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Journal

Diamond and Related Materials, 14(1)

ISSN

0925-9635

Authors

Tremsin, A S
Siegmond, OHW

Publication Date

2005

Peer reviewed

UV photoemission efficiency of polycrystalline CVD diamond films

Anton S. Tremsin^{*}, Oswald H.W. Siegmund

Experimental Astrophysics Group

Space Sciences Laboratory

University of California at Berkeley

Berkeley, CA 94720

Abstract

The absolute quantum efficiency of polycrystalline diamond films grown on silicon substrates by chemical vapor deposition (CVD) is reported in the range of 25-200 nm. The efficiency of boron-doped and hydrogen-activated by microwave plasma reflective photocathodes peaked at 37% at 40 nm with the sensitivity cut off observed at ~190 nm. We confirmed that hydrogen-activation is relatively stable in air: the efficiency of the photocathode degraded by less than 15% after an 18-hour air exposure. It was found that diamond photocathodes can be reactivated multiple times to the same high QE values even after extended ultrasonic cleaning in both water and alcohol. The sensitivity of a diamond photocathode coated with a high dipole moment 4 nm thick CsI layer was found to be slightly better than that of hydrogenated films, especially at longer wavelengths, while the sensitivity cut off shifted to ~200 nm. The observed high efficiency of thin CVD diamond films and relatively high stability of surface activation makes them a very attractive alternative to many existing UV

^{*} Corresponding author.

E-mail address: ast@ssl.berkeley.edu; Telephone: (510) 642 4554

photocathodes, especially taking into account other useful features of diamond (mechanical and chemical stability and radiation hardness).

Keywords: Diamond film; Electron affinity; Optical emission

1. Introduction

The novel deposition techniques (e.g. hot filament or microwave plasma chemical vapor deposition [1]) allowed the growth of polycrystalline diamond thin films on non-diamond substrates, thus providing a basis for a possible use of diamond films in a broad range of applications. The wide band gap of diamond (5.47 eV, 227 nm) matches the energy of ultraviolet photons, which makes this material very attractive for efficient UV photodetection with a high out-of-bandpass light rejection (e.g. solar blind UV detection). At present due to their high photoconversion efficiency (higher than 70 % at 110 nm) [2] alkali halides still remain the preferable materials of choice for most UV photodetection applications. However, alkali halide films are not stable enough and degrade under exposure to moisture [3] and intense radiation [4],[5]. Polycrystalline diamond films can become an alternative to alkali halide photocathodes, especially in the applications where the photocathode stability is one of the main concerns. Other attractive features of diamond are chemical and mechanical stability under harsh external conditions, heat dissipation properties and radiation hardness [6]. It has also been shown that hydrogenated and cesiated diamond surfaces exhibit negative electron affinity (NEA) [7],[8], which is a very important parameter for cold electron emitting and photoemitting applications.

Until late 1980s, natural and synthetic diamond were available in the form of small crystallites only, and their properties varied substantially from sample to sample. Since late 1980s tremendous progress has been made in growing diamond films and their application in electron emitters. However, only limited success was achieved in applying and characterizing thin diamond films as effective UV photoconverters [7],[9]-[12]. The efficiency of hydrogen-

activated diamond reflective photocathodes in the range 140-210 nm was studied by Laikhtman et. al. [10],[11] and the quantum photoyield (QPY) was shown to be as high as ~12% at 140 nm. Although the efficiency of diamond films could not be increased to the level of CsI photocathodes the stability of diamond films under air exposure was found to be much higher than that of alkali halides. In this paper we studied several diamond thin films grown by two different vendors in the extended spectral range of 25-200 nm and investigated the dependence of QPY on the angle of incoming photons. The angular dependence of photocathode response is essential for application of diamond films as opaque photocathodes in imaging photon-counting detectors with microchannel plates.

In addition to hydrogen-activated diamond films we tested another method of lowering photocathode's work function by depositing a thin film of a material with a high electric dipole moment, as suggested by Wong et. al. [13],[14]. We have also confirmed the stability of hydrogen-activated diamond photocathode performance under a relatively long air exposure.

2. Experimental techniques

The diamond reflective planar photocathodes used in the present study were provided by Crystallume Inc. and Nanosciences Corporation and they were grown by chemical vapor deposition (CVD) method. Samples from Nanosciences Corp. were grown on 2" silicon substrates (n-type Si, phosphorous doped, resistivity $\sim 1 \Omega \cdot \text{cm}$) and were boron doped to $\sim 10^{17} \text{ cm}^{-3}$ during deposition. The sample from Crystallume Inc. was deposited on a 4" diameter silicon substrate held at $\sim 800 \text{ C}^\circ$ during deposition, and was later doped with boron in a furnace with solid boron wafers (100mm GS-139 BORON+ source wafers from Owens-Illinois

Technical Products) at UC Berkeley Microfabrication Laboratory. All the reported quantum efficiency measurements of diamond photocathodes were performed in a reflective mode in a vacuum chamber at pressures of about 1×10^{-6} Torr. Following each treatment (surface-activation or aging), the diamond samples were 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 diamond photocathodes for the photoelectron collection. 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. The electrometer with a photocathode was then mounted on a manipulator with a rotation stage. Monochromatic radiation (25-200 nm) 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 films were repeated for untreated, activated, air-exposed and reactivated photocathode.

2.1. Surface activation of diamond photocathode

It is well known that photocathode efficiency depends on three parameters: the photon absorption length, the photoelectron escape length (its diffusion to the surface) and the photoelectron escape probability (the surface work function or electron affinity). Diamond has a proper band gap energy, providing efficient photon-electron conversion in the bulk of the material. For a particular electron energy the electron escape length is also fixed. For positive

electron affinity surfaces the escape length is the inelastic mean free path of electrons, while for samples with negative electron affinity the escape depth is determined by the diffusion length of electrons, which was reported to be on the order of 50 nm [7] and can be as high as few micrometers. The presence of grain boundaries in the polycrystalline film may reduce the electron escape length. However, Laikhtman *et. al.* [11] observed that possible defects at grain boundaries and geometrical structure of diamond crystallites did not influence the photoemission properties of diamond photocathodes. Thus only chemical composition of the film and electronic structure of its surface are likely to determine the efficiency of a particular photocathode. Therefore activation of the photocathode surface into a negative electron affinity is an effective technique for the improvement of photoemission from existing diamond films. Activation of the surface leads to lowering the vacuum level below the bulk conduction-band minimum, providing efficient surface emission of electrons excited above the conduction-band minimum. Several techniques are currently used for lowering the electron affinity. Deposition of Cs combined with pre-exposure to oxygen results in a true negative electron affinity of the surface and, consequently, an electron escape probability of nearly unity [7]. However this activation technique has only limited use due to an extremely high chemical reactivity of cesiated surfaces. Another widely used method of lowering the electron affinity of diamond films is hydrogen termination of its surface [9],[15],[16], leading to NEA. Hydrogen passivation (formation of C-H chemisorbed bonds on the diamond surface) leads to a negative electron affinity due to a dipole layer which is induced by the heteropolar carbon-hydrogen bonds of the surface atoms. 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.

In our study all samples were first cleaned chemically and by an argon microwave plasma in order to remove possible contaminations on the diamond surfaces, and then activated by a hydrogen plasma for about 20 minutes with hydrogen purged at 4 cubic feet per hour (CFPH) through the microwave vacuum chamber with pressure of about 75 Torr. Following activation, the photocathodes were exposed to ambient air (with a relative humidity of <50%) for several minutes during their transfer and installation into the calibration chamber.

3. Measurement results

3.1. Absolute quantum efficiency

Absolute quantum efficiency of as-deposited and hydrogen-activated photocathodes was first measured at normal incidence, Fig. 1. Non-activated photocathodes peaked at about 16 % @ 58 nm with sensitivity cut off at ~150 nm (8.26 eV). Although the efficiency of such a photocathode is substantially lower than that of alkali halide films or hydrogenated CVD diamond, they may still find some applications where chemical and air-exposure stability is very important. The efficiency of hydrogenated film from Crystallume (circles) and from Nanosciences Corp. (diamonds) was substantially higher and peaked at 37 % @ 40 nm with the sensitivity cut off at ~190 nm (6.53 eV). The difference in the performance of photocathodes grown by two different companies can be attributed to the variance in the bulk structure of the films and concentration of electron-trapping impurities. We emphasize here that after hydrogenation the samples were exposed to ambient air for several minutes during their transfer into the calibration chamber. This proves that the hydrogen-activation of diamond photocathodes is relatively stable in air, which simplifies the process of their assembly into a detection device. Since the surface

hydrogenation process is unlikely to change the bulk properties of the photocathode, the photon absorption and the electron escape length of untreated and activated films should remain the same. Thus we conclude that hydrogenation did reduce the electron affinity to the value lower than 1 eV. Production of negative electron affinity by surface cesiation should result in an even better photoyield from diamond photocathode. We are currently in the process of characterizing cesium-activated films.

3.2. Stability under air exposure and photocathode recycling

Previous measurements of hydrogen-activation stability indicated that the efficiency of photocathode at 140 nm drops by ~13% after 2 hour air exposure [10],[11]. A high purity free-standing polycrystalline diamond film with large crystallites (20-50 μm in size) was used in that study. 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 film inhomogeneity. It was found in the latter experiments that some oxygen atoms did adsorb on the sample surface and substantially reduced the photocathode quantum efficiency. The reduction of the efficiency is likely to be explained by upward band bending connected with the occurrence of surface conductivity. Indeed, it was established recently that a strict correlation exists between the photoelectron emission spectra and the surface conductivity of hydrogenated diamond surfaces [17].

In our study of air stability we used standard off-the-shelf samples, rather than a specially prepared high quality film. After the efficiency measurements (results of which are shown in Fig. 1) we exposed the Crystallume hydrogen activated film to air with a relative humidity of 40-50

%) for 18 hours and then re-measured the photocathode performance. Fig. 2 shows the quantum efficiency of the hydrogenated diamond film before (circles) and after (crosses) this air exposure. We observed that the film efficiency degraded by $\sim 15\%$ at 140 nm (in agreement with the results of Laikhtman *et. al* [10],[11]) and by only 7-16 percent in the entire spectral range of 40-190 nm.

We continued with the study of the irreversibility of air damage to diamond photocathodes. It was found that the air-damaged photocathode efficiency can be completely restored by subsequent hydrogenation. Moreover, these processes can be repeated many times without any loss of the efficiency of hydrogen-activated films. Following these measurements, the photocathode was subjected to ultrasonic cleaning in water for ~ 10 minutes and then in isopropyl alcohol and methanol mixture for ~ 15 minutes. The subsequent hydrogen-activation of this film completely restored its sensitivity, thus proving that CVD diamond film is mechanically robust and chemically stable and can be recycled many times.

3.3. Lowering electron affinity by a high dipole momentum thin film

In addition to semi-stable surface activation by hydrogen and very unstable cesiation it was suggested by Wong *et. al.* [13],[14] to use thin (0.3 - 2 nm) layers of other materials with a high electric dipole momentum, such as LiF (6.33 D [13]) and RbF (8.55 D [14]). To test this method of increasing the photocathode's efficiency, we deposited a ~ 4 nm thick layer of CsI on hydrogen activated diamond film used in previous measurements. CsI has a high value of electric dipole momentum (10.4 D [18]) and is relatively easily deposited by vacuum evaporation. Although we did not verify the optimum thickness of CsI layer on diamond photocathode, as it was done for

RbF and LiF, we believe the film reduced the electron affinity of diamond surface and at the same time was not too thick to dominate over the photoemission from the diamond photocathode. We estimated from CsI absorption data that the film was not too thick to dominate over the response of the diamond photocathode. We calculated the probability of photon absorption in CsI layer from the optical constants data [19],[20]. Even if each absorbed photon would produce a photoelectron emitted in vacuum (which would correspond to the unphysical CsI efficiency of 100%) the emission from CsI would still be below measured response from our sample. Triangles in Fig. 2 correspond to the efficiency measured with 4 nm CsI-coated diamond photocathode. The improvement in the efficiency indicates that CsI film further lowered the electron affinity of the hydrogen-terminated diamond photocathode, but still not to a negative electron affinity. As expected, the biggest improvement of sensitivity was observed at longer wavelengths (Fig. 3) and the cut off wavelength was shifted from ~190 nm to ~200 nm.

3.4. Angular variation of quantum efficiency

As described in Section 2.A, 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 further improved once the photocathode is installed in a particular detecting device. The photon absorption length and photoelectron escape length are also intrinsic characteristics of the photocathode. However, in some cases detector sensitivity can still be improved using optimization of the angle of radiation incidence. For instance, smaller angles of photon incidence in reflective (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.

We studied the angular variation of the photoyield from the same polycrystalline diamond film used in the previous measurements. In these experiments the electrometer with the sample was mounted on a ~ 1 degree accuracy rotation stage, which had the range of $+60,-20$ degrees. Fig. 4 shows both the experimentally measured relative variation of sensitivity with angle (individual markers) and the results of our calculations (lines) for different photon wavelengths.

The calculated relative angular QE variation represented in Fig. 4 is found from the following equation:

$$\frac{QE(\alpha) - QE_0}{QE_0} = \frac{1}{2} \frac{QE(\alpha)_s + QE(\alpha)_p}{QE_0} - 1 \quad (1)$$

where $QE(\alpha)_s$ and $QE(\alpha)_p$ are quantum efficiencies of s- and p-polarized light incident at angle α relative to the photocathode normal, and QE_0 is the efficiency at a normal incidence. The efficiency $QE(\alpha)$ of the photocathode is calculated with the help of the model suggested by Fraser [21]:

$$\frac{QE(\alpha)_x}{QE_0} = \frac{1 - R(\alpha)_x}{1 - R_0} \frac{1 + (\mu L)^{-1}}{1 + \cos \alpha'_x (\mu L)^{-1}} \frac{1 - \exp\left[-T\left(\frac{\mu}{\cos \alpha'_x} + \frac{1}{L}\right)\right]}{1 - \exp[-T(\mu + L^{-1})]}; x = s, p \quad (2)$$

where $R(\alpha)_s$ and $R(\alpha)_p$ are the reflection coefficients for s- and p-polarization, L is the secondary electron escape length, μ is the linear absorption coefficient of the photocathode material

($\mu = \frac{4\pi k}{\lambda}$), α'_s and α'_p are the refraction angles for s- and p-polarization, respectively, and T is the photocathode thickness. The photocathode reflectance of the photocathode at an angle of incidence α , measured from the surface normal is related to the complex index of refraction ($\tilde{n} = n + ik$) by the generalized Fresnel reflection coefficients [22]:

$$R_s = \frac{(A - \cos \alpha)^2 + B^2}{(A + \cos \alpha)^2 + B^2}; \quad R_p = R_s \frac{(A - \sin \alpha \tan \alpha)^2 + B^2}{(A + \sin \alpha \tan \alpha)^2 + B^2} \quad (3)$$

where

$$A^2 = \frac{1}{2} \left\{ \sqrt{(n^2 - k^2 - \sin^2 \alpha)^2 + 4n^2 k^2} + (n^2 - k^2 - \sin^2 \alpha) \right\} \quad (4)$$

$$B^2 = \frac{1}{2} \left\{ \sqrt{(n^2 - k^2 - \sin^2 \alpha)^2 + 4n^2 k^2} - (n^2 - k^2 - \sin^2 \alpha) \right\} \quad (5)$$

Refraction angles for two different polarization can be found from the following equations [23]:

$$\cos \alpha'_s = \frac{A}{\sqrt{\sin^2 \alpha + A^2}} \quad \tan \alpha'_p = \frac{2A(n^2 - k^2) \sin \alpha}{2A^2(n^2 - k^2) + 4k^2 n^2} \quad (6)$$

In calculations we used the value of electron escape length L of 50 nm reported by Niigaki *et. al* [7] and the optical constants for diamond film were approximated from references [19] and [20] to fit the experimental data: $n=(1, 1.05, 1.1, 0.9, 1.2, 1.3)$ and $k=(0.02, 0.025, 0.3, 0.39, 0.7, 0.8)$ for $\lambda=(25.6, 30.4, 40.5, 58.4, 83.4, 98.8)$ nm, respectively.

The efficiency of the photocathode increased by as much as 50 % for 25.6 and 30.4 nm photons arriving at 50 degrees relative to the normal. Almost no angular variation was observed for the wavelengths of 80 nm and larger, since the absorption length becomes quite small for such low energy photons and they all are absorbed close to the escape surface.

4. Conclusions

We measured the response of CVD diamond photocathodes in the extended spectral range of 25-200 nm and found that efficiency of these photocathodes is as high as 37 % at 40 nm. Such a high efficiency was obtained with relatively stable (under air exposure) hydrogen-terminated films. The efficiency degraded only by less than 15% after 18-hour exposure to air. It was shown that air-damaged or even alcohol washed photocathodes can be reactivated many times into the same high sensitivity-state by subsequent hydrogen-plasma surface activation. Cesium of diamond films should lead to an even higher sensitivity due to the possibility to achieve true negative electron affinity, but an extremely high instability of cesiated films makes them suitable only for a limited number of detecting instruments, such as sealed-tube devices. We have also shown that the efficiency of diamond photocathodes coated with a thin film of material with a high electric dipole momentum (4 nm CsI film in our experiments) is superior to hydrogen-activated diamond surfaces especially near the sensitivity cut off. Although deposition of CsI layer does increase the photocathode sensitivity to moisture exposure, such films are still much more stable than cesiated surfaces and do not degrade after a few minute exposure to ambient air during the instrument assembly, which eliminates the need for in-vacuum installation of activated photocathodes. Besides, more stable materials with a high dipole momentum (such as RbF or LiF used by Wong et. al. [13],[14]) can be used for surface activation. However, before this activation technique can be used in applications with large radiation fluxes, the radiation hardness of the activated surfaces should be investigated.

The present study of angular variation of quantum efficiency indicates that diamond opaque photocathodes deposited directly on the surface of silicon microchannel plates [24], which can

survive deposition temperatures over 800 °C, may produce UV imaging devices with a very high efficiency and stability. Most of the photons in such a device will be falling on the photocathode at a grazing angle, producing photoelectrons closer to the surface, and thus increasing the probability of escape into the MCP pore, especially for low energy photoelectrons. We conclude that the high quantum efficiency, chemical stability, mechanical robustness, excellent heat dissipation properties and radiation hardness all make diamond photocathode a very attractive candidate for a large number of UV detecting applications.

Acknowledgments

This work was supported by NASA grant NAG5-3913. The authors would like to thank Dr. Charles P. Beets of Nanosciences Corp. for growing the diamond films used in this study and Siavash Parsa of Berkeley Microfabrication Laboratory for his help with boron doping.

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Figure Captions

Fig. 1. The absolute quantum efficiency of a polycrystalline diamond planar reflective photocathodes as a function of the wavelength measured at normal incidence. Crosses – non-activated (as-deposited) photocathode grown by Crystallume Inc. Circles – the same photocathode activated by microwave hydrogen plasma. Diamonds - hydrogen-activated photocathode grown by Nanosciences Corp.

Fig. 2. The absolute quantum efficiency of hydrogen-activated (circles) and air exposed for 18 hours (crosses) diamond photocathode. The efficiency of the same photocathode was increased by evaporation of a thin CsI film (4 nm thick), serving as an effective dipole layer lowering the electron affinity (triangles).

Fig. 3. Relative increase of hydrogen-terminated photocathode sensitivity by evaporation of 4 nm CsI film. Reduction of electron affinity is most pronounced at longer wavelengths.

Fig. 4. The angular variation of the quantum efficiency of the diamond photocathode (normalized to the efficiency measured at normal incidence) for different wavelengths. Individual markers correspond to the measured data, while the curves represent the results of calculations with the parameters described in the paper.

Fig. 1

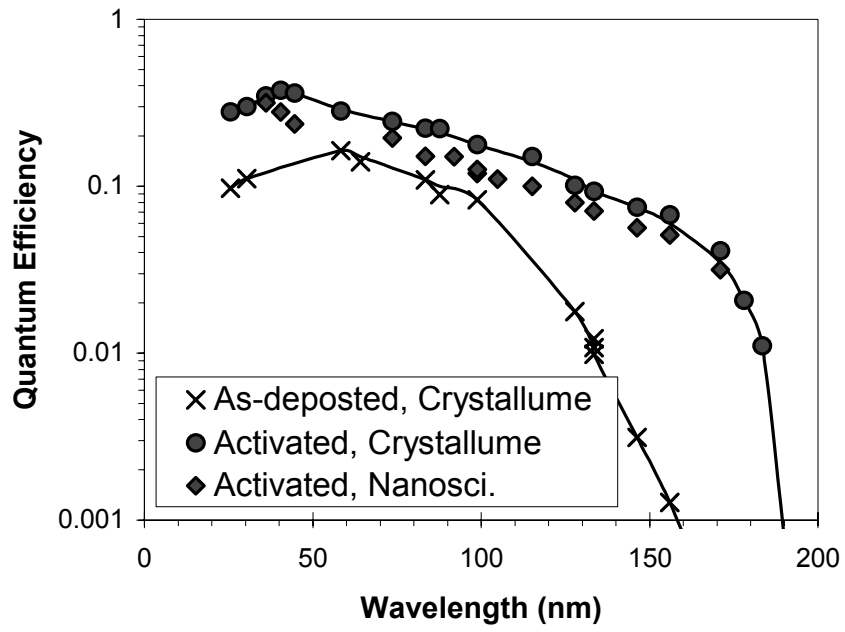


Fig. 2

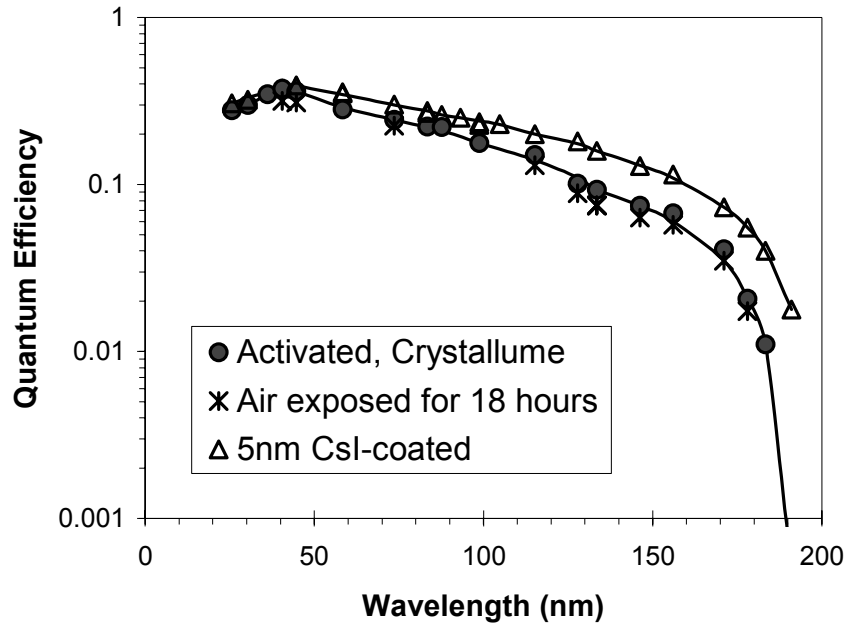


Fig. 3

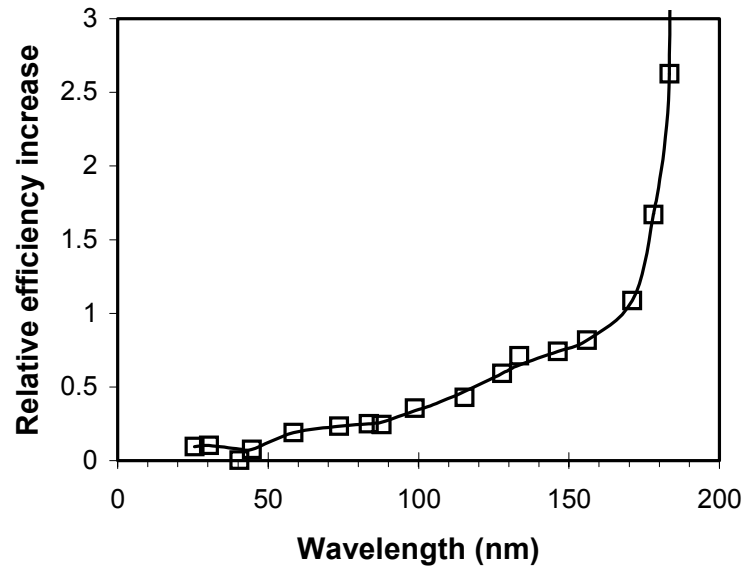


Fig. 4

