Optical and structural properties of CsI thin film photocathode

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Abstract

Performance of cesium iodide (CsI) thin film photocathode is reported in the present work. Optical absorbance CsI have been analyzed in the spectral range of 190 nm to 900 nm. The optical energy band gap of CsI films are calculated using Tauc plot from absorbance data. The values refractive index was estimated using envelope plot of transmittance data, proposed by Swanepoel. Absolute quantum efficiency (QE) measurement of CsI have been carried out in the wavelength range of 150 nm to 200 nm. Crystallographic nature and surface morphology of CsI investigated by the means of X-ray diffraction (XRD), transmission electron microscopy (TEM) and atomic force microscopy (AFM) are also presented. In addition, elemental composition result of CsI thin film is gained by energy dispersive X-ray analysis (EDAX) is also reported in the present work.

Keywords: Cesium iodide, quantum efficiency, XRD, TEM, AFM, EDAX, absorbance, transmittance, energy band gap, refractive index, texture coefficient, crystallite size and grain size.

1. Introduction

Photocathode devices in the soft X-ray and ultraviolet (UV) wavelength range are very important in the particle physics experiments for particle identification [1, 2, 3, 4]. In soft X-ray and UV wavelength regions alkali halide photocathodes are known to be very efficient photo converters. Cesium Iodide (CsI) is one of the most efficient among them, because CsI photocathode is relatively stable under short exposure to air and has the highest QE among alkali halide photocathodes [5]. Therefore it is widely used in many UV-detecting devices [6, 7]. These devices consist films of thicknesses varying from few nanometer (nm) to micrometer (µm), depending upon the mode of operation and application of photocathode. It is very much important to know the absorbance, transmittance and refractive index as a function of wavelength to predict the photoemissive behavior of a photocathode device. Knowledge of these optical constants is also necessary to determine the optical energy band gap of the film.

In the present work, optical absorbance of CsI thin films were measured and analyzed. Optical transmittance and energy band gap were estimated from optical absorbance data of CsI thin films. Dispersive behavior of 500 nm thick CsI film was studied by using refractive index. The value of refractive index has been determined by using Swanepoel’s method. Photoemission properties of 500 nm thick CsI photocathode is shown in the spectral range of 150 nm to 200 nm. Structural, morphological and elemental composition analysis of CsI film are also reported in the present work.

2. Experimental Details

CsI thin films evaporation was carried out into a high vacuum stainless steel chamber. Evaporation chamber was pumped with a turbo-molecular pump (Model: TMU 521 P from Pfeiffer vacuum) having a pumping speed 510 Ltr/Sec for N2 gas. Prior to CsI evaporation residual atmosphere of the chamber was monitored through a residual gas analyzer (RGA) (model: SRS RGA 300), under a high vacuum environment (3 × 10⁻⁷ Torr). It is observed that large amount of water molecules have been evacuated from the evaporation chamber after 08 hours of pumping (see Figure 1) and main constituent of residual gases (at partial pressure 3 × 10⁻⁷) were N2 (58.2%), H2 (11.0%), H2O (16.2%), O2 (9.9%) and CO2 (1.4%). After 08 hours of pumping, the majority of residual gas was N2, which does not affect CsI photocathode during the film preparation. Small amount of CsI crystals (Alfa Aesar, 5N purity)}
were placed in a tantalum (Ta) boat inside the vacuum chamber and carefully heated to allow out gassing from the outer surface of the CsI crystals. After proper out gassing and melting, CsI thin films deposited from Ta boat on quartz, Aluminium (Al) and formvar coated copper grid substrates. For uniform deposition, distance between Ta boat and substrate was kept about 20 cm. The films were deposited at a typical rate of 1 nm to 2 nm per second. The thickness of the films was controlled by a quartz crystal thickness monitor (sycon STM 100 thickness/rate monitor). After the sample preparation, vacuum chamber was purged with dry nitrogen gas, in order to avoid the interaction of water vapor present in humid air to the prepared sample. Immediately after the chamber opening under constant flow of nitrogen gas, CsI films were placed into a vacuum desiccator and further moved to characterization setup.

Figure 1: Residual gas composition inside the vacuum chamber: After 30 minutes of pumping (left panel) and after 08 hours of pumping (right panel).

The schematic diagram of experimental setup for QE measurement is shown in Figure 2. The experimental setup for quantum efficiency (QE) measurement, includes a high vacuum stainless steel (S.S.) chamber (pumped with a TMP to $10^{-5}$ Torr), coupled to a vacuum ultra violet (VUV) monochromator (MC)( model -234/302 VUV monochromator, McPherson). The experimental setup is equipped with a 30 Watt (W) magnesium fluoride (MgF2) windowed deuterium ($D_2$) lamp (model 632 deuterium light source, having entire spectral range from 113 nm to 380 nm). The QE was measured in a reflective mode, under vacuum. A positive voltage was applied from high voltage power supply (CAEN - N471A) to a mesh electrode placed at a distance of $\sim 3$ mm from the photocathode surface. The photocurrent, induced by monochromatic UV photons to photocathode, was recorded from a picoampereter (Keithley -6485). The absolute QE value, which is the ratio of number of emitted photoelectrons ($N_e$) to number of incident photons ($N_p$) i.e. $QE = N_e/N_p$, derived from the ratio of the current measured from the photocathode to the current measured from a calibrated photomultiplier (Cal. PMT). This was done by alternatively directing the UV beam to both Cal. PMT interchangeable via a photocathode. This PMT was calibrated against a NIST vacuum-photodiode [8]. The stability of $D_2$ lamp was monitored throughout the measurements by a second reference photomultiplier (Ref. PMT) (Hamamatsu PMT, Model: 658), of the same type, and the measured photocurrent values were corrected correspondingly.

Optical properties measurement of CsI thin film photocathodes were carried out using Perkin Elmer λ25 UV/Vis spectrophotometer in the wavelength range of 190 nm to 900 nm. Structural properties was studied by using X’Pert PRO PANalytical X-Ray diffractometer (XRD), based on Brag-Brentano para-focusing geometry, operated at 30 kV and 40 mA with Cukα (λ = 1.54056 Å) radiation. CsI film deposited on formvar coated copper (Cu) grid was moved to transmission electron microscopy (TEM) lab where morphological and structural features of the CsI thin film was studied by FEI Technai 20 G2 TEM operated at 200 kV accelerating voltage. Elemental composition of CsI photocathode was studied by means of energy dispersive X-ray spectroscopy (EDAX) technique.
3. Optical properties of CsI thin films

3.1. Optical absorbance

UV/Vis absorption of CsI films, deposited on quartz (Qz) substrate, due to its transparency in the spectral region of 190 nm to 900 nm, performed in spectral range 190 nm to 900 nm as shown in Figure 3. It is observed that the absorbance of CsI films varies in between 0 to 2 for the thicknesses 10 nm to 100 nm, while for thicknesses more than 100 nm absorbance varies in between 0 to 3.5 (shown in inset of Figure 3). Two strong absorption peaks was observed in the UV-region at a wavelength smaller than 225 nm for thinner CsI films. Similar optical absorbance results are reported in previous literature \[9, 10, 11\] for thinner and thicker CsI films.

The absorption coefficient ($\alpha$) was also calculated from the absorption spectrum using the relation:

$$\alpha = \frac{1}{l} \ln \frac{1}{T}$$  

(1)

where $t$ is the thickness of the film and $T$ is the transmittance of the film. Absorption coefficient ($\alpha$), estimated using equation (1), lies in between 0.02 to 0.04.

![Figure 3: Optical absorption of CsI thin films in the wavelength range of 190 nm to 900 nm and zoomed view of absorbance in UV spectral region (inset)](image)

3.2. Optical transmittance

Optical transmittance of CsI films are derived from absorbance data in the wavelength region of 190 nm to 900 nm. Transmittance of CsI films is shown in Figure 4, are in good agreement with the previous reported work \[12, 13\]. Transmittance of CsI films have been derived from the absorbance data using the relation:

$$T = \exp(-A)$$

(2)

Where $A$ is the absorbance. Several transmittance peaks are observed in the wavelength region 190 nm to 900 nm, as already shown in reference \[12, 13\]. CsI films of thicknesses more than 100 nm, was found to be opaque in the spectral region 190 nm to 225 nm, having transmittance is about only 2-3% (see inset of Figure 4). While CsI film of thicknesses below 50 nm, found to be semitransparent in the spectral region 190 nm to 225 nm, where transmittance varies from 20% to 40%. A sharp increase in transmittance was observed near a wavelength $\lambda \approx 225$ nm indicates crystalline nature of CsI films. Thinner and thicker CsI films are found to be transparent in the spectral region 225 nm to 900 nm, having more than 80% transmittance.

![Figure 4: Optical transmittance of CsI thin film in the wavelength range 190 nm to 900 nm.](image)

The surface quality and homogeneity of CsI films are analyzed from the existence of interference fringes (oscillatory nature in transmittance spectra) in the transmittance spectra. In transparent spectral region ($\lambda > 225$) nm, for thinner and thicker CsI films shows distinct characteristics, which impute to inhomogeneities in the films. In transparent spectral region CsI film of thicknesses smaller than 100 nm does not shows any interference fringes pattern in the transmission spectrum, which reveals that the CsI layer does not appear to be continuous, exhibiting small surface area coverage. While CsI film of thicknesses 100 nm and more shows interference fringes patterns, which indicates existence of continuous and homogeneous CsI layers, exhibiting large surface area coverage (see Figure 4). It is also observed fro
Figure 4, that oscillatory nature in transmittance spectra of CsI films increases with an increase in the thickness of the film. Oscillatory nature in transmittance spectra of CsI films indicates that homogeneity, continuity surface area coverage, of CsI films increases with an increase in the thickness of the film.

500 nm thick CsI film found to be more homogeneous and continuous, than the thinner CsI films. Transmission spectrum for 500 nm thick CsI film (shown in Figure 5) depict a sharp fall in transmission near the fundamental absorption, which is an identification for the good crystallinity of film [14, 15, 16, 17]. The oscillatory nature of the transmission spectrum observed for 500 nm thick CsI film is attributed to the interference of light transmitted through the thin film and the substrate.

3.3. Optical energy band gap for 500 nm thick CsI film

The energy band gap of the photocathode is one of the key parameter determining the range of its most efficient operation, in particular the sensitivity cutoff. In addition to proper band gap energy of a good photocathode material should allow an efficient electron transport to the emission surface and should have low or negative work function/electron affinity.

The absorption in the UV region is attributed to energy band gap absorption of CsI thin film. An obvious increase in the absorption of wavelength less than ~225 nm (see inset of Figure 6) can be assigned to the intrinsic band gap absorption of CsI film due to the electron transmission from the valence band to conduction band. The absorption band gap \((E_g)\) has been calculated by using the Tauc relation [18, 19, 20].

\[
(\alpha h\nu)^n = A(h\nu - E_g)
\]

where \(A\) is the edge width parameter, \(h\) is the Planck’s constant, \(\nu\) is the frequency of vibration, \(h\nu\) is the photon energy, \(\alpha\) is the absorption coefficient, \(E_g\) is the band gap and \(n\) is either 2 for direct band transitions or 1/2 for indirect band transitions [21]. The direct band gap energy estimated from a Tauc plot of \((\alpha h\nu)^2\) versus photon energy \(h\nu\) according to the K. M. Model is shown in Figure 6. The value of photon energy \((h\nu)\) extrapolated to \(\alpha = 0\) gives an absorption edge which corresponds to a band gap \(E_g\). The extrapolation gives band gap \(E_g \approx 5.4 eV\) corresponds to absorption peak of 500 nm thick CsI film. The energy band gap determined from Tauc relation can be compared with energy band gap \(E_g = 5.9 eV\) derived from experimental QE dependence on wavelength [22] for heat-enhanced CsI thick film photocathode.

3.4. Determination of refractive index

The optical properties of 500 nm thick CsI film can be evaluated from transmittance data using the method proposed by Swanepoel [23, 24]. The applicability of this method is limited to thin film deposited on transparent substrate much thicker than the CsI film. The application of this method entails, as a first step, the calculation of the maximum \(T_{Max}\) and minimum \(T_{Min}\) transmittance envelope curves by parabolic interpolation to the experimentally determined positions of peaks and valleys (shown in inset of Figure 5). From maximum of transmittance \(T_{Max}\) and minimum of transmittance \(T_{Min}\), value of refractive index \((n_i)\) is determined by using the expression proposed by Swanepoel [23] is
given below:

\[ n = \sqrt{N + \sqrt{N^2 - n_s^2}} \]  

(4)

In the weak and medium absorption regions, the value of \( N \) is given by

\[ N = 2n_s \frac{T_{\text{Max}} - T_{\text{min}}}{T_{\text{Max}}T_{\text{min}}} + \frac{n_s^2 + 1}{2} \]  

(5)

with \( n_s \) being the refractive index of the substrate. In general, \( n_s \) is determined by the maximum of the transmission in the transparent region \( T_{\text{Max}} \) using the relation:

\[ n_s = \frac{1}{T_{\text{Max}}} + \sqrt{\left(\frac{1}{T_{\text{Max}}^2} - 1\right)} \]  

(6)

It is observed that the value of refractive index decreases with increasing wavelength as shown in Figure 7. Table 1 shows the values at the extremes of the spectrum of \( \lambda, T_{\text{Max}} \), and \( T_{\text{min}} \) obtained from envelope plot of Figure 5 (see zoomed view, inset image). The values of refractive index \( n_{\lambda} \) with the wavelengths is shown in Table 1. The variation of the refractive index \( n_{\lambda} \) with the wavelengths is shown in Figure 7. We observe a sharp fall in refractive index at lower wavelength side and a gradual destruction in refractive index corresponds to higher wavelength side. This variation in refractive index indicates normal dispersive behavior of 500 nm thick CsI film.

### Table 1: Values of \( \lambda, T_{\text{Max}} \), and \( T_{\text{min}} \) for the transmittance spectrum of CsI (Figure 6) and the value of refractive index \( n_{\lambda} \) to the corresponding wavelength \( \lambda \):

| \( \lambda \) (nm) | \( T_{\text{min}} \) | \( T_{\text{Max}} \) | \( n_{\lambda} \) |
|-----------------|-----------------|-----------------|----------------|
| 275             | 0.81792         | 0.8455          | 1.930          |
| 283             | 0.83039         | 0.85802         | 1.860          |
| 300             | 0.85110         | 0.87923         | 1.800          |
| 312             | 0.86194         | 0.89029         | 1.740          |
| 336             | 0.87685         | 0.90815         | 1.690          |
| 359             | 0.88617         | 0.91966         | 1.655          |
| 390             | 0.89547         | 0.92872         | 1.610          |
| 423             | 0.90294         | 0.93507         | 1.570          |
| 479             | 0.91155         | 0.94488         | 1.554          |
| 532             | 0.91658         | 0.95134         | 1.513          |
| 622             | 0.92120         | 0.95850         | 1.489          |
| 735             | 0.92360         | 0.96364         | 1.478          |
| 900             | 0.92467         | 0.96731         | 1.464          |

3.5. Photoemission properties CsI film

Photoemission properties of 500 nm thick thermally evaporated CsI film is studied in wavelength region of 150 nm to 200 nm, with a scan step size of 2 nm. Absolute QE, which is the ratio of emitted photoelectrons to incident photons, is determined by illuminating the CsI surfaces with photon flux of a given frequency and the resulting photocurrent is measured by a picoammeter (Keithley-6485). Because the observables are current, it is necessary to relate these to QE, using the relation:

\[ QE(\%) = \frac{I_{pc}}{I_{pm}} \times QE_{pm} \times G_{pmt} \]  

(7)

Where, \( I_{pm} \) is the PMT current, \( I_{pc} \) is the photocathode current, \( QE_{pm} \) is known QE of calibrated PMT and \( G_{pmt} \) is gain of PMT.

It is clearly observed that from the plot of Figure 8, maximum QE obtained is \( \sim 40\% \) at wavelength 150 nm. The QE was found to decrease with an increase in wavelength of incident photon. experimentally determined QE is in good agreement with the most of literature data for the CsI photocathode [26, 27].

4. Structural properties of CsI film

4.1. Crystallographic analysis

The crystal structure and orientation of the CsI thin film was investigated by X-ray diffraction (XRD) patterns. Figure 9 shows the typical X-ray diffraction patterns of 500 nm thick CsI film deposited on Al substrate. XRD patterns indicate that the CsI film is purely
Figure 8: Absolute quantum efficiency as a function of wavelength for 500 nm thick CsI photocathode deposited on Al disc.

crystalline in nature. XRD pattern of CsI deposited on Al substrate, contains an intense peak at Bragg’s angle $2\theta = 27.06$, assigned to (110) crystallographic plane and three other XRD peaks of CsI found at Bragg’s angle $2\theta = 38.87, 48.30$ and $56.49$ corresponds to (200), (211) and (220) crystallographic planes respectively. As CsI is deposited on Al substrate, so XRD pattern also contains four Al peaks as shown in Figure 9. The crystallographic orientations eventually obtained allow to attribute a body centered cubic (bcc) structure to the CsI.

The lattice constant of crystalline CsI film is calculated using the analytical relation (for cubic crystal system):

$$a = d \times \sqrt{(h^2 + k^2 + l^2)} \quad (8)$$

The lattice constant for crystalline CsI thin film is found to be about $a = 4.66\text{Å}$, which is in good agreement with lattice constant reported in International Center for Diffraction Data (ICDD, File number - 060311).

The crystallite size is calculated using a well known Scherrer’s equation [28, 29].

$$D = \frac{k\lambda}{\beta\cos\theta} \quad (9)$$

where $D$ is the size of crystallite, $k (=0.9)$ is the crystal constant, $\lambda (= 1.5406\text{Å})$ is the wavelength of X-ray used, $\beta$ is the broadening of diffraction line measured at half of its maximum intensity in radians and $\theta$ is the angle of diffraction. The crystallite size obtained for most intense (110) crystallographic plane of CsI thin film is about 55 nm, which matches very well with previous reported articles [30, 31].

Table 2 shows the values of Bragg’s angle ($2\theta$), interplanar spacing($d$), full width at half maximum(FWHM),

Figure 9: X-ray (XRD) pattern of 500 nm thick CsI film deposited on Al substrate. The diffraction pattern is taken in a Bragg Brentano parafocusing geometry.

texture coefficient (TC) and crystallite size($D$), corresponds to their lattice (hkl) planes for 500 nm thick CsI film.

Figure 10: Average crystallite size and texture coefficient of CsI thin film calculated from X-ray diffraction pattern.

The XRD pattern of CsI film shows a highly intense peak at $2\theta = 27.06$ indicating a strong preferred orientation along the (110) plane. The texture coefficient (TC) of CsI determined from XRD data represents the texture of a particular plane. The deviation in TC from unity implies the preferred growth. The texture coefficient factor can be calculated for each crystallite orient-
Table 2: Crystallographic properties of 500 nm thick CsI film obtained from XRD:

| (hkl) | 2θ[deg] | d[Å] | FWHM | \( \frac{I(hkl)}{I_0(hkl)} \) | TC[%] | D(nm) |
|-------|---------|------|------|-----------------------------|------|-------|
| (110) | 27.06   | 3.295| 0.1476| 1.00                        | 1.59 | 55    |
| (200) | 38.87   | 2.315| 0.1968| 0.37                        | 0.59 | 43    |
| (211) | 48.30   | 1.884| 0.1968| 0.45                        | 0.72 | 44    |
| (220) | 56.49   | 1.628| 0.2460| 0.69                        | 1.10 | 46    |

The texture coefficient was calculated using the following equation \[32\]:

\[
TC(hkl) = \frac{I(hkl)/I_0(hkl)}{N^{-1} \sum_n I(hkl)/I_0(hkl)} \times 100\% \tag{10}
\]

where TC(hkl) is the texture coefficient, \(I(hkl)\) is the measured relative intensity of a plane (hkl) and \(I_0(hkl)\) is the standard intensity of the plane (hkl) taken from the ICDD (card no: 060311) data and ‘n’ is the number of reflections taken into account.

By using the above equation, the preferred orientation of the lattice plane can be understood. TC(hkl) is expected to be unity for films with randomly oriented crystallites, while higher values indicate the abundance of grains oriented in a given (hkl) direction. The variation of TC(hkl) and crystallite size for the peaks of the CsI film is presented in Table 2. TC(hkl) and average crystallite size of different planes of CsI film are shown in Figure 10. Average crystallite size corresponds to the various crystal plane of CsI is found to be about 47 nm which varies from 43 nm to 55 nm. It is clear from the plot that the average pertaining to (110) reflection, is higher than that of the other planes. This indicates that the preferential orientation of (110) plane in CsI film.

4.2. Morphological analysis of CsI film

A transmission electron microscope (TEM) is a powerful microscope that produces a high-resolution, black and white image from the interaction that takes place between samples and energetic electrons in the vacuum chamber. TEM measurement of 500 nm CsI film deposited on formvar coated copper (Cu) grid was carried out. In order to observe the surface morphology of CsI film, few regions were scanned by TEM, one of them is shown in Figure 11 (top panel). Figure 11(top panel) shows that CsI film surfaces have homogeneous and continuous grain like morphology, with more than 95% surface area was covered by CsI grains. It is observed that 500 nm thick CsI film have grains of various sizes, ranges from 110 nm to 860 nm. Average grain size of CsI film is found to be about 300 nm, as shown in histogram of Figure 11 (bottom panel). The electron diffraction pattern shown in inset of Figure 11(top panel)) indicate that the 500 nm thick CsI film is crystalline in nature and having single crystal like domains. A cubic structure with lattice constant \(a = 4.66\,\text{Å}\) was found to have good match between experimental and calculated values of inter-planar distances.

4.3. Elemental composition analysis of CsI film

The energy dispersive X-ray (EDAX) is used to detect elements present in considerable amount (quantitative determination of bulk element composition) of thermally evaporated CsI thin film. The EDAX analysis
Fig. 12: Chemical composition of CsI film was determined by EDAX. The spectra suggests that grains have chemical composition of Cs and I having Cs:I ratio is 1:1.

5. Conclusions

Photoemissive properties of thermally evaporated 500 nm thick CsI film was investigated by the means of VUV monochromator. Photoemission measurement was performed in the wavelength range of 150 nm to 200 nm and the maximum quantum efficiency achieved is ~ 40% at the wavelength $\lambda = 150$ nm.

Optical properties measurement has been performed on Perkin Elmer $\lambda$ 25 UV-Vis spectrometer. Optical absorption of CsI thin film deposited on quartz substrate was performed in the spectral range 190 nm to 900 nm. Two strong absorption peaks is observed in the UV wavelength region, one is at 207 nm and another is at 222 nm. Transmittance of CsI film has been derived from absorbance data and it is found that CsI film having only about 3% transmittance in the spectral range of 190 to 225 nm, which reveals that 500 nm thick CsI film is opaque in the spectral range 190 to 225 nm. However in the spectral range of 225 nm 900 nm CsI film having more than 80% transmittance, which shows CsI film is transparent in the spectral range of 225 nm 900 nm.

Appearance of interference fringes pattern in transparent spectral region indicates, existence of continuous and homogeneous grain like morphology with maximum surface area coverage for 500 nm thick CsI film. Optical energy band gap has been calculated from absorbance data using the Tauc plot of K. M. model and found to be about 5.4 eV. The values of refractive index calculated from envelop plot of optical transmittance data, varies from 1.82 to 1.30 in the spectral range of 275 nm to 900 nm. This variation of refractive index indicates, dispersive behavior of CsI film.

Surface morphology, bulk structure as well as crystallographic nature of CsI was studied by the means of TEM and XRD techniques. TEM results reveals that the CsI film have homogeneous and continuous grain like morphology, with more than 95% surface area coverage by CsI grains. Average grain size (composed of many coherent domains) of CsI thin film, obtained from TEM micro structure is about 300 nm. Diffraction pattern of obtained from XRD and TEM measurement reveals that CsI thin film is purely crystalline in nature and having body centered cubic (bcc) structure. The value of lattice constant obtained is about $a = 4.66$ Å. The coherent scattering domain size (crystallite size) calculated using Scherrer’s method is found to be about 55 nm. EDAX result indicates that, CsI film having mainly Cs and I elements. The atomic ratio of Cs and I is found to 1:1, which is consistent with the stoichiometry of CsI.

Acknowledgments

This work was partly supported by the Department of Science and Technology (DST), the Council of Scientific and Industrial Research (CSIR) and by Indian Space Research Organization (ISRO), Govt. of India. Triloki acknowledges the financial support obtained from UGC under research fellowship scheme for meritorious students (RFSMS) program. Richa Rai acknowledges the financial support obtained from UGC under research fellowship scheme in central universities.
