

Cathodoluminescence study of ArF excimer laser-induced planarization of large grain diamond films

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(Received 25 October 1995; accepted for publication 14 February 1996)

Planarization of large grain diamond films has been induced by 193 nm excimer laser irradiation. Secondary emission images and cathodoluminescence (CL) in the scanning electron microscope have been used to characterize the irradiated area. Irradiation causes changes in the structure of defects involving nitrogen and vacancies. Evolution of the CL signal with the number of pulses indicates that the luminescence intensity tends to stabilize when a smooth film surface is obtained.

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In some applications of chemical vapor deposited (CVD) diamond films the rough surface is a drawback that needs to be reduced. One of the methods to achieve a smooth surface is laser irradiation (e.g., Refs. 1–5). However, besides the desired film modifications, laser induces local structural changes which can influence the film properties. For this reason, studies of laser-induced changes using different characterization techniques have been reported in the literature.^{2,4,6} A number of previous reports on laser irradiation of diamond films refer to film thickness under 30 μm and grain sizes in the range 1–5 μm (Refs. 1–4, 7, and 8). In this work, the effect of excimer laser irradiation with a wavelength of 193 nm on thick (130 μm) diamond films with a grain size in the range 40–50 μm is investigated by using the cathodoluminescence (CL) technique in the scanning electron microscope. These films present advantages compared to thinner films as their properties approach those of single crystals with increasing thickness of the columnar growth deposit. In particular, the influence of a high fluence irradiation, producing smooth surface, on the luminescence emission and hence on the defect structure has been investigated. The fluences used in the present work are higher than those usually reported in the literature and their effect on the films is to a large extent not known.

The samples used were self-standing CVD diamond films with a thickness of 130 μm and 40–50 μm grain size. The as-received samples were covered with a 100 nm gold layer. The samples were irradiated in air with 12 ns ArF excimer laser pulses at wavelength of 193 nm. The excimer laser beam is partially focused in the sample by means of two cylindrical lenses with focal lengths of $f_1=30$ cm and $f_2=11$ cm. The use of a mask allows to select an irradiation area of 1.5 mm \times 0.25 mm with a nearly homogeneous irradiation profile. Several regions of the sample were irradiated with a number of pulses ranging from 1 to 1000. Two different fluences were selected for the experiment: 20 and 37 J/cm². We applied a number of pulses necessary to produce a smooth surface. We considered that a smooth surface is obtained when the original crystal grain structure is lost and the surface appears smooth as observed in the secondary electron

mode of the scanning electron microscope. However, we did not carry out quantitative measurements of surface roughness. The samples were observed in the emissive and CL mode in a Hitachi S-2500 scanning electron microscope at accelerating voltage of 25 kV and temperatures between 80 and 300 K. The CL experimental arrangement has been previously described.⁹

The secondary electron mode of the scanning electron microscopy shows that first laser pulses (between 5 and 20 pulses, depending on the fluence value) remove the metallization without modifying the grain shape [Fig. 1(a)]. In a next step, edges and tops of grains are rounded [Fig. 1(b)] and a smoothing process takes place during the subsequent pulses. A smooth surface is observed [Fig. 1(c)] after about 500 pulses for the lower fluence and 50 pulses for the high fluence irradiations. After this treatment only traces of the original grains remain. Increasing the number of pulses causes additional material removal and a smoother surface.

Figure 2 shows a CL spectrum of the untreated crystal and the spectral evolution with the number of pulses. In Fig. 2(b) spectra after 1, 50, and 500 pulses with the fluence 20 J/cm² are represented. The behavior upon irradiation with a fluence of 37 J/cm² is qualitatively similar but less pulses are in this case necessary to produce the same effect. The CL intensity has been found to change with the number of pulses, as Fig. 3 shows. Comparison with secondary electron images shows that the maximum of CL intensity is attained when the gold layer has been removed by irradiation and the grains show the rounded appearance of Fig. 1(b). The minimum observed after 500 pulses corresponds to a high grade of planarization [Fig. 1(c)]. The qualitative shape of this evolution is similar for both series of irradiations.

The present results show that the use of a 193 nm excimer laser at large fluences enables an effective polishing of the rough surface of large grain diamond films. Besides smoothing, irradiation causes some structural changes detected by CL microscopy. The luminescence bands observed in the untreated CVD diamond have been often reported in the literature (e.g., Refs. 9–14). A band peaked at about 430 nm has been attributed to dislocations while a band peaked at

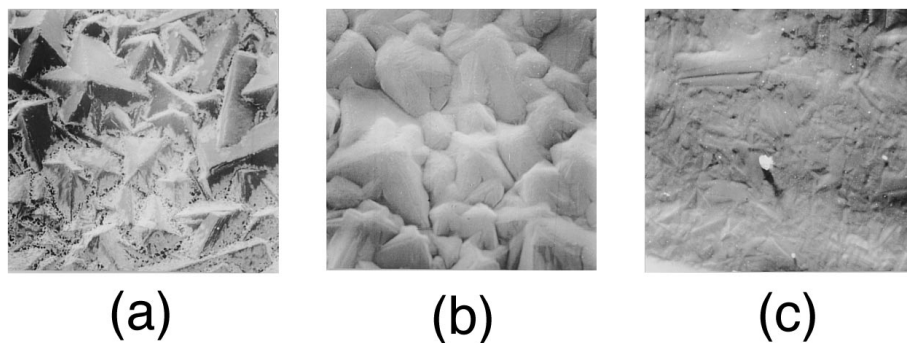


FIG. 1. Secondary electron image of a sample after (a) 1, (b) 20, and (c) 500 pulses at a fluence of 20 J/cm^2 .

about 530 nm is thought to be associated with centers containing nitrogen atoms and vacancies. As Fig. 2 shows, laser irradiation modifies the original spectrum with a complex emission in the blue–green region, and causes the appearance of a dominant band centered at about 600 nm . The recorded CL bands have been previously attributed to different mechanisms in diamond. The luminescence is generated in a layer of about $5 \mu\text{m}$ (Ref. 10), by 25 keV electrons, and is emitted through the thin layer, estimated in some hundreds of nm ,^{2,3} of graphite formed during laser irradiation. In the

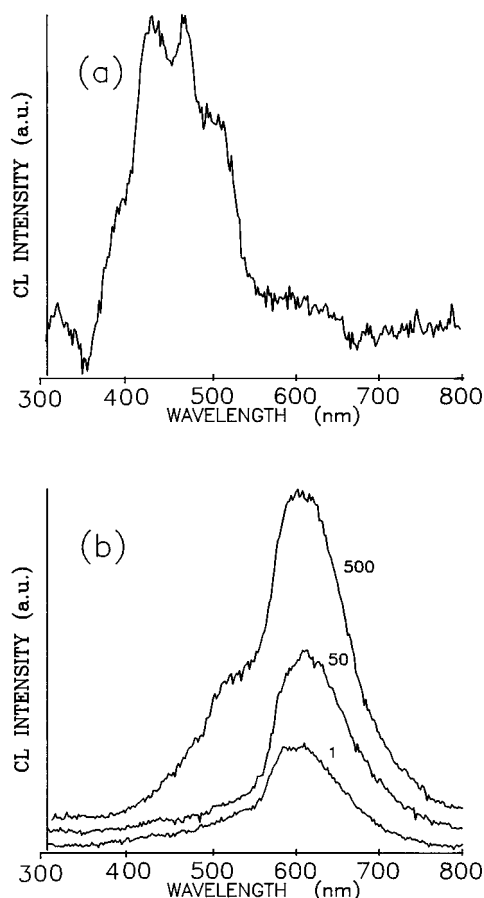


FIG. 2. CL spectra of (a) untreated sample and (b) of samples after 1, 50, and 500 irradiation pulses, respectively, with the fluence of 20 J/cm^2 at 220 K . The 575 nm zero phonon line is observed in spectra recorded at low temperatures down to 80 K (not shown in this figure).

spectra recorded after high number of pulses (500 pulses in Fig. 2), a shoulder at about 515 nm is observed. The prominent 600 nm band has been previously reported as a vibronic band with zero phonon line at 575 nm ^{10,13,15} and is attributed to a substitutional nitrogen atom and a vacancy.¹⁶ The band at 515 nm is also attributed to nitrogen-vacancy complexes.^{17,18}

The CL results show that laser irradiation causes changes in the structure of defects involving nitrogen and vacancies. In particular the concentration of centers with substitutional nitrogen increases while the centers involved in the original blue–green emission are partially annealed. Consequently planarization of diamond films with excimer laser causes changes in their optical properties.

The evolution of CL intensity with the number of pulses (Fig. 3) is not only a consequence of changes in the defect structure but also of differences in the composition, structure, and topography of the surface at different stages of the irradiation process. In particular, during the first pulses the gold overlayer is removed which implies an increase of the CL intensity. In the next pulses competing processes which influence the absorption, planarization and formation of graphite in the surface, take place. Both mechanisms, together with the changes in luminescent centers concentration would determine the variation of CL intensity. Comparison of secondary electron images and CL signal indicate that CL intensity tends to stabilize when a smooth surface has been obtained.

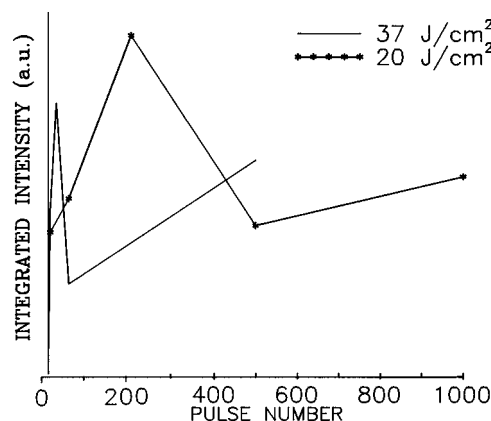


FIG. 3. Evolution of the total CL intensity with the number of pulses during irradiation at fluences of 20 and 37 J/cm^2 .

ACKNOWLEDGMENT

This work has been supported by DGICYT (Projects Nos. PB-93-1256 and HP94-098).

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