

Absolute photoyield from chemical vapor-deposited diamond and diamond-like carbon films in the UV

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Abstract: The absolute photoyields of chemical vapor-deposited (CVD) diamond and amorphous hydrogen-free diamond-like carbon (DLC) films, in the range of 140-300 nm, are reported. CVD diamond films exhibit a large photoyield, of a few percent in the range 140-180 nm. DLC films have a 20-50 times lower yield. Post growth hydrogenation is found to substantially increase the photoyield of CVD diamond films. We discuss the applicability of these films as UV photocathodes coupled to electron multipliers based on gaseous charge multiplication

Chemical vapor-deposited (CVD) diamond and diamond-like carbon (DLC) films have attractive mechanical, electrical and optical properties, which lead to a broad spectrum of possible applications. Using film growing techniques with controllable parameters, a variety of amorphous and polycrystalline carbon-based materials with specially tailored properties can be realized. CVD diamonds and DLC films, like natural diamonds, are chemically stable and radiation resistant¹. Monocrystal diamonds and CVD diamond films have a wide energy band gap of 5.47 eV and some of them, like type IIb <111> diamond², hydrogenated diamond surfaces³ and H-terminated CVD diamond films⁴ have negative electron affinity (NEA). These properties make CVD diamond films good candidates for new applications such as photon detectors and field emitters. The unique semiconducting properties of diamonds and the efficient charge transport in the bulk have led to the development of novel UV imagers^{5,6} and particle tracking detectors⁷ capable of withstanding very high radiation flux. The good electron emission properties of diamond have triggered intensive research in field-emission devices such as flat panel displays and in secondary electron emission for cold cathode devices. CsI-treated CVD diamond films were recently proposed as secondary emission converters for particle tracking⁸.

Unlike polycrystalline CVD diamonds, DLC films are amorphous and exhibit a mixture of sp² (graphite-like) and sp³ (diamond like) bonds. The film properties depend on the sp² fraction (0% to 90%) and on the local order of the sp² bonded atoms, which can be controlled by the growth conditions. The energy band gap of DLC with sp³ >60% is about 2 eV. The DLC surface is rich with defects and is characterized by an sp²-rich layer, its thickness depends on the growth conditions. Consequently the semiconducting and emission properties of DLC films are rather different from those of CVD diamond films⁹. DLC films nevertheless may possess interesting electron emission properties, a matter currently investigated.

The photoemission properties of natural diamonds and CVD diamond films have been extensively studied. Early works of Himpfel et al.² provide information about the quantum efficiency (QE) of <111> natural type IIb diamond: 20% at 9 eV and 40-70% at 12-35 eV. Whereas many authors have studied the relative photoemission properties of synthetic diamond films^{4,10-12} and hydrogenated amorphous DLC films¹³, noting a

high photoyield, no absolute values of the QE were provided, neither for CVD diamond nor for hydrogen-free DLC, to the best of our knowledge.

We report here on the absolute photoyield in the UV range, of 140-300 nm (4.1 to 8.8 eV), from several CVD and hydrogen-free DLC films, grown in different conditions and subjected to different post growth treatments.

The good photoemission properties of diamond films suggest their use as UV-photocathodes in photomultipliers based on gas multiplication^{14, 15}. These are attractive, offering sub-millimeter imaging accuracy and sub-nanosecond time resolution over a very large active area. The robustness and chemical stability of diamond films could reduce the usual photocathode aging by gas impurities and ion bombardment. Such gas photomultipliers will be solar-blind, due to the high energy cutoff of diamond. Knowledge of the absolute QE of diamond films is therefore required for this application.

The field-emission, secondary electron emission and photoemission properties of CVD diamond films could be related. The measurement of the absolute photoemission QE of diamond films may help to clarify the relation between the different electron emission processes.

The measurements were performed under vacuum, using two complementary systems:

1). A VUV vacuum-operated monochromator (Jobin-Yvon H20 VUV), with a 30W / MgF₂ window deuterium lamp. The absolute light flux was calibrated, with 10% accuracy, in the range 140-240 nm, relative to a calibrated primary standard NIST UV-photodiode (Ball Aerospace). The vacuum operated sample chamber was coupled to the monochromator via a CaF₂ window. Each diamond sample was attached to a stainless-steel holder; electrical contacts were made with silver paint. An 81% transparent stainless steel anode mesh was mounted 2 mm above the sample and held at 200V, providing the electric field needed to efficiently collect the photoelectrons. The sample was connected to ground via an electrometer.

2). A UV, air-operated double, blazed monochromator (Oriel 77250), with a 1000W Xe lamp (Oriel 6269). The absolute light flux was normalized in the range of 200-300 nm relative to a UDT UV-100 calibrated photodiode. The calibration was verified in the overlapping range of the two systems, 200-240

nm. The vacuum chamber and the sample handling were identical to the above.

The sensitivity was limited by the dark current, of 0.1 pA, permitting the measurement of absolute photoyield of 10^{-4} and 2×10^{-10} in the first and the second systems, respectively.

Samples of three different kinds were measured in this work: 1). A variety of CVD diamond films (total of 13 samples) deposited at the Weizmann Institute¹⁶ and at the Technion laboratories on p-type Si, by microwave assisted plasma (1%CH₄, 850°C) and by hot filament (1-1.25%CH₄, 750-930°C). The samples were 4-5 μm thick and with area of 25-100 mm². Some were doped by 1000-1500 ppm of B. The resistivity of CVD diamond samples, measured between the surface and the metal holder, varied between a few tens of Ohms (Boron doped) to hundreds of megaohms (undoped).

2). A variety of hydrogen-free DLC films with different fractions sp²/sp³ (total of 13 samples) produced at Soreq NRC by mass selective ion beam deposition, (mostly on p-type Si) at room temperature, with the C beam energy varying between 10 to 1000 eV. The sample thickness was typically 60-300 nm. The sp³ fraction of these DLC films was determined by EELS¹⁷ to be between 0-85%, with specific resistivity between 10³ to 10¹¹ Ω-cm.

3). Undoped, highly resistive natural diamond <111>, 4x4 mm².

Representative results are shown in figure 1. The QE of CVD diamond films is about 20-50 times higher than that of DLC films. This may be related to the difference in the structure of the layers, implying a difference in the energy bands and in the electron transport properties. The QE of a DLC film with

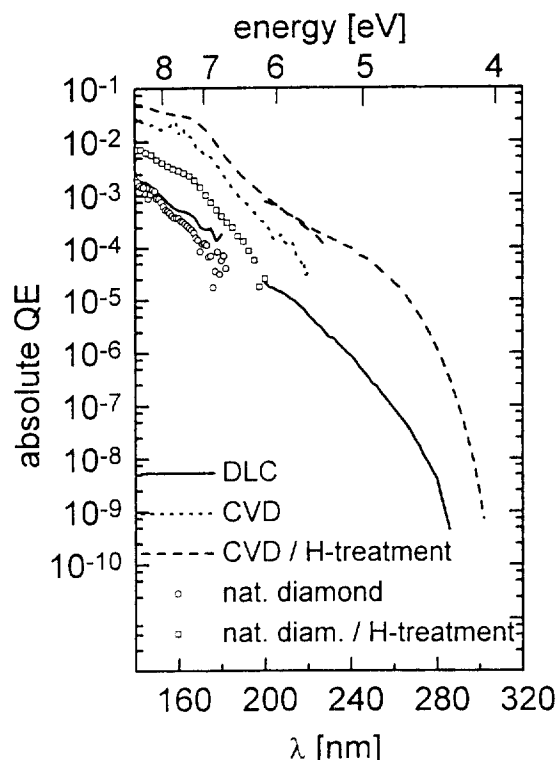


Figure 1. Typical absolute photoyield of a CVD diamond, DLC film and type IIb undoped natural diamond. The CVD and the natural diamond, treated by post-growth H₂ plasma, exhibit an enhancement of the photoyield. DLC films are etched by H₂ plasma. The gap in the DLC data results from the sensitivity limit in the VUV system.

85% sp³ is indeed considerably higher¹⁸ than the QE of all other DLC samples, having 0-70% sp³, in the wavelength range $\lambda > 200$ nm, but yet it is similar for $\lambda < 200$ nm. Nevertheless it is much smaller than the average QE of CVD diamond films. The fact that all DLC films measured in this work have rather similar QE values in the far UV, irrespective of their sp²/sp³ ratio, suggests that the main factor determining their QE may not be the sp³ fraction but the sp²-rich surface layer. For more details on the photoemission of DLC films (mainly around the band gap: 180-300 nm) and its correlation with other film characteristics see ref. 18.

The untreated natural diamond, measured for comparison in the VUV system only, has low QE, similar to that of DLC. We suspect that this undoped crystal, being a good insulator, suffered from considerable upcharging during this measurement and therefore we cannot compare this result with the one given for the lower-resistivity B-doped diamond². H₂ Plasma treatment, discussed below, reduced the surface resistivity of the natural diamond and increased the QE values.

CVD diamonds exhibit an absolute QE of a few percent in the far UV. The best value measured is 6% at 140 nm from a hot-filament grown, undoped CVD film; other CVD samples have 4-5% at 140 nm. This QE is inferior to the QE of other UV photocathodes, e.g. CsI (50% at 150 nm¹⁹) nevertheless it could be interesting for applications where the QE can be sacrificed in favor of radiation hardness and robustness. The high QE of all CVD diamond films studied here was found to be rather similar, i.e. independent of their doping level and therefore of their resistivity. It is interesting to note that the CVD films have photoemission at photon energies lower than the energy gap, of 5.47 eV. These photoelectrons may originate from amorphous carbon constituents or from defect states. In our future studies we will try to correlate the photoemission with Raman and photoluminescence analysis in order to clarify this effect. The issue is of significance for the understanding of the photoemission mechanism and for the possibility to tailor the layer properties for future applications in photoemission and secondary emission devices.

Considering the possible dependence of the CVD photoemission on the surface structure, purity and termination we have studied the effect of treating the sample with H₂ plasma. This process has two roles: on one hand it is etching the remnants of graphitic material from the sample and on the other hand it is H-terminating the surface, preventing surface reconstruction of the diamond, providing a low surface resistivity²⁰ and often negative electron affinity. We suspected that although the film is continuously etched during the deposition process, some residual sp²-rich material could be present on the surface following the film growth. Figure 1 also shows the change in photoemission yield from a CVD diamond, measured in the far UV system only, due to the post growth H₂ plasma treatment (50 Torr H₂, 350W microwave plasma, for 30 minutes at 800°C). This plasma treatment significantly enhanced the QE in the far UV and reduced the resistivity, as already observed²⁰. In contrast, an excessive H₂ etching at the end of the growth process in the hot-filament system¹⁶, had only little effect on the QE mainly at the longer wavelengths. Probably the microwave plasma, being much more aggressive, is more effectively modifying the sample surface. The natural diamond, known to have some spontaneous surface reconstruction, also exhibits an enhancement of the photoyield following the same H₂-plasma treatment (fig. 1), due to

elimination of the surface reconstruction and its hydrogenation. The same plasma treatment was found to etch the DLC films. Milder and more controlled H₂ treatment will be tested in the future for the removal of the sp²-rich layer and termination of the surface sp² bonds in DLC films.

In summary, we have reported here, for the first time, experimental results for the absolute photoemission yield of various synthetic diamond and diamond-like films in the UV range. The highest QE values, measured on CVD diamond films were typically a few percent at 140-170 nm. We have shown that subjecting the CVD films to post-growth H₂ plasma treatment enhances their photoyield, although the exact nature of the surface modification is yet unclear and is a subject for further study. Bearing in mind the need for an efficient and stable photocathode for fast detection of UV light with large area gaseous detectors, the substantial QE obtained so far with CVD diamond films in the far UV is most promising.

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