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BAND ALIGNMENT OF ULTRATHIN GIZO/SiO_2/Si HETEROSTRUCTURE DETERMINED BY ELECTRON SPECTROSCOPY

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Abstract

Amorphous GaInZnO (GIZO) thin films are grown on SiO_2/Si substrate by the RF magnetron sputtering method. By the combination of measured band gaps from reflection energy loss spectroscopy (REELS) spectra and valence band from X-ray photo-electron spectroscopy (XPS) spectra, we have demonstrated the energy band alignment of GIZO thin films. The band gap values are 3.2 eV, 3.2 eV, 3.4eV and 3.6eV for the concentration ratios of Ga: In: Zn in GIZO thin films are 1:1:1, 2:2:1, 3:2:1 and 4:2:1, respectively. These are attributed to the larger band gap energy of Ga_2O_3 compared with In_2O_3 and ZnO. The valence band offsets (ΔE_v) decrease from 2.18 to 1.68 eV with increasing amount of Ga in GIZO thin films for GIZO1 to GIZO4, respectively. These experimental values of band gap and valence band offset will provide the further understanding in the fundamental properties of GIZO/SiO_2/Si heterostructure, which will be useful in the design, modeling and analysis of the performance devices applications.

Keywords: band alignment, band gap, GIZO, REELS, XPS

1. Introduction

Zinc oxide (ZnO) based semiconductive oxides have been widely used as electrodes in optoelectronic devices, transparent thin film transistors (TFTs), and solar cells. Recently, there have been more extensive investigations and fabrications on ZnO based oxide including other ZnO based compounds such as gallium indium zinc oxide (GIZO), indium zinc oxide (IZO), and zinc cadmium oxide (ZnCdO) [1-5]. In particular, considerable attention to GIZO has led to improvement in analysis of the properties of these materials. GIZO thin films have several advantages. They have high field-effect mobility (>10 cm^2/V s) and are suitable for fabrication in various substrates such as; silicon, glass, plastic, polyimide, polyethylene terephthalate (PET), cellulose paper, and flexible substrates [1-5]. In addition, they have superior uniformity, low processing temperature, possibility of large-area deposition and long term stability, and moreover they are cost effective [4-5].

Kang *et al*. [6] and Tahir *et al.* [7] obtained the optical band gap for a-GIZO while varying the compositions of Ga and Zn by using spectroscopic ellipsometry and reflection electron energy los spectroscopy (REELS), respectively. They showed that the optical band gap was strongly correlated to the electrical performance of a-GIZO thin film transistors, i.e., the turn-on voltage of the drain-source current versus gate voltage increased with the increase of the optical gap energy as the Ga/In ratio increased. In recent years, a large progress has been done toward high performance TFTs based on a-GIZO as channel layers [1-6].

High mobility of GIZO TFTs reported Kang *et al*. [6] could be associated with both the generation of majority carriers in the films and the path formation at the interface heterostructure (band alignment) for carrier transport. Amorphous oxide semiconductors have defect states originating from structural disorder and defect [7], which strongly affects the carrier transport properties and devices performances [8]. The carrier transport strongly influence to the leakage current in devices, which depend on how large the band offset at the interface heterostructure. In general, when the band offset (conduction and valence) of oxide layer on the semiconductor was larger than 1 eV, the leakage current could be reduced significantly [9].

Although the fundamental transport properties, electronic and structural properties of a-GIZO have been reported, many physical properties are still not well understood. Band alignment is one of the physical properties which are essential for the heterojunction materials and useful in the design, modeling and analysis of the performance devices applications have

not been experimentally investigated adequately. Therefore, the investigation of band alignment and electronic properties of GIZO thin films are very important.

XPS and REELS are surface sensitive and they are capable of characterizing the electronic (band gap, valence band and chemical state and electron transition) and optical properties of oxide semiconductor because the low energy loss region reflects the structure of the valence and conduction electrons [10]. REELS has great potentials for determining the band gap of thin films. The experiment is simple and can be performed under ultra high vacuum conditions. In fact, REELS and XPS have previously been successfully used to obtain the electronic of several materials, including ultra thin dielectrics, semiconductor, transparent oxide films, polymers and metal oxides [7-8,11-16].

In the present paper, the valence band maximum was characterized by XPS spectra and the band gap as well as electronic properties we obtained from an analysis of REELS spectra. We report these properties in term of band alignment of GIZO/SiO_2/Si heterostructure thin films.

2. Experiment

GIZO thin films were deposited by RF magnetron sputtering on SiO_2/Si substrates with the rf power of 200 W at room temperature in the argon gas ambience with 1% of oxygen added. The composition ratios of Ga:In:Zn in GIZO thin films were 1:1:1(GIZO1), 2:2:1(GIZO2), 3:2:1(GIZO3), and 4:2:1(GIZO4), which were estimated by using the inductively coupled plasma (ICP) method [6]. The composition ratios were also confirmed with a quantitative analysis of XPS spectra [7]. The physical thickness of deposition for all compositions was 70 nm. To obtain the band alignment and electronic properties of GIZO thin films, XPS and REELS experiments were carried out by using the VG ESCALAB 210. XPS spectra were measured using an Al source and the analyzer pass energy of 20 eV. The incident and take-off angles of electrons for both REELS and XPS were 55^o and 0^o from the surface normal, respectively. XPS binding energies were referenced to C 1s peak of carbon contamination at 285eV. REELS were measured with the primary electron energy of 1.5 keV 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.

3. Results and Discussion

In REELS system, the exited electrons passing through oxide thin films can suffer inelastic losses due to Plasmon and band-to-band excitations. The Plasmon

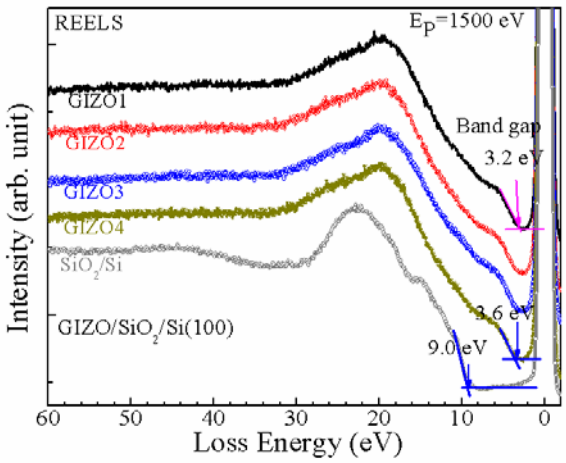

Figure 1. REELS Spectra of GIZO and SiO_2 for Primary Energies of 1500 eV

loss energy is observed with a rather broad spectrum ~18 eV for GIZO or more for SiO_2. The electron excitation from the valence to conduction bands is also measured in the energy region separated from the elastic peak by the corresponding loss energy. Thus, the band gap energies for oxide thin films can be determined from the threshold energy of the energy loss spectrum.

Figure 1 show REELS spectra for GIZO thin films. The arrow in each spectrum shows the threshold energy of band-to-band excitation, i.e., the band gap energy, which is defined as an intercept of the line with a maximum negative slope near the edge to the background level, indicated with the horizontal line. The crossing point gives the band gap value. The method was described in our previous paper [7-8,11,13-16]. The band gap values for GIZO1, GIZO2, GIZO3 and GIZO4 are 3.2eV, 3.2eV, 3.4eV and 3.6eV, respectively. The band gap values for GIZO1, GIZO2, GIZO3 and GIZO4 obtained by using spectroscopic ellipsometry are 3.17eV, 3.14eV, 3.22 eV and 3.36 eV respectively [6]. The band gap values for GIZO1 and GIZO2 are almost same, but for GIZO3 and GIZO4 are about 0.2 eV smaller than that obtained from REELS spectra. Details about the band gap from REELS spectra and composition from XPS spectra of GIZO thin films on SiO_2/Si(100) can be found in Tahir *et al*. [7]. The band gap depends on the ratio of Ga to In in GIZO thin films. This phenomenon can be explained in term of the increase of Ga_2O_3 phase with the increase in the Ga content because the band gap of Ga_2O_3 is about 4.9 eV, which are larger than that of In_2O_3 and ZnO (see Ref. [7] for detail explanation). Ga/In ratio of the GIZO films plays an important role in the band gap energy, refractive indexes and device performance [6].

Figure 2 shows the valence band spectrum GIZO/SiO_2/Si heterostructure by using reference spectra which were separately measured for SiO_2/Si substrate.

The valence band maximum (VBM) is determined from the intersection of two straight lines, where one line fits the valence band leading edge while the other line fits the background [17-19]. The valence band offset (ΔE_v) at the interface of GIZO and SiO_2 is the energy difference between VBM of SiO_2/Si and VBM of GIZO/SiO_2/Si heterostructure as shown in the insert of Fig. 2 for GIZO4. The valence band maximum of Si is positioned at 0.24 eV.

The VBM increase with increasing the amount of Ga in GIZO films are indicated the surface Fermi level shifted toward conduction band [9]. This result was attributed to decrease of the valence band offset with increasing the amount of Ga in GIZO thin films. The valence band offsets (ΔE_v) are 2.18, 1.98, 1.78, and 1.68 eV for GIZO1, GIZO2, GIZO3, and GIZO4, respectively.

The band gap and valence band offset (ΔE_v) allow us to determine the conduction band offset (ΔE_c) by using relation: $\Delta E_c = E_g(SiO_2) - \Delta E_v(GIZO/SiO_2/Si) - E_g(GIZO)$ [17-19]. The conduction band offset of GIZO1, GIZO2, GIZO3, and GIZO4 are 3.62 3.82, 3.82, and 3.72 eV, respectively. The band alignment parameters for these GIZO are listed in Table 1. By considering the measured GIZO band gap value in Figure 1, the valence band in Figure 2, and the conduction band offset in Table 1, the

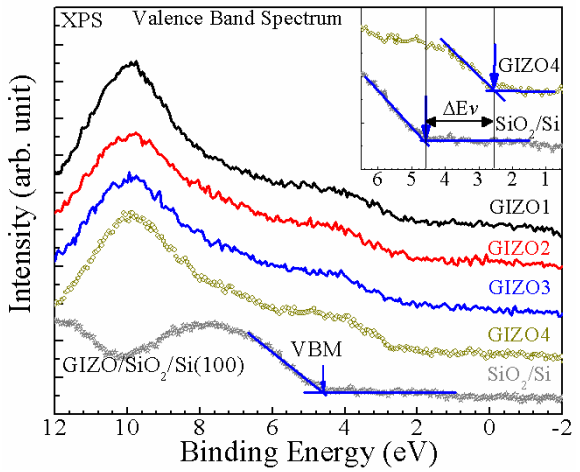

Figure 2. Valence Band Spectra for GIZO and SiO_2 Thin Films, the Insert Figure Shows Valence Band Offset (ΔE_v) of GIZO4 Thin Films

Table 1. Band Gap (E_g), Valence Band Maximum (VBM), Valence Band Offset (ΔE_V), and Conduction Band Offset (ΔE_c) of GIZO Thin Films

Sample	E_g (eV)	VBM (eV)	ΔE_V (eV)	ΔE_c (eV)
GIZO1	3.2	2.1	2.18	3.62
GIZO2	3.2	2.3	1.98	3.82
GIZO3	3.4	2.5	1.78	3.82
GIZO4	3.6	2.6	1.68	3.72

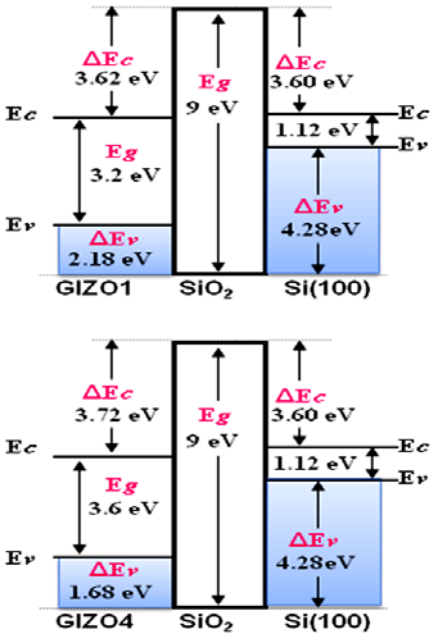

Figure 3. Energy Band Diagram for Thin Films of GIZO1 on SiO_2/Si(100) Substrate and GIZO4 on SiO_2/Si(100) Substrate

band diagram of GIZO1 and GIZO4 can be drawn as display in Figure 3. The energy band lineup between GIZO, SiO_2 and Si(100) as confirmed by the analysis the valence band spectrum of GIZO/SiO_2/Si(100) heterostructure.

4. Conclusion

In summary, we investigated the band gap and valence band via REELS and XPS analysis, respectively. The results showed the band gap increases from 3.2 eV to 3.6 eV with increasing amount of Ga atoms in the GIZO thin films but the valence band offsets (ΔE_v) decrease from 2.18 to 1.68 eV with increasing amount of Ga in GIZO thin films for GIZO1 to GIZO4, respectively. Also, we demonstrated the determination of the energy band profiles of thin films GIZO/SiO_2/Si hetero-structure, which will be useful in the design, modeling and analysis of the performance devices applications.

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