

Polycrystalline diamond films as prospective UV photocathodes

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ABSTRACT

Polycrystalline diamond films grown by chemical vapor deposition have been considered recently for a number of UV detection applications. Negative electron affinity, chemical and mechanical stability and relative ease of fabrication make such films attractive candidates for effective and stable UV photoconverters. In this paper we present our study of the absolute quantum efficiency of a thin film diamond reflective photocathode in the spectral range of 25-200 nm. Modification of the surface by microwave hydrogen plasma etching resulted in a substantial increase of the photocathode sensitivity. The quantum efficiency of the photocathode at ~40 nm was as high as 37 percent and the sensitivity cut off was found to be about 200 nm. We also verified that the photocathode is relatively stable under air exposure. The relative QE degradation in the spectral range studied did not exceed 15 percent after the sample was left in ambient air for 18 hours. In addition, the diamond photocathode appeared to be chemically stable and mechanically robust: alcohol and water ultrasonic cleaning, followed by the same surface activation in hydrogen plasma, did not result in any degradation of the sample UV sensitivity. The photoyield from the diamond film at 256 Å exhibited an increase with the angle of radiation incidence, which is in agreement with the results of our calculations.

Keywords: Photocathodes, Polycrystalline Diamond, Quantum Efficiency

1. INTRODUCTION

Prospective instruments present new challenges for cathode development, particularly in the production of efficient UV photocathodes with high out-of-bandpass light rejection and stability under radiation and gas exposure. The wide band gap of diamond (5.47 eV, 227 nm) matches the energy of ultraviolet photons, which makes this material very attractive solar blind UV detection. Other well-known features of diamond are chemical and mechanical stability under harsh external conditions, heat dissipation properties and radiation hardness¹. It has also been shown that hydrogenated and cesiated diamond surfaces exhibit negative electron affinity (NEA)²⁻⁴, which is a very important parameter for electron emitting and photoconverting applications. Natural and synthetic diamond were available only in the form of small crystallites until late 1980s, and their properties varied substantially from sample to sample. Development of new techniques allowed growth of polycrystalline diamond films on non-diamond substrates (i.e. hot filament or microwave plasma chemical vapor deposition⁵), thus providing the basis for possible wide use of diamond films in photodetectors. There has been tremendous progress in growing diamond films and in their application in electron emitters. However, only limited success was achieved in applying and characterizing thin films of diamond as effective UV photoconverters⁶⁻⁹.

The substrate temperature during deposition is an important parameter determining the stoichiometry, purity and crystal structure of the coating obtained, which, in turn, are the crucial parameters for the photocathode quantum efficiency. The

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widely used chemical vapor deposition (CVD) technique requires rather high substrate temperatures (over 600 C°), which is not acceptable for many detection devices. In fact, application of a photocathode material directly on top of a microchannel plate in order to increase its quantum detection efficiency has become standard practice. However, glass microchannel plates can not be heated to temperatures higher than ~350 C° and therefore opaque CVD diamond films on standard glass MCPs can not be utilized in current imaging/spectrographic detectors. State-of-the-art technologies, such as Silicon MCP production^{10,11}, offer new possibilities in terms of deposition conditions and therefore extend the spectrum of materials which can be used for both opaque and semitransparent photocathodes, including polycrystalline diamond films. Si MCPs can actually be heated to a much higher temperature (>800 C°) than glass MCPs, and the Si MCP surface should be less chemically reactive.

Besides CVD deposition methods, which generally produce diamond films with excellent physical properties, other relatively cheap deposition methods are available, such as dielectrophoresis¹² coating or spraying technique¹³. Xu *et. al.*¹⁴ deposited a nanostructured diamond film on etched silicon and reported negative electron affinity of the diamond surface. In addition, Kyung-Suk Shim *et. al.*¹⁵ also showed that quality films could be grown by pulsed laser deposition with substrate temperatures as low as 300 C°, which is acceptable for common glass microchannel plates.

1.1. Diamond photocathode surface activation

It is well known that photocathode efficiency depends on three parameters: photon absorption length, photoelectron escape length (its diffusion to the surface) and photoelectron escape probability (surface work function or electron affinity). Diamond has a proper band gap energy, providing efficient photon-electron conversion in the bulk of the material. As far as photoelectron escape length is concerned, it was reported that crystal orientation has no influence on the low-energy electron transport properties¹⁶, i.e. that low-energy electrons are transported and emitted very efficiently regardless of crystal orientation. Furthermore, Laikhtman *et. al.*⁹ observed that possible defects at grain boundaries and geometrical structure of diamond crystallites did not influence the photoemission properties of diamond photocathodes, thus proving that only chemical composition and electronic structure of the surface determine the efficiency of a particular film. Thus modification of the photocathode surface can be used as an effective technique for the improvement of photoemission. Photocathode surfaces can be activated in order to achieve negative electron affinity, so that the vacuum level is lowered below the bulk conduction-band minimum, and the electrons excited to the conduction-band minimum are emitted from the surface. It has been reported in a number of publications that an effective NEA was achieved for diamond films. There are several techniques currently used for lowering the electron affinity. Deposition of Cs combined with pre-exposure to oxygen reduces the electron affinity of diamond films, resulting in a true NEA of the surface and, consequently, an electron escape probability of nearly unity⁸. Extremely high chemical reactivity of cesiated surfaces constitutes a great difficulty for the application of this activation technique. Another widely used method of lowering the electron affinity of diamond films is hydrogen termination of its surface^{8,9,17}, leading to efficient negative electron affinity, with an electron escape probability of 0.25-0.3. Hydrogen passivation (formation of C-H chemisorbed bonds on the diamond surface) leads to negative electron affinity due to a dipole layer which is induced by the heteropolar carbon-hydrogen bonds of the surface atoms. Hydrogenation reduces the amount of sp² bonded carbon at the surface, which turns out to be a crucial parameter determining the position of the surface Fermi level, and therefore the surface band bending in diamond¹⁸. The hydrogenation of diamond surface can be accomplished by treating samples with microwave hydrogen plasma, which etches off the remnants of graphitic material from the sample and H-terminates the surface.

2. SAMPLE PREPARATION AND MEASUREMENT TECHNIQUE

2.1. Photocathode preparation and surface activation

The diamond reflective planar photocathode used in the present study was provided by Crystallume Inc.¹⁹ and was prepared by chemical vapor deposition. Polycrystalline diamond was deposited on a 4" diameter silicon substrate held at ~800 C° during deposition. The film thickness was 5 μm. The choice of the silicon substrate was dictated only by the availability of the diamond film samples. The measured photoyield from the diamond photocathode should not depend on the properties of Si substrate, since the absorption length of the incident UV photons is several orders of magnitude lower than the thickness of the diamond film under study²⁰.

Upon receiving the sample from the manufacturer, one half of it was cleaned by immersion into hydrofluoric acid diluted (25:1) by DI water in order to eliminate possible contaminants on the diamond surface. The film was then doped with boron (100mm GS-139 BORON+ source wafers from Owens-Illinois Technical Products) at UC Berkeley Microfabrication Laboratory. The temperature during deposition was 800 C°.

The quantum efficiency of as-grown boron doped photocathode was then measured in the reflective mode, followed by the subsequent surface activation by microwave hydrogen plasma. For the activation the sample was placed in a microwave plasma cleaner equipped with a vacuum pump and controlled gas flow. The entire system was then evacuated and purged with argon at a flow rate of 3 cubic feet per hour (CFPH) in order to eliminate all remaining oxygen. The photocathode was then subjected to microwave argon plasma for about 15 minutes in order to reduce possible contaminants on its surface. Subsequently the volume of the plasma cleaner was purged with argon gas while the sample cooled down to room temperatures, and argon purging was substituted by hydrogen purging performed over an extended period of time. Following that, the surface of the photocathode was activated by hydrogen plasma for about 20 minutes with hydrogen purged at 4 CFPH through the chamber with pressure of about 75 Torr. Finally, the sample was left to cool down to room temperature in the oven still being purged by hydrogen. Following hydrogenation, the photocathode was exposed to ambient air (with a relative humidity of <50%) for several minutes during its transfer and installation into the calibration chamber.

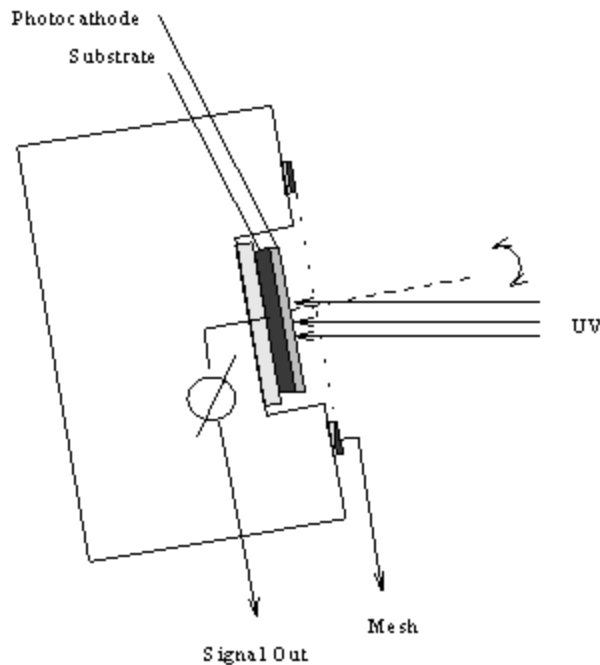


Fig.1. A schematic view of the experimental setup.

2.2. Measurement technique

All the reported quantum efficiency measurements of diamond reflective photocathode were performed in a vacuum chamber at pressures of about 1×10^{-6} Torr. Following each treatment, the diamond sample was mounted directly onto the front face of a custom-made electrometer with a sensitivity of about 5×10^{-16} Amps. A 90% transmissive nickel mesh was installed ~ 3 mm in front of the cathode for the photoelectron collection. The electrometer with the photocathode was then mounted on a manipulator with a rotation stage. A positive voltage of 200 V, which was initially verified to be sufficient for the plateau regime of the photoelectron collection, was applied to the mesh. Monochromatic radiation (25-200 nm, with a beam of 4 mm in diameter at the photocathode) was provided by a gas discharge hollow cathode source in combination with a 1 m grazing incidence monochromator. The absolute quantum efficiency was determined from the ratio of the observed photocurrent from the samples to the flux measured by NIST-calibrated standard photodiodes. The angular dependence of the mesh transparency was calibrated prior to all QE measurements and was subsequently used to normalize the incident flux variation. The measurements with the same diamond film were repeated for untreated, activated, air-exposed and reactivated photocathode.

3. EXPERIMENTAL RESULTS

3.1. Absolute quantum photoyield

Fig.2 shows the absolute values of the quantum efficiency (QE) of the diamond photocathode before (circles) and after the surface activation (triangles) by microwave hydrogen plasma, described in Section 2.1. We emphasize here that after hydrogenation the sample was always exposed to air for several minutes during its transfer into calibration chamber. This proves that the activation of the photocathode is relatively stable in air. The latter fact makes photocathodes made of this material easy to handle and therefore very attractive for many detection applications.

The measurements of quantum efficiency presented in Fig.2 were performed at normal incidence. The as-deposited diamond film had the highest efficiency of 16.3% at ~ 580 Å and a sensitivity cut off at an energy of about 8 eV. Therefore the surface of the untreated film exhibited a positive electron affinity. As reported by Laikhtman *et. al.*⁹, the presence of oxygen on the surface is correlated with the decay in quantum photoyield: the photocathode efficiency decreases exponentially with the increase of the oxygen concentration on the sample surface. The surface oxygen concentration of only 1 percent reduced the sensitivity of their photocathode by a factor of 3. It is likely that our diamond sample had some oxygen adsorbed on the surface during its deposition and/or subsequent high temperature boron doping.

The sample cleaning by argon plasma might have reduced the amount of surface oxygen and therefore improved the photocathode sensitivity by reducing the electron affinity. It is unlikely that this process changed the photon absorption length and the electron escape length. We did not measure the efficiency of the photocathode after the argon plasma cleaning, which was followed by hydrogenation.

Triangles in Fig.2 show the efficiency of hydrogenated diamond reflective photocathode. The electron affinity of the sample is substantially reduced by hydrogen passivation and therefore the sensitivity of the activated photocathode is considerably higher, with a quantum efficiency of as high as 37% at about 450 Å and a sensitivity cut off energy of about 6.2 eV. The observed dips of sensitivity at 988 and 520 Å (and probably not observed at ~ 670 Å) is likely to correspond to $2x E_{\text{gap}} + E_{\text{aff}}$, $4x E_{\text{gap}} + E_{\text{aff}}$, and $3x E_{\text{gap}} + E_{\text{aff}}$, respectively. A much better spectral continuity of the illumination source is required in order to study the UV absorption fine structure.

As described in Section 2.1, one half of the diamond photocathode sample was cleaned with hydrofluoric acid prior to boron doping. Mounting the photocathode on a translational stage allowed us to measure the quantum efficiency within both sides of the sample. We did not observe any difference in the photocathode response, which indicates that hydrofluoric acid surface cleaning during initial sample preparation neither improved nor deteriorated the photocathode performance.

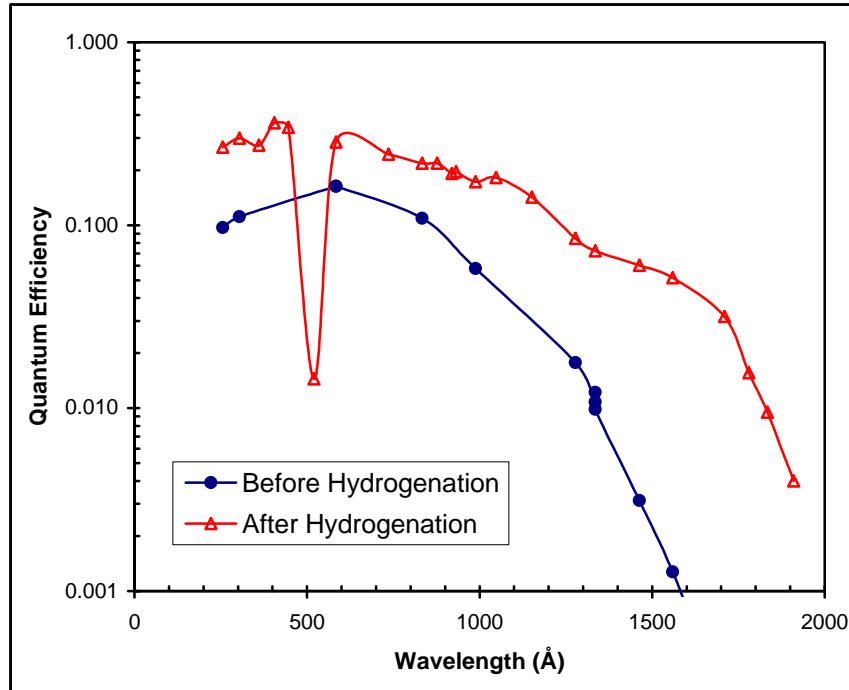


Fig.2. The quantum efficiency of a polycrystalline diamond planar reflective photocathode (5 μm thick, deposited on a 4'' silicon substrate) as a function of the wavelength measured at a normal incidence. Circles – non-activated (as-deposited) photocathode. Triangles – photocathode's surface modified by microwave hydrogen plasma activation. The electron affinity is lowered by hydrogen passivation of the diamond surface.

3.2. Stability of the surface activation under air exposure

The stability of the hydrogenated diamond surface is a crucial parameter for many possible applications of this material in photon detecting devices. The measurements of the activation stability of a free-standing polycrystalline diamond film, characterized by large crystallites (20-50 μm in size) of high purity showed that the quantum efficiency at 140 nm dropped by ~13% after air exposure of 2 hours⁹. The QE degradation with further exposure was slower. Exposure to ambient air for 100 hours resulted in a sensitivity decrease of only 33%. The measurements of activation stability were deliberately performed on a high purity film in order to eliminate the influence of amorphous components and impurities, as well as inhomogeneity. It was found in the latter experiments that some oxygen atoms do adsorb on the sample surface and substantially reduce the photocathode quantum efficiency by increasing the electron affinity of the surface since oxygen is a highly electronegative atom.

We investigated the stability of hydrogenation of our diamond photocathode, which comprised a standard off-the-shelf sample, rather than a specially prepared high quality film. The photocathode sample was exposed to ambient air (with a relative humidity of 40-50 %) for 18 hours. Fig.3 shows the quantum efficiency of the hydrogenated diamond film before and after this air exposure while the relative QE degradation is presented in Fig.4. The efficiency of the film degraded only by 7-16 percent in the spectral range of 400-1900 Å. The degradation at 140 nm was about 15 percent, which is in agreement with the results of Laikhtman *et. al.*⁹ obtained with a high quality large-crystallite film. The observed high stability of the activated diamond surface makes it a very attractive alternative to many current UV photocathodes, especially if one takes into account other outstanding features of this material, such as a high mechanical and chemical stability and radiation hardness.

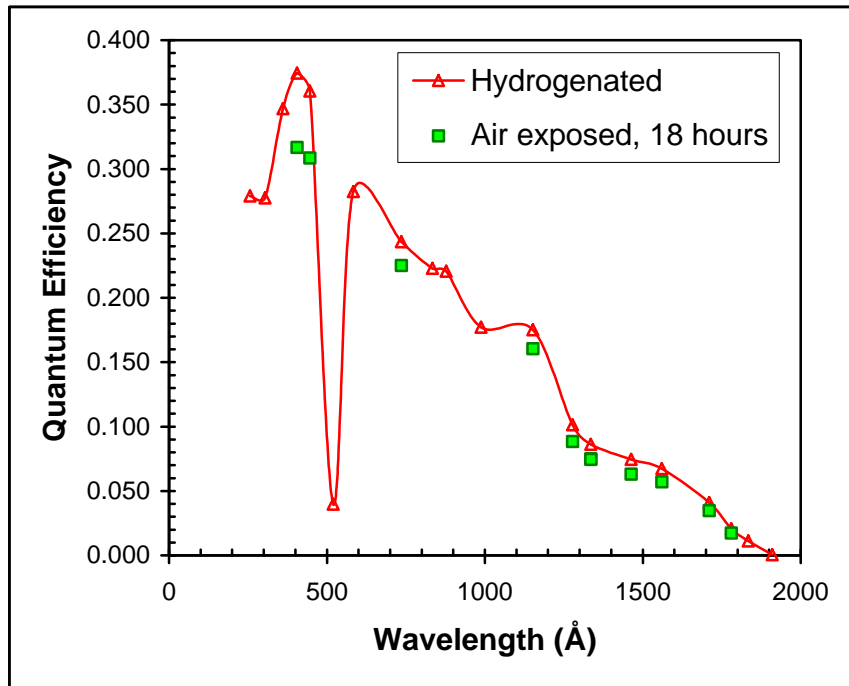


Fig.3. The absolute quantum efficiency of diamond reflective photocathode before and after exposure to ambient air for 18 hours (relative air humidity of 40-50%). No significant degradation of the sensitivity was observed.

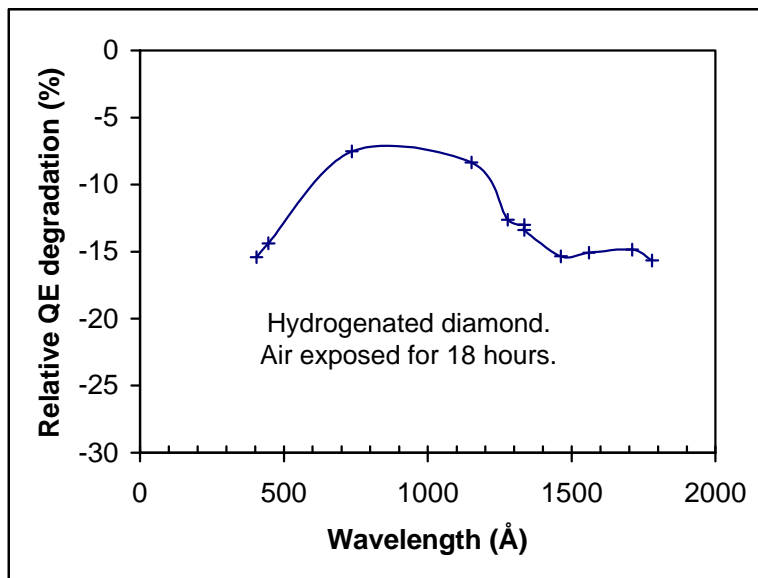


Fig.4. Relative variation of the quantum efficiency of the activated diamond photocathode with air exposure as shown in Fig.3. The sensitivity of air exposed sample is normalized to the initial QE values.

3.3. Photocathode reactivation and chemical and mechanical stability

We also investigated whether sensitivity degradation is irreversible after air exposure, and found that the photocathode efficiency can be restored by subsequent hydrogenation. After the diamond photocathode sample was exposed to air and its quantum efficiency was found to be lower than that of unexposed film, we applied the same surface activation procedure to the degraded sample. The photocathode was transferred to the microwave plasma cleaning chamber and subjected to hydrogen plasma activation for about 20 minutes, as described in Section 2.1. No additional cleaning or argon plasma etching was used before surface hydrogenation. The sensitivity of the reactivated photocathode was completely restored to pre-exposed values.

We continued with investigation of the surface chemical stability in terms of photocathode quantum efficiency. The diamond sample was subjected to ultrasonic cleaning in water for ~10 minutes and then in isopropyl alcohol for ~15 minutes. Following that, we applied the same hydrogenation of the surface as described previously and remeasured quantum efficiency of the sample. No sensitivity degradation was observed, indicating that CVD diamond film is mechanically robust and chemically stable.

3.4. Angular response

As described in Section 1.1, the efficiency of a particular photocathode is determined by its photon absorption length, photoelectron escape length and photoelectron escape probability. The photoelectron escape probability, improved by surface activation, cannot be remodified once the photocathode is installed in a particular detecting device. The photon absorption length and photoelectron escape length are intrinsic characteristics of the photocathode. However, in some cases detector sensitivity can be improved using optimization of the angle of radiation incidence. For instance, shallower angles of photon incidence in reflective and opaque photocathodes result in photons being absorbed closer to the surface, and therefore the distance which a photoelectron has to travel in order to escape to the vacuum, is shorter. The improvement in diamond sensitivity should be more pronounced at shorter wavelengths, where the photon absorption length is larger.

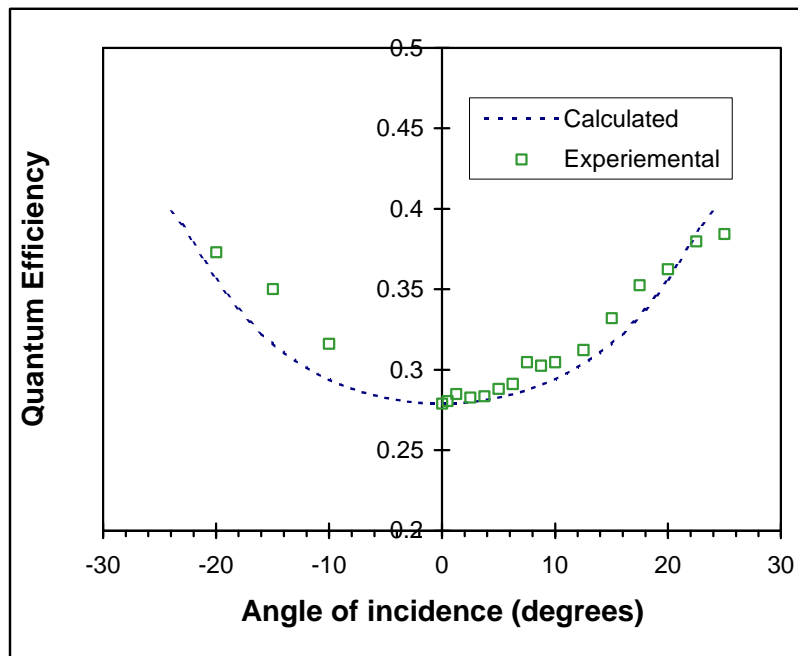


Fig.5. The angular variation of quantum efficiency of polycrystalline diamond photocathode at 256 Å. Separate points represent the experimental data. The curve corresponds to the calculation results with the parameters described in the text (Section 3.4).

We measured the angular variation of the quantum efficiency of a polycrystalline diamond film at 256 Å. The electrometer with the sample was mounted on a manipulator with a rotation stage, which allowed rotation with ~1 degree accuracy. The separate data points in Fig.5 show the results of these angular QE variation measurements. At an angle of UV incidence of 25 degrees the quantum efficiency increased by as much as 37 percent relative to normal incidence. However, at longer wavelengths the efficiency did not vary as much as at 256 Å, as was expected, since the photon absorption length decreases with increasing wavelength. The curve in Fig.5 represents the results of our calculations of the relative angular response of a diamond photocathode, normalized to the absolute value of the efficiency measured at a normal incidence. The model used in these calculations of a relative QE variation with angle is described in detail in Ref.²¹. We used the value of electron escape length of 50 nm reported by Niigaki *et. al*⁸. The missing optical constants were interpolated from the data reported in the handbook of optical constants of solids²⁰ and we found that the calculations with values of $(n,k) = (0.43,0.033)$ fit the experimental data, although independently measured values of the optical constants of polycrystalline diamond would be desirable for these calculations.

4. CONCLUSIONS

The present study of the quantum efficiency of a polycrystalline diamond reflective photocathode showed that for some applications CVD diamond can be a very attractive alternative to the currently used materials. Although the diamond UV sensitivity is somewhat lower than the sensitivity of other widely used photocathodes (e.g. alkali halides), this material could be preferable for applications where QE can be sacrificed in favor of chemical and mechanical stability, radiation hardness and robustness.

As reported earlier^{6,7,9}, the sensitivity of as-deposited diamond thin film is relatively low and the surface of the film can be activated by microwave hydrogen plasma in order to improve the efficiency. We measured that the normal incidence QE of as-deposited diamond photocathode peaked at about 16 percent (~580 Å) and the sensitivity cut off was at about 1500 Å, while the hydrogenated film showed an efficiency of as high as 37 percent at 400 Å with the sensitivity cut off at ~2000 Å. We have also verified that the hydrogenation of the polycrystalline CVD diamond surface is quasi-stable under ambient air exposure. Relative degradation of the sensitivity is on the order of ~10 percent after the activated photocathode has been held in air for several hours. The reduction of UV sensitivity after air exposure can be completely compensated by subsequent surface hydrogenation (we consistently measured the same high QE values for the photocathode reactivated after prolonged air exposure). The latter fact significantly broadens the range of possible applications of diamond photocathodes in UV detection devices and reduces the overall cost of such detectors.

The chemical and mechanical stability of diamond photocathode was verified by comparing the quantum efficiencies of the sample before and after ultrasonic cleaning in both water and alcohol, followed by surface activation. We did not observe any QE degradation, which indicates that, if required, devices with diamond photocathodes can be ultrasonically cleaned.

The quantum efficiency variation with the angle of radiation incidence for reflective diamond photocathode measured at 256 Å proved that at these wavelengths QE increases substantially at small incidence angles. The observed increase in QE was 27 percent for an incidence angle of 25 degrees to normal. The model of QE angular dependence based on the absorption length of photons and the escape length of photoelectrons appears to be in a good agreement with the measured data, although the photoelectron escape length and optical constants of polycrystalline CVD diamond films yet have to be measured in order to verify the parameters used in our calculations.

Application of opaque diamond photocathode directly on the front surface of microchannel plates can produce very stable and robust, and also relatively efficient UV detection devices. Such an opportunity can be provided with the anticipated introduction on the market of silicon microchannel plates, which can sustain much higher process temperatures.

5. ACKNOWLEDGEMENTS

This work was supported by NASA grant NAG5-3913. The authors would like to thank Siavash Parsa of Berkeley Microfabrication Laboratory for his help with boron doping and Jim Malloy and Joseph Stock of Experimental Astrophysics Group at SSL for their help with the MW plasma hydrogenation of the diamond photocathode.

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