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Blue shift in the optical band gap of amorphous Hf–In–Zn–O thin films deposited by RF sputtering

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ABSTRACT

Amorphous Hf–In–Zn–O (*a*-HIZO) thin films were grown by radio frequency (RF) magnetron sputtering in a mixed atmosphere of Ar and O_2 at fixed 5 mTorr working pressure. A 13% enhancement (blue shift) in band gap from 3.59 eV to 4.06 eV was obtained as O_2/Ar flow ratio increased from 5% to 50%. *a*-HIZO films deposited at higher O_2/Ar gas flow ratio were more resistive. Oxygen-incorporation-induced reduction of oxygen vacancies is suggested to explain the band gap and resistivity increase.

1. Introduction

Recently, oxide semiconductors such as amorphous In–Ga–Zn–O (*a*-IGZO) and amorphous Hf–In–Zn–O (*a*-HIZO) are subject of intensive investigation due to their high potential for thin film transistor (TFT) applications in flat panel displays [1–4], because of their relatively high field effect mobility values above 5 cm^2/V s compared to those of amorphous Si counterparts (0.5 cm^2/V s). *a*-HIZO TFTs have shown good electrical performance and stability under long-term bias stresses. *a*-HIZO has a sufficient on-to-off ratio compared with *a*-IGZO TFT [5]. In *a*-HIZO, compared to Ga (electronegativity, EN = 1.81) in *a*-IGZO, Hf (EN = 1.30) can form stronger chemical bonds with O (EN = 3.44) due to high electronegativity difference with O and hence may play an important role in the suppression of charge carrier generation, i.e., suppression of the formation of oxygen vacancies [6,7]. Hf may also suppress the carrier generation more readily due to the lower standard electrode potential (−1.70 V) than that of Ga (−0.52 V) [5]. Thus, it may be interesting to investigate how Hf atoms control the net electron carrier density in *a*-HIZO thin films as well as how Hf atoms improve the stability of TFTs, which can be enhanced by the Hf atom's high oxygen bonding ability [8] and lower standard electrode potential [5].

For device application it is important to tune the band gap during the deposition process. The band gap of the films is generally affected by preparation conditions such as deposition methods, working pressure, substrate temperature, types of substrate, thickness of films and O_2/Ar flow ratio. O_2/Ar flow ratio is one of the most significant parameters to tune the optical band gap. Kim et al. [9] have reported the influence of O_2/Ar flow ratio on the performance and stability of HIZO TFTs under illumination. Jeong et al. [10] have also reported the effect of Hf on the optical band gap of HIZO TFTs. However, still, current understanding of the detailed tuning of the band gap with O_2/Ar flow ratio for *a*-HIZO films is incomplete.

Here we present unreported engineering of optical band gap in *a*-HIZO thin films with O_2/Ar flow ratio. We provide the synthesis details, sheet resistivity and optical band gap variation of *a*-HIZO thin films with O_2/Ar flow ratio from 5% to 50%. It was found that O_2/Ar flow ratio changed the sheet resistivity and optical band gap of *a*-HIZO thin films. The increase of optical band gap and sheet resistivity was suggested to be related with oxygen-incorporation-induced reduction of oxygen vacancies.

2. Experimental

80 nm-thick *a*-HIZO films were grown onto *p*-type Si wafers (for AFM, XRD, XRR, sheet resistivity measurements) and Corning glass (for transmittance measurement) substrates by RF magnetron sputtering, using a single target (with composition HfO_2:In_2O_3:ZnO = 1:1:1 mol%). The deposition was done at room temperature in a

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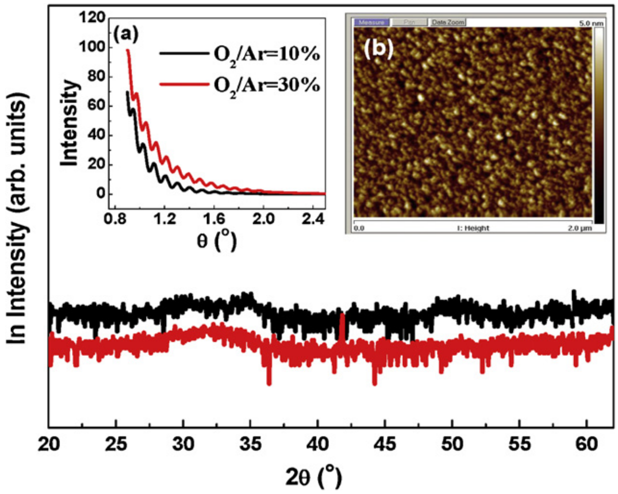

Fig. 1. XRD patterns of amorphous Hf–In–Zn–O (*a*-HIZO) thin films. The inset (a) shows XRR pattern of *a*-HIZO thin films deposited at 10% and 30% of O_2/Ar ratio, and inset (b) shows AFM pattern of *a*-HIZO thin films deposited at 10% of O_2/Ar ratio.

mixed atmosphere of Ar and O_2 at fixed total pressure of 5 mTorr, where the O_2/Ar gas flow ratio was varied from 5% to 50%. The amorphous nature of *a*-HIZO thin films was investigated using high-resolution X-ray diffraction (HR-XRD) with $\lambda = 1.5425$ Å at the 10B KIST-PAL beamline of the Pohang Light Source (PLS). The thickness of all the films was calculated by using X-ray reflectivity (XRR) measurement at the PLS's 3C2 beamline.

3. Results and discussion

Fig. 1 shows the XRD patterns for the films deposited at O_2/Ar gas flow ratio, 10% and 30%. The patterns show no characteristic peaks of In_2O_3, HfO_2, ZnO or Hf–In–Zn–O, confirming that these films were amorphous in nature. The XRR interference patterns for these 10% and 30% films are shown in inset (a) of Fig. 1. The estimated thickness of these films from the period of interference patterns was approximately equal to 80 nm. The XRD patterns and the XRR period of interference patterns for the other thin films were almost similar to those of the above films (results not shown here). The XRR patterns also indicate that the deposited films were highly smooth, which was consistent with the AFM results. An AFM image of the thin film deposited at 10% O_2/Ar ratio is shown in the inset (b) of Fig. 1. The root mean square roughness values were 0.19, 0.39, 0.88, 1.58, 2.42 and 2.87 nm for the thin films grown at 5%, 10%, 15%, 20%, 30% and 50% O_2/Ar ratio, respectively. At high O_2/Ar ratio the sputtered atoms or clusters would reach the substrate with reduced kinetic energies, which may explain the observed roughness increase.

The normal incidence transmission spectra of the substrate with and without *a*-HIZO thin films were measured by a spectrophotometer (Varian-Cary100), in the transmission range of 200–800 nm. Fig. 2 shows the optical transmittance for the films deposited at different O_2/Ar gas flow ratio. The average transmittance for all thin films in the visible range was higher than 85%. The inset of Fig. 2 shows that the absorption edge was shifted toward shorter wavelength at higher O_2/Ar gas flow ratio.

The absorption coefficient α can be calculated from Beer's law

$$I = I_o e^{-\alpha d} \qquad (1)$$

where I is the transmitted intensity, I_o is the incident intensity and d is the thickness of the thin film. In a direct transition semiconductor, the absorption coefficient α and optical band gap (E_g) are related

$$(\alpha h\nu)^2 = \beta(h\nu - E_g) \qquad (2)$$

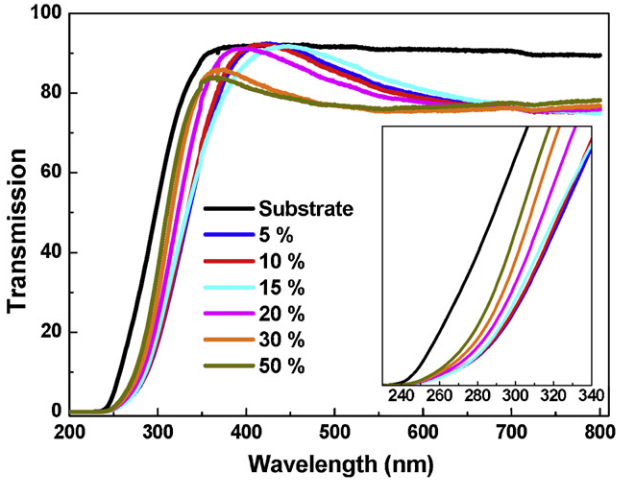

Fig. 2. Variation of transmittance with wavelength at different O_2/Ar ratio.

where h is Planck's constant, β is energy independent constant and ν the frequency of incident photon. The E_g can be obtained by extrapolating the straight line portion of $(\alpha h\nu)^2$ vs. $h\nu$ plot to the energy axis [11]. The relationship between $(\alpha h\nu)^2$ and $h\nu$ for *a*-HIZO films deposited at various O_2/Ar gas flow ratio is shown in Fig. 3. The inset of Fig. 3 clearly shows that band gap increased with the O_2/Ar gas flow ratio. Burstein [12] suggested that for degenerate semiconductors the optical band gap increases with increase in carrier density [13], which is not likely applicable to our study as discussed below.

Recently Kamiya et al. [14] reported that oxygen vacancies in amorphous oxide semiconductors form defect levels within the band gap based on first principle calculations. The oxygen vacancies can act as shallow donors and supply conduction electrons in *a*-HIZO films, meanwhile the vacancies or defects can also act as scattering centers, reducing some amount of charge carrier conduction [15]. The oxygen vacancies and surface defect states can also induce deep subgap state (DSS) [16–18]. The density of the DSS was estimated to be $\sim 10^{21}/\text{cm}^3$ [18], which may effectively increase the charge carrier density. From the above considerations, we may suggest that the increase of O_2/Ar gas flow ratio would lead to decrease of oxygen vacancies and therefore the carrier density. Our resistivity measurements using a conventional four-probe method showed that resistivity increased from $7.5 \times 10^1\ \Omega$ cm to

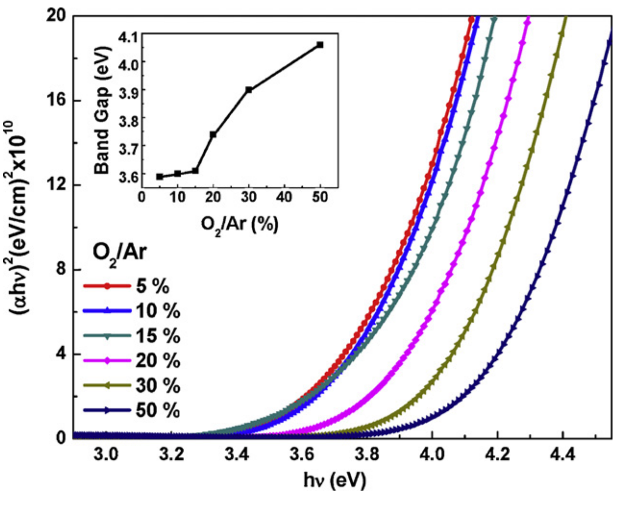

Fig. 3. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for *a*-HIZO thin film at different O_2/Ar ratio. The inset shows the variation of band gap with O_2/Ar ratio.

$5.7 \times 10^3\ \Omega$ cm as O_2/Ar ratio increased from 5% to 50%, confirming that higher O_2/Ar gas flow ratio effectively resulted in lower charge carrier density and therefore higher resistivity.

The band gap increase at higher O_2/Ar gas flow ratio may also be understood by the higher oxygen environment than that with lower oxygen gas flow. Thin films deposited with higher O_2/Ar gas flow ratio have higher oxygen incorporation because the impinging rate of the sputtered particles at the substrate drops and, thus, the oxidation efficiency increases [19]. Thus, besides the reduction of charge carrier density by the decrease of oxygen vacancy, the oxygen incorporation also makes more oxidized *a*-HIZO [1,20]. Orikasa et al. [21] has also reported that $(ZnO)_3In_2O_3$ thin films becomes more oxidized at higher oxygen contents, resulting in reduction of oxygen vacancies and increase in the band gap. The oxygen incorporation particularly with Hf would form stronger bonding configuration which would then result in larger separation of energy band and the increase in the energy gap [22]. Considering the ZnO (~3.3 eV), In_2O_3 (~3.6 eV), and HfO_2 (~5.7 eV) optical band gaps [10], the observed band gaps (shown in Fig. 3) maybe within a reasonable range.

4. Conclusion

In conclusion, we present that a 13% enhancement and hence a blue shift in optical band gap in *a*-HIZO thin films can be realized by varying O_2/Ar gas flow ratio from 5% to 50%. All the films are amorphous in nature and have a smooth surface. Oxygen incorporation-induced reduction of oxygen vacancies is suggested to be the cause of the band gap and resistivity increase. The controllability of band gap tuning by using deposition condition may add one advantageous feature for the potential TFT material.

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