

Determination of the band gap energy for ternary material Sn-In-Zn-O thin films by electron spectroscopy and ultra-visible spectrometer

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Abstract:

The SnInZnO thin film was prepared at room temperature by RF magnetron sputtering. The band gap of this film was investigated by REELS and UV-Spectrometer analysis. By using REELS with low energy (500 eV) and high energy (1500 eV) electron beams, the surface band gap as well as and the bulk energy band gap were measured. The result shows that the band gaps are affected by the primary electron energies. The transmittance value of 80% in the visible light region has been achieved. The optical band gap was calculated by using Tauc's relation from UV-Spectrometer analysis and compared to that of the band gap obtained by the REELS spectra.

Keywords: transparent conducting oxide; REELS; UV-Spectrometer; band gap energy.

Introduction

ZnO-based films have applications as active channel for transparent conducting oxides (TCO) materials in thin film transistors (TFTs). This is due to their higher carrier mobility and transparency in the visible light region compared to the conventional TFTs, which are based on hydrogenated amorphous silicon (a-Si:H) having a carrier mobility of less than $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [1]. Tin indium zinc tin oxide (SnInZnO) films, particularly, can be one of the possible alternatives for transparent electrodes of various optoelectronic devices such as flat-panel displays, solar cells, and organic light-emitting diodes because of their good electrical conductivity, chemical stability, and low deposition temperature [2, 3]. There are several deposition techniques to deposit SnInZnO thin films such as electron beam evaporation, laser deposition, spray pyrolysis, organic chemical vapor deposition, and sputtering. However, the sputtering method takes advantages of relatively high deposition rate and a high uniformity so that this method has been used in large-area and high quality depositions. In this paper, the SnInZnO thin film was deposited with RF magnetron sputtering. We used both REELS spectra and UV-Spectrometer to determine the band gap of the SnInZnO thin films.

Experiments

SnInZnO thin films were deposited on glass substrates at room temperature in argon mixed with oxygen gas (Ar: O₂ = 15: 85) by RF magnetron sputtering with the RF power of 200 W. The target composition ratios of In: Zn: Sn in IZTO thin films is 13: 60.2: 26.8. Thin film was annealed at 350 °C for an hour in air. The band gap of SnInZnO thin films will be examined with two different methods such as REELS spectra and UV-Spectrometer. REELS spectra were obtained by using a VG ESCALAB 210 equipment. The REELS spectra were measured with the primary electron energy of 500 and 1500 eV for excitation and with the constant analyzer pass energy of 20 eV. The full width at half maximum (FWHM) of the elastic peak was 0.8 eV. The transmittance and absorbance spectra of the IZTO thin films were measured by Genesys 6 model from Thermo Electron Corporation in the wavelength range of 300 to 1000 nm at RT at increments of 0.1 nm.

Results and discussion

The basic principle of REELS spectra can be explained in Fig. 1. The REELS spectra consist in bombarding the surface of a sample with a beam of monoenergetic electrons and detecting the energy distribution of the backscattered electrons [4]. The REELS spectra contains of two area, the elastic peak is due to electron that have lost no energy (elastic backscattering electrons) and at lower kinetic energies refer to electrons that have lost part of their energy through electronic excitations or phonons excitations within the solid as being shown in the Schematic of Fig. 1. The losses produced by the interactions with phonons can be observed only if the experimental set-up is high enough. Hence, this study were performed an experimental resolution of typically 0.8 eV, which can be estimated from full width at half maximum (FWHM) of the elastic peak from REELS experiment.

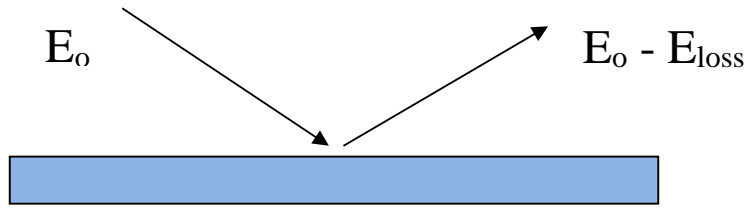


Figure 1. The basic principle of REELS spectra.

The response of a solid to an external field can be characterized by the dielectric response function (\bar{q}, ω) of the solid. The energy loss probability that an electron loses energy and transfers momentum \bar{q} in a single collision in the bulk of the solid is proportional to $1/(q^2)\text{Im}(-1/(\bar{q}, \omega))$. Despite the fact that in a REELS experiment non-zero momentum transfers occurred this technique has been known however shown to be a powerful tool to obtain information on the gap energy of materials oxide. The shape of the loss spectrum corresponding to single losses is in this case identical to that of the optical loss function $\text{Im}(-1/(\bar{q}, \omega))$ and then optical absorption defect related bands can be compared to defect-related losses. The flat part of the loss spectrum near the elastic peak of the REELS spectra is related to the energy gap [5].

REELS spectra of SnInZnO thin films on the glass substrate can be shown in Fig. 2. It shows that REELS spectra contain both elastically backscattered electrons and inelastically backscattered electrons. The kinetic energy corresponds to the energy of electrons that coming out from the surface of thin films. For the elastic peak case, the value of kinetic energy is similar as the primary energy. Thus, there is no loss energy for the elastic peak (zero energy loss). The loss energy can be calculated by subtracting the kinetic energy with the primary energy. In addition, the REELS also consist of the Plasmon peak (known as plasma oscillation) [6]. The Plasmon peak can be explained as follows: the valence electron in a solid can be thought of as a set of coupled oscillators which interact with each other and with reflected or transmitted electron via electrostatic forces. In the simplest situation, the valence electrons behave essentially as free particles and constitute a “free-electron gas” also known as “Fermi sea” or “jellium”. The collective excitation of valence electrons is called plasmon. The long-range Coulomb interactions then make possible collective oscillation of large number of electrons. The plasmon loss signals are observed with a rather broad spectrum shifted toward the lower kinetic energy side of the primary elastic peak by plasmon energy of ~15 eV or more as can be seen from Fig. 2. The plasmons peak show up as broad, smooth replicas of the peaks shifted to lower kinetic energy by an amount equal to the bulk plasmon energy ω_p . In the free-electron approximation, the bulk plasmon energy is related to the valence electron density as $(\omega_p)^2 = (e^2/m)N$, where m is the electron mass, e is the electron charge, and \hbar is Plank’s

constant, the N valence electron density [6]. This peak experimentally can be observed in the REELS spectra.

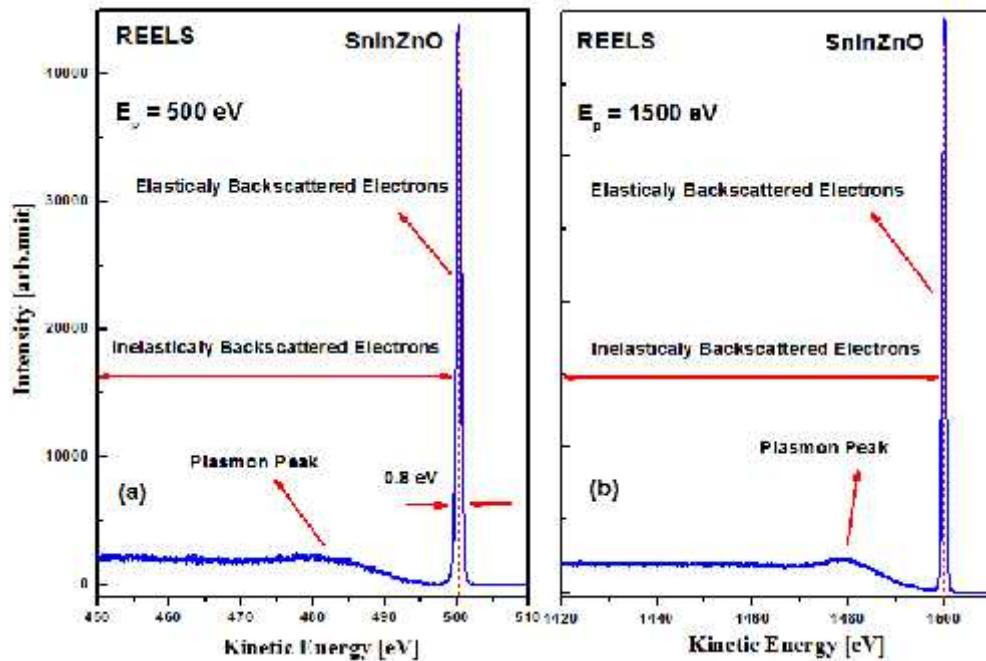


Figure 2. REELS spectra as a function of kinetic energy for different primary energies ($E_p = 500$ dan 1500 eV).

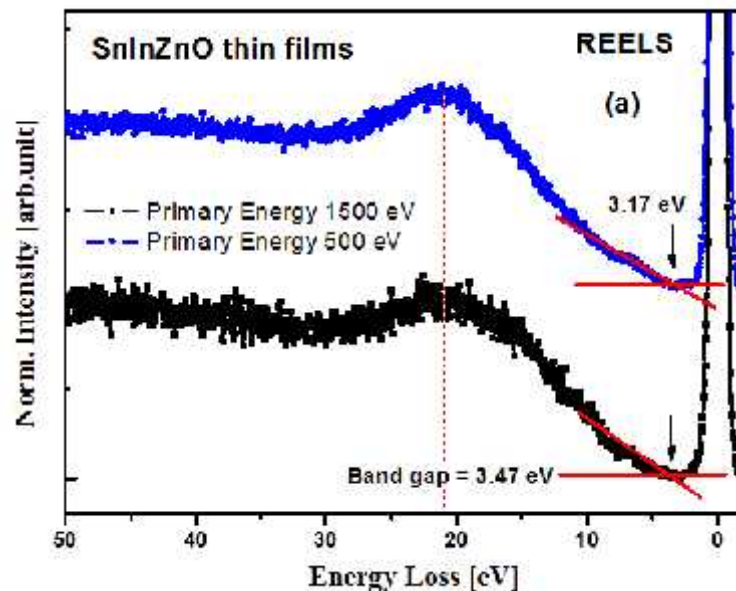


Figure 3. Reflection electron energy loss spectra of SnInZnO thin films in different primary energy of 500 and 1500 eV.

We made use of REELS to investigate the dependence of the band gap energy E_g of SnInZnO thin films with different primary energies. Figure 3 shows the REELS spectra with different primary

energies. As can be seen in Fig. 3, the Plasmon loss peak form SnInZnO thin films located at loss energy of 23 eV and it was no changed correspond to the different primary energy. The REELS spectra were used to estimate the energy band gaps of the SnInZnO thin films by the method described in our previous work [7,8]. The band gap value of the probed region of the excited solid was estimated by the extrapolating the linear part of maximum negative slope to the background level. The onset of the loss signal refers to the band gap value. The result shows that the band gap of SnInZnO thin films were 3.17 and 3.47 eV for the primary energy of 500 and 1500 eV, respectively within the uncertainty of ± 0.1 eV. Previous study reported that the band gap value of ZnO, SnO₂, and In₂O₃ were 3.37, 3.60, dan 3.70 eV, respectively. Hence, the band gap of SnInZnO thin film is closed to the band gap of ZnO. Therefore, in the band structure of of SnInZnO thin film, there will be an upper band level states (known as conduction band) that derived from Zn 2p filled states and an lower band level states that derived from O 2p states (known as valence band) that are partially occupied. This result suggests the band gap value of SnInZnO thin film could be improved by changing the composition ratio of the ZnO. On the other hand, for SnInZnO, the inelastic mean free paths (λ) of electron energy of 500 eV and 1500 eV are 0.5 nm dan 2.2 nm, respectively [8]. Thus, the energy spectrum for 500 eV gives the surface sensitive information. On the other hand, the energy spectrum for 1500 eV gives the bulk sensitive information. By comparing the band gap values with different primary energy, it can be seen that the surface band gap of SnInZnO thin films is about smaller 0.3 eV than that of the bulk band gap. Overall, this result indicates that the band gaps are affected by the primary energy of electron.

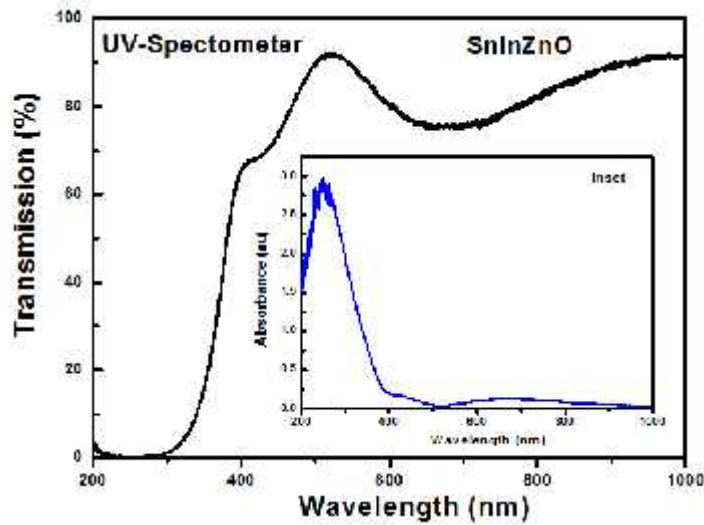


Figure 4. Transmittance spectra of SnInZnO thin films (inset: the absorbance of the film).

For comparison, the band gap was also measured by utilizing a UV-spectrometer. Figure 4 shows the transmittance and absorbance spectra of SnInZnO thin film. The measured transmittance spectra of the films shows that the film is transparent with the transmittance exceeding 80% all over the spectral range 300 to 1000 nm as shown in Fig. 4. The absorbance spectra were used to estimated the absorption coefficient, (α), by the relation [9]:

$$\alpha \omega = \frac{1}{d} \ln \frac{I_0}{I_t} = \frac{2.303A}{d} \quad (1)$$

where d and A are the thickness of the films and absorbance, respectively, also I₀ and I_t are the

intensities of incident and transmitted radiation, respectively. In the high absorption region, (α) 10^4 cm^{-1} , Mott and Davis proposed the following relation for amorphous materials [9]:

$$= A (h\nu - E_{opt})^m \quad (2)$$

where E_{opt} is the optical band gap, $h\nu$ is incident photon energy, and m is the index which can have different values (1/2, 3/2, 2 and 3) corresponding to direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively. A is a constant called the band tailing parameter and is related to speed of light (c), the refractive index (n), the extrapolated D.C conductivity at $T = 0 \text{ K}$, and the band tailing energy (E_e). It was noticed from Fig. 4 (a) that for $m = 2$, the extrapolation of the linear part gives the value of the direct band gap. The value shows that the direct band gap of SnInZnO thin films is about 3.08 eV. In addition, the extrapolation of the linear part of $(\alpha h\nu)^{1/2}$ versus $h\nu$ plot is shown in Fig. 4 (b), the indirect band gap is deduced as 3.48 eV. The values of direct band gap and indirect band gap agree with the reported value of other literatures [10,11]. A comparative study of the band gap by REELS spectra and UV-Spectrometer with the same previous finding is given in Table 1. It can be seen from the data in Table 1 that the band gap obtained from the preliminary analysis of the REELS spectra with the primary energy of 1500 eV is comparable to that of the optical band gap from indirect transitions. Similarly, the band gap from the REELS spectra with the primary energy of 500 eV closed to that of the optical band gap from direct transitions. These findings of this study suggest that the direct band gap from UV-Spectrometer can give the surface band gap information; meanwhile the indirect band gap gives the bulk band gap information.

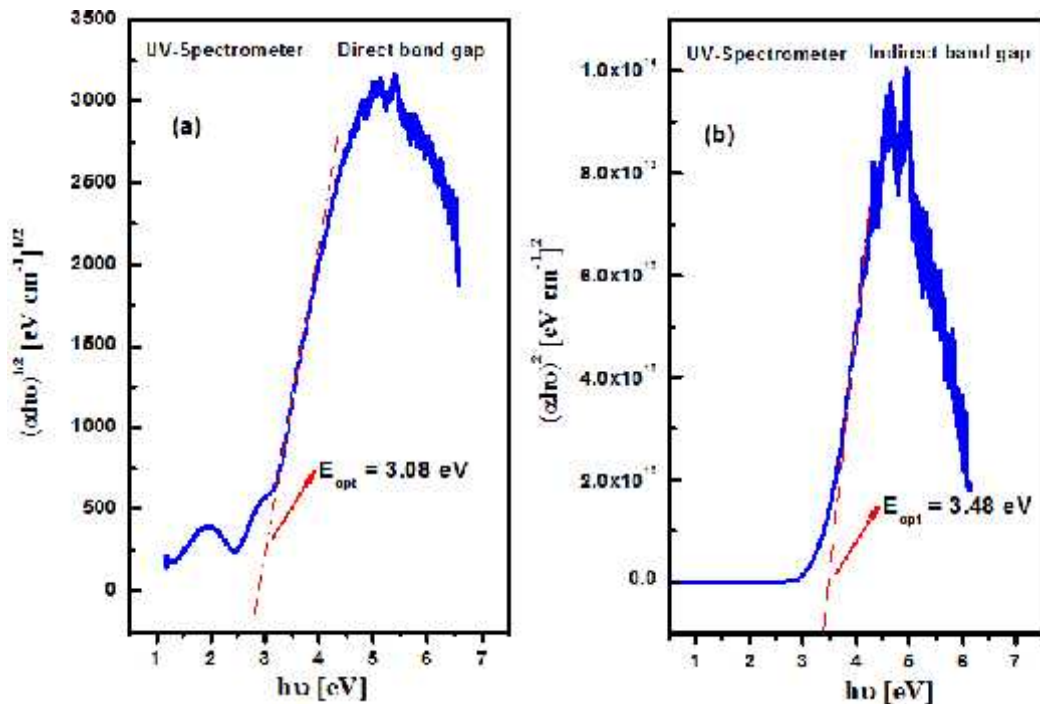


Figure 4. Transmittance spectra of SnInZnO thin films (inset: the absorbance of the film).

Table I. A review of some published data on the optical energy gap and its comparison with the present findings.

Energy Gap (eV)	Method	Preparation technique	Ref.
3.50	Indirect band gap	Electron beam evaporation	[10]
3.00	Direct band gap	Co-sputtered DC Sputtering	[11]
3.44	Indirect band gap	Co-sputtered DC Sputtering	[11]
3.08	Direct band gap	RF magnetron sputtering	Present work
3.48	Indirect band gap	RF magnetron sputtering	Present work
3.17	REELS with $E_p = 500$ eV	RF magnetron sputtering	Present work
3.47	REELS with $E_p = 1500$ eV	RF magnetron sputtering	Present work

Conclusion

In this study, we investigated the band gap of SnInZnO thin film by using different method REELS spectra and UV-Spectrometer. The REELS spectra showed that the band gap values are strongly affected by primary energy. In the visible light region, the transmittance coefficients SnInZnO thin film is approximately 80%. Furthermore, we found that the direct band gap from UV-Spectrometer analysis can give surface band information; meanwhile the indirect band gap gives the bulk band gap information. We believe that our results can be a good guide for those growing SnInZnO thin films with the purpose of device applications, which require TFTs good transparency and a proper the band gap values.

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