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Study of photocathode protection with thin dielectric films

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Long-term stability of air-sensitive solid photocathodes operating in gas could be reached by coating their surface with a thin solid dielectric film. The protection film should have good electron transmission properties. We present data on LiF, NaF, CsF, MgF₂, BaF₂, SiO₂ and Al₂O₃ films. The electron escape length and the films protection properties were studied on relatively stable photocathodes, namely CsI, CuI and Al. We observed a reduction of the electron affinity due to an adsorption of polarized water molecules on alkali fluorides. We report on the stability of CsI photocathodes coated with thin films, under exposure to air and under gas multiplication conditions. The possible protection of visible photocathodes is discussed.

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I. INTRODUCTION

The extension of the spectral sensitivity of gaseous photo-multipliers [1], currently operating in the UV range with CsI convertors [2], towards the visible range is highly desirable. It will permit their coupling to various scintillators and will enable the detection of a larger portion of the Cherenkov spectrum in RICH detectors. However their development [3, 4] has met with difficulties: one of the obstacles is the sensitivity to residual H₂O and O₂ molecules in the detector gas. A few attempts to protect visible photocathodes with a CsI film have been done [5, 6], but with a limited success.

Recently we have proposed to coat the sensitive photocathodes with a thin (≤ 20 Å) dielectric protection film and reported [7] on the results obtained with LiF or MgF₂ used in the past for protection of Al coated UV mirrors from oxidation [8]. It is known that dielectric materials with a large energy gap should have good electron transport properties [9]. In the present article we present the results on a more detailed study of LiF and MgF₂ protection films, as well as some other large-energy-gap materials like alkali-halides (NaF, CsF), alkali-earth halides (BaF₂) and oxides (SiO₂, Al₂O₃). The last were tested since it is known that native layers of 15-20 Å of SiO₂ [10] and 30-35 Å of Al₂O₃ [11] provide sealing from further oxidation of the Si and Al bulk.

We report here on the results obtained with thin films evaporated mostly on CsI. This relatively air-stable photocathode [12] is used as a test bench only, for the understanding of the experimental procedures and properties of possible protection films. In the future the same procedure should be applied to mono- and multi-alkali visible photocathodes. A more detailed article on the photoemission from coated photocathodes is under preparation [13].

II. EFFECTS OF COATING WITH THIN FILMS

All films studied were produced by a vacuum evaporation technique. The experimental setup consists of a high vacuum (1×10^{-7} Torr) evaporation chamber coupled to a vacuum monochromator. Important feature of this system is that after preparation of the sample it can be brought into the measurement area in the same vacuum chamber, without contact to air. The photoyield from the sample was measured in a reflective mode in vacuum.

Fig.1 shows the atomic-force microscope (AFM) images of uncoated CsI and CsI coated with a 20 Å thick LiF film. The surfaces were exposed to air for few minutes prior to their imaging, also done in air. The coated surface is smoother, the CsI grain structure is almost not seen under the LiF and the roughness decreases. These images give an indication that the LiF coating is probably continuous even at a thickness of a few atomic layers. This is not necessarily true with the other materials studied.

The effect of the coating is mainly the attenuation of the photoemission due to trapping and scattering of electrons inside the film. In addition a modification of the interface potential between the two materials can either enhance or further attenuate the emission yield.

Electron transport properties of films, evaporated on the CsI photocathode, were studied by measuring the quantum yield (QY) as a function of the film thickness. Fig.2 gives an example of the thickness dependence of the QY, for almost all protection materials investigated, measured at 170 nm.

For thicknesses larger than about 10 Å, the attenuation of the photoemission follows an exponential law for all films, indicating that they are basically continuous. This allows to determine an electron escape length, defined as a slope of the exponential fit to the QY-thickness dependence; it is shown in Fig.2b. As one can see, CsF has the best electron transport properties: an escape length of

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Figure 1: AFM images of uncoated CsI (bottom) and CsI coated with 20 Å thick LiF film (top).

an electron with an initial kinetic energy of 2 eV (photon energy 8 eV) is equal to 30 Å. All other materials have much smaller escape lengths at this electron energy, varying from 8 Å for SiO₂ to 14 Å for NaF.

At a thickness below 10 Å the QY-thickness dependence in some materials deviates from that exponential law, indicating at either discontinuity of the film (MgF₂) or a modification of the interface potential (CsF and Al₂O₃). The CsF coating slightly enhances the photoemission from CsI at wavelengths above 190 nm. This can be related to the ability of CsF layer to reduce the work function of a substrate, as observed earlier for GaAs [14]. We found this effect also for CuI and Al. Fig.3 shows the QY spectra of the CuI, CuI/CsF, Al, Al/CsF photocathodes, measured in vacuum after preparation, together with the QY spectra of CsI and TMAE. The effect of the CsF layer is much more pronounced for Al and CuI photocathodes, as compared to CsI. Moreover, the CuI/CsF photocathode, which was found to be stable to a short-term exposure to air, has higher QY than CsI or TMAE, at wavelengths longer than 205 or 225 nm correspondingly.

III. WATER ADSORPTION ENHANCEMENT OF THE PHOTOYIELD

During the study of the sample aging in humid air we have revealed an interesting phenomenon of the quantum yield enhancement due to a water adsorption on the photocathode surface [15]. An exposure of the sample to

Figure 2: a) Quantum yield of CsI photocathodes coated with CsF, MgF₂, NaF, LiF, SiO₂, Al₂O₃ films as a function of the film thickness, measured at 170 nm (points). Solid lines are the exponential fit to the data points (points at zero thickness excluded from the fit). b) Photoelectron escape length in the dielectric film, evaporated on top of CsI, as a function of the photon energy.

Figure 3: Quantum yield spectra of various UV solid photocathodes: CsI, CuI, CuI/CsF(10 Å), Al, Al/CsF(10 Å). The quantum yield spectrum of the TMAE vapour [17] is shown as well.

Figure 4: Quantum yield spectra of CsI photocathodes coated with (a) hygroscopic films of LiF(22 Å), NaF(23 Å), CsF(102 Å) and (b) with nonhygroscopic films of MgF₂(22 Å, heat treated), BaF₂(28 Å), before and after exposure to humid air at room temperature inside the chamber. Relative air humidity varied from 35% to 60% and air exposure time varied from 5 minutes to 22 hours. The quantum yield spectrum of the unexposed uncoated CsI photocathode is shown as well.

Figure 5: Air-stability test of CsI, CsI/LiF, CsI/MgF₂ photocathodes, stored in laboratory conditions. Shown are the quantum yield spectra normalized to that of the unexposed uncoated CsI. Relative air humidity during the test was 60-70%.

Figure 6: Gas gain curves, measured in 1 atm CH₄ in the multiwire proportional chamber with CsI or CsI/NaF(19 Å) photocathode.

H₂O vapour was performed inside the chamber, by filling it with ambient air of 35-70% relative humidity.

Fig.4 shows the QY spectra of CsI coated with hygroscopic (LiF, NaF, CsF) and non-hygroscopic (MgF₂, BaF₂) protection films, before and after exposure to humid air. For non-hygroscopic films the effect of the exposure is minor. However, for hygroscopic films there is a dramatic enhancement of the photoemission, the magnitude of the effect increasing from LiF to NaF and to CsF, in accordance with the increase of their solubility in water. This enhanced photoemission is rather stable after further exposure to vacuum or ambient air. The magnitude of the effect was found to be independent of the exposure time (5 minute to 20 hours, inside the chamber) and of the humidity level.

The results obtained suggest the enhancement of the photoemission to be caused by a decrease of the LiF, NaF or CsF electron affinity, induced by a polarized adsorption of H₂O molecules. Indeed, orientation effects in water adsorption are predicted to be strong on alkali halides due to their highly polar structure [16]. The value of the decrease of the electron affinity was estimated by us, for LiF and NaF, to be about 0.4 eV [13].

IV. DEGRADATION IN AIR AND PERFORMANCE UNDER GAS MULTIPLICATION

We have studied the degradation of photocathodes by exposing them to ambient air outside the chamber, at room temperature. It should be noticed that in these conditions the photocathodes degraded much faster, compared to an exposure to air inside the chamber, under almost equal humidity conditions. The reason could be related to different conditions of exposure to light, presumably influencing the defect formation rate in CsI, or to the large surface covered by CsI deposit inside the chamber, possibly acting as a getter.

Fig.5 shows the results of these tests for CsI, CsI/LiF

and CsI/MgF₂ photocathodes (the latter was additionally heat-treated before air exposure [7]). The QY spectra are normalized to that of an unexposed CsI. The air humidity in all tests was about 60-70%. The conclusion from Fig.5 is that the coated CsI photocathode is more stable than the uncoated one. Indeed, while after 6 hours in air the uncoated CsI degrades considerably, CsI/LiF shows still a high QY, of about 60% of the initial value of uncoated CsI. Also, after 20 hours in air the QY of the CsI/MgF₂ is very little affected. However, one can see that a full protection is not yet achieved by such thin (≤ 20 Å) coating films: the QY of these photocathodes decreases significantly after 30 hours for CsI/LiF and after 9 days for CsI/MgF₂.

The performance under gas multiplication was studied with a multiwire proportional chamber (MWPC) coupled to CsI photocathodes, uncoated and coated with MgF₂ or NaF films. The chamber has a 20 μ m in diameter anode wires plane, with a 2 mm wire spacing, symmetrically placed between a mesh cathode and a photocathode plate, at a distances of 2 mm. The chamber was run with CH₄ at 1 atm, under constant flow.

Fig.6 shows the chamber gain as a function of the anode voltage, for CsI and CsI/NaF photocathodes. No significant difference is observed between the two photocathodes up to gain of 10^5 , and very stable operation was obtained with the CsI/NaF photocathode up to gain 10^6 . The photocathode aging under gas multiplication with gain 10^5 , was measured with a Hg(Ar) lamp by monitoring the photocurrent collected on the cathode. The current density was kept below 0.05 nA/mm². A decay of 20% in QY was observed after 1.3 μ C/mm² in CsI and 0.8 μ C/mm² in CsI/NaF and CsI/MgF₂ [18]. After the aged photocathode was removed and exposed to air, the damage was clearly visible indicating the illuminated area.

V. SUMMARY

Based on the results of this work, thin films of CsF, NaF, LiF, MgF₂ and SiO₂ can be considered for protection of air-sensitive photocathodes. Moreover, CsF may even increase the quantum yield of the photocathode. It should be noted that the long exposure times to humid air were done for the sake of the study. In practice, the exposure of photocathode to air or to low-humidity gas during transfer to the detection could be limited to a few minutes. Therefore, we hope that visible photocathodes coated with such films could be used in a stable way in gaseous photomultipliers. They would have rather high quantum yield, of the order of few percents for blue light and are expected to operate well under gas multiplication.

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