Performance of cesium iodide (CsI) as a reflective photocathode is presented. Absolute quantum efficiency (QE) measurement of 500 nm thick CsI film has been carried out in the wavelength range of 150 nm to 200 nm. Optical absorbance of 500 nm thick CsI film in the spectral range of 190 nm to 900 nm is analyzed and optical energy band gap is calculated using Tauc plot. To see the dispersive behavior of CsI film, refractive index has been determined by envelop plot of transmittance data, using Swanepoel method. Additional information on morphological and elemental composition results of CsI film, gained by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively are also reported in present work.

Keywords: Cesium iodide, optical absorbance, transmittance, optical energy band gap, quantum efficiency, atomic force microscopy, grain size, XPS, elemental composition

1. Introduction

Various photocathodes are currently used to improve the sensitivity of photon counting or imaging detectors. The choice of photocathode material is determined by the spectral range where the device sensitivity is crucial. Alkali halide photocathodes have been shown to be very efficient photo-converters in the ultraviolet (UV) wavelength range. 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 quantum efficiency (QE) among other alkali halide photocathodes. Therefore it is widely used in many UV-detecting devices. These devices consist of films of thickness varying from few nanometer (nm) to micrometer (µm), depending upon the mode of operation of photocathode. Therefore it is important to know the absorbance, transmittance and refractive index as a function of wavelength to predict the photoemissive behavior of a photocathode. Knowledge of these optical constants is also helpful to determine the optical band gap of the film.
In the present work, we have measured optical absorbance of 500 nm thick CsI film in the spectral range of 190 nm to 900 nm. Transmittance, refractive index and optical energy band gap of CsI film were estimated from absorbance of CsI film. Photoemission measurement was done in the wavelength range of 150 nm to 200 nm. Surface morphology of CsI film, studied by atomic force microscopy (AFM) is also reported in present work. In addition, elemental composition result obtained from XPS is also reported.

2. Experimental Details

CsI film was deposited by thermal evaporation technique in a high vacuum ($3 \times 10^{-7}$ Torr) evaporation chamber. Prior to deposition, typical compositions of different residual gases including water vapor inside the evaporation chamber were monitored through a residual gas analyzer (SRS RGA 300 unit). CsI crystal of high purity (99.999%) from Alfa Aesar, placed into a tantalum boat inside the deposition chamber and heated carefully to allow outgassing from the outer surface of the crystals, if any. After proper outgassing and melting of CsI crystals, 500 nm thick CsI film was deposited on quartz (Qz) and aluminum (Al) substrates. The film was deposited at a typical rate of 1 nm to 2 nm per second. The thickness of the film as well as deposition rate was controlled by a quartz crystal thickness monitor (Sycon STM 100). After the film preparation, vacuum chamber was purged with nitrogen ($\text{N}_2$) gas, in order to avoid the interaction of humidity on the prepared CsI film. Immediately after the chamber opening under constant flow of $\text{N}_2$ gas, CsI film was placed into a vacuum desiccator and further moved to the characterization setup.

Photoemission measurement of CsI was performed on 234/302 VUV monochromator, in the wavelength range 150 nm to 200 nm. UV/Vis measurement of CsI films was carried out on Perkin Elmer UV/Vis spectrometer (Model: λ 25) in the wavelength range 190 nm to 900 nm. Further, for morphological study, CsI film deposited on Al substrate was used for AFM measurement. AFM scanning was done by NEXT ND-MDT. Elemental composition analysis of CsI film was done by x-ray photoelectron spectroscopy (XPS).

3. Photoemissive properties of CsI

Absolute quantum efficiency (QE) measurement of thermally evaporated 500 nm thick CsI photocathode was performed on 234/302 vacuum ultra violet (VUV) monochromator (Details are similar to the reference [3]) setup available in our laboratory. Absolute QE, which is the ratio of emitted photoelectrons to incident photons, is determined by illuminating the cathode with photon flux of a given frequency and the resulting photocurrent measured by a picoammeter (Keithley-6485). Absolute QE measurement of as-deposited CsI photocathode was performed in the wavelength range 150 nm to 200 nm, with a step size of 2 nm. It is clearly observed from the plot of Figure 1, maximum QE obtained is about 40% at wavelength 150 nm. QE of CsI photocathode was found to decreases with an increase in wavelength of incident photon. our observed QE data is in good agreement with the most of available literature data for the CsI photocathode [4].
4. Optical properties of 500 nm thick CsI film

Optical absorbance and band gap

UV/Vis absorption of CsI film, deposited on quartz substrate was measured in the spectral range of 190 nm to 900 nm, as shown in inset of Figure 2. Absorption peak of 500 nm thick CsI film obtained in the UV wavelength region (wavelength smaller than 225 nm) and found to be \( \sim 3.5 \). Absorbance lies in the UV-region at a wavelength smaller than 225 nm. Similar result for absorbance spectra has been previously reported by Lu and McDonald [5] for 200 nm thick CsI film. The 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 optical energy band gap, a good photocathode material should allow an efficient electron transport to the emission surface and should have low or negative work function or electron affinity.

The absorption of incident photons in the UV region is attributed to band gap absorption of CsI film. An obvious increase in the absorption of wavelength less than 225 nm 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 [6].

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

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. The absorption coefficient \(\alpha\) has been determined using the relation \(\alpha = 1/t \ln(1/T)\) [7], where \(t\) is thickness of the film and \(T\) is the optical transmittance. The optical energy band gap 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 2. It has been observed that the plot of \((\alpha h\nu)^2\) vs. \(h\nu\) is linear over a wide range of photon energies indicating a direct type of transitions. The value of photon energy \((h\nu)\) extrapolated to \(\alpha = 0\) gives an absorption edge which corresponds to a optical energy band gap \(E_g\). The extrapolation gives optical energy band gap \(E_g \approx 5.43\) eV, which can be compared with energy band gap \(E_g \approx 5.9\) eV derived from experimental QE dependence on wavelength [8] for heat enhanced CsI thick films.

**Optical transmittance and refractive index**

![Transmission spectrum of 500 nm thick CsI film](image)

Figure 3: Transmission spectrum of 500 nm thick CsI film (solid line), including the maximum \(T_{max}\) and minimum \(T_{min}\) transmittance envelope curve (dashed and dotted lines).

Optical transmittance of CsI photocathode deposited on quartz (Qz) substrate is measured in dependence of wavelength in the region of 190 nm to 900 nm. Transmittance of 500 nm thick CsI film is shown in Figure 3 (solid line). Transmittance of CsI film has been calculated from the absorbance data using the relation: \(T = \exp(-A)\);

where \(A\) is the absorbance of CsI film. In the wavelength range of 190 nm to 225 nm, maximum transmittance (%) is found to be about 3.5%, while in the wavelength range beyond 225 nm to 900 nm, more than 80% transmittance is observed. Thus the CsI photocathode is opaque below the wavelength 225 nm, whereas, for wavelength more than 225 nm, CsI photocathode is transparent.

The surface quality and homogeneity of CsI film was analyzed from the existence of interference fringes in the transmission spectra as shown in Figure 3. In transparent spectral region (\(\lambda 222\) nm), CsI film shows interference
fringe pattern, which reveals the existence of continuous and homogeneous CsI layers. The spectrum shown in Figure 3 depicts a sharp fall in transmission near the fundamental absorption, which is an identification for the good crystallinity of the film [9]. The oscillatory nature of the transmission spectrum observed for CsI film attributed to the interference of light transmitted through the thin film and the substrate.

The optical properties of CsI film can be evaluated from transmittance data using the method proposed by Swanepoel [10 11]. 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 transmittance ($T_{\text{max}}$) and minimum transmittance ($T_{\text{min}}$) envelope curves by parabolic interpolation to the experimentally determined positions of peaks and valleys. From $T_{\text{max}}$ and $T_{\text{min}}$, refractive index ($n_\lambda$) can then be calculated by using the expression [11].

\[
\begin{align*}
    n &= \sqrt{N + \sqrt{N^2 - n_s^2}} \\
    N &= 2n_s \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{max}} T_{\text{min}}} + n_s^2 + \frac{1}{2}
\end{align*}
\]

In the weak and medium absorption regions, the value of $N$ is given by

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

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 $T_{\text{max}}$ [12] using the relation:

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

Swanepoel’s envelope [10] method is employed to estimate the refractive index from the transmittance spectra of 500 nm thick CsI film. It is observed that the value of refractive index decreases with increasing wavelength (Figure 4), which shows film has normal dispersive behavior.

![Figure 4: Refractive index as a function of wavelength for 500 nm thick CsI film photocathode deposited on quartz substrate.](image)

\[
n = \sqrt{N + \sqrt{N^2 - n_s^2}}
\]
5. Morphological properties of CsI

In order to analyze the microscopic details of surface structure of CsI thin film, such as grain size, average roughness and the arrangement of grains, atomic force microscopy (AFM) measurement has been adopted. Atomic force microscopy is a high-resolution type of scanning probe microscopy for morphological information analysis. AFM measurement technique offers digital images which allow quantitative measurements of surface features, such as root mean square (RMS) or average roughness and the analysis of images from different perspectives, including three dimensional (3-D) views. Top panel and bottom panel respectively, of Figure 5 show two dimensional (2-D) and (3-D) AFM surface images of 500 nm thick CsI film. The AFM surface images of CsI film was recorded by scanning over an area of 5×5 µm². 2-D AFM surface image of CsI film exhibits uniform film surface with pin hole free, crack free and densely packed morphology. The observed image shows clearly the grainy structure with ridge and valley features having an average roughness of about 39 nm and the grain size varying from 220 nm to 1700 nm. The low roughness of the film indicates the film quality is good. The average grain size calculated for CsI film is found to be about 350 nm approximately and the z-height is found to be about 171 nm. The morphological result of CsI film obtained from atomic force microscopy can be compared with earlier published results [13, 14]. Average grain size for 500 nm thick CsI film estimated from AFM (i.e. ~ 350 nm) is comparable with earlier published result determined from transmission electron microscopy (i.e. ~ 300 nm).

6. Elemental composition of CsI

The X-ray photoelectron spectroscopy (XPS) technique was used to detect elements present in considerable amount (quantitative determination of bulk element composition). The XPS analysis of 500 nm CsI thin film deposited on Al substrate was carried out. Figure 6 shows the XPS survey scan of 500 nm thick CsI film. The Cs3d and I3d transition at a binding energy of 723.9 eV and 618.3 eV respectively (5/2 peaks of 3d spin-orbit doublet) are the dominant peaks. Carbon and Oxygen were also detected as a strong C1s signal at 285 eV and a weak O1s at 532 eV.
Figure 6: Elemental composition of CsI film was determined by XPS. The spectra suggests that CsI film mainly having Cs and I elements. The signals of Carbon and Oxygen might be due to the atmospheric exposure during the sample transfer in the XPS chamber. The relative elemental concentrations are calculated from peak intensities. The atomic ratio of I and Cs is found to be $\sim 1.02$, indicating the deposition of almost stoichiometric by thermal evaporation (TE). Stoichiometry of CsI deposited by TE is in good agreement with previous XPS result [15] using same evaporation technique. However for CsI film deposited by pulse laser deposition (PLD) technique, ex situ XPS measurement shows atomic ratio of I and Cs to be relatively smaller value (0.52) reported by Fairchild [16], indicating Cs-enriched surface.

7. Conclusions

Photoemission measurement of thermally evaporated 500 nm thick CsI film was done in the spectral range of 160 nm to 200 nm. Maximum value of absolute QE is obtained $\sim 40\%$ at wavelength $\lambda = 150$ nm. The combined data from the optical measurements shows a optical energy band gap of about 5.43 eV in the UV spectral region with QE of about 6% to 20%. The UV/Vis Optical data reveals that, CsI film is opaque in the spectral range of 190 nm to 222 nm, where as in the spectral range of 222 nm to 900 nm, it is found to be almost transparent. The oscillatory nature in transmittance data shows that the existence of continuous and homogeneous CsI layers. The value 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. The variation of refractive index indicates a dispersive behavior of CsI film. The AFM results reveals that the CsI films have crystalline, homogeneous and continuous grain like morphology. The average value of grain size and average film roughness was found to be about 350 nm and 39 nm respectively. XPS wide spectra suggests that CsI film is mainly having Cs and I elements. The atomic ratio of Cs and I is found to be $\sim 1:1$, which is consistent with the stiochiometry of CsI.
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