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EVALUATION OF BAND GAPS AND URBACH ENERGIES FOR ZnO THIN FILMS BY THERMAL EFFECT

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Abstract

Zinc Oxide (ZnO) nanoparticles were synthesized by the sol-gel technique. As prepared ZnO thin films were deposited by spin coating method on different annealing temperatures at200 °C and 300 °C. Optical properties of ZnO thin films were investigated by Ultraviolet–visible spectroscopy (UV–VIS). Energy gaps were decreased from 3.27 eV at 200 °C to 3.18 eV at 300 °C with increasing temperature. On the contrary, Urbach energy was decreased from 180 meV (300 °C) to 92 meV (200 °C) due to effect of annealing temperature.This mainly comes from decreasing of interatomic spacing and the average potential energy by defects and imperfection of semiconductor materials. Hence, Lower Urbach energy and higher transmittance of ZnO nanoparticles thin film is suitable electron transport layer in low temperature processed for flexible perovskite solar cells.

Keywords: Energy Gap, Urbach energy, Zinc oxide, thin film, Annealing temperature

Introduction

Perovskite solar cells (PSCs) initially investigated from methylammonium lead halide which are promising light harvesters in the field of next-generation solar cells. In 2009, Miyasaka (Kojima et al., 2009) applied an organic-inorganic lead halide perovskite compounds as visible-light utilized in ETLs structure and received an initial power conversion efficiency (PCE) of 4%. Later on, power convention efficiency has drastically improved up to 22.7% due to adorable optical and electrical properties such as long diffusion length up to 175 μm, high carrier mobility, direct optical band gap, extensive absorption range (Ansori, 1972; Brivio et al., 2013; D'Innocenzo et al., 2014; Etgar et al., 2012; Jeong et al., 2021; Saliba et al., 2016; Stranks et al., 2013; Tao et al., 2015).

In order to improved perovskite solar cell efficiency, different types of electron transport layers (ETLs) have been studied in recent year. The ETLs normally used in perovskite-based solar cells as titanium dioxide TiO_2 **(**Gao et al**.**, 2015; Hadouchi et al**.**, 2016**)**. TiO_2 films need high temperature 500 C° which is not suitable for flexible perovskite solar cells **(**Kim et al**.**, 2012; Liu et al**.**, 2013**)**. This problem is one of the boundaries for commercialization of perovskite solar cells. As an alternative, Zinc oxide (ZnO) can be substituted instead of TiO_2 as an ETLs in PSCs (Luo et al., 2018). In addition, ZnO is a wide band gap semiconductor and electron mobility higher than that of TiO_2, which is favorable for electron transport layers **(**Zhang et al**.**, 2009**)** and it need low temperatures process, which have great advantages in tandem and flexible devices **(**Seo et al**.**, 2019**)**. Furthermore, ZnO has a high exciton binding energy of 60 meV that contributes to its excellent optical properties (Gu et al., 2013) and It has a favorable conduction level of 4.4 eV (Wright and Uddin, 2012) which facilitates electron extraction from LUMO level (3.9 eV) (Choi et al., 2015) of methylammonium iodide perovskite. Thus, ZnO can simultaneously play a role of n-type conducting layer in a perovskite solar cell and deposited by spin coating for flexible substrates at low temperature to achieve smooth and high- quality films (Hadouchi et al., 2016).

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However, it is not clear that what is scientific reason for low temperature process is used for ZnO thin film compared than that of high temperature sintering.

In our work, ZnO colloidal nanoparticle solution was synthesized by sol gel method. Resulted ZnO thin films were deposited by spin coated method under different temperature of 200 °C and 300 °C. The effect of thermal annealing on their optical properties were studied.

Materials and Method

Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, 99%), Potassium hydroxide (KOH,99%), and methanol (CH_3OH, 96%) are purchased from Sigma-Aldrich and Merck sources.

Synthesis of ZnO nanoparticles

ZnO_x nanoparticle was synthesized following by the sol gel method (Dehghan and Behjat, 2019). 0.11 M of Zinc acetate dihydrate $Zn(CH_3COO)_2.(H_2O)_2$ was dissolved in methanol (CH_3OH) under magnetic stirrer at 60 °C for 30 min to obtain a clearly solution. Potassium hydroxide (KOH) (0.45M) was dissolved in methanol with another vial and stirred for 30 min at 60 °C. Finally, KOH clearly solution was slowly added to the zinc acetate solution at 60°C while vigorous stirring. The white solution was formed within 5 min then transformed into clearly solution within 30 min. Colloidal solution was precipitated after 2 h stirring at 60°C. ZnO nanoparticle solution was obtained and ready to use by spin coating method.

Sample preparation

Glass substrates (2.5×2.5 cm^2) were ultrasonically cleaned with distilled water, acetone, ethanol and isopropanol for each 15 minutes. The cleaned glass substrates were further treated with UV/ozone for 15 minutes before film deposition.

Films deposition

The ZnO colloidal solution was deposited onto the glass substrate by spin coating method using spinning speed at 2000 rpms for 30 s and annealed at 200 °C and 300 °C for 30 minutes each.

Characterization of ZnO thin films

The absorption and transmission spectra of ZnO films were recorded from the spectral range of 300 nm to 900 nm using UV-Vis spectrophotometer (Genesys 10S). The baseline scan was taken using a bare glass substrate (for thin films) prior to the measurement.

Results and Discussion

Figure 1 shows the prepared ZnO colloidal solution is deposited on the glass substrate by spin coated method and then annealed for 200 °C and 300 °C for 30 min each.

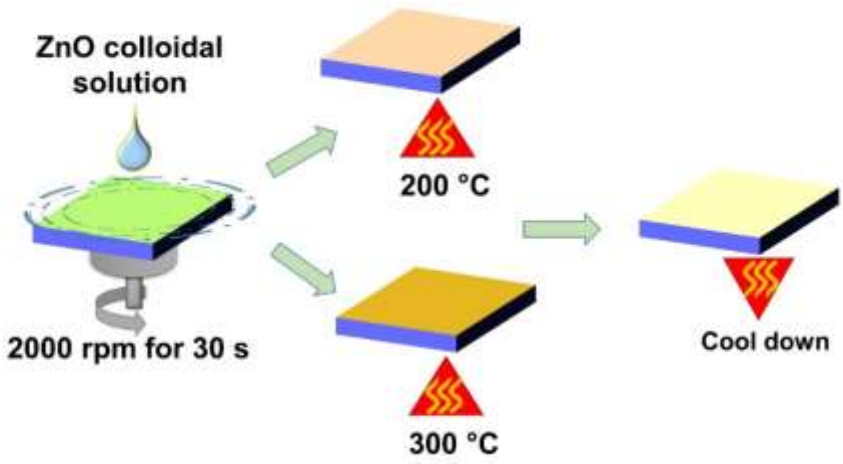

Figure 1. Schematic illustration of deposited ZnO thin films

The optical properties of deposited films were characterized by UV- vis spectrophotometry. Figure 2 shows the measured transmittance, absorption spectra of ZnO films and corresponding Tauc's plot. These results exhibit the optical transmission and absorption of ZnO film with varying temperatures at 200 °C and 300 °C. The higher optical transmission of ZnO film is observed when temperature is set at 200 ^{o}C (see Figure 2a). On the contrary, transmittance is decreased with increasing temperature at 300 °C. The low temperature deposited film can be attributed to lower energy loss due to highest transmittance for suitable electron transport layer in perovskite solar cells. Higher absorption of ZnO films (300 °C) can be observed in the wavelength of 300–350 nm range as shown in Figure 2b. Lower absorption spectrum of annealing film (200 °C) exhibits a UV shift character corresponding to the higher energy bandgap. Furthermore, energy gaps of ZnO annealing films is also estimated from Tauc's plot equation (Makuła et al., 2018): $(\alpha h\nu)^n = A\,(h\nu\text{-}E_g)$, where α is absorption coefficient, hν is incident light energy, and E_g is the band gap of the material. The exponent 'n' is the transition type of the material. The n value is 2 for direct transition for ZnO (Dehghan and Behjat, 2019). The optical band gap of ZnO annealed films are decreased with increasing annealing temperatures in Figure 2c. The band energies of resulted films are obtained by extrapolating the linear portion of the curve to photon energy axis. The calculated energy gap for low temperature (200 °C) annealed film is 3.29 eV (C. Nehru et al., 2012; Srikant and Clarke, 1998). The band gap energy is decreased to 3.21 eV when temperature is increased to 300 °C. It may increase grain sizes of ZnO film due to decrease energy gap with increasing temperature.

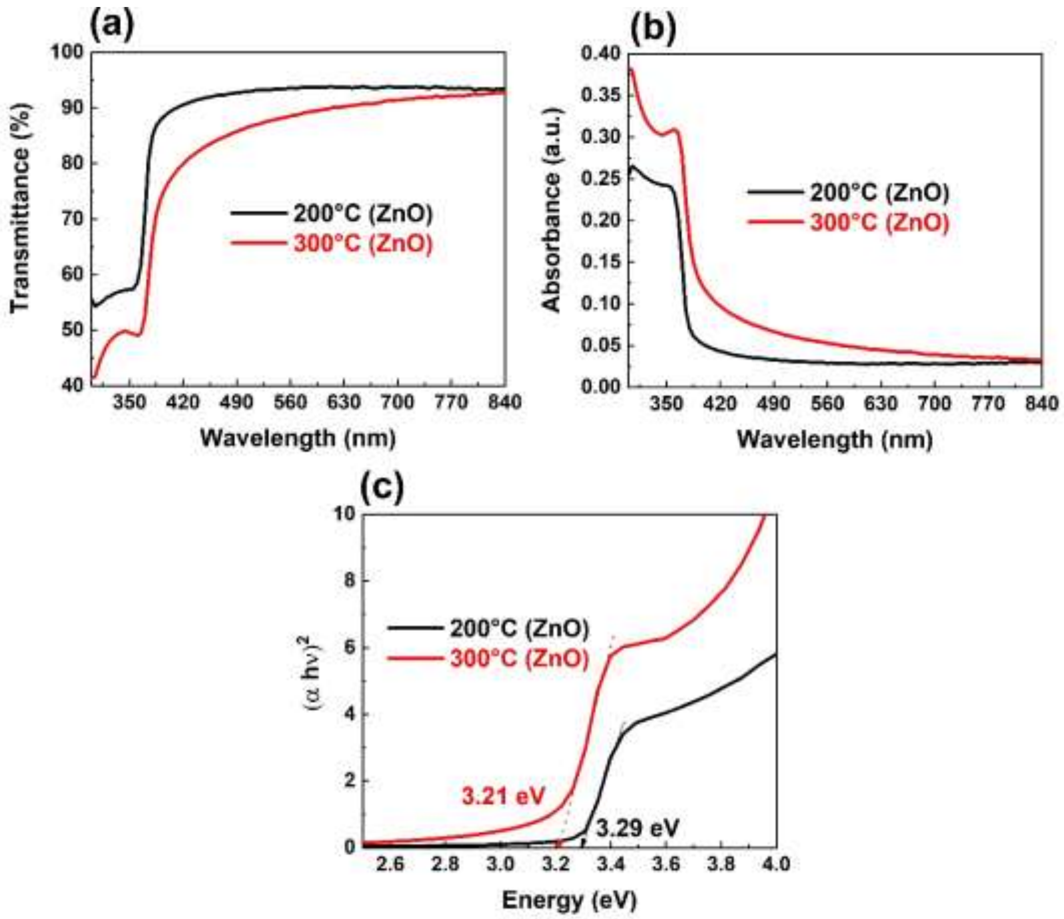

Figure 2. UV-Vis spectra of different annealing temperature (a) optical transmittance (b) absorption spectra (c) plot of $(\alpha h\nu)^2$ versus $h\nu$ of ZnO films

This results can be further analyzed upon different temperature by a combination of the thermal effect and the Urbach effect (Skettrup, 1978; Urbach, 1953). The origin of the Urbach energy mainly comes from the impurities, defects and imperfection of growth thin films by annealing temperature (Rai et al., 2012). Figure 3 exhibits the Urbach tails from the Sgreen region for 200 °C and yellow region for 300 °C. It can be clearly seen the broadened behavior by thermal effect at increased temperatures (300 °C). The Urbach energy can be determined from Urbach tails which refers charge excition transition between the valence band tail to the conduction band edge in the semiconductor following equation: $\alpha = \alpha_0 \exp [(h\nu)/E_U]$ (Skettrup, 1978). From the slope of simplified equation: $\text{Ln}(\alpha) = \text{Ln}(\alpha) + [1/(E_U)] \times h\nu$, E_U can be determined. Urbach energy is increased from 91 meV (200 °C) to 182 meV (300 °C). Lower Urbach energy indicates in the range of 80–100 meV, suggesting that low defect and disorder in the semiconductor materials (Rai et al., 2012). Interestingly, low temperature prepared ZnO thin film has lower Urbach energy and higher transmittance which are appropriate for electron transport layer utilized in the flexible perovskite solar cells.

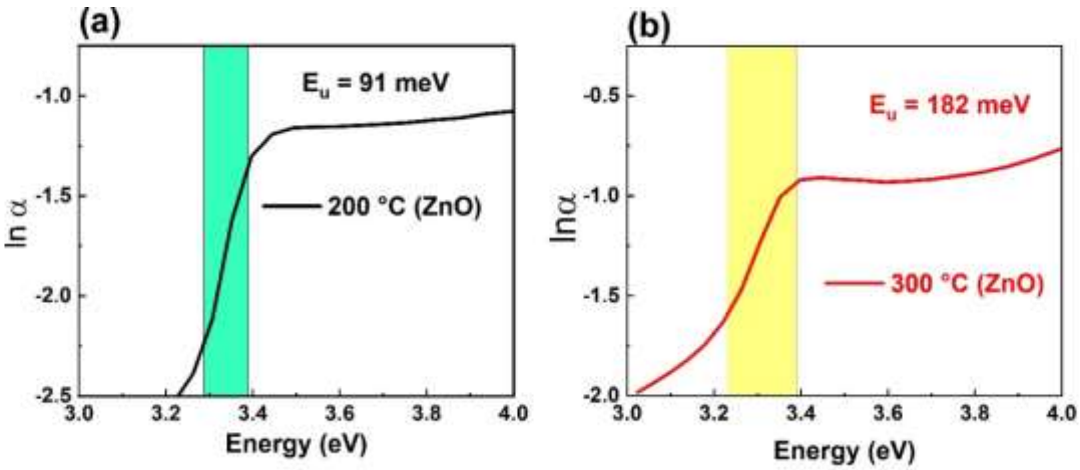

Figure 3. Estimated Urbach energies from Ln α vs photon energy's plot, where E_u is Urbach energy

Conclusion

In this work, ZnO nanoparticles colloidal solution has been synthesized by sol gel method. And ZnO thin films were prepared by spin coated method under different annealing temperature at 200 °C and 300 °C. The resulted ZnO film annealed at 200 °C was higher transmittance and lower Urbarch energy. However, the transmittance of ZnO film decreased and its Urbach energy increased when it was annealed at 300 °C. This result shows that higher defect and disorder form in high temperature annealed film. Hence, ZnO thin film annealed at low temperature (200 °C) is a suitable electron transport layer for flexible perovskite solar cells.

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