Preparation of cuprous iodide transparent thermoelectric materials by SILAR method

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Abstract. Thermoelectric generator can obtain electric energy from waste heat, which is one of the best ways to recycle the energy from waste heat. At present, most thermoelectric materials tend to be opaque, so the preparation of transparent thermoelectric materials is one of the research directions of thermoelectric materials. In this work, p-type transparent CuI films were prepared by successive ionic layer adsorption and reaction (SILAR) method. The crystalline structure of the film was determined to be γ-CuI by X-ray diffraction. The surface morphology of the film analyzed by scanning electron microscope was flat. In the wavelength of visible light, the average transmittance of CuI film is 60-70%. The energy band of the prepared CuI film is calculated by the formula to be about 3.04 eV. The results show that the CuI film prepared by the SILAR method has excellent optical transparency.

1. Introduction
Thermoelectric technology, as an environmentally friendly solid-state technology that can directly convert temperature difference into voltage, has attracted extensive attention. In fact, due to the small band gap (Eg <2eV), most of the identified thermoelectric materials tend to be optically opaque, such as the Bi2Te3 family. Several types of non-transparent thermoelectric materials with attractive thermoelectric properties, including silicon telluride and semi-quartz, have been recently reported for use in renewable energy power generation. So far, optical transparency is known (Eg >3eV) thermoelectric devices are rare, and the realization of such cloaking devices could open new areas in a range of new applications.

Loureiro, J. et al. deposited transparent aluminum zinc oxide (AZO) films at room temperature by using rf and pulsed DC magnetron sputtering, and prepared N-type transparent thermoelectric films with ZT value greater than 0.1 by adjusting the doping concentration of aluminum and film thickness [1]. Tomeda. Atsuki et al. prepared GZO films with light transmittance higher than 80% by sol-gel method and pulse-laser deposition method, respectively, and tested the thermoelectric properties of GZO films, with the highest power factor reaching 2.8μWcm⁻¹K⁻² and the lower thermal conductivity 8.4Wm⁻¹K⁻¹ [2]. Brinzari, V. et al. reported n-type transparent thermoelectric thin films doped with tin indium oxide, with the highest power factor up to 4.7 mW/(m·K²) [3]. Coroa, J. et al. prepared transparent CuI thermoelectric films with a thickness of 300nm and increased their ZT value to 0.29 [4].
Cuprous iodide (CuI) is a wideband gap semiconductor (3.1 eV), whose crystal structure is closely related to temperature. When the crystal structure is lower than 643K, it shows the structure of sphalerite (γ phase); when the crystal structure is 643K-673K, it shows the structure of wurtzite (β phase); when the crystal structure is higher than 673K, it shows the structure of plane cube (α phase). γ-CuI is a p-type semiconductor, which has a wide band gap. It can be used as a transparent material and has potential applications in many fields [5]. For example, hole-transporting layers in solar cells [6]; various catalysts for organic conversion [7]; as materials for P-type thermoelectric generators [8].

In this work, successive ionic layer adsorption and reaction (SILAR) method was used to prepare P-type transparent thermoelectric material CuI. The crystalline structure of the film was determined to be γ-CuI by X-ray diffraction. The surface morphology of the film was analyzed by scanning electron microscope, and the optical properties of the CuI film were measured with a UV–vis–NIR spectrophotometer. The results show that the SILAR method is a feasible preparation to obtain transparent cuprous iodide thin film.

2. Experimental

2.1. Fabricating CuI thin film

CuI thin film was deposited onto intrinsic ITO substrate (10 × 10 × 0.65 mm, Zhejiang Lijing Technology Ltd.) at room temperature by SILAR method. The solution of cationic precursor contains 100ml CuSO₄⋅5H₂O (0.1 mol/dm³) and 40ml Na₂S₂O₃ (0.1 mol/dm³). Aqueous solution of KI (0.025 mol/dm³) was used as an anionic precursor. ITO substrate ultrasonically cleaned in 95% ethanol and acetone for 15 minutes, respectively. Firstly, the ITO substrate was immersed in a cationic precursor for 10 s. Then copper ions were absorbed on the surface of the substrate and the un-absorbed ions were removed by rinsing the ITO substrate in de-ionized water (18 MΩ cm) for 5 s. For the reaction with iodine ions, the substrate was immersed in an anionic precursor for 20 s. The last step, powdery material or loosely bounded ions were removed by rinsing the substrate in de-ionized water for 5 s. The above steps were a cycle, which was repeated 40 times. Finally, the γ-Cul thin film was dried in air at room temperature.

2.2. Characterization and measurements

The crystalline structure of CuI films is confirmed by X-ray diffraction. Surface morphology of CuI films was photographed by field emission scanning electron microscope. The optical properties of the CuI film were measured with a UV–vis–NIR spectrophotometer (UV-3600, Shimadzu). All the measurements are done at room temperature.

3. Results and discussion

Fig. 1 showed morphology of CuI thin films prepared by the SILAR method. The dense fine-grained CuI structure for the SILAR deposited film shown in Fig. 1 (a) was similar to the one reported previously by N.P. Klochko et al [9]. Fig. 1 (b) showed a large number of irregular holes formed on the surface of the film. In a cross-sectional view (at an angle of 30 degrees to the bottom) of Fig. 1 (c), the bottom showed the layered network structure, while the schistose and granular structures were arranged vertically on the network structure. The film thickness was about 1.73μm, which was much higher than the 0.33μm reported previously [10]. With the increase of the number of cycles, the network structure cannot be superimposed stably. Simultaneously, voids have formed inside the film, resulting in a significant increase in thickness.
Fig. 1. SEM images of the CuI thin film deposited on ITO substrate. (a) and (b) top view, (c) cross-sectional view.

Fig. 2 showed the X-ray diffraction pattern of the CuI thin film. The main diffraction peaks were identified as (111), (220), and (311) of the zinc blende structure of γ-CuI, which was consistent with the values in the standard cards (PDF Card No.77-2391). All the diffraction peaks were assigned to a pure face-centered cubic structure of γ-CuI. Note that the peak (111) was the highest of the three narrow and pointed peaks, which indicated that γ-CuI single crystals were grown on ITO substrate by preferred growth orientation of 111. No other impurities were detected in the γ-CuI thin film. This indicated that the γ-CuI thin film prepared by the SILAR method had the high purity.

Fig. 3 showed the optical transmittance spectra of the γ-CuI film. It can be seen from Figure 3 that the γ-CuI film had a high light transmittance and considerable absorption. The transmittance in the visible range is generally above 60%. The optical band gap is estimated using Tauc's equation: $\alpha h\nu = B(h\nu - E_g)^x$, where $\alpha$ is the optical absorption coefficient, $B$ is a constant, $x$ is 1/2 for a direct band transition and 2 for an indirect band transition, and $h\nu$ is the photon energy. The inset in Fig. 4 showed the relationship between $(\alpha h\nu)^2$ and $h\nu$, indicating a direct energy bandgap of the γ-CuI thin film. The value of $E_g$ is determined to be about 3.04 eV, which is corresponding to relevant literature [11].
Fig. 3. Transmission spectra of CuI films deposited on ITO substrates. The corresponding $(\alpha h \nu)^2$ and $h \nu$ curves are presented in the inset.

Fig. 4 showed the output voltage as a function of temperature difference for the samples. We measured the sample output voltage under different temperature difference conditions. As the increase of temperature difference, the output voltage of sample increased gradually, which agreed with the characteristic of thermoelectric effect. The substrate is made of intrinsic glass and $\gamma$ cuprous iodide is a P-type semiconductor [12]. Therefore, the thermoelectric voltage is mainly caused by cuprous iodide. We calculated the Seebeck coefficient of CuI according to the red curve through the equation: $S = \frac{V}{\Delta T}$ where $V$ is the voltage at both ends of the sample, $\Delta T$ is the temperature difference between the cold end and the hot end, $S$ is Seebeck coefficient of CuI. The value of $S$ is estimated to $70 \mu V*K^{-1}$ which is less than relevant literature $(160 \mu V*K^{-1})$ [13].

Fig. 4 Thermoelectric voltage as a function of temperature difference.

4. Conclusions
In summary, CuI thin films were prepared on the surface of ITO by SILAR method. X-ray diffraction patterns of the thin film showed all the diffraction peaks were assigned to a pure face-centered cubic structure of $\gamma$-CuI. The scanning electron micrograph of the film shows that the film prepared by the SILAR method has a compact surface morphology and a layered stack structure. The reflectance diagram of the film shows that the film has a high transmittance (60%-70%) in the visible light range. At the same time, the energy band (3.04eV) of the film prepared by the SILAR method is calculated using the Taco formula. The resistivity measurement results show that the film has high conductivity. The experiments were performed to measure the output voltages of thermoelectric effect.

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