Synthesis and Characterization of Zinc Tin Oxide Thin Film Application in Perovskite Solar Cells

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Abstract

Zinc Tin Oxide, ZTO thin films were synthesized by sol-gel spin-coating method. They are aimed to be exploited as interfacial layer in perovskite solar cells. The structural property of ZTO was studied by X-ray Diffractometry, XRD, the optical transmission of ZTO films were examined by UV-vis spectroscopy, UV-1600, surface morphology of ZTO films were investigated by Atomic Force Microscopy, AFM and wettability of ZTO on perovskite film were measured by content angle measurement. XRD pattern indicates that ZTO has cubic structure at 700°C. In addition, the optical band-gap energy of ZTO film is about 3.48 eV. From AFM microphotographs, the shape of grains are popcorn-like on ZTO films were observed. The result of wettability measurement observe that the contact angle decreases at the lower concentration of ZTO film, and the surface becomes more hydrophilic. According to the experimental results, ZTO might be promising, credible and applicable in use for perovskite solar cells.

Keywords: sol-gel, spin-coating, perovskite solar cell, XRD, AFM, band-gap energy.

1. Introduction

Energy supply has become one of the most important problems facing humanity. Due to the exponential increase of population and economic rise of many un-developed countries, the world energy consumption is going problem. Electrical energy is most useful forms of energy, since it can be used for almost everything. Against this bottle-neck, scientists and engineers have been widely investigated to develop alternative and sustainable sources of energy especially using solar power. Solar energy is one of the most important resources in our life. Photovoltaic is the most important technology to represent the conversion from the solar energy into electrical energy. Solar cells' technology are promising renewable energy. It is very important to improve the Power Conversion Efficiency, PCE and reduce the cost. organic-inorganic hybrid Perovskite Solar Cells, PSCs, as the third-generation solar cells, are attracting due to low-cost, flexibility and high output. Most technologies in this generation have not yet been commercialized, but there is a lot of research going on in this area. The most commonly studied perovskite absorber is methylammonium lead trihalide with a band-gap between 2.3 eV and 1.48 eV [1, 2]. In order to enhance the photovoltaic performance of PSCs, the researchers have been extensively studied to the perovskite deposition methods, perovskite composition engineering, interface engineering, device architecture, etc. In perovskite of solar cell, the perovskite can harvest the light on the basis of electron excitation. Afterwards, the electron and hole are collected at the charge transport materials. The electron and hole transport layers play, therefore, as a crucial role in determining the light harvesting and charge transport properties.

There are many kinds of metal oxides and ternary metal oxides are used as charge transport layers. The favorable characterize of charge transporting window layer in solar cells are high optical transmittance, high electrical conductivity, mobility and good energy level alignment. The prior reports showed that ZTO have high-electron Hall mobility of 10-30 $cm^2V^{-1}s^{-1}$, wide optical band-gap of 3.8 eV, and relatively low refractive index nearly 1.37 and transmittance about 95% in the visible region [3]. Thus it is expected that ZTO would have better electron transporting, hole blocking capacities, reduced recombination probabilities, thermally and chemically more stable than ZnO and TiO_2. At present, the ZTO have received attention of the researchers as interfacial layer in solid state devices including solar cells, combustible gases and sensors for humidity. Employing the optimizing steps, varying the deposition method, using advanced characterization are becoming of key importance to realize cost effective and efficient ZTO materials for real-world applications. The difference methods of synthesis of ZTO are thermal evaporation, high-temperature calcination, hydrothermal reaction, ion-exchange reaction and sol-gel synthesis. The aim of this present work is to synthesis ZTO film by sol-gel spin coating method and also to investigate the phase identification, to study the optical transmission and band gap energy, to clear understand surface morphology and composition elements of thin films. Annamalia et al. reported the synthesis of highly crystalline ZTO nanoparticles could easily be controlled by adjusting the concentration of the mineralizer, enabling band-gap engineering [4]. Zeng et al. studied systematically the influence of operating conditions such as reaction temperature, duration time and addition of surfactants on the phase composition, particle size, and crystal morphology of ZTO nanocrystals synthesized by a hydrothermal process [5].

2. Experiment

Zinc chloride, $ZnCl_2$ and tin chloride, $SnCl_2$ were used as precursor solution to prepare ZTO solution. In order to get ZTO solution, same molarity of $ZnCl_2$ and $SnCl_2$ were dissolved in acetonitrile solvent. The mixed solution was stirred at room temperature until the precursor salt was dissolved completely. The obtained solution was heated at 200°C for 3 hr in air to get powder form. The resultant powders were annealed at different annealing temperature for 3hr at the furnace. Annealed samples were analyzed by using XRD (RIGAKU Multiflex) (Japan) using CuK_α radiation, the Bragg angle is 1.5418 °A, to investigate the phase identification of the samples. In order to synthesis ZTO films, glass substrates were cut in 1.5 x 2.5 cm and ultrasonically cleaned with detergent, distilled water, acetone and isopropyl alcohol for 15 min successfully and dried by nitrogen flow. And then these glasses were treated with 1 M NaOH solution to make it hydrophilic nature. Glass surfaces were treated by UV light in order to remove the organic contamination on them. Sol-gel spin coating was performed up onto the prepared glass substrates according to the following process. In first step, ZTO solution was dropped on a cleaned glass and spun-coat at 3000 rpm for 30 s. In second step, after each deposition, the covered substrate was heated at 200°C for 2 min. In third step, the coating procedure was repeated three times to increase the thickness, before a post annealing process was performed at different annealing temperature for 3 hr at the furnace during which the thin films were converted to metal oxide. In addition, the optical transmittance measurements of thin films were performed with UV-1600 at wavelength range 300-900 nm, then the optical band gap energy were calculated with it. The surface morphology of ZTO films were studied by AFM in this work. The wetting properties of ZTO on perovskite films were measured by content angle measurement.

3. Results and Discussion

3.1 XRD Analysis

We have studied the phase identification of ZTO samples annealed at different temperature 500°C-700°C. When the ZTO samples were annealed at 500°C and 600°C, the observed peaks were not sharp and included undesired peaks. Figure 1 illustrates ZTO sample annealed at 700°C, most of the peaks were consistent with JCPDS 28-1486 data of ZTO. The sample has sharp and narrow diffraction peaks, and it is attributed that the materials exhibit high crystallinity and the average lattice constant about 7.7617 Å. The strongest peak was selected to determine the crystallite size of using Debye-Schere's equation (1):

$$t = \frac{0.9\lambda}{\beta cos\theta} \quad (1)$$

where, t is the crystallite size, λ is the X-ray wavelength, β is the full-width half-maximum of the peak and θ is the Bragg's angle. The calculated crystallite size was 21.64 nm and it indicated the cubic structure for ZTO sample at 700°C. The calculated crystallite size is confirmed with the reference [4].

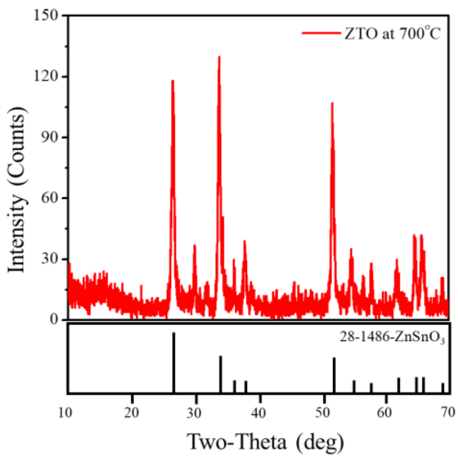

Figure 1. XRD pattern of ZTO

3.2 UV-vis Spectroscopy Measurement

We studied the transmission properties of ZTO films with difference thickness in the wavelength range (300-900 nm) by using UV-Vis Spectrophotometry. Figure 2. show the optical transmission spectra and optical band-gap energy of ZTO films with difference thickness. The optical transmission is about 97% for ZTO films. The optical band-gap energy is main point to select the material which can match or not with that of photosensitizer. We calculated band–gap energy E_g from absorption spectra of ZTO films by using the following equation (2):

$$\alpha h\nu = A (h\nu - E_g)^n \quad (2)$$

where α is absorption coefficient, hν is the incident photon energy, A is the proportionality constant, Eg is the band-gap energy and n is either 1/2 for direct band-gap semiconductor or 2 for indirect band-gap semiconductor [1]. The calculated band-gap energies of ZTO films with different thickness are 3.68 eV, 3.64 eV and 3.48 eV.

Table 1. Optical transmission and band-gap energies of ZTO films with different thickness

ZTO Films	Transmission (%)	Optical Band-gap Energy (eV)
13 nm	99	3.68
26 nm	98	3.64
51 nm	97	3.48

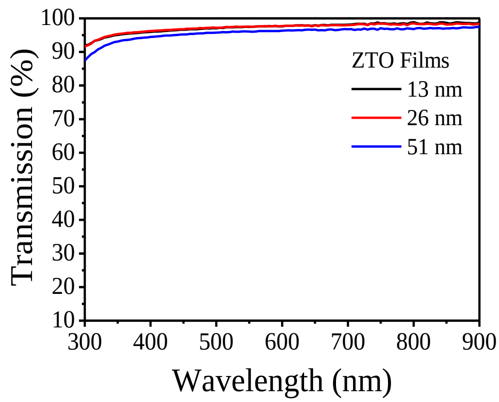

Figure 2. Optical transmission spectra of ZTO films with different thickness

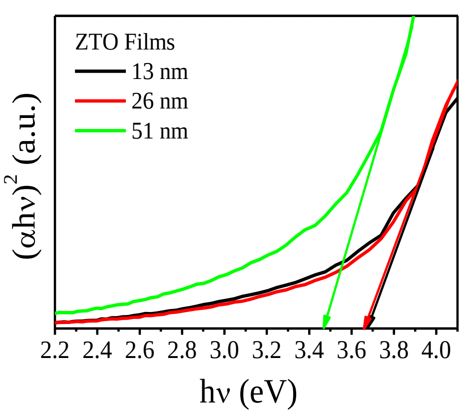

Figure 3. Optical band-gap energies of ZTO films with different thickness

3.3 AFM Analysis

A detail analysis on size and shape of the grains on the surface of ZTO films was performed by the AFM images with higher magnification. Figure 4 depicts AFM micrographs (20 µm × 20 µm) of ZTO films with different thicknesses (13 nm, 26 nm and 51 nm) (Figure 3 a-c), we observed the grains are popcorn like and size of the grains are nearly the same on surface. The line profiles shown on the right side of AFM images were obtained by scanning across the length of the grains on the surface of the film. The line profiles show that the length of the grains ranges from 1.2-1.4 µm.

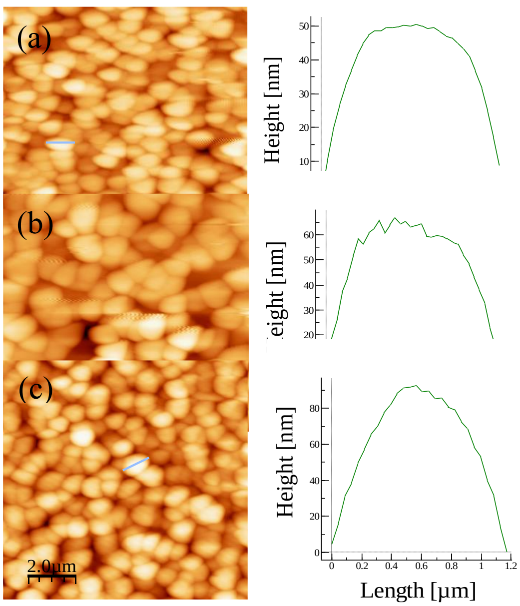

Figure 4. Two-dimensional and line profiles AFM (20 µm × 20 µm) images of multilayered ZTO thin films (a) 13 nm (b) 26 nm (c) 51 nm

3.4 Wettability of Perovskite towards ZTO Films

The determination of wetting properties of perovskite solution, $CH_3NH_3PbI_3$ on ZTO films is based on measurement of contact angle. All contact angle measurements were performed immediately after the formation of $CH_3NH_3PbI_3$ drop at the substrate. The obtained contact angles at three different locations of the same sample were averaged out. In Figure 4, the contact angles of $CH_3NH_3PbI_3$ solution on ZTO films were measured. We observed there is a little change in contact angles of $CH_3NH_3PbI_3$ solution on ZTO films with different concentration. The contact angle of $CH_3NH_3PbI_3$ on a ZTO surface is considerably influenced by changing concentration, i.e. as the lower concentration, the contact angle decreases and the surface becomes more hydrophilic.

Table 2. Contact angle measurement with different concentrations

ZTO films (different concentrations)	Contact Angle (Degree)
0.07 M	11
0.24 M	14

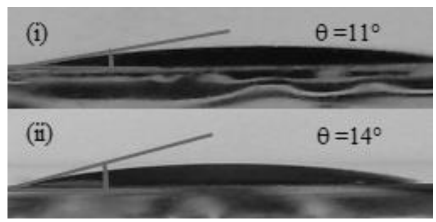

Figure 5. Contact angles of $CH_3NH_3PbI_3$ solution on ZTO thin films with different concentrations

4. Conclusion

In this research work, synthesis and characterization of ZTO film by sol-gel spin coating method has been successfully studied. From XRD analysis, ZTO was found with cubic structure and $ZnSnO_3$ phase. The average crystallize size of ZTO is about 21.64 nm. As a result of UV-vis spectrum, the optical transmission is about 97% and band-gap energy is 3.48 eV at 51 nm thickness. The AFM images indicate that popcorn like morphology of ZTO grains were uniformly distributes on the surface. In addition, the contact angle decreases at the lower concentration of ZTO film, and the surface becomes more hydrophilic.

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