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ARTICLE

Preparation of Copper Indium Sulfide Film by Electro-Deposition Method

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Abstract: Copper indium sulfide ($CuInS_2$, CIS_2) film was prepared by an electro-deposition method. Uv-vis spectrophotometer test result shows that the band gap of the electroplated CIS_2 film is 1.5 eV. X-ray photoelectron spectroscopy (XPS) analysis reveals that the Cu, In and S signals corresponded to valence state （+1, +3 and -2）of three elements in CIS_2 film, respectively. The photoelectrical properties of the CIS_2 film were characterized by linear sweep voltammetry measurements under the dark and illumination. The *I–V* characteristic is linear under the dark and illumination, and the slope gap is 0.6×10^{-3}. We also simulated the band gap (1.5 eV) of the CIS_2 film with chalcopyrite structure prepared by electroplating experiment using DMol3 and CASTEP modules, respectively. The molecular structure model of electroplated copper indium sulfide film has been established, and the X-ray diffraction simulative spectrum has been obtained by Materials Studio, which has good agreement with the experiment result.

Key words: CIS_2 film; electro-deposition; structure; band gap

A number of ternary semiconductors which crystallize in the chalcopyrite structure appear to be sustainable for future large scale energy production[1,2]. The highest conversion efficiency of solar cells made with $CuInS_2$ material is around 12% until now[3], which have many advantages, such as good anti-jamming and anti-radiation ability, stable performance and long service life. Also the CIS_2 thin-film is used for quantum dot-sensitized solar cells[4]. So the CIS_2 is one of the most promising materials for solar cells. CIS_2 is a compound semiconductor belonging to I-III-VI_2 chalcopyrite family, and is available for an advanced absorber material due to its excellent material properties, such as proper band-gap energy of 1.4 ~1.5 eV and large over 10^5 cm^{-1} absorption coefficient[3]. Many experimental techniques have been employed for preparing CIS_2 thin films: RF reactive sputtering[5], reactive magnetron sputtering[6], spray pyrolysis technique[3,7], sequential evaporation[8], and solvothermal process[9,10]. However, these methods have some problems such as complicated apparatus and even some toxic byproducts. It is necessary to produce CIS_2 films through an eco-friendly and scalable process for mass production of films for photovoltaic applications. Eelectrodeposition deserve special attention because they have been shown to be inexpensive, low-temperature and non-polluting methods[11-14].

1 Experiment

The CIS_2 films were electro-deposited in potentiostatic system (1.5 V). A two-electrode-cell was supplied, with a graphite as anode and a conductive glass substrate (area: 1.5 cm × 3 cm) as a working electrode. The electrolyte compositions of electroplating CIS_2 were $CuSO_4\cdot5H_2O$ 25 g/L, $In_2(SO_4)_3$ 50 g/L, $Na_2S_2O_3\cdot5H_2O$ 25 g/L and $C_6H_5O_7Na_3\cdot2H_2O$ 25 g/L. The solution was well stirred so

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that a claret-red homogeneous solution was formed. The pH of the solution was controlled at approximately 2.5 with the addition of HCl. The clean substrate (FTO glass) was placed vertically inside the beaker at 25 ºC. After 1 h, the substrate with the deposited film was taken out from the solution, and washed with deionized water, then dried and preserved. Finally, the $CuInS_2$ thin film was heat-treated at 300 ºC for 0.5 h under the nitrogen atmosphere in a furnace to improve the structural quality and the adherence of the film. After annealing, the sample was cooled to room temperature naturally in the furnace.

In order to determine the main composition and the state of the surface film, the D/max-B rotating anode X-ray diffraction analyzer (XRD, Japan neo-confucianism kabushiki kaisha) was used. The optical absorption of CIS_2 film was recorded in the wavelength range from 200 to 1100 nm by Uv-vis spectrophotometer (Purkinje General TU-1950). The photoelectrical properties of the CIS_2 film were tested by linear sweep voltammetry in a three-electrode cell using a potentiostat/galvanostat (PARSTAT2273) at 25 °C under the dark and illumination, separately. Atomic force microscopy (AFM, BIOSCOPE) was used to study the surface morphology of the electroplated CIS_2 films. X-ray photoelectron spectroscopy (XPS, PHI-5700, ESCA System) with an Al Kα X-ray source (1486.6 eV) and at 45º take-off angle was used to analyze the surface electronic states; the pass energy used to record the wide scan XPS spectra was 187.85 eV and the pass energy was 29.35 eV for high resolution scans. All XPS peaks were referenced to the C1s signal at a binding energy of 285 eV.

Fig.1 indicates an optimized chalcopyrite structure model of CIS_2 by Materials Studio simulation. The coordinate of atom Cu was (0.000, 0.000, 0.000), In was (0.500, 0.500, 0.000), and S was (0.750, 0.750, 0.125). The lattice parameter of CIS_2 was $a=b$=0.5545 nm, c=1.1084 nm and $\alpha=\beta=\gamma$=90°; it belonged to 122 SG, which meant I-42D; tetragonal groups. The X-ray diffraction simulation calculation was carried out by the Powder Diffraction function in Reflex module included in software Materials Studio. Step size was 0.0200, the geometry was Bragg-Brentano, the function was David Voigt Approx, and the correction of Asymmetry was Rietveld. The band gap of CIS_2 was simulated by DMol3 and CASTEP modules. First principles simulations had been performed using DMOl3 code. After the geometry optimization, GGA with Becke exchange plus Perdew (BP) functional were employed. The TS method was used for DFT-D correction, the Gamma point only was selected as k-point. CASTEP modules were based on Density Function Theory (DFT). Electronic exchange association energy used the PBE, plane wave basis set cut-off 310.0000 eV, and the K-point set 3×3×4. The Pseudopotentials was Ultrasoft, and the Pseudopotential representation was Real space.

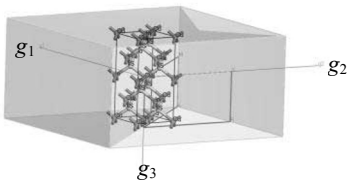

Fig.1 Optimized molecular structure of CIS_2 by Materials Studio simulation

2 Results and Discussion

Fig.2a is X-ray diffraction patterns of CIS_2 films gained through the experimental test. The sharp peaks at 26.59°, 45.95° and 54.41° correspond to (112), (220) and (312) crystal planes of tetragonal structure $CuInS_2$, respectively. Fig.2b shows the $CuInS_2$ structure of simulation results of X-ray diffraction. There is little difference between the simulative and experimental spectra, confirming the accuracy of established model structure. So the CIS_2 prepared by electroplating method is chalcopyrite structure. S atom is in the middle of the structure, while In and Cu atoms are symmetrical around the S atom.

Fig.3a shows the band gap of CIS_2 calculated with DMol3. There is no crosspoint among conduction band and valence band and E_g=1.5 eV. The bottom of conduction band and the top of valence band belong to the same G point in Brillouin zone, indicating that CIS_2 is a direct band gap semiconductor. Due to the less valence band fluctuation, a comparative narrow band shows that the eigenstate is mainly composed of lattice point atomic orbital composition, and the electron locality is very good and effective mass is great. PDOS can be used as visualization result of energy band structure. From the diagram, we can clearly see the band gap, valence band and conduction band. And there are peaks of d and s orbitals (Fig.4a and 4b) in the top of valence band, which explains that electronics in d and s orbitals are relatively localized. Around 0.2 Ha, conduction band is occupied by p and d orbitals (Fig.4a and 4c).

Fig.3b shows the band gap of CIS_2 by CASTEP, which is 1.5 eV. After the geometry optimization, we use GGA to accurate the result because GGA considers the exchange association role. The more intensive the curve is, the denser the density of states is, indicating that there are more electrons in the area. The electrons are the most aggregate in the field of –10~ –15 eV, and electrons take the second place between –5 eV and 0 eV (Fig.4d). Fermi energy is 0 Ha (Fig.4d), which shows semiconductor property of the CIS_2 film.

The optical absorption of the annealed CIS_2 sample is determined by ultraviolet visible spectrum. E_g can be achieved using the following formula[3]: $(\alpha hv)^n=A(hv-E_g)$, where A is a constant and n characterizes the transition