knöpfle, M. Krammer, T. J. Llewellyn, P. F. Manfredi, D. Meier, L. S. Pan, H. Pernegger, M. Pernicka, V. Re, S. Roe, D. Roff, A. Rudge, M. Schaeffer, M. Schieber, S. Schnetzer, S. Somalwar, V. Speziali, R. Stone, R. J. Tapper, R. Tesarek, W. Trischuk, R. Turchetta, G. B. Thomson, R. Wagner, P. Weilhammer, C. White, H. Ziock, and M. Zoeller, Nucl. Instrum. Methods Phys. Res. A **383**, 64 (1996).
[9] W. Shockley, J. Appl. Phys. **9**, 635 (1938).
[10] S. Ramo, Proc. IRE **27**, 584 (1939).
[11] K. Hecht, Z. Phys. **77**, 235 (1932).
[12] M. A. Plano, S. Zhao, C. F. Gardinier, M. I. Landstrass, D. R Kania, H. Kagan, K. K. Gan, R. Kass, L. S. Pan, S. Han, S. Schnetzer, and R. Stone, Appl. Phys. Lett. **64**, 193 (1994).
[13] S. Zhao, Ph.D. dissertation, Ohio State University (1994).
[14] W. Adam, C. Bauer, E. Bedermann, F. Bogani, E. Borchi, M. Bruzzi, C. Colledani, J. Conway, W. Dabrowsky, P. Delpierre, A. Daneuville, W. Dulinsky, B. van Eijk, A. Fallou, D. Fish, F. Foulon, M. Friedl, K. K. Gan, E. Gheeraert, E. Grigoriev, G. Hallewell, R. Hall-Wilton, S. Han, F. Hartjes, J. Hrubec, D. Husson, H. Kagan, D. Kania, J. Kaplon, R. Kass, K. T. Knöpfle, M. Krammer, P. F. Manfredi, D. Meier, M. Mishina, F. Le-Normand, L. S. Pan, H. Pernegger, M. Pernicka, S. Pirollo, V. Re, J. L. Riester, S. Roe, D. Roff, A. Rudge, S. Schnetzer, S. Sciortino, V. Speziali, H. Stelzer, R. Stone, R. J. Tapper, R. Tesarek, G. B. Thomson, M. Trawick, W. Trischuk, R. Turchetta, A. M. Walsh, R. Wedenig, P. Weilhammer, H. Ziock, and M. Zoeller, Proceedings of the Electrochemical Society's 5th Symposium on Diamond Materials (1998), p. 491.
[15] E. Bedermann, K. Blasche, P. Moritz, H. Stelzer, and F. Zeytouni, Proceedings of the 36th International Winter Meeting on Nuclear Physics (1998), p. 216.
[16] G. Balestrino, M. Marinelli, E. Milani, A. Paoletti, I. Pinter, and A. Tebano, Appl. Phys. Lett. **62**, 879 (1993).
[17] M. Marinelli, E. Milani, M. Montuori, A. Paoletti, P. Paroli, and J. Thomas, Appl. Phys. Lett. **65**, 2839 (1994).