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Photoemission through thin dielectric coating films

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Abstract

Photoemission through thin coating films was studied in the scope of protection of sensitive photocathodes. The transmission of low energy ($\sim 1\text{eV}$) electrons was measured for a large number of dielectric films (LiF , NaF , CsF , NaI , MgF_2 , BaF_2 , SiO_2 , Al_2O_3 , $n\text{-C}_{36}\text{H}_{74}$), evaporated in vacuum on CsI and CuI photocathodes. Some films like CsF , NaI and $n\text{-C}_{36}\text{H}_{74}$ were found to have a fairly large electron attenuation length, varying from about 20 to 100 Å at a maximum initial electron energy of 1 eV. A thin CsF layer deposited on top of CuI and Al photocathodes was found to significantly increase their quantum yield. An enhancement of the photoyield following exposure to water vapor has been observed for alkali fluoride-coated photocathodes. We interpret this effect as a decrease of the electron affinity by about 0.3-0.4 eV, induced by adsorption of polarized H_2O dipoles.

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1 Introduction

Coating photocathodes with thin dielectric films is relevant in the field of photodetection, in particular for detectors combining solid photocathodes with gaseous electron multipliers [1, 2, 3]. Gaseous photomultipliers, currently operating in the ultraviolet (UV) range with CsI convertors [4], have important potential applications in the field of photon imaging, mostly in Ring Imaging Cherenkov (RICH) Detectors [5] and in the readout of gaseous [1] and solid [2] scintillators. There has been a growing interest in extending the spectral response of gaseous photomultipliers towards the visible range. The few attempts to operate visible photocathodes in gas media [6, 7, 8] have so far had limited success. We have recently proposed protecting air-sensitive photocathodes with thin solid dielectric films, to permit their short exposure to air and long-term operation in pure gas media [9, 10].

The requirements for coating films are contradictory: on one hand the film should be thin enough to provide good electron transmission; on the other hand it should be sufficiently thick and homogeneous to protect the photocathode against deterioration by chemical reaction with active species such as water, oxygen etc. There are several reasons that influenced our choice of dielectric protective films. It is known that dielectric materials with a large energy gap should have good electron transport properties [11]. Some dielectric films like LiF, MgF₂ and SiO are being used for protection of Al-based mirrors and optical filters from oxidation [12, 13]. Also, thin dielectric layers of native oxides, such as SiO₂ and Al₂O₃, provide sealing from further oxidation of the bulk [14, 15].

The initial photoelectron energy relative to the vacuum level, typical for photoemission from visible and UV photocathodes, varies in the range of 0-3 eV. There exist considerable experimental data on electron transmission through solids for electron energy above 10 eV (see for example [16] and references therein). However there are only a few theoretical [17, 11, 18] and experimental [19, 20, 21, 22, 23, 24, 25, 26] works on photoemission and electron transport through thin dielectric films, other than SiO₂, in the low energy (~ 1 eV) range. Of particular relevance are refs. [17, 18] providing theoretical calculations for alkali halides, and a few experimental works concerning the photoemission through Al₂O₃ films [21], SiO₂ films (for energies above 8 eV) [23] and organic films of hexatriacontane [24] and cadmium stearate [25]. Some works deal with electron transport in solid Ar, Kr and Xe films [27, 28, 29].

There is ample literature on low energy electron transport, in Si/SiO₂ systems due to their technological importance (see for example [30, 31, 32, 33] and references therein). Few works in the past considered a field-induced vacuum emission from Al/Al₂O₃/Al systems [34, 35], containing some information on the electron transport in Al₂O₃. To the best of our knowledge there are no experimental data on low energy (a few eV) electron transmission, neither through alkali and alkali-earth halide films nor through oxide films, produced by a vacuum evaporation technique. The present work tries to fill this gap.

In the present article we survey the photoelectron transmission properties of a number of films: alkali halides (LiF, NaF, CsF, NaI), alkali-earth halides (MgF₂, BaF₂), oxides (SiO, SiO₂, Al₂O₃), and organic films (hexatriacontane). The films were prepared by vacuum evaporation at our laboratory. We measured the quantum yield (QY) spectra of CsI and CuI

photocathodes coated with these films of different thicknesses, and determined the electron attenuation length for each of them. We found that some of the coating films like CsF, NaI and $n\text{-C}_{36}\text{H}_{74}$ (hexatriacontane) exhibit rather high electron transmission, and that CsF deposited on CuI and Al can even increase their quantum yield.

Effects of exposure to water vapor of coated photocathodes were also studied. During this study we observed an interesting effect of the photoyield enhancement of alkali fluoride-coated photocathodes after their exposure to water vapor [36]. We discuss a possible interpretation of the enhancement as being due to polarized H_2O dipole adsorption, leading to an effective drop of the electron affinity of the photocathode. We are not aware of any work on the direct measurement of the electron affinity decrease by water adsorption. However, there are some indications that it could happen; for example, it has been observed that the QY of LiF, CsBr and RbI photocathodes in the vacuum ultraviolet region is higher after a short-term contact with ambient air, compared to the QY of the same photocathodes prepared without contact with air [37, 38]. Based on this interpretation and using a simple model of the photoemission from dielectric films, we estimated the drop of the electron affinity induced by water adsorption.

Results reported in this work were obtained with thin films evaporated mostly on CsI and CuI surfaces. These relatively air-stable photocathodes are used only as a testing ground, for the understanding of the experimental procedures and properties of potential coating films. At present, similar experimental procedures are being successfully applied by us to visible photocathode coating [39, 40, 41].

2 Experimental procedures

All films investigated were produced by a vacuum evaporation technique. The main experimental setup consists of a high vacuum (1×10^{-7} Torr) evaporation chamber, coupled via a CaF_2 window to a vacuum monochromator, equipped with a D_2 lamp (see Fig.1a). An important feature of the setup is that after preparation of the sample its QY can be measured *in situ*: the sample is brought from the evaporation site to the measurement position by manipulating the substrate support in vacuum.

The absolute QY of each sample was measured in a reflective mode, in vacuum, as a function of wavelength, in steps of 2-5 nm; a positive voltage is applied to a mesh electrode, placed at a distance of 2 mm above the photocathode, and the photocurrent induced by a calibrated UV-photon flux is measured on the photocathode. The electric field strength at the photocathode surface was usually maintained at 1.2 kV/cm. A more detailed description of the calibration and measurement procedures can be found elsewhere [42, 43]. The error in measurement of the QY of a given photocathode sample, defined by fluctuations of the dark current, was about 4×10^{-4} . The systematic error due to photon flux calibration was about 5% of the absolute QY value.

A typical procedure for preparation and characterization of the sample under investigation included the evaporation of a 5000 Å thick CsI or 1000 Å thick CuI film on a polished stainless steel substrate (pre-coated with a 500 Å thick Al film in the case of CsI), its con-

ditioning by heating in vacuum for few hours [44], measurement of the QY, evaporation of the coating film, and re-measurement of the QY. The last two steps were repeated several times, measuring the QY dependence on the film thickness. All the steps are carried out in the same chamber without breaking the vacuum.

The thickness of the film and its deposition rate are monitored with a quartz crystal oscillator [45], with an accuracy of about 0.3 Å and 0.03 Å/sec respectively. The film thickness was calculated relative to the bulk density of the deposited material, i.e. it was not corrected for the possible reduced packing-density, which in principle could take place [13, 46]. Most materials were evaporated from Ta or Mo boats, closed with a perforated cover. The evaporation material is typically a powder of high purity [47].

A few words should be said about SiO₂ and Al₂O₃ films, since their preparation techniques were different. Two techniques were used: a reactive evaporation [48] from a resistive source and an electron beam evaporation. In the reactive evaporation, SiO or Al were evaporated from the boat in the presence of oxygen gas, providing fast oxidation of the deposit. The O₂ was introduced into the chamber through a needle valve up to a pressure of about 10⁻⁴ Torr. The electron beam evaporation was performed in a different setup, and in this case, the CsI photocathode was exposed to ambient air for a few minutes during transfer. We firmly believe that this transfer did not affect the results, because of the proven stability of CsI [4] and, moreover, of CsI/SiO₂ photocathodes to a short-term exposure to ambient air.

The preparation conditions for the various films are summarized in Table I.

Heating of the substrate in the temperature range of 50-90°C was performed *in situ* in vacuum, with a built-in water heat-exchanger (see Fig.1b). In this case the sample had no contact with air. For heating to higher temperatures, the sample was transferred, through ambient air, to another chamber, heated by a halogen lamp from its rear side, and retransferred to the main vessel for characterization.

An exposure of the sample to water vapor was performed by filling the chamber with distilled water vapor or with humid air, up to a certain pressure (see Fig.1c), and keeping the sample at this pressure for a given time at room temperature (22°C). Water vapor pressure inside the chamber was carefully monitored with a hygrometer [49], down to 4×10⁻⁴ Torr.

3 Coating of photocathodes with thin dielectric films

3.1 General considerations

The coating of a photocathode with a thin dielectric film results in the attenuation of photoemission. This can be due to quasielastic and inelastic electron scattering on acoustic and optical phonons within the film (see for example [18]). In addition, a modification of the surface potential barrier can occur, which either enhances or further attenuates the emission yield. Finally, vacuum-deposited dielectrics can contain a large density of electron trapping centers, which can strongly influence the electron transport properties.

In general, the energy band structure notion can be applied to thin dielectric films, similar to that of bulk materials and regardless of their crystalline form, since the essential features of the band structure are determined by the short-range order within the solid [50]. Fig.2

shows a possible example of the simplified energy-band diagram at the CsI/LiF/vacuum interfaces. Since both the substrate and the coating film are insulators, they are incapable of supplying sufficient charge to the interface to cause significant band bending [50, 51]. The photoemission process is depicted schematically in the figure as well.

The principal photocathodes used in the present study were CsI and CuI. The measurements were performed over a spectral range of 150-250 nm (8.3-5 eV). Taking into account the photoemission threshold of 6.1 eV and 5.5 eV [44] for CsI and CuI, respectively, the initial energy of the photoelectrons injected into the coating film and measured with respect to the vacuum level ranges between 0-2.2 eV for CsI and 0-2.8 eV for CuI. These values are valid only under the assumption that the coating film does not affect the relative position of the bottom of the conduction band of the substrate and the vacuum level. Otherwise, one should take into account the modification of the surface barrier induced by the coating film, to estimate the electron energy correctly.

Both CsI and CuI evaporated photocathodes are polycrystalline films. CsI film consists of a mosaic of crystallites of sizes varying typically between 0.3 and 3 μm ; the crystalline structure was confirmed by Atomic Force Microscopy (AFM) and X-ray diffraction studies [52, 53]. It was reported that CuI films evaporated on different substrates consist of crystallites with a typical dimension of 1 μm [54], preferentially oriented with the $\langle 111 \rangle$ axis perpendicular to the substrate [55, 56].

In the case of an epitaxial growth of a crystalline material on top of a crystalline substrate, the matching of their lattice constants plays a major role. Similarly, a good lattice matching between CsI or CuI and the coating material may favour the formation of a layer which replicates the structure of the photocathode underneath. This could also affect the electron transport properties through the coating film. Lattice constants, energy gaps and electron affinities of materials used in the present work are presented in Table II.

Almost all films investigated formed coatings on CsI and CuI which were stable in vacuum at room temperature, for at least a few days. The only exception is $n\text{-C}_{36}\text{H}_{74}$, which slightly improved its electron transmission properties after a few hours of storage in vacuum. Some coating films, namely MgF_2 and NaI , were found to change their properties after undergoing heat-treatment for a few hours [9, 44]. In what follows the data are presented for freshly evaporated films, within half an hour after deposition.

For thicknesses above 5-10 $\text{\AA}$ most of the coating materials studied exhibit an exponential decrease of the QY with thickness. The exponential behaviour allows one to define the attenuation length L of the photoyield:

$$Y(x) \sim \exp(-x/L) \quad , \quad (1)$$

where $Y(x)$ is the QY of a photocathode coated with a film of thickness x .

$$1/L = 1/L_e + 1/L_{ph} \quad (2)$$

where L_e and L_{ph} are the electron attenuation and photon absorption lengths of the film. If the coating film does not contribute to the photon adsorption, L is determined by the electron attenuation length: $L = L_e$. All thin coating films studied, except NaI , SiO and

Al_2O_3 , are very transparent to photons over the spectral range considered in this work. We also ignore the photoemission from the coating film itself, since it is negligible for all the studied materials, except for NaI.

In the following sections the properties of each coating film investigated are given in detail. The following data are presented: QY spectra for a series of coatings, QY versus film thickness for a few selected films and a summary of the thickness-dependence of the QY and the escape length, for all the films.

3.2 Alkali halide films

LiF

Among alkali halides, LiF has the smallest lattice constant. It is used as a protective film for Al mirrors in the extreme ultraviolet [12, 13, 57].

A surface microanalysis was carried out on a few samples using atomic force microscopy. AFM images of uncoated CsI and CsI coated with about 20 Å thick LiF film are shown in Fig.3. The surfaces were exposed to air prior to and during their analysis. The surface of uncoated CsI shows a polycrystalline texture, inherent in CsI films produced by vacuum evaporation [53]. The CsI surface coated with LiF is smoother compared to the uncoated one: the CsI grain structure is almost invisible under the thin LiF film. These images indicate that the LiF film coating is continuous even at very small thickness (few atomic layers). This is not necessarily true for the other materials and other substrates studied.

QY spectra of the CsI photocathode coated with LiF films of different thicknesses are shown in Fig.4. Fig.5 shows the QY as a function of LiF thickness, measured at different wavelengths. For each wavelength the data points fit the exponent. The exact exponential decrease of the QY, including the data points at a "zero" thickness, and the dependence of the attenuation slope on the wavelength (Fig.5) provide an indication that the contribution of photoemission through holes in the film is not dominant even in very thin layers, i.e. that the film is basically continuous.

The monotonic decrease of the QY with thickness also indicates that the LiF coating does not change the position of the vacuum level with respect to the bottom of CsI conduction band. This allows one to determine the maximum initial photoelectron energy in CsI with respect to the vacuum level by subtracting a photoemission threshold of CsI from the incident photon energy.

The electron attenuation length, determined according to eq.(1), is shown in Fig.10; it depends on the photon wavelength and varies from 5 to 10 Å at the maximum initial electron energy of 0.4 and 2.2 eV correspondingly. We are not aware of any available attenuation-length data by other authors.

NaF

NaF has a lattice constant which is close to that of CsI (see Table II); the lattice mismatch is only 1%. Therefore one could expect a more regular structure of NaF on the CsI crystallites, compared to that of LiF on CsI. The electron attenuation length of the NaF film is by a

factor of 1.5 larger compared to that of LiF and varies from 7 to 14 Å over the investigated spectral range (Figs.9,10). In other aspects NaF coating is very similar to that of LiF.

CsF

CsF coating was studied on CsI and CuI photocathodes and on an Al surface. Unlike other materials studied, the coating of CsI and CuI with thin (10 Å) film of CsF results in the enhancement of the photoyield (Fig.4). For CsI photocathode the effect is small and takes place at wavelengths longer than 190 nm. For CuI photocathodes the substantial QY enhancement occurs over the whole spectral range. The shift of the red boundary by a value of about 0.4 eV indicates a similar decrease of the surface barrier. Similar to CuI/CsF, the effect of the CsF overlayer on Al was found to be strong, compared to that of CsI/CsF (see Fig.3 in ref. [10]). It is important to note that the CsF-induced enhancement is conserved after a short-term (half an hour) exposure to ambient air.

The observed effect could be connected to the ability of the CsF layer to reduce the work function of the metal or semiconductor substrate, as reported earlier for W [58] and GaAs [59]. The reduction of the work function of W by the CsF adsorption was explained by a dissociation of CsF molecules [58] resulting in a cesiation of the surface, which is known to be an effective way to reduce the work function of solids.

For CsF films thicker than 10 Å the QY decreases with film thickness. The QY attenuation can be described by an exponential law up to a thickness of about 40-50 Å, both for CsI and CuI substrates (Figs.6,9). However for larger thicknesses, in the case of CsF on CsI, the damping rate is appreciably slower than that of an exponent (see Fig.6). This could be explained by the transition from an amorphous or very small microcrystal structure near the CsI/CsF interface to a more organized polycrystalline structure at larger film thicknesses, similar to that observed for LiF [46].

The electron attenuation length determined in the thickness ranges of 9-36 Å and 10-50 Å for CsI/CsF and for CuI/CsF respectively, using expression (1), is presented in Fig.10. For CsI/CsF it varies from 14 to 30 Å in the respective photon energy range of 6.5-8.3 eV.

Attenuation length of CsF on the CuI substrate is considerably larger compared to that on CsI, varying from 65 to 170 Å over the respective photon energy range of 5.6-8.3 eV. The corresponding range of the maximum initial electron energy is equal to 0.5-3.2 eV, assuming a post-coating surface barrier drop equal to 0.4 eV as discussed above. There are no other experimental data on the electron transport in CsF in this energy range. However, it is interesting that for ideal CsI crystals, theoretical calculations [11] suggest an electron escape length of about 250 Å at an electron energy of 3 eV and 30 Å at 0.5 eV, which is not far from our results for CsF.

We suppose that the effect of lattice matching could be the cause for the difference in attenuation lengths of CsF on CsI and CuI substrates. Indeed, CsF has a lattice constant which is very close to that of CuI (see Table II): the mismatch is of only 0.3%, while the mismatch between CsF and CsI is large, of 32%. Notice, that a lattice matching between the substrate and the coating film is usually considered as a major condition for an epitaxial growth of a perfect crystalline structure. Thus one could expect better electron transmission

of CsF on CuI, compared to CsF on CsI.

NaI

We found NaI to be one of the most transmissive materials for low energy electrons. NaI coating was studied on both CsI and CuI photocathodes. In contrast to other coating materials, the contribution of photon absorption in NaI to the photoyield attenuation, below 240 nm, can be substantial. The absolute light absorption coefficient of NaI films was measured in refs. [60, 61]: the absorption length varies from 1000 to 300 Å at photon energies 5.2-6.7 eV.

CsI/NaI films show a decrease rate of the QY with a thickness which is slower-than-exponential (Fig.4). The reason is that apart from the light absorption, NaI contributes electrons from its own photoemission, at wavelengths shorter than 180 nm [44]. This contribution was taken into account and subtracted, while estimating the electron attenuation length using formula (1). For that purpose it was independently evaluated by measuring the QY spectra of NaI films freshly deposited on a stainless steel substrate. These spectra are shown in Fig.4 as dot-dashed lines in CsI/NaI and CuI/NaI plots. We did not observe substantial differences in the QY for NaI thicknesses varying from 100 to 500 Å. Comparing the QY spectra of a 100 Å thick NaI film on a stainless steel substrate and 250 Å thick layer of NaI on CsI (Fig.4, CsI/NaI plot), one can see that for the latter the photoemission of the NaI itself dominates.

QY-thickness dependences for CsI/NaI films, after subtraction of the photoemission contribution of NaI, are shown in Fig.7 and are well described by an exponential attenuation. It becomes clear from the figure that a very thin NaI layer slightly increases the surface barrier. The effective attenuation length determined for NaI thickness larger than 10 Å, is shown in Fig.10; it varies from 14 to 70 Å in the photon energy range 6.5-8.3 eV. The attenuation length is smaller than the photon absorption length, approximately by a factor of 4. Therefore, in a first approximation, with an accuracy of 25%, the total attenuation length measured can be identified as the electron attenuation length. We may conclude that among all coating films on CsI investigated in this work, NaI has the highest electron transmission.

NaI coating on CuI gives mysterious results: even for very thick NaI film, of 1000 Å, the QY of CuI/NaI is significantly larger than the QY of NaI itself, as seen in Fig.4 (CuI/NaI plot). Also, the attenuation length, obtained by applying a similar procedure to that applied to CsI/NaI, is surprisingly large, being in complete contradiction with the data on light absorption in NaI [60]. For example, at photon energies of 6.7 eV the attenuation length of NaI on CuI is 420 Å. i.e. larger than the light absorption length of NaI (equal to 300 Å), which violates expression (2).

A possible explanation of these results could be an ion diffusion between CuI and NaI layers: CuI is known to be a superionic conductor with extremely high mobility of Cu^+ ions [62], and both CuI and NaI have the same type of anion. This could lead to an easy cation exchange between CuI and NaI films. Consequently, the CuI content in the topmost layers could be enriched, acting as a source of the observed photoemission. This possible

mechanism should be confirmed by further X-ray spectroscopy (XPS) and X-ray diffraction studies.

3.3 Alkali earth halide films

MgF₂

MgF₂ is the most widely used optical coating material. Protective MgF₂ films of thickness of 250 Å provide long-term stability to Al mirrors in air [57].

In very thin layers the MgF₂ coating provides an example of a discontinuous film : the QY of CsI after coating with 5 Å thick layer is practically unchanged, almost independently of the wavelength (Figs.4,9). This should be the case when the photoemission occurs through holes in the coating film, as discussed before. The discontinuity of thin MgF₂ films can be related to its lower lattice symmetry: it has a tetragonal structure, while all alkali halides have a cubic structure.

For thicknesses larger than 5 Å the QY drop obeys an exponential law, indicating film continuity, and allowing for the determination of the electron attenuation length, shown in Fig.10. The latter is one of the smallest among the materials investigated in this work and it decreases with wavelength faster than for the other fluorides.

It is known [13, 46] that MgF₂ tends to form films with low packing density, of about 0.7, if deposited on a substrate at room temperature. The packing density could be increased by evaporation at elevated substrate temperatures, of about 300°C , or by annealing the film after deposition [13]. We proceeded with a post-evaporation heat treatment in vacuum at 60°C , and found that the QY was indeed considerably enhanced. It should be remarked that of all coating materials investigated here, MgF₂ and NaI turned out to be the only ones which significantly changed their properties under heating.

BaF₂

Not much can be said about BaF₂ , since it turned out that the QY spectra of CsI/BaF₂ were not easily reproducible from sample to sample. We can only state that the electron transmission properties of BaF₂ films are situated between those of MgF₂ and NaF.

3.4 Oxide films

Oxides can be very effective protective films, even in extremely thin layers, if well prepared. Indeed, native layers of 15-20 Å thick SiO₂ and of 35 Å thick Al₂O₃ provide efficient sealing from further oxidation of Si and Al [14, 15, 21]. Evaporated SiO, SiO₂ and Al₂O₃ films are amorphous.

SiO

SiO films are widely used for optical [13] and dielectric [63] applications. Since the photon absorption length of the SiO film, in the UV region, is above 250 Å [64], i.e. much larger

than the thicknesses used in our study, the photoyield attenuation can be fully attributed to the electron attenuation. Thus, the electron attenuation length of SiO is situated between that of MgF₂ and LiF, varying from 3 to 9 Å (Fig.10).

SiO₂

We prepared SiO₂ films using both a reactive evaporation of SiO and an electron beam evaporation of quartz. For some of the CsI/SiO₂ samples prepared with the SiO₂ film produced by reactive evaporation, we proceeded with an X-ray photoelectron spectroscopy (XPS) of the surface. Distinct XPS-signals of Cs, I, Si and O were detected, confirming that SiO was indeed deposited on top of CsI. The shape and the position of the Si peak corresponds to 85% of Si bound as SiO₂, and approximately 15% bound as Si₂O₃. This confirms that most of SiO was transformed into SiO₂ during the reactive evaporation. The estimation of the SiO₂ layer thickness, derived from the relative intensity of signals for Cs, I and Si species, was in agreement with the quartz oscillator data.

Fig.9 shows the QY as a function of the SiO₂ thickness, obtained with different CsI samples. Both preparation techniques give rise to similar results: electron damping with thickness can be described by an exponent.

The electron attenuation length of SiO₂ (Fig.10) is close to that of MgF₂: at the maximum initial photoelectron energy of about 2.2 eV, it is equal to 8 Å. This value is fairly consistent with the attenuation length of a SiO₂ film thermally grown on Si and measured in a photoemission experiment [23] for photoelectron energy of 8 eV. This is, however, somewhat smaller than the electron energy relaxation length in SiO₂, of 30 Å, reported in ref. [30] obtained in a field emission experiment.

Al₂O₃

Al₂O₃ films were prepared by reactive evaporation of Al and by an electron beam evaporation of sapphire. Both preparation techniques gave rise to consistent results.

Al₂O₃ coating on CsI provides a good example for increase of the surface barrier (Fig.9): the QY of CsI drops considerably after coating with 7 Å thick Al₂O₃ layer. For larger thicknesses the QY decrease is moderate and can be described by an exponent. The attenuation length of Al₂O₃ determined for this exponential fit has an intermediate value, between that of LiF and NaF (Fig.10): at a photon energy of 8.3 eV it amounts to 10 Å. The photon absorption length of the Al₂O₃ film varies between 250 and 1000 Å in the relevant wavelength range [21], therefore the photoyield attenuation can be attributed to the electrons.

Since the Al₂O₃ layer significantly modifies the surface barrier, the initial electron energy with respect to the vacuum level is also changed, as compared to the uncoated CsI film. The change is estimated from the red boundary shift, to be of the order of 0.7 eV. Therefore the maximum initial electron energy corresponding to the photon energy of 8.3 eV is about 1.5 eV.

The extracted electron attenuation length can be compared to the value of 130 Å, measured by photoemission from Al through Al₂O₃ films grown by anodization, for a maximum initial photoelectron energy of 7.8 eV [21]. The large discrepancy could result from the large

difference in electron energy and the different film preparation techniques. On the other hand we can use the data of energy loss for hot electrons in Al_2O_3 [34, 35], measured in $\text{Al}/\text{Al}_2\text{O}_3/\text{Al}$ tunnel structures. It gives an electron energy-relaxation length of the order of 10-30 Å at an energy of 1 eV, which is consistent with our data.

3.5 Organic films

$n\text{-C}_{36}\text{H}_{74}$

$n\text{-C}_{36}\text{H}_{74}$ (hexatriacontane, HTC) is the only organic coating film studied in the present work. This long-chain paraffin insulator was reported [65] to have a negative electron affinity (NEA) and to be a model substance for polyethylene. Its important advantages are the possibility of preparation by vacuum evaporation and the stability in ultra-high vacuum and in ambient air conditions [24].

Fig.8 shows the QY as a function of the HTC film thickness at different wavelengths, measured for two different CsI samples. HTC has a relatively large electron attenuation length, of 40 Å at the maximum electron energy of 2.2 eV, slowly decreasing to 35 Å at 0.8 eV (see Fig.10). It should be noted that our results are in good quantitative agreement with the results obtained in another photoemission experiment [24], where the electron attenuation length of HTC varied from 45 Å at the electron energy of 2.2 eV to 30 Å at 1 eV.

4 Effects of exposure to water vapor

4.1 Experimental results

Fig.11a shows the evolution of the QY of a CsI photocathode coated with a 22 Å thick LiF film, following an exposure to humid air, re-exposure to vacuum, heating and further long exposure to air. One can see a dramatic enhancement of the photoemission after an exposure to humid air inside the chamber; the difference in the QY can reach a factor of 20 at 190 nm. The stability of the effect should be emphasized: once the sample has been subjected to a H_2O vapor "treatment", its enhanced photoemission is rather stable when further exposed to vacuum (even at elevated temperatures) and to ambient air, for a few days. However, long-term (1 month) exposure to ambient air destroys the photoemission enhancement.

We verified that the effect is due to LiF and not to CsI, by treating an uncoated CsI surface in a similar way. No enhancement has been found; after the treatment the QY either remained unchanged or decreased, depending on the degree of humidity and the exposure time.

It has also been proved that the observed QY enhancement is due to H_2O vapor and not to other impurities in air, by exposing a CsI/LiF sample to a controlled amount of H_2O vapor in the vacuum chamber (see Fig.11b). In this experiment the exposure varied from 2 minutes at 0.3 Torr H_2O to 2 hours at 7 Torr H_2O . Further exposure to H_2O vapor did not increase the photoyield, indicating a saturation of the enhancement. A major increment of the photoyield takes place after an exposure to 7 Torr H_2O , which could indicate the

necessity for a certain density of H_2O molecules to initiate the effect. Comparing Figs. 11a and 11b we conclude that the magnitude of the water-exposure effect is the same in humid air and in pure H_2O vapors, i.e. the presence of air does not noticeably affect the process.

The magnitude of the enhancement decreases with a decrease of the film thickness. This is seen in Fig.12 showing the results for a 10 Å thick LiF film. Nevertheless, for thinner films the QY after exposure to H_2O vapor can even exceed that of uncoated CsI for wavelengths above 190-200 nm (see Figs.12,14a).

Very similar results were obtained for CsI photocathodes coated with NaF and CsF films and CuI photocathodes coated with CsF films. In particular, the final magnitude of the photoyield enhancement was found to be roughly the same for the three alkali fluorides, if they have the same initial QY values. However, the saturation was found to be faster compared to LiF. This is seen in Fig.13 showing the dependence of the QY of CsI/LiF, CsI/NaF and CsI/CsF photocathodes on the water "dosage" expressed in Langmuirs (L) ($1 \text{ L} = 10^{-6} \text{ Torr-sec}$). Due to our simplified experimental arrangement we could provide a controlled water dosage above 10^5 L . But as one can see, the photoyield signal does not change at this dosage; the signal starts increasing only at 10^7 L and saturates at about 10^8 L for CsF, 10^9 L for NaF and 10^{10} L for LiF. Note that the saturation dosages appear to follow a descending order from LiF to CsF, in correlation to the increase of their water solubility.

It is also interesting to note that the effect slightly enhances from LiF to NaF and then to CsF, in accordance with their increasing solubility in water (Fig.14a). These three alkali fluorides are known to be hygroscopic. For comparison non-hygroscopic alkali-earth fluoride films like MgF_2 and BaF_2 on CsI were studied (Fig.14b). The water adsorption effect for them was found to be negligible, which supports the assumption for the enhancement being related to H_2O .

We studied the effect of exposure to H_2O vapor for other photocathodes like NaI, CsI/ SiO_2 , CsI/ Al_2O_3 , CsI/NaI and CuI/NaI. A little enhancement of the photoyield was observed for CsI/ SiO_2 and it took several days to reach a photoyield saturation. The other photocathodes had no distinct response to short-term contact with H_2O .

4.2 Polarized water adsorption

We propose to interpret the photoemission enhancement results in terms of modification of the electron affinity, induced by surface adsorption of polarized H_2O molecules. Indeed, it is well known that the electron affinity of solids can be reduced by a surface adsorption of molecules with either a low ionization potential, for example Cs [70, 71], or a high polarizability, such as noble gases [72]. Qualitatively, the effect of the electron affinity reduction is explained by attraction of the electrons of the adsorbed molecules towards the solid. This leads to a formation of a double-charged layer, providing a drop of the surface potential barrier.

In principle there should exist another way to create such a double layer structure, namely by a polarized adsorption of molecules with a high dipole moment. A surface potential step induced by an adsorbed layer of oriented dipoles is equal to

$$\Delta U = 4\pi n\mu_{\perp} \quad (3)$$

where n is the number of adsorbed molecules per unit area, $\mu_{\perp}$ is the average component of the molecular dipole moment in the direction perpendicular to the surface plane. If $\mu_{\perp}$ is antiparallel to the surface normal, the surface barrier is reduced resulting in the enhancement of the photoyield. The water molecule is one of the best candidates for this task, because of its particularly high dipole moment of 1.84 D (1 Debye = 10^{-18} esu). Orientation effects in water adsorption should be particularly strong on ionic salts like those of halides, due to their highly polar structure.

However, little is known about water adsorption on alkali halides (LiF, NaF, NaCl) [73, 74, 75] and alkali-earth halides (BaF_2 , CaF_2) [76] and even less about H_2O molecule orientation on their surfaces. The latter has been recently studied in refs. [76, 77, 78] with an optical second-harmonic generation (SHG) technique. The following interpretation of their results [76, 78] is particularly relevant to our work:

- Water adsorbs on NaCl(100) and BaF_2 (111) both in air and in vacuum, even at room temperature. This is in contrast to previous expectations [74], where only cooling of crystals much below 0 °C could induce water adsorption, and in accordance with our observations for LiF, NaF and CsF.
- Water adsorption on NaCl(100) is predicted to have a polarized nature. At small water coverage, below 0.5 monolayer, the dipole moment of H_2O molecules is expected to be oriented antiparallel to the surface normal. This dipole orientation should strongly reduce the work function of the electrons.
- It is predicted that beyond one monolayer coverage a 2D-ice bilayer is formed on NaCl(100) surface at room temperature, still having a non-vanishing perpendicular component of the H_2O dipole moment, of the order of 0.4 D (Fig.4 in ref.[78].) This concept implies that the highly polar character of alkali halides stabilizes 2D-ice layers on their surfaces, even at room temperature.

Substituting the value of 0.4 D into (3) and taking into account the H_2O molecule concentration within one 2D-ice layer ($17.5 \text{ \AA}^2$ area per H_2O molecule) [79], we can roughly predict a work function drop at the alkali-halide/ice interface to be about 0.9 eV. This should be compared to our estimations of the electron affinity decrease of 0.4 eV obtained from experimental data for LiF and NaF, as discussed in the next section.

We suggest that quasistable conditions might exist, at which a certain H_2O dipole orientation, namely towards the film, could considerably reduce the electron affinity of alkali halides.

4.3 Estimation of the electron affinity decrease

Motivated by these arguments, we tried to estimate the value of the electron affinity decrease for CsI/LiF and CsI/NaF films using a simplified three-step model [80] of the photoemission from dielectric films, similar to that used in [81, 66]. Fig.2 shows a possible energy diagram at the CsI/LiF/vacuum interface. Note that the difference between the vacuum level and the bottom of the CsI conduction band, $E_a(\text{CsI})$, does not change after coating with LiF;

this assumption, supported by photoelectron transmission data presented in section 3.2, is also valid for the CsI/NaF system. This is however not the case for CsF coatings: thin CsF overlayer reduces the surface barrier of CsI and especially of CuI. Since the exact value of this reduction is generally unknown, we excluded CsF from the following calculations.

A photoemission process consists of three steps [80]: photoexcitation of an electron from the valence band to the conduction band of CsI, a transport through the CsI and LiF films to the surface, and an escape to vacuum. The main simplification of the model is the assumption that electrons in the conduction band of both CsI and LiF are distributed isotropically in angle and uniformly in energy. This assumption has been successfully applied to explain a threshold behaviour of the photoemission from metals (Fowler dependence) [81] and to describe a field-enhancement effect in the photoemission from CsI [66]. In deriving the expression for the QY we followed these references; the derivation is presented in the Appendix.

The QY of the photoemission from CsI/LiF films is given by

$$Y = \frac{f}{2\Delta E} \left[g^{1/2} E_m^{1/2} - E_0^{1/2} \right]^2 . \quad (4)$$

Here E_m and ΔE are respectively the initial maximum energy and the initial energy spread of photoelectrons in the CsI conduction band. E_0 is the surface potential barrier at the LiF/vacuum interface; measured from the bottom of the LiF conduction band, it is equal to the LiF electron affinity E_a . f and g are the normalization and electron transport parameters depending on the LiF thickness.

First, the experimental QY spectra before contact with H_2O , for a certain LiF thickness, are used to fit the parameters f and g . During this fit an arbitrary fixed value is assigned to E_0 (in particular we used $E_a = 1$ eV which is close to that quoted in the literature [71]). Supposing that the electron transport properties in LiF remain unchanged after contact with H_2O and that the only effect of H_2O is the modification of the surface barrier, we then fit the spectra measured after exposure to H_2O with fixed values of f and g obtained before exposure and with E_0 being a single free parameter. The difference between the initial value and that of the fitted one provides us with the desired value of the electron affinity variation ΔE_a . The wavelength range for the fits was 160-190 nm and 160-200 nm for the data before and after exposure to H_2O correspondingly. A similar procedure was applied to NaF-coated films.

An example of the model fit to experimental data is shown as solid lines in Fig.12. For uncoated CsI the model successfully describes the shape of the QY spectrum below 200 nm, the wavelength corresponding to the sum of the energy gap and electron affinity of CsI. However, at longer wavelengths the model has limitations due to other mechanisms, for example the decay of excitons on F-centers [60, 19], which are not taken into account.

The model describes reasonably well the increment in quantum yield between the data obtained before and after contact with H_2O , in the range 160-190 nm. Estimations of ΔE_a are presented in Table III. The values for LiF and NaF are very similar; they are smaller for thinner films, 0.15-0.17 eV, while above 10 Å they tend to be constant, of the order of 0.3-0.4 eV. According to (3) this is by a factor of 10-20 less compared to a hypothetical limit,

which might be reached if all H_2O molecules would form a layer with their dipole moment directed antiparallel to the surface normal.

5 Summary and conclusions

The aim of this research is the study of physical properties of thin dielectric film coatings, for possible protection of sensitive photoemissive materials, i.e. visible photocathodes. In this work we presented the results of a systematic study of photocathode coating with various thin films: alkali halides, alkali-earth halides, oxides and organics. All films were prepared and studied in the same way, applying vacuum deposition techniques and measuring the attenuation of the quantum yield (QY) spectra of coated photocathodes at different film thicknesses. For reasons of simplicity, we deposited the films on relatively air-stable photocathodes, namely CsI and CuI.

Though the QY data provide only an integral information on the photoemission (for example, only the maximum photoelectron energy can be evaluated), these measurements directly estimate the QY attenuation due to coating, which is of prime interest for practical applications. We have extracted the electron attenuation length from the QY-thickness dependences; for some of the films (LiF, NaF, CsF, NaI, MgF_2) the attenuation length (in the 1 eV energy range) was determined for the first time.

The observed QY dependence on the thickness of various coating films can be summarized as follows (see Fig.9). One should distinguish the effects measured at film thicknesses of the order of 1-2 monolayers, i.e. below 10 Å, from that observed above 10 Å. For some films, like LiF, NaF, SiO, SiO_2 and $n\text{-C}_{36}\text{H}_{74}$, the QY decreases, below 10 Å, by the same law as that observed for larger thicknesses. This could be interpreted as possible evidence for continuity of the film and for non-modification of the surface barrier after coating. For other films, whose thickness dependence in very thin layers differs from that of thicker ones, three types of behavior are observed: 1) the QY stays practically constant independently of the wavelength (MgF_2), obviously indicating the discontinuity of the film; 2) the QY increases (CsF), indicating the decrease of the surface barrier; 3) the QY abruptly drops (Al_2O_3 and NaI), indicating the increase of the surface barrier.

An important experimental result is the chemical stability of most of the dielectric coatings on CsI and CuI photocathodes. Another observation is that CsF, NaI and $n\text{-C}_{36}\text{H}_{74}$ have fairly large electron attenuation length, varying, on CsI substrates, from 20 to 50 Å at a maximum initial electron energy of 1 eV. Moreover, the electron attenuation length of CsF on CuI was found to be considerably larger than that on CsI. The possible interpretation could be an epitaxial growth of CsF on CuI due to the matching of their lattice constants. Thus, CsF, NaI and $n\text{-C}_{36}\text{H}_{74}$ films can be good candidates for protective coatings of sensitive photocathodes.

Intriguing results were obtained with ultrathin CsF coating: a 1-2 monolayer thick CsF film considerably increases the QY of CuI and Al photocathodes, shifting the red boundary, in the case of CuI, by about 0.4 eV. The possible explanation is a dissociation of CsF molecules on metal or semiconductor substrates resulting in a partial cesiation of the surface

[58]. The fact that the increase in QY was found to be stable in air for tens of minutes is not very surprising, if we take into account relative stability of cesiated diamond film surfaces, reported recently [82].

Exposure of alkali-fluoride-coated photocathodes to water vapor gives rise to an interesting effect of QY enhancement. We explain this effect by a possible reduction of the electron affinity of the coating film, induced by adsorption of polarized H₂O molecules. We estimated the order of magnitude of this reduction to be of 0.3-0.4 eV, using a simplified model of photoemission. More precise estimates of the effect will be obtained after the elaboration of more rigorous model including microscopic approach. Of particular interest are the study of the temperature dependence of the effect and the possible use of other liquid or gaseous adsorbants with high molecular dipole moment. If successful, these investigations will result in the production of new, highly efficient, negative-electron-affinity photocathodes.

An example of the ultimate application of the results obtained in the present work is the coating of visible Cs₃Sb photocathodes with thin dielectric protective films [39, 41]. It was confirmed that few coating films, namely NaI, CsF and *n*-C₃₆H₇₄, preserve their good electron transmission properties on Cs₃Sb photocathodes. Moreover, it was found that NaI films provide protection of Cs₃Sb photocathodes against exposure to a considerable amount (tens of Torr) of oxygen, which could permit handling in dry air or operation in gas media. This may open new ways in the development of large-area imaging detectors for visible photons.

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Appendix

Quantum yield of coated photocathodes

Let us consider, as an example, the CsI photocathode coated with a LiF film. Fig.2 shows a simplified energy diagram at the CsI/LiF/vacuum interface. If the initial electron energy distribution dN/dE in CsI and the final electron energy distribution dN/dE' in LiF near the surface are assumed constant, then a relation between them, as well as between initial E and final E' electron energies, should be linear:

$$dN/dE = g \, dN/dE', \quad E' = g \, E, \quad (5)$$

where the factor g depends on the LiF thickness. Let E_m and $E'_m = g E_m$ be the initial and final maximum electron energies, and ΔE the initial energy interval within which they are distributed: $\Delta E = h\nu - E_g(\text{CsI})$, where $h\nu$ is the photon energy and $E_g(\text{CsI})$ the energy gap of CsI.

The escape probability of an electron with energy E over the potential barrier E_0 is [81]:

$$P(E) = \frac{1}{2} \left[1 - (E_0/E)^{1/2} \right] . \quad (6)$$

Assuming that one absorbed photon produces one electron in the CsI conduction band, then the quantum yield (QY) of the photoemission from CsI/LiF film is given by

$$\begin{aligned} Y &= f_1 \frac{\int_{E_0}^{E'_m} dN/dE' P(E') dE'}{\int_{E_m - \Delta E}^{E_m} dN/dE dE} = \\ &= \frac{f}{2\Delta E} \left[g^{1/2} E_m^{1/2} - E_0^{1/2} \right]^2 . \end{aligned} \quad (7)$$

Here f_1 and f are the normalization factors depending on the LiF thickness; E_0 , measured from the bottom of the LiF conduction band, is simply equal to the LiF electron affinity $E_a(\text{LiF})$. Both E_m and E_0 should be measured from the same energy level. The relation between them, assuming a non-modification of the surface barrier due to LiF coating as discussed in section 3.2, is as follows: $E_m = \Delta E + E_0 - E_a(\text{CsI})$.

We have only two parameters in the model, f and g , which in fact describe the electron transport properties through LiF film. All these expressions are also valid for CsI/NaF and other films. The model is not sensitive to the absolute value of the LiF or NaF electron affinity since it is automatically accounted for by f and g . For the energy gap and electron affinity of CsI, the values $E_g(\text{CsI})=5.9$ eV and $E_a(\text{CsI})=0.2$ eV were used, derived from recent data on CsI absorption spectra [26] and field-enhanced photoemission [66].

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Figure captions

- Fig.1** Experimental setup. a) Photocathode evaporation and characterization. b) Heat treatment of the sample. c) Exposure to water vapour and ambient air.
- Fig.2** Simplified energy-band diagram at the CsI/LiF/vacuum interfaces, before and after exposure to water vapour. $E_a(\text{CsI})$ and $E_a(\text{LiF})$ are the initial electron affinities of CsI and LiF respectively.. The photoemission process is depicted schematically as well.
- Fig.3** Atomic force microscopy (AFM) images of uncoated CsI (bottom) and CsI coated with 20 Å thick LiF film (top).
- Fig.4** Absolute quantum yield spectra of CsI and CuI photocathodes coated with dielectric films of LiF, MgF_2 , CsF and NaI. The thicknesses of the coating film are indicated. Dot-dashed lines in plots for CsI/NaI and CuI/NaI represent the quantum yield spectra of NaI films, of a thickness of 100 Å and 500 Å respectively, deposited on stainless steel substrates.
- Fig.5** Absolute quantum yield of CsI/LiF photocathodes as a function of thickness of the coating film, measured at different wavelengths. Solid lines are the exponential fits to the data points.
- Fig.6** Absolute quantum yield of CsI/CsF photocathodes as a function of thickness of the coating film, measured at different wavelengths.
- Fig.7** Absolute quantum yield of CsI/NaI photocathodes, after subtraction of the photoemission of NaI, as a function of thickness of the coating film, measured at different wavelengths. Solid lines are the exponential fits to the data points.
- Fig.8** Absolute quantum yield of CsI/ $n\text{-C}_{36}\text{H}_{74}$ photocathodes as a function of thickness of the coating film, measured at different wavelengths. Solid lines are the exponential fits to the data points.
- Fig.9** Absolute quantum yield of CsI photocathodes coated with various films LiF, NaF, CsF, NaI, MgF_2 , SiO_2 , Al_2O_3 and $n\text{-C}_{36}\text{H}_{74}$ (HTC), as a function of the film thickness, measured at 170 nm (points). Solid lines are the exponential fits to the data points (points at zero thickness are excluded from the fit).
- Fig.10** Attenuation length of the photoyield in LiF, NaF, CsF, NaI, MgF_2 , SiO, SiO_2 , Al_2O_3 and $n\text{-C}_{36}\text{H}_{74}$ films deposited on CsI, and in CsF film deposited on CuI, as a function of the photon energy.
- Fig.11** a) Evolution of the quantum yield during the exposure test of a CsI/LiF photocathode to humid air. Quantum yield spectra are shown for: (1) uncoated CsI; (2) CsI coated with 22 Å thick LiF film; (3) 22 hours exposure to 1 atm of humid air with H_2O pressure of about 10 Torr, at room temperature inside the evaporation chamber;

(4) 3 days exposure to high vacuum; (5) further heating in vacuum at 60 °C for 2 hours; (6) 33 days storing in ambient air.

b) Evolution of the quantum yield during the exposure test of a CsI/LiF photocathode to H₂O vapour in vacuum. Quantum yield spectra are shown for: (1) uncoated CsI, (2) CsI coated with ≥ 15 Å thick LiF film, (3) 2 min at 0.3 Torr H₂O , (4) further 4 min at 1 Torr H₂O , (5) further 10 min at 7 Torr H₂O , (6) further 2 hours at 7 Torr H₂O .

Fig.12 Quantum yield spectra of CsI/LiF photocathodes for LiF thicknesses 10 Å, before and after exposure to 1 atm of humid air with H₂O pressure of about 10 Torr, for 20 hours. The quantum yield of CsI before coating is shown as well. Points are experimental data, curves are model fits.

Fig.13 Water dosage dependence of the quantum yield of CsI/LiF (LiF thickness ≥ 15 Å), CsI/NaF (NaF thickness 15 Å) and CsI/CsF (CsF thickness 44 Å) photocathodes. Exposure to H₂O vapour was done in vacuum for CsI/LiF and in air for CsI/NaF and CsI/CsF.

Fig.14 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 [9]), BaF₂ (28 Å), before and after exposure to 1 atm of humid air, at room temperature inside the evaporation chamber. Exposure time and H₂O pressure were respectively 30 min and 10 Torr for CsF, 5 min and 6 Torr for NaF, 22 hours and about 10 Torr for LiF, 16 hours and 11.5 Torr for MgF₂ , 5 min and 7 Torr for BaF₂ . A typical quantum yield spectrum of an uncoated CsI photocathode is shown as well.

Table I: Film preparation conditions.

Deposited material	Purity %	Evaporation source	Substr. temp. °C	Deposition rate Å/sec	Remarks
CsI	ultrapure	Mo boat	60	50-120	
CuI	ultrapure	Mo,Ta boat	70	10-25	Poor quality for higher rate.
LiF	99.99, 99.9	Mo,Ta boat with cover	60	0.05-0.1	Poor quality for higher rate.
NaF	99.995, 99	Mo boat with cover	70	0.1-1	Poor quality for 99% purity.
CsF	99.9	Mo boat with cover	22	0.1-1	
NaI	99.5	Ta boat with cover	70	0.5-1.5	Poor quality for rate 5Å/sec.
MgF ₂	99.99	Mo boat with cover	60	0.2-0.8	
BaF ₂	opt.grade	Mo,Ta boat with cover	60	0.2-0.3	Not well reproducible.
SiO	99.9	baffle Ta box	90	0.05-0.1	Poor quality for higher rate.
SiO ₂ 1)	SiO, 99.8	Mo boat with cover	22	0.1-0.5	Reactive evaporation of SiO at $(1-3) \times 10^{-4}$ Torr O ₂ . Weak Si XPS-signal for lower rate.
2)	quartz	electron beam		0.3-1	
Al ₂ O ₃ 1)	Al, 99.98	W wire	22	0.3-6	Reactive evaporation of Al at $(0.5-1.6) \times 10^{-4}$ Torr O ₂ .
2)	sapphire	electron beam	22	1	
<i>n</i> -C ₃₆ H ₇₄	99	Ta boat with cover	22	0.5-1.5	

Table II: Lattice constants a and c , energy gap E_g and electron affinity E_a of the film materials used in the present work. Data on E_g for CsI and on E_a for CsI and CuI are given for the heat-treated films^{a)}; for NaI the E_a is given for a fresh (non heat-treated) film^{b)}. For other films the data are compiled from elsewhere^{c)}.

Material	CsI	CuI	LiF	NaF	CsF	NaI
a [Å]	4.57	6.04	4.03	4.62	6.02	6.47
E_g [eV]	5.9	3.0	≥ 12	11.5	10.0	5.8
E_a [eV]	0.2	2.5	≤ 1	-	-	1.4
Material	MgF ₂	BaF ₂	SiO ₂	Al ₂ O ₃	n -C ₃₆ H ₇₄	
a, c [Å]	4.62, 3.05	6.20	-	-	-	
E_g [eV]	≥ 14	11	8.8	7	8.8	
E_a [eV]	-	-	0.9	1	-0.5	

^{a)} Refs. [44, 66]

^{b)} Ref. [44]

^{c)} Refs. [71, 67, 68, 69, 31, 21, 65]

Table III: Model estimations of the electron affinity reduction due to H₂O adsorption.

Film	ΔE_a [eV]
CsI/LiF(6 Å)	0.17 $\pm$ 0.01
CsI/LiF(10 Å)	0.32 $\pm$ 0.01
CsI/LiF(22 Å)	0.35 $\pm$ 0.04
CsI/NaF(7 Å)	0.15 $\pm$ 0.01
CsI/NaF(23 Å)	0.37 $\pm$ 0.05

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

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Fig.11

Fig.12

Fig.13

Fig.14