Study of humidity on the structure and optical properties of cesium iodide thin film

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Abstract. We report the influence of 70% 5% humid exposed air at room temperature on the structure of 500nm thick CsI film. By means of scanning electron microscopy (SEM) and X-ray diffusion (XRD) analysis, the surface morphology and polycrystalline structure were investigated. After 24 hour exposure to humid air, the grain size of CsI film has a drastic change, and so as to the preferential growth orientation. Infrared spectra showed a hydroxyl absorption peak after 3h exposure. And in long term exposure (24h), the absorption peak broadened with the band center shifting toward lower wavenumbers.

1. Instruction

With the high Quantum Efficiency (QE) in VUV/UV and X-ray energy range, cesium iodide (CsI) thin film are widely used as photoelectron converters in medical imaging, particle physics, position emission tomography and other various fields [1-2]. In recent years, CsI-based devices have been successfully applied in Ring Imaging Cherenkov experiments, such as A Large Ion Collider Experiment at the CERN LHC, High Acceptance Di-Electron Spectrometer at Gigascale Integration [3-6]. CsI thin film is sensitive to its surrounding. All of those experiments need CsI complete insulation from air. The problems of CsI thin film exposed to humidity air have been studied and discussed. Most of the studies concern the effects of the exposure to air on surface morphology and the quantum efficiency (QE) of CsI thin film. However, the grain-size mechanism of crystal column is still uncertain [7-12]. The theory of CsI recrystallization caused by water molecules [11] and the fusion of crystal surface caused by chemical reaction between water and CsI were put forward [12].

The aim of the present work is to examine the influence of humidity on the structure and optical properties of CsI thin film. In particular, the surface morphology and structure of CsI thin films, exposed to 70% 5% humidity air, were studied. Results of ultraviolet transmittance and infrared absorption rate affected by the water were also reported.

2. Experimental technique

The films were prepared by resistive heating evaporation in a high vacuum spherical chamber. CsI crystals were grinded into powder and placed into a molybdenum boat, under a shutter, inside the vacuum chamber. The quartz slides were used as substrates. After more than 6 hours soaked in chromic acid lotion, the substrates were ultrasonic vibration cleaned with acetone, alcohol and deionized water then dried. After creating a vacuum condition at 2.5 x 10⁻³ Pa (the order of 10⁻⁵ Torr), the shelf whirled at the rate of 10 r/min and the CsI crystals films of 3μm were deposited at a typical evaporation rate of 1-2nm/s. After the deposition completed, high-purity argon gas was filled into the vacuum chamber as a protective gas. And the films were transferred into a vacuum box immediately after the chamber opened.
Scanning electron microscopy (SEM, QUANTA FEG 450) and X-ray diffraction (XRD, PHILIPS HR-XRDScan) were used to investigate the surface morphology and inspect the structure of the films. The properties of transmittance and absorptance of the films were measured by UV Spectrophotometer (UV-1700) and Fourier Transform Infrared Spectroscopy.

3. Results

3.1. Surface morphology and structure analysis

In order to study the humidity impact, the surface of CsI film, scanned by SEM, are shown in Fig. 1. Fig. 1a shows the fresh film has a typical crystal columnar structure, with high grain density and small grain size. The SEM images of same deposition process samples with exposure to 70% 5% humid air for 3 h, 12 h and 24 h are shown in Fig. 1b, Fig. 1c and Fig. 1d respectively. As shown in the images, the grain density decreased obviously and the grain size increased rapidly. After being exposed to humid air for 3 h, the average grain size grew from 0.25μm to 0.68μm as is shown in Fig. 2. As can be seen in Fig. 2, the boundaries of the grains gradually become blurred due to the coalescence process.

It is considered the short-circuit diffusion played an important role in the process of the grains growing up. The spreading activation energy of atoms in the boundaries can be reduced by the diffusion of the attracted water molecules. That lends to the bending and moving of the grains boundaries, which causes the increasing of grain size [11].

The large difference of electronegativity between Cs and I makes CsI show a strong polarity. Therefore, the polar water molecules would be easily adsorbed on the surface of the grains. Moreover, the distortion and sparse of the grain boundaries tends to lower diffusion activation energy, but greater vacancy diffusion. Thus more and more water molecules are attracted. Its kinetics and presented morphology obey the Fick’s law and the basic laws of thermodynamics.

The chemical reaction as: \( \text{CsI} + \text{H}_2\text{O} = \text{CsOH} + \text{HI} \uparrow \) on the surface of grains is proved in Xie’s work [12]. Considering the diffusion-water mainly being molecular state, the chemical equation rewritten as: \( \text{CsI} + \text{H}_2\text{O(gas)} \rightleftharpoons \text{CsOH} + \text{HI(gas)} \), is more reasonable. Since the adsorption and chemical reaction happened with exothermic phenomenon, which lends to the increasing kinetic energy. And according to Fick’ law [13] the surface self-diffusion coefficient D could be expressed as:

\[
D = C_e \exp(-\Delta E / kT)
\]

Where \( \Delta E \) is the diffusion activation energy, \( k \) is the Boltzmann constant, is the intrinsic factor unrelated to temperature. The larger kinetic energy and lower cause the more intense diffusion. Regarding to three particle junction system [14]

\[
\frac{\gamma_{12}}{\sin \phi_3} = \frac{\gamma_{23}}{\sin \phi_1} = \frac{\gamma_{31}}{\sin \phi_2}
\]

Where \( \phi_1, \phi_2, \phi_3 \) is the junction angle; \( \gamma_{12}, \gamma_{23}, \gamma_{31} \) is the coefficient of the interfacial energy of the sector. When the junction angle is , the columnar has a shape with a hexagonal base and a straight boundary; otherwise the junction system is unstable and that makes the boundary bend to
small-angle direction. In this case, the bending boundary moves along the curvature center, with interface decreased, to reduce the system free energy. According to the Young-Laplace equation, the movement of the boundary is driven by the unequal pressure of the different sides [15]. The smaller grains were consumed to promote the bigger-around to grow. The larger grains annexed the smaller by the concave boundaries merging the convex, as shown in Fig. 3.

![Fig. 3. A model for CsI grain growth boundary change](image)

Fig. 3 shows the altered XRD spectra among the fresh, 3h, 12h and 24h exposed films. The spectra clearly shows that the diffraction intensity of (110), (211) and (220) crystal planes is enhanced with the exposure time, while the (200) is weakened. That mainly because the recrystallization process made by water molecules lends the grains to grow along the (110) and (211) direction.

![Fig. 4. XRD spectra of CsI film (a) without exposure (b) 3h exposed (c) 12h exposed (d) 24h expose](image)

3.2. Optical properties analysis.

As a function of wavelength, Fig. 5a and Fig. 5b show the trends of the transmittance percentage $T$ and the reflectance percentage $R$ in the range of 190-500 nm, respectively, with two curves for 500μm thick CsI films without exposure and with 24h exposed to 70% 5% humid air.

The measurements for handling substrates were done to calibrate the figures. Thus the $T$ and $R$ curves are only referred to the CsI film.

The 24h exposed film shows a lower but smoother $R$ curve. It is obviously to see the transmittance spectra relative to 24h exposure, which the average transmittance in the UV spectral range is about 50% is lower than the unexposed one while that is 78%. After exposure in the humid air, a white substance called milky effect is formed on the surface of the film [16]. That mainly due to the chemical reaction with water molecular mentioned in (1), do favor to cause the reflectance and transmittance reduction. In particular, considering the recrystallization crystalline structure introduced optical absorption centers lends to an increased absorbance in the UV range [17].
3.3. Infrared absorptance analysis

Absorption spectra of CsI films without exposure, 3h exposed and 24h exposed to 70%+5% humid air are shown in Fig 6 (10% panned up). Spectra shown in Fig.6 of obtained sequentially for increasing time depicts the apparent absorption of water molecules in corresponding coverages of 3760cm⁻¹-2840cm⁻¹. The OH (free) stretching vibration band centers are at 3652 and 3756cm⁻¹, while that of liquid water is at 3400cm⁻¹ [18]. It can be concluded the properties of water molecules on the surface of the grains are changed by the film. The affection by cation and anion of the film and the chemical reaction between CsI and water fracture the hydrogen bonding. Ion-dipole bond affects the hydroxyl vibration. Thus the spectra are more likely to exhibit the OH (free) absorption peak. With exposure time increasing, the absorption peak broadens with the band center shifting toward lower wavenumbers. That suggests the hydrogen bonding network in the film is more closed to liquidlike. Thus the absorption spectrum results in a state of liquid water.

4. Conclusion

In this paper, scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to study the surface morphology and structure of 500nm freshly evaporated and humid-air (70%+5%) exposed CsI film. Adsorbed water diffusion between the particles boundary reduce the film tensile stress. The particles boundaries bent and moved showed a significant change in the grain size and preferential growth orientation. The average grain size grew from 0.25μm to 0.68μm. The affected transmittance and reflectance of the films in the band of 190-500nm due to the change, the 24h exposed film showed a lower but smoother R curve and also a reduce T spectrum. Infrared spectra showed a hydroxyl absorption peak after 3h exposure. And in long term exposure (24h) the absorption peak broadened with the band center shifting toward lower wavenumbers.

Acknowledgments
This work was supported by 973 Program of China (2012CB315701), the National Natural Science foundation of China (61177035), Sichuan Provincial International Cooperation Project (2013HH0002), and Sichuan Provincial Science and Technology Support Project (12ZC0245, 2012GZ0051). The authors would like to thank CCD Research Center of China Electronics.

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