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Protection of cesium-antimony photocathodes

A.Buzulutskov *, A.Breskin, R.Chechik, M.Prager †, E.Shefer

Department of Particle Physics

The Weizmann Institute of Science, 76100 Rehovot, Israel

Abstract

In order to operate gaseous photomultipliers in the visible range it was suggested to protect sensitive photocathodes against contact to air and counting gases by their coating with a thin solid dielectric film. We present data on coating of cesium-antimony photocathodes with alkali-halide (NaI, CsI, CsF, NaF), oxide (SiO) and organic (hexatriacontane, calcium stearate) films. The photoelectron transmission through these films and their protection capability have been studied in detail. Cesium-antimony photocathodes are shown to withstand exposure to considerable doses of oxygen and dry air when coated with NaI films. This opens ways to their operation in gas media.

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*presently at Budker Institute of Nuclear Physics, 630090 Novosibirsk, Russia

†El-Mul Technologies, Soreq, P.O. Box 571, 81104 Yavne, Israel

1 Introduction

Studies in the field of photocathode protection have been motivated, on the one hand, by the remarkable progress in far ultraviolet (UV) photon gaseous detectors [1, 2, 3], and on the other hand, by serious difficulties encountered in the development of gaseous detectors for visible photons [4, 5, 6]. The problem is that alkali photocathode materials used in the near UV and the visible range are not stable in air or in commonly used counting gases.

This problem could be overcome if one would manage to protect photocathodes with a thin solid film. The idea of protection is based on the property of some thin dielectric films to transmit photoelectrons from the photocathode underneath to the vacuum level and at the same time to prevent a diffusion of unfavourable molecules such as oxygen and water from the gaseous media to the photocathode. The following protective films were considered in the past: CsI [6, 7] and LiF, MgF₂, NaF, CsF, NaI, BaF₂, SiO, SiO₂, Al₂O₃, and *n*-C₃₆H₇₄[8, 9]. However, the few attempts [6, 7, 10] to protect visible photocathodes were not successful so far.

Recently, we have presented an evidence that visible cesium-antimony (Cs₃Sb) photocathodes coated with thin NaI and CsI films can withstand contact with considerable amount of oxygen and dry air [11]. In the present article we continue to investigate various coating films on Cs₃Sb photocathodes, such as NaI, CsI, NaF, SiO, hexatriacontane (*n*-C₃₆H₇₄: HTC) and calcium stearate ([CH₃(CH₂)₁₆COO]₂Ca: CaSt). We present data on their photoelectron transmission and protection properties as well as on key elements of their preparation procedure. The choice of these protective films was based on our latest investigations of a large number of dielectric coating films on CsI UV-photocathodes [9, 12].

2 Experimental setup

The experimental setup for preparation and characterization of protected visible photocathodes consists of a high vacuum (10⁻⁹ Torr) chamber coupled to a monochromator. An important feature of the setup is that the photocathode can be displaced, without breaking the vacuum, between three positions inside the chamber: the photocathode preparation

position, the protective film evaporation position and the quantum yield (QY) measurement position. The absolute QY is measured, with an accuracy of 10 %, in a reflective or transmittive mode in vacuum, by recording the photocurrent and normalizing it to the response of a solid-state photodiode.

The Cs₃Sb photocathodes are prepared using a standard technique [13]. First, a thin Sb layer with a thickness corresponding to the attenuation of white light transmission down to 50-70% is deposited on a polished quartz substrate. Then, the Sb layer is activated with Cs vapour, by running current through a Cs dispenser [14], at a photocathode temperature of 150-170 °C, until the photocurrent reaches a peak value. After cooling and stabilizing the photocathode, it can be coated with a protective film, under controlled film-deposition-rate and temperature. Other details of the setup and the films preparation are presented in refs. [15] and [9] respectively.

The exposure of the photocathode to gas (oxygen, methane, air) was performed inside the chamber at room temperature; the pressure and the humidity were carefully monitored. The photocathode was exposed to gas for 5 min at each measurement point, after which the chamber was pumped and the QY measured. Gas purities were 99.5% for oxygen and 99.99% for methane. Water partial pressure was below $4 \cdot 10^{-4}$ Torr in oxygen and was equal to $1.1 \cdot 10^{-2}$ Torr in air.

3 Photoelectron transmission through coating films

The following coating films on Cs₃Sb were chosen for detailed investigations: NaI, CsI, CsF, NaF, SiO, HTC and CaSt.

Few words should be said about the preparation of the films. For NaI films, a post-evaporation heat-treatment, at 60-70 °C for a few hours, turned out to be a key element for attaining the highest photoelectron transmission. The particular advantage of organic films studied, HTC and CaSt, is the possibility of their vacuum evaporation [16, 17]. In order to obtain organized CaSt films, which should have very good electron transport properties [18], with a vacuum-evaporation technique, we followed the procedure reported in [17] - the films were deposited at a very small rate, of about 0.1 Å/sec, and at an elevated substrate temperature of about 70 °C.

Figs.1,2 illustrate photoelectron transmission properties of various coating films on

Cs₃Sb photocathodes. Fig.1 shows the QY spectra of a reflective Cs₃Sb photocathode uncoated and coated with 14-150 Å thick NaI films.

The observed QY-thickness dependence for various coating films on reflective Cs₃Sb photocathodes, measured at a wavelength of 365 nm, is summarized in Fig.2. The attenuation of the photoemission yield for film thicknesses above 15 Å is exponential, with an attenuation slope increasing from shorter to longer wavelengths. The photoelectron transmission of different materials, defined by the attenuation slope, follows an ascending order in SiO, NaF, HTC, CaSt, CsF, NaI, CsI. Among the coating materials studied, CsI turned out to be one of the best in terms of electron transport properties, in agreement with theoretical estimations [19].

In addition we observe a QY drop for film thicknesses below 15 Å (Fig.2). We believe that a modification of the surface potential barrier due to the formation of a dipole layer at the Cs₃Sb/coating-film interface is responsible for this effect.

Contrary to CaSt films deposited on CsI photocathodes (data shown in Fig.2 for comparison), which exhibit the highest photoelectron transmission ever observed by us [9], CaSt films deposited on Cs₃Sb photocathodes have a rather moderate electron transmission. This may indicate that organized CaSt films are formed on CsI and not on Cs₃Sb photocathodes. This could be due to high chemical activity of Cs₃Sb compared with the relative chemical stability of CsI, as well as to possible impurities of the CaSt material evaporated. On the other hand, for NaI films we observed rather similar attenuation slopes on both Cs₃Sb and CsI photocathodes, for similar photoelectron energies [11].

4 Protection properties of coating films

It should be emphasized that all the coating films were found to be stable in vacuum for few days. We also observed that uncoated photocathodes and those coated with NaI were stable for at least one week when the chamber was filled with 1 atm of methane of 99.99% purity. This confirms previous observations [5, 6, 20, 21] that Cs₃Sb is inert to methane atmosphere.

Fig.3 shows the QY of an unprotected reflective Cs₃Sb photocathode, measured at 436 nm, as a function of the integral amount of oxygen (expressed in Torr·cm³) injected into the chamber (the exposure time at each data point is 5 min). One can see that the QY

drops rapidly for oxygen doses and residual pressures larger than $100 \text{ Torr}\cdot\text{cm}^3$ and 10^{-5} Torr, respectively.

NaF, SiO and CsF films did not protect Cs_3Sb photocathodes: the photocathodes, coated with 30 Å thick NaF and SiO films or 150 Å thick CsF film (for larger thicknesses the attenuation of the photoyield is unacceptable), degraded as fast as the uncoated photocathode.

Better results were obtained for organic films, HTC and CaSt, 100 Å thick: the coated photocathode decays slower than the bare one. However such films did not provide effective protection.

NaI and CsI films showed the highest protection capability, and their thickness was found to be critical for the photocathode stability. As shown for example in Fig.3, a Cs_3Sb photocathode coated with a 100 Å thick NaI film, withstands an oxygen dose larger by a factor of 5, as compared to a bare one, while a 151 Å coating allows at least 10^4 times larger oxygen doses. Although such thickness of the coating film reduces the QY by factors of 10-100 (see Figs.1,2), the yields remains at reasonable values, varying from 0.2% at 405 nm to above 1% at 312 nm. One should note that the last point in Fig.3 corresponds to residual pressure of oxygen of 150 Torr (top scale in the figure), which is equal to its partial pressure in air.

We also found that the state of the Cs_3Sb layer, or most probably its smoothness, is another critical parameter. For example, if a Cs_3Sb photocathode was prepared on top of a previous one (i.e. the total thickness is twofold larger and obviously the roughness is larger), it could not be well protected with NaI films even at a thickness of 172 Å (see Fig.3).

The protection capability of CsI films was found to be comparable with that of NaI, for a similar post-coating attenuation of the photoyield (the corresponding CsI thickness is in the range of 200-300 Å) and for oxygen pressures below 10^{-2} Torr. However for higher pressures it is appreciably smaller compared to NaI. This is seen in Fig.4, showing the QY of Cs_3Sb photocathodes coated with 250 Å thick CsI and 155 Å thick NaI films, as a function of the residual oxygen pressure (the exposure time at each data point is 5 min).

We also found that NaI-coated photocathodes degraded by exposure to air, with water

content of about 10^{-2} Torr, could be fully recovered by heating them at 70-80 °C in vacuum for few hours [11].

5 Discussion and conclusions

Following the results presented above we can point at three important aspects which define whether the photocathode can be protected with a given coating film:

The nature of the film. This includes its capability to transmit photoelectrons, to prevent diffusion of oxygen and water molecules and probably to form an epitaxial structure on a particular photocathode surface. For example, despite of the comparable electron transmission, CsF does not protect while NaI does protect the photocathodes.

The thickness of the film. In the case of NaI we found that the thickness should exceed 150 Å.

The state of the photocathode to be protected. A Cs_3Sb photocathode consists of a mosaic of crystallites [13]. Since the surface of such a photocathode is not smooth, the thickness of the coating film needed for effective protection should exceed some threshold value, most probably of the order of the variation of the photocathode thickness. This value depends on the smoothness of the surface, i.e. on the crystallites size and on the thickness.

So far NaI showed the most successful protection properties among the materials investigated by us. On Cs_3Sb photocathodes it provides a reasonable quantum yield (QY), of 0.1-1 % at 300-400 nm, and a stability over minutes in dry air and oxygen, at pressures reaching hundreds of Torrs. It is of great advantage that NaI-coated photocathodes, degraded by exposure to a moderate amount of water vapour, can be fully recovered by heating in vacuum [11].

The degree of protection of Cs_3Sb photocathodes obtained is sufficient for their handling in glove-box. This permits easy manipulation of visible photocathodes while assembling and operating the detectors and open new directions in large-area position-sensitive light detectors.

For low oxygen pressures, below 10^{-2} Torr, the CsI protective film is comparable to NaI.

It has been observed that some saturated hydrocarbons, such as methane gas and hexatriacontane film, do not deoxygenate Cs₃Sb photocathodes. This indicates that visible photocathodes can be operated in counting gases containing organic quenching additives and suggest searching for new organic protective films. Organized organic films, such as salts of stearic acid, seem to be very promising, providing the highest photoelectron transmission ever reached. The possibility of epitaxial growing of these films on visible photocathodes should be investigated.

It should be emphasized that for the purpose of this study, the photocathodes were exposed to very large amount of oxygen and air. When handled and operated in relatively clean gases, thinner protective films can be used, resulting in considerably smaller attenuation of the initial QY.

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Figure captions

Fig.1 Quantum yield spectra of a reflective Cs_3Sb photocathode, uncoated and coated with NaI films of different thicknesses.

Fig.2 Quantum yield of reflective Cs_3Sb photocathodes coated with CsI, NaI, CsF, SiO, hexatriacontane (HTC) and calcium stearate (CaSt) films as a function of the film thickness, measured at 365 nm (points). Solid lines are the exponential fit to the data points. Data for the CaSt film on a reflective CsI photocathode, measured at 170 nm, are shown for comparison.

Fig.3 Evolution of Cs_3Sb photocathodes, coated with NaI films of different thicknesses, under exposure to oxygen. Shown are the quantum yield values of Cs_3Sb photocathodes measured at 436 or 365 nm: uncoated (reflective) and coated with NaI films of a thickness of 100 Å (transmittive), 130 Å (reflective) and 151 Å (reflective), as a function of the integral oxygen dose. The corresponding residual pressure is presented on the top scale. Data for a Cs_3Sb photocathode prepared on top of the previous one, coated with a 172 Å thick NaI film, are shown as well. Exposure time to gas at each data point is 5 min, followed by measurement in vacuum.

Fig.4 Evolution of NaI- and CsI-coated Cs_3Sb photocathodes under exposure to oxygen. Shown are the quantum yield values of reflective Cs_3Sb photocathodes coated with 155 Å thick NaI and 250 Å thick CsI films, measured at 312 and 405 nm, as a function of the residual oxygen pressure during the exposure. Exposure time to gas at each data point is 5 min, followed by measurement in vacuum.

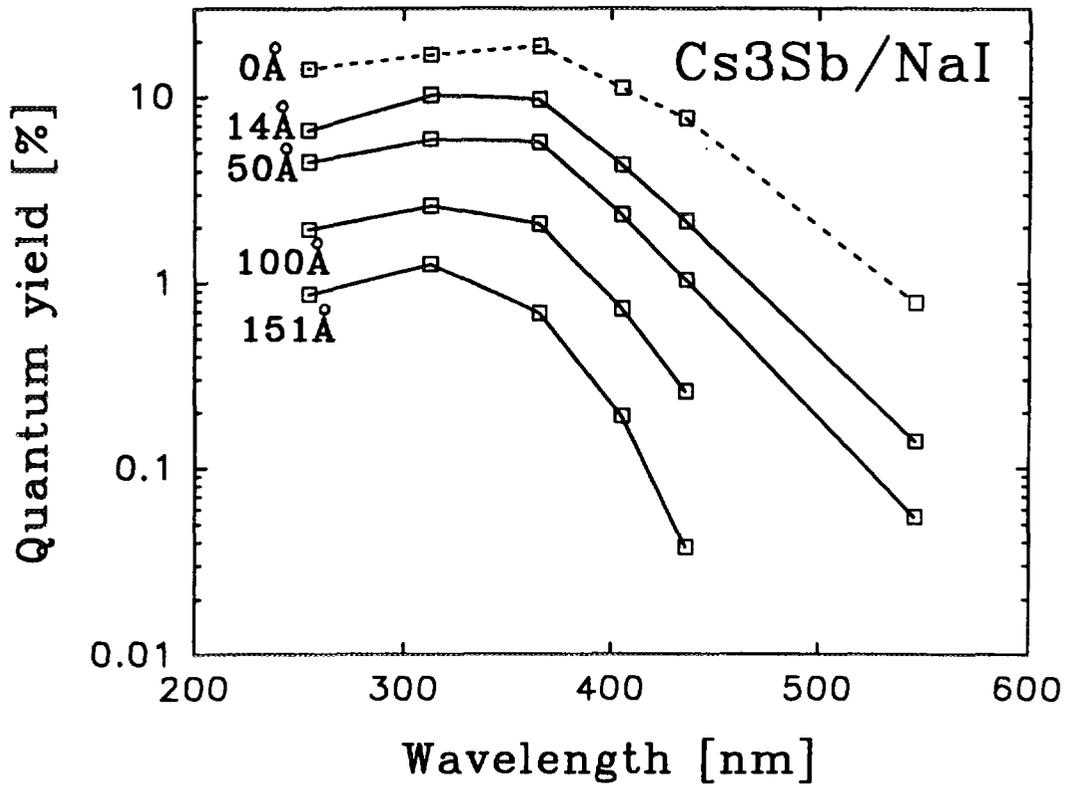


Fig. 1

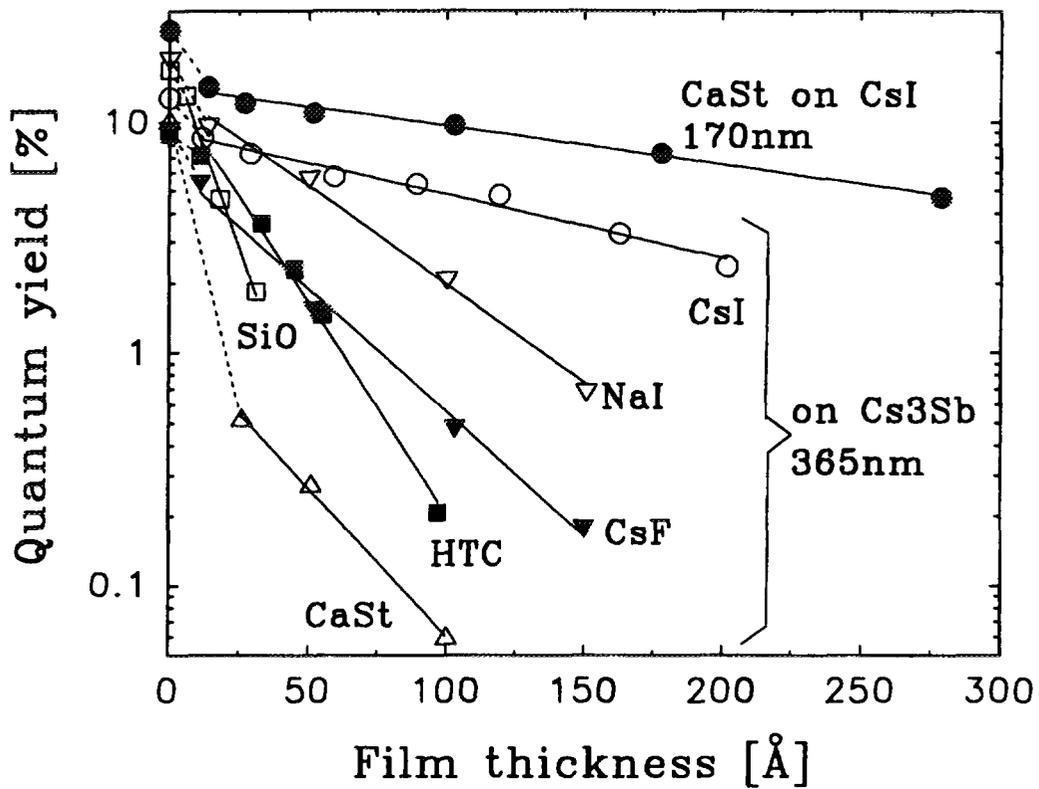


Fig. 2

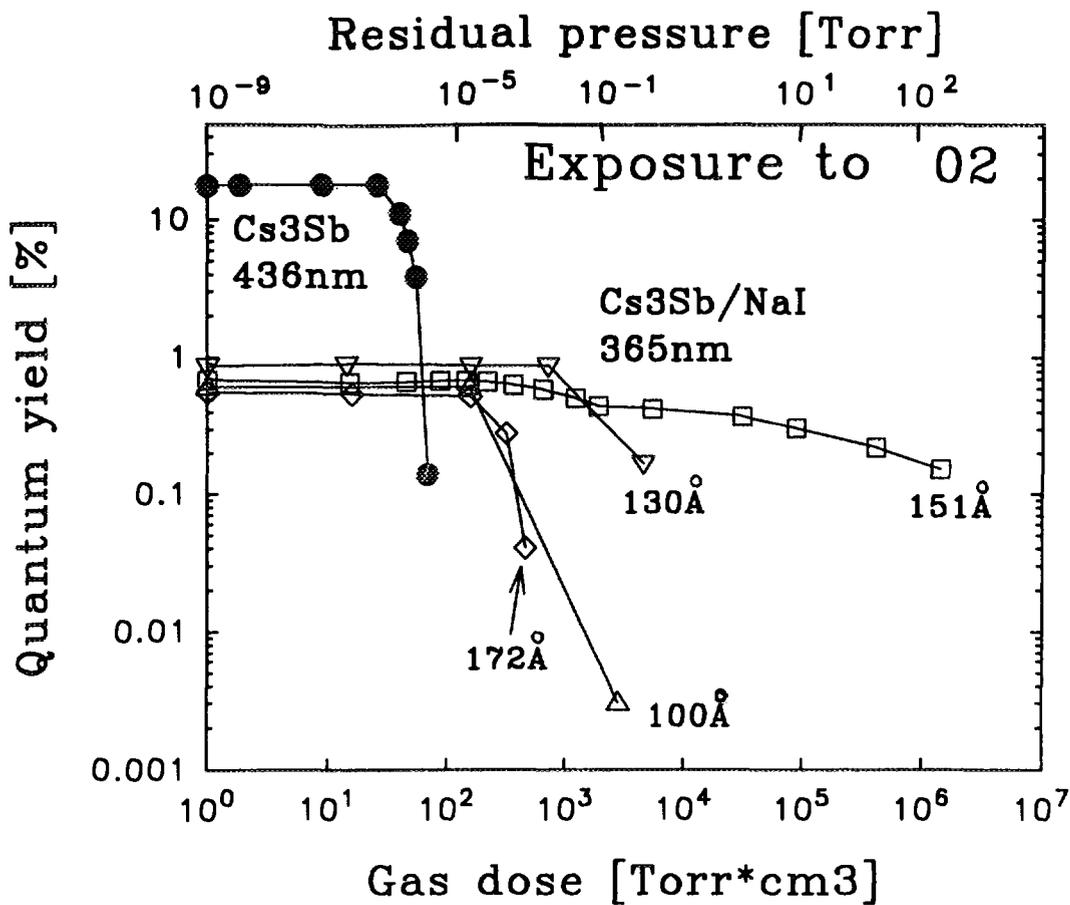


Fig.3

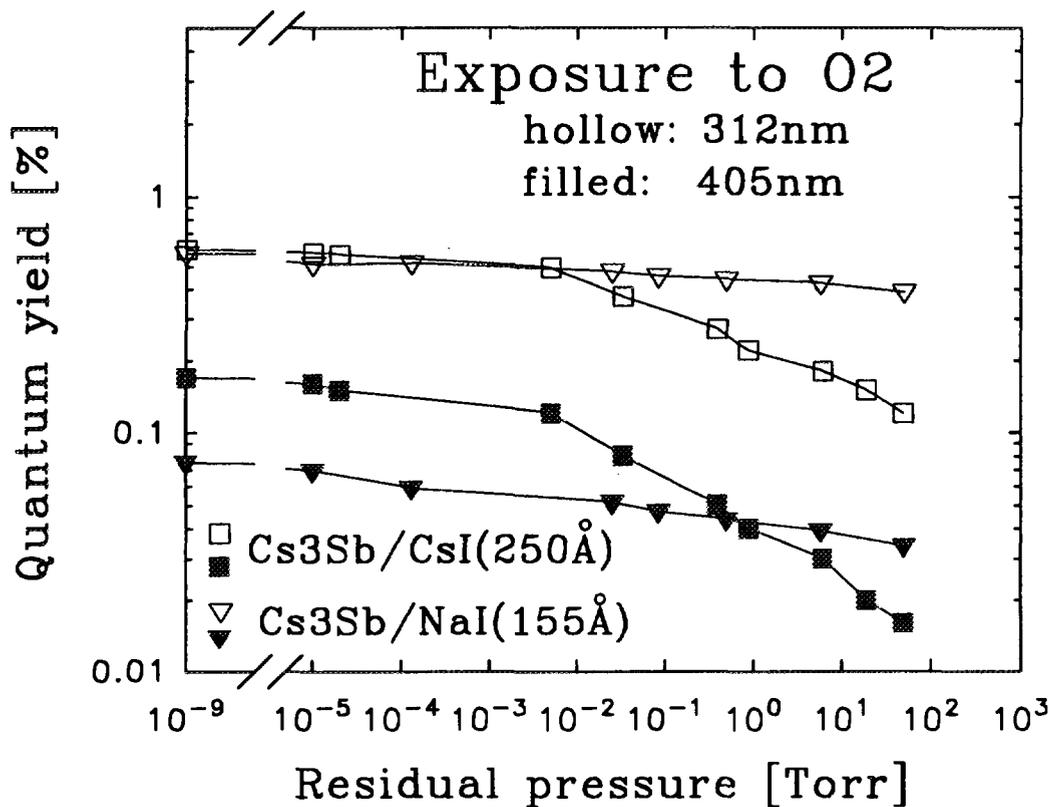


Fig. 4