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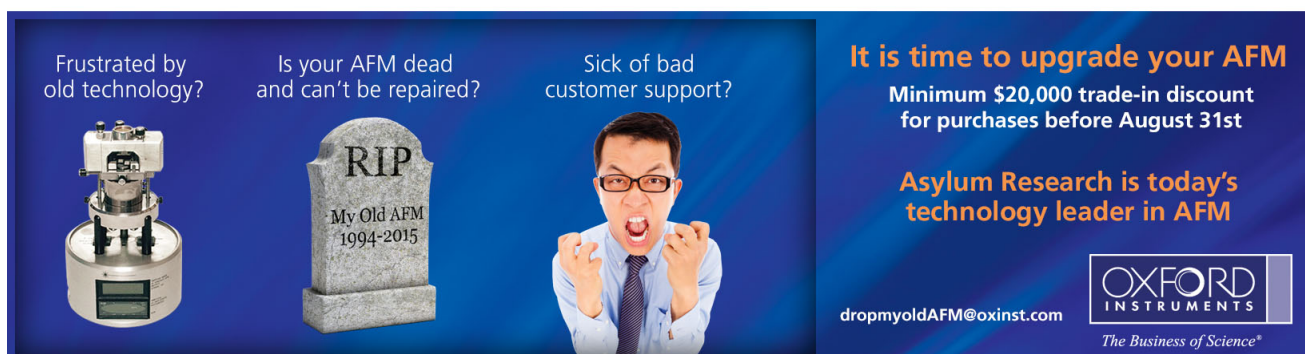
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Cathodoluminescence of diamondlike films deposited by glow discharge

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The room-temperature cathodoluminescence of diamondlike films produced by glow discharge is reported. The material was deposited onto dc biased substrates maintained at relatively low temperature ($< 100^\circ\text{C}$). Two visible peaks around 2.3 eV (green) and 2.7 eV (blue-violet) were identified which are commonly found in natural and synthetic diamond, indicating the presence of crystalline particles in the films. Moreover, x-ray diffraction spectra of the samples before cathodoluminescence studies are identical to the ones reported for natural powder diamond.

In recent years, considerable effort has been devoted toward the growth of films of crystalline diamond on a variety of substrates. The tendency of carbon to form a graphite-type structure during growth is a serious impediment to diamond fabrication at low pressure by plasma-assisted decomposition of hydrocarbons. A major breakthrough in depositing polycrystalline diamond was the discovery that the presence of atomic hydrogen inhibit graphite formation.¹ It was demonstrated also that oxygen incorporation in the plasma discharge enhances both the crystallization and deposition rates. Attempts have been made to find particular experimental conditions for avoiding the formation of unwanted nontetrahedral bonds. Thus, several techniques are currently used to deposit polycrystalline diamond films, but all of them generally require temperatures above 700–900 °C.^{2–5} Preseeding the substrate with diamond powder, different gaseous hydrocarbon/argon mixtures, and chemical etching are some of the reported techniques which seem to induce the crystalline phase. Recently, using microwave plasma-enhanced chemical vapor deposition, polycrystalline diamond was obtained at lower temperatures ($\sim 350^\circ\text{C}$), opening the possibility of using substrates which are unstable at higher temperatures.⁶ There is a general consensus that the deposition of thin films from a low-temperature plasma at low substrate temperature and/or pressure produce an amorphous material. This is generally called “diamondlike carbon” (DLC) and possesses variable amounts of sp^2 and sp^3 bonds. Recently, however, Amaratunga *et al.*⁷ reported the presence of single-crystal diamond in thin films deposited from CH_4/Ar rf plasma onto *n*-type crystalline Si. These authors presented experimental results obtained from transmission electron microscopy showing evidence of crystalline diamond grains over the entire film.

In this communication we report the room-temperature cathodoluminescence (CL) spectra of glow-discharge-deposited thin films on biased stainless-steel (SS) substrates from a 80% gaseous mixture of CH_4/Ar . The CL spectra exhibit the green and blue-violet emission which is characteristic of natural and synthetic diamond, indicating the existence of crystalline particles in the films. Also, x-ray diffraction spectra of as-deposited samples are coincident with those reported in the literature for natural powder diamond, confirming the existence of crystalline particles.

The deposition system was a standard capacitively cou-

pled glow-discharge reactor. In order to perform visible and infrared (IR) studies, the samples were simultaneously deposited onto both quartz and polycrystalline silicon. SS substrates 19, 29, and 39 were etched with a 50% volume solution of HF and HNO_3 until isolated small pits resulted evident by visual inspection. SS substrate 49 was etched with the same solution until it became completely roughened. The substrates were temperature controlled and a dc bias was applied during the deposition. Sample 19 (deposited at 50°C) shows a rough structure while samples 29 and 39, which were deposited at 100°C , have mirrorlike surfaces. Sample 49, which was also deposited at 100°C , shows a hazy appearance. The deposition rate was approximately $0.3 \text{ \AA}/\text{s}$. Table I shows some fabrication parameters, the optical gap E_T , determined using the Tauc plot, and E_{04} , the energy where the absorption coefficient takes the value 10^4 cm^{-1} . The thickness of the samples and the estimated plasma-substrate potential are also listed. The former was obtained from the interference fringes of the visible transmission spectra and the latter followed from the method proposed by Corbun and Kay.⁸ A standard television electron gun was used for the CL studies. The electron beam was electronically chopped and a phase-sensitive detection system used. The electron beam hits the sample at 45° to the normal and the emission is collected at a right angle to the incident electron beam.

The IR spectra of all the samples show similar features

TABLE I. The substrate temperature used during the deposition and samples thickness are indicated. E_{04} and E_T are the energy where the absorption coefficient is 10^4 cm^{-1} and E_T is the optical gap from a Tauc plot, respectively. The plasma-substrate potential was varied biasing the sample holder and its estimated value (see Ref. 8) is indicated.

Sample	Substrate temp. ($^\circ\text{C}$)	Plasma substrate potential (V)	E_{04} (eV)	E_T (eV)	Thickness (Å)
19	50	- 100	4.0	3.8	2400
29	100	- 100	4.2	3.8	2000
39	100	- 15	4.0	3.8	3700
49	100	-- 100	4.1	3.9	1400

and absorption bands at 3000, 2956, 2924, and 2872 cm^{-1} were always found. We note that the IR absorption spectra were taken on samples grown on crystalline silicon and the CL experiments performed for films deposited onto SS. Although differences in the structure are expected, an attempt to identify the observed absorption bands was made. The comparison of our results with those of Dischler, Bubenzer, and Koidl⁹ allows us to assign the vibrational bands as follows.

The sp^2 (CH) bond is expected to contribute to absorption near 3000 cm^{-1} and is associated with a graphite structure. The 2956- cm^{-1} peak is associated with sp^3 (CH_3) (asymmetric stretching) bonds, the 2924- cm^{-1} peak with sp_3 (CH_2) (asymmetric stretching) bonds and the 2872- cm^{-1} peak with sp^3 (CH_3) (asymmetric stretching) bonds. In order to estimate the sp^2 (CH) bonds contribution, the spectra were deconvoluted following the procedure proposed by Dischler *et al.*,⁹ which involves the fitting of an equal number of Gaussian curves to the absorption bands associated with sp^2 and sp^3 bonds, respectively, and by calculating their relative area. For our samples, we obtained 25%–30% density of sp^2 bonds contributing to the total.

Figure 1 shows the normalized room-temperature CL of three of the studied samples. The accelerating voltage was 7 kV, the cathode current 4 μA , and the spot size 0.5 mm^2 . Samples 29 and 39 are much more efficient than sample 19. The strongest emission was obtained in sample 49, the one deposited onto a completely roughened substrate. The emission of all the samples could be observed with the naked eye in a normally illuminated room. Samples 19 and 49 emitted light uniformly while the other ones showed CL from different spots distributed on the surface.

Two peaks between 2.0–2.5 eV (green) and 2.6–3.0 eV (blue-violet) were observed. Samples 29 and 49 manifested a blue shift of the stronger (green) peak as compared to samples 19 and 39. These variations are most likely due to different substrate bias and preparation conditions. The full width at half maximum (FWHM) for this peak, however, is similar for all the samples (0.3 eV). The blue peaks are coincident for samples 29, 39, and 49, having a FWHM of 0.4 eV. The weakness of the signal of this peak in sample 19 does not allow us to locate its position accurately.

Yamamoto, Spence, and Fathy¹⁰ studied the CL of natural ("type II_a") diamond and found two broad peaks centered at 2.85 and 2.35 eV with a relative intensity which is in good agreement with that obtained in our samples. The observed CL structure is generally interpreted as a combination of the luminescence of the so-called bands A and H3, which are commonly found in natural and synthetic diamonds. Band A is considered to arise from a deep donor-acceptor pair recombination while the H3 one is associated with a nitrogen-vacancy complex.¹¹

Recently, Kawarada *et al.*¹² observed CL from crystalline films produced by plasma-assisted chemical-vapor-deposition (CVD) deposited onto substrates kept at 850–900 °C. These investigators observed visible emission between 2.3 and 2.6 eV in different samples and suggested that its origin was in band A with some small contribution of the type H3 luminescence.

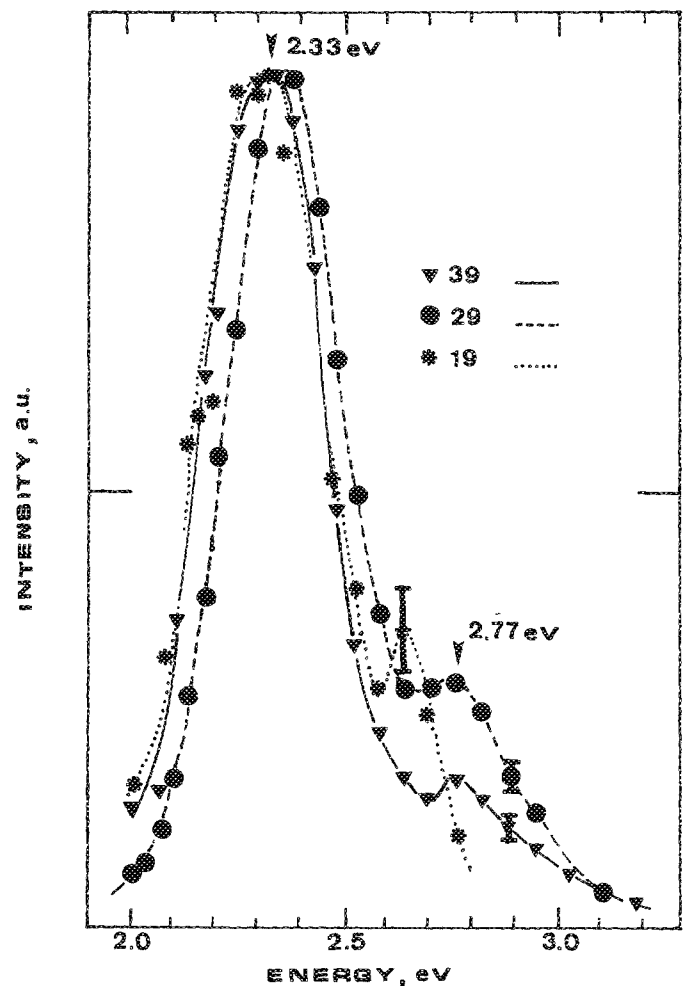


FIG. 1. Room-temperature cathodoluminescence spectra from some of the studied samples. The curves are normalized to one. The experimental curve of sample 49 (none indicated) is coincident with the one of sample 29.

Robins *et al.*¹¹ observed a CL band peaking at 2.83 eV in diamond films grown by hot-filament CVD which they suggest arises from dislocations. This value is very similar to the 2.77-eV emission found in our samples 29, 39, and 49.

Rand and DeShazer¹³ discussed two centers related to the nitrogen impurity in natural and synthetic diamonds. They are called N3 and, as before, H3, having emission bands at 2.75 and 2.3 eV, respectively.

We point out that the widths of the emission bands we observed (0.4 and 0.3 eV for the blue and green peak, respectively) are in good agreement with the reported ones by the above mentioned authors.

Luminescence from DLC was previously reported to emit a broad band which was attributed to the wide-band-gap amorphous phase.^{14,15} In our results, however, this possibility is ruled out because of the observed relative narrow emission bands and energy range of the emission. In fact, the CL results suggest the presence of crystalline particles in the material. Moreover, x-ray diffraction experiments confirm the existence of a crystalline phase. Within 1%, x-ray diffraction patterns of our samples were identical to the ones obtained in natural powder diamond (ASTM 6-675). Fur-

thermore, within the sensitivity of the x-ray apparatus, not even one peak corresponding to the graphite diffraction spectrum was found. The lack in our samples of the characteristic narrow zero-phonon line of a crystalline phase could be understood, perhaps, as due to the low resolution of our measurement system. Experiments in progress to improve the resolution are under way.

To summarize, CL and x-ray spectra indicate the existence of crystalline diamond particles in glow-discharge-deposited carbon from a gaseous mixture of argon and methane onto biased low-temperature substrates. The strength of the emission is related to the morphology of the substrate. The strongest emission was observed in a material deposited on a completely roughened substrate. No major changes were observed in the shape of the CL spectrum for samples deposited under different substrate bias conditions. This can be understood because after a few minutes in the plasma, the SS substrates become coated with a thin insulating layer. After this layer is formed the growing material is essentially at the floating potential, independent of the applied bias.

As we stated previously, the role of the atomic hydrogen seems to be crucial in the "etching" of the unwanted graphite bonds. We suggest that in the formation of our material, the argon-ion bombardment probably assists in the breaking of this type of bond due to preferential sputtering.

The ratio of the density of sp^3 bonds to the total one ($sp^2 + sp^3$) obtained from analysis of the IR spectra is approximately $\frac{1}{3}$. The CL probably arises from centers related to the inclusion of nitrogen impurities.

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- ¹K. E. Spear, *J. Am. Ceram. Soc.* **72**, 171 (1989).
- ²C. V. Deshpandey and R. F. Bunshah, *J. Vac. Sci. Technol. A* **7**, 2294 (1989).
- ³J. Shang Ma, H. Kawaraga, T. Yonchara, J. I. Suzuki, J. Wei, Y. Yokota, and A. Hiraki, *Appl. Phys. Lett.* **55**, 1071 (1989).
- ⁴J. Mort, D. Kuhman, M. Machonkin, M. Morgan, F. Jansen, K. Okumura, Y. M. Le Grice, and R. J. Nemanich, *Appl. Phys. Lett.* **55**, 1121 (1989).
- ⁵C. V. Angus, F. A. Buck, M. Sunkara, T. F. Groth, C. C. Hyman, and R. Gat, *Mater. Res. Soc. Bull.* **38** (1989).
- ⁶Y. Liou, A. Inspektor, R. Weimer, and R. Messier, *Appl. Phys. Lett.* **55**, 631, (1989).
- ⁷G. Amaratunga, A. Putnis, K. Clay, and W. Milne, *Appl. Phys. Lett.* **55**, 634 (1989).
- ⁸J. W. Corbun and E. Kay, *J. Appl. Phys.* **43**, 4955 (1972).
- ⁹B. Dischler, A. Bubenzer, and P. Koidl, *Solid-State Commun.* **48**, 105 (1983).
- ¹⁰N. Yamamoto, J. C. H. Spence, and D. Fathy, *Philos. Mag. B* **49**, 609 (1984).
- ¹¹L. H. Robins, L. P. Cook, E. N. Farabaugh, and A. Feldman, *Phys. Rev. B* **39**, 13 367 (1989).
- ¹²H. Kawarada, K. Nishimura, T. Ito, J. Suzuki, K. Sheng Mar, Y. Yokota, and A. Hiraki, *Jpn. J. Appl. Phys.* **27**, L683 (1988).
- ¹³S. C. Rand and L. G. DeShazer, *Opt. Lett.* **10**, 481 (1985).
- ¹⁴I. Watanabe and M. Inoue, *J. Appl. Phys.* **21**, 856 (1982).
- ¹⁵S. B. Kim and J. F. Wager, *Appl. Phys. Lett.* **53** 1880 (1988).