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The effects of high-energy electron beam irradiation on the properties of IGZO thin films prepared by rf magnetron sputtering

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This work demonstrates that high-energy electron beam irradiation (HEEBI) performed in air at room temperature (RT) affected remarkably the properties of indium-gallium-zinc oxide (IGZO) films grown on glass substrates at RT by radio frequency magnetron sputtering techniques. Hall, photoluminescence, and X-ray photoelectron spectroscopy (XPS) measurements revealed that the *n*-type conductivity was preserved in HEEBI treated films with a low dose of 10^{14} electrons/cm^2 and converted to *p*-type conductivity with further increase in the amount of dose, which was attributed to the strong reduction of donor-like oxygen vacancy defects as a result of formation of either oxygen interstitial or zinc vacancy acceptor defects. In addition, Hall and XPS results revealed that the mobility and the amount of In compared to Ga decreased for films treated by HEEBI with a low dose while they increased for those with a high dose. The halo peak at around 34 $^{\circ}$ observed from X-ray diffraction analysis is attributed to the amorphous IGZO films, indicating that all films prepared in this study have an amorphous structure. These results would contribute to developing high-quality IGZO-based materials and devices for space applications.

Key words: Indium-gallium-zinc oxide (IGZO) films, High-energy electron beam irradiation (HEEBI), Radio frequency (rf) magnetron sputtering, Photoluminescence, Hall measurements, X-ray photoelectron spectroscopy.

Introduction

Nowadays, indium-gallium-zinc oxide (IGZO) thin films have attracted tremendous attention as high performance active materials for active matrix organic light emission diode (AMOLED) driving transparent thin film transistors (TTFTs) because of their high field-effect mobility, atmospheric stability, excellent uniformity, good transparency to visible light, amorphous nature, and low fabrication temperature [1-8].

On the other hand, recently, it was demonstrated that the optical, structural, and electrical properties of GaN [9, 10], undoped ZnO [11-15], and Al-doped ZnO films [16, 17] had been changed remarkably by treatment with high-energy electron beam irradiation (HEEBI) at room temperature (RT). Furthermore, high-performance, stable oxide TTFTs are required in a high radiation environment, such as X-rays, gamma-rays, electron beams, etc., which suggests that researches on the variation of the electrical, optical, and structural properties in the radiation environment are very important for space application of IGZO based materials and devices [12]. However, in the case of IGZO thin films, there is, at present, no detailed information in the literature on demonstrating a systematic study of the effects of HEEBI treatment at RT on the properties of IGZO thin films grown by a radio-frequency (rf) magnetron sputtering. Therefore, we demonstrated in this study the effects of HEEBI on the electrical, optical, and structural properties of IGZO films grown on the glass substrate at RT with an rf magnetron sputtering technique.

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Experimental

IGZO thin films were deposited onto 400-nm-thick alkaline-free glass substrates by rf magnetron sputtering from IGZO (In_2O_3 : Ga_2O_3 : ZnO = 1 : 1 : 1 at %) target. The mixtures of 99.999% pure Ar and O_2 gases were used as the reaction gases. The O_2 fraction [O_2/(O_2 + Ar)] and the total gas pressure were 0.2 and 0.5 mTorr, respectively. The substrate was rotated at 10 rpm and unheated during deposition. The IGZO target power was fixed at 400 W. Typical film thicknesses were around 30-100 nm. Then IGZO thin films were treated by HEEBI in air at RT with electron beam energy of 0.8 MeV and doses in range from

Table 1. Summary of the Hall measurement results at RT for a series of IGZO films prepared in this study.

Sample description	Resistivity (Ωcm)	Carrier concentration ($1/cm^3$)	Mobility (cm^2/Vs)	Type of conductivity
As-grown IGZO films untreated with HEEBI	11.2	3.80×10^{16}	14.7	n
HEEBI treated IGZO films with a dose of 10^{14} electrons/cm^2	20.6	1.37×10^{17}	2.21	n
HEEBI treated IGZO films with a dose of 10^{16} electrons/cm^2	40.3	1.62×10^{16}	9.55	p

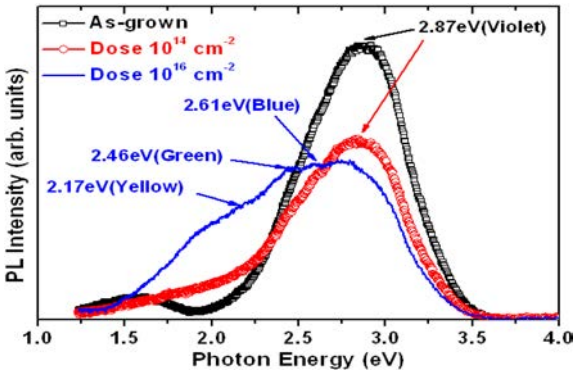

Fig. 1. RT PL spectra of IGZO films prepared in this work: the open square symbol is for as-grown films untreated with HEEBI, the open circle symbol is for HEEBI treated films with a low dose of 10^{14} electrons/cm^2, and the solid line is for HEEBI treated films with a high dose of 10^{16} electrons/cm^2.

1×10^{14} to 1×10^{16} electrons/cm^2.

The electrical properties of IGZO films were measured at RT by Hall measurements system using a van der Pauw configuration after Ohmic contacts were formed by coevaporation of a 50-nm-thick Ni and a 100-nm-thick Au, followed by alloying at 450 °C in N_2 for 1 min. The Hall measurements were repeated more than ten times with a special care for each film in order to obtain reliable results. They were very carefully performed to understand in particular the conduction type or the polarity of Hall voltage using small applied voltages so that we can avoid errors arising from the thermal effects caused by local heating at the contacts and/or high-resistance regions. We also changed the magnetic field in the opposite direction to check the changes of polarity of Hall voltage. Furthermore, we ensured that the observed current (~ 1 nA) is much less than the measure limit of 100 mA for Hall measurements. The optical properties of the films were analyzed by photoluminescence (PL) measurements at RT using a He-Cd 325 nm laser as the excitation source. X-ray photoelectron spectroscopy (XPS) measurements were conducted to examine the contents (at. %) and the chemical bonding states of In, Ga, Zn, and O in IGZO films treated with HEEBI at RT. The structures and surface morphologies of the films were characterized by x-ray diffraction (XRD) with a Cu $K\alpha_1$ radiation source ($\lambda = 0.15406$ nm) and field emission scanning electron microscope (FE-SEM), respectively.

Results and Discussion

Table 1 summarizes the Hall measurement results for a series of IGZO films prepared with an O_2 fraction of 0.2, indicating that the n-type conductivity was preserved in HEEBI treated films with a low dose of 10^{14} electrons/cm^2 and converted to *p*-type conductivity with further increase in the amount of dose. It is also shown in Table 1 that as the dose of irradiation is increased, the decrease in the product of the mobility (μ) and the carrier concentration (n) takes place, resulting in the increase in the resistivity (ρ) on the basis of the relation $\rho = 1/(nq\mu)$, where q is the charge of electron. It has been reported that when selecting a channel material for a TTFT, important considerations are the need for high carrier mobility (≥ 10 cm^2/Vs) and controllable and low carrier concentration ($\leq 10^{17}$ cm^{-3}) [1, 18, 19]. Thus, it was suggested from Table 1 that the high dose of 10^{16} electrons/cm^2 in HEEBI process played a key role in realizing a *p*-type channel IGZO film.

Fig. 1 illustrates the RT PL spectra of IGZO films prepared in this work. For as-grown IGZO films untreated with HEEBI, a dominant violet emission (VE) peak at 2.87 eV is observed. The VE peak at 2.87 eV is related to a transition between the shallow donor level of zinc interstitial (Zn_i) [12, 20-22] (or double ionized oxygen vacancy (V_o^{2+}) [23]) and the valence band. This suggests that all as-grown samples revealed *n*-type conductivity as evident in Table 1. After HEEBI treatment with a low dose of 10^{14} electrons/cm^2, *n*-type conductivity was still maintained, whereas the intensities of all PL peaks observed in as-grown films were reduced. The additional strong yellow emission (YE) peak at 2.17 eV, a dominant blue emission (BE) peak at 2.61 eV, and a green emission (GE) peak at 2.46 eV were exhibited for IGZO films treated by HEEBI with a high dose of 10^{16} electrons/cm^2. Here YE peak at 2.17 eV, BE peak at 2.61 eV, and GE peak at 2.46 eV are ascribed to a recombination between free electrons and deep acceptor defect levels (i.e., oxygen interstitial (O_i)) [21, 24, 25], a transition between the conduction band and the shallow acceptor level of zinc vacancy (V_{zn}) [12, 24, 25], and a single ionized V_o level (V_o^+) [21, 26, 27]. In the case of IGZO films treated by HEEBI with a high dose, it is noticeable from Fig. 1 that the outstanding difference depending on HEEBI treatment seems to be the appearance of strong YE and BE. Hence, we suggest that *p*-type

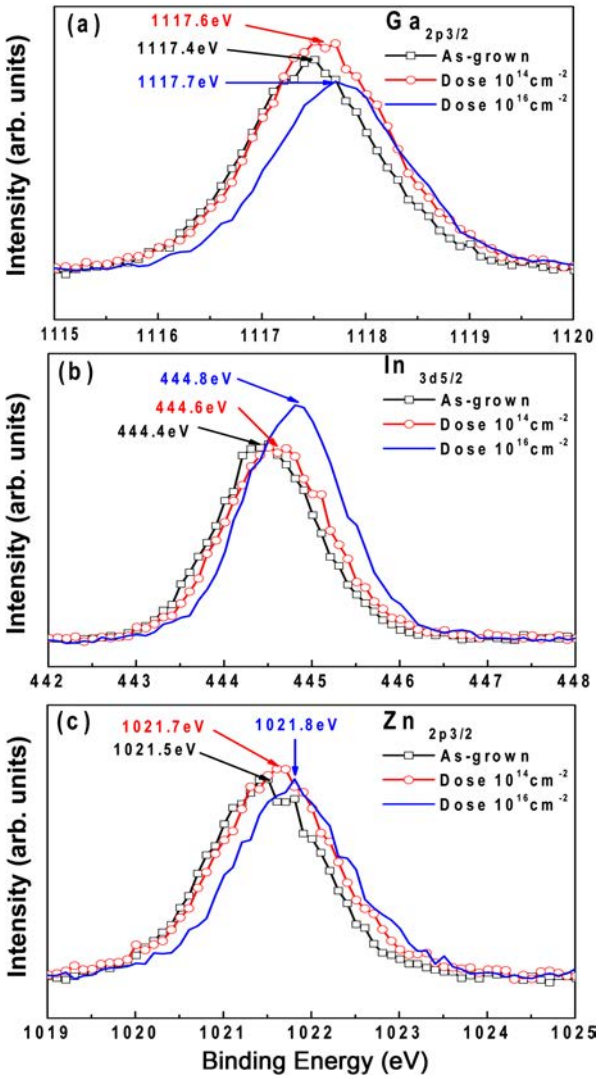

Fig. 2. (a) $Ga_{2p3/2}$, (b) $In_{3d5/2}$, and (c) $Zn_{2p3/2}$ narrow scan XPS spectra of IGZO films prepared in this work: the open square symbol is for as-grown films untreated with HEEBI, the open circle symbol is for HEEBI treated films with a low dose of 10^{14} electrons/cm^2, and the solid line is for HEEBI treated films with a high dose of 10^{16} electrons/cm^2.

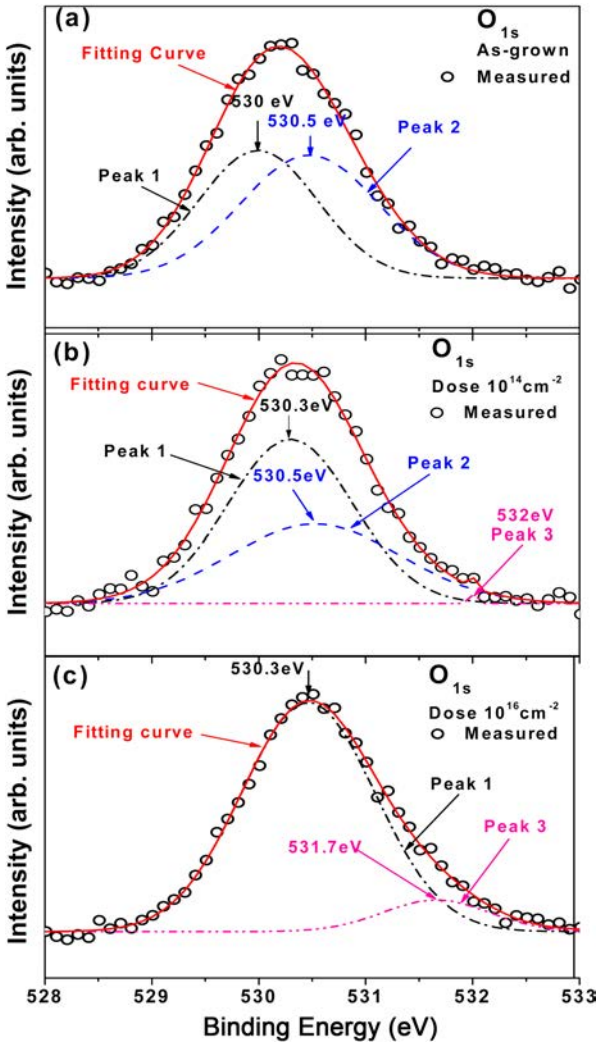

Fig. 3. O_{1s} narrow scan XPS spectra of (a) as-grown IGZO films untreated with HEEBI, (b) HEEBI treated IGZO films with a low dose of 10^{14} electrons/cm^2, and (c) HEEBI treated IGZO films with a high dose of 10^{16} electrons/cm^2. The O_{1s} peaks were fitted by two or three Gaussian peaks (GPs).

conductivity can be realized for films treated by HEEBI with a high dose due to a result of formation of O_i and V_{zn} acceptor defects as well as the density of O_i and V_{zn} acceptor defects, as evident in Table 1.

Raw XPS data indicated that considerable electrostatic charging took place because of the nonconducting substrates used. Therefore, we calibrated the observed spectra taking C_{1s} peak (284.6 eV) as the reference. The XPS data revealed that the chemical compositions of the films untreated, the films treated by HEEBI with a low dose of 10^{14} electrons/cm^2, and those with a high dose of 10^{16} electrons/cm^2 were In : Ga : Zn : O = 16 : 25.82 : 8.98 : 49.2, 14.67 : 26.34 : 8.8 : 50.19, and 18.92 : 22.79 : 8.91 : 49.39 in atomic percentage ratio, respectively. This XPS result and Hall data (see Table 1) suggest that the mobility and the amount of In compared to Ga decreased for films treated by HEEBI with a low dose while they increased for those with a high dose, indicating that the mobility increases with increasing the amount of In.

Fig. 2 shows the calibrated results of XPS analyses for $Ga_{2p3/2}$, $In_{3d5/2}$, and $Zn_{2p3/2}$ obtained from as-grown and HEEBI treated IGZO films. As is shown, for as-grown IGZO films untreated with HEEBI, a $Ga_{2p3/2}$ peak at 1117.4 eV, an $In_{3d5/2}$ peak at 444.4 eV, and a $Zn_{2p3/2}$ peak at 1021.5 which correspond to In-In, Ga-Ga, and Zn-Zn bonds, respectively [1, 28], are observed. These peaks at 1117.4, 444.4, and 1021.5 eV shifted to higher binding energies such as 1117.7, 444.8, and 1021.8 eV, which are attributed to In-O, Ga-O, and Zn-O bonds, respectively [1] as a consequence of HEEBI treatment with a high dose. Hence, we suggest that HEEBI treatment with a high dose causes either O_i formation due to in-diffusion of O from the ambient or V_{Zn} formation due to out-diffusion of Zn from the films. This result confirms that *p*-type con-

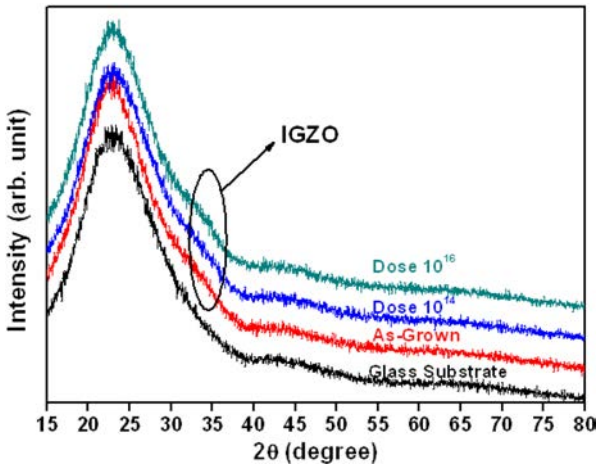

Fig. 4. XRD patterns of IGZO films and glass substrates used in this work.

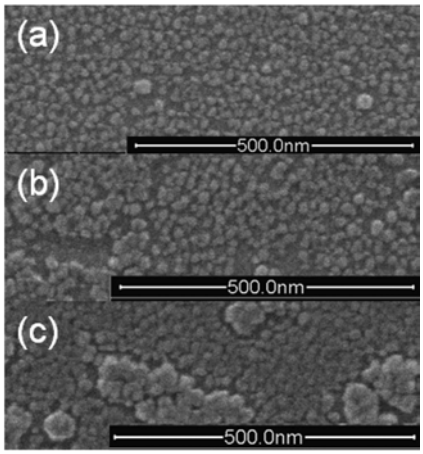

Fig. 5. SEM top images of IGZO films prepared in this work as a function of the dose of irradiation; (a) dose = 0 (as-grown films), (b) dose = 10^{14} electrons/cm^2, and (c) dose = 10^{16} electrons/cm^2.

ductivity can be realized for films treated by HEEBI with a high dose, as evident in Table 1 and Fig. 1.

Fig. 3 also shows the results of XPS analyses for O_{1s} obtained from all samples prepared in this study. The O_{1s} peak was fitted by two or three Gaussian peaks (GPs). For as-grown IGZO films, two dominant GPs at 530 (peak 1) and 530.5 eV (peak 2), which are respectively attributed to O^{2-} ions in the wurtzite structure of hexagonal Zn^{2+} ion array, surrounded by In, Ga, and Zn atoms [1, 5, 7, 21] and O^{2-} ions in oxygen deficient regions within the IGZO matrix [5, 7, 21], were observed. These results suggest that all as-grown samples have ionized V_o (due to peak 2) and reveal *n*-type conductivity as evident in Table 1. After HEEBI treatment with a low dose, the intensity of a GP at 530.5 eV (peak 2) was reduced while that at 530. 3 eV (peak 1) was enhanced. We believe that the origin of GP at 530.3 eV is the same as that at 530 eV because peaks in the range of 529.8 - 530.3 eV are usually assigned to O^{2-} ions in the wurtzite structure of hexagonal Zn^{2+} ion array, surrounded by In, Ga, and Zn atoms [1, 5, 7]. Moreover, additional weak GP at around 532 eV (peak 3) which is associated with loosely bound oxygen on the surface of film belonging to O-H bonding [5] was barely observed. These suggest that donor-like V_o defects are decreased by acceptor-like O_i formation due to in-diffusion of O from the ambient. For IGZO films treated by HEEBI with a high dose, however, a GP at 530.5 eV (peak 2) was vanished while a dominant GP at 530.3 eV (peak 1) and an enhanced GP at 531.7 eV (peak 3) were exhibited, indicating that *p*-type conductivity can be realized for films treated by HEEBI with a high dose due to strong reduction of donor-like V_o defects as a result of formation of O_i acceptor defects, as evident in Table 1.

Fig. 4 shows XRD patterns of IGZO films and glass substrates used in this work. As shown in Fig. 4, two halo peaks at around 22 ° and 43.3 °, which were from glass substrates, were observed. The additional halo peak at around 34 ° was also exhibited only in IGZO films and its intensity increased slightly with the increase of an irradiation dose. These indicate that the halo peak at around 34 ° is attributed to IGZO films and all IGZO films prepared in this study have an amorphous structure. The angles and the widths of halo peaks observed in Fig. 4 are in good agreement with those in the previous results in Refs. [4] and [6].

Fig. 5 shows the SEM top images of IGZO films prepared in this work as a function of the dose of irradiation. As can be seen, HEEBI treated films with a low dose had the smooth morphologies while those with a high dose had the rough surface morphologies. We can suggest that the rough morphologies in IGZO films treated by HEEBI with a high dose are due to the surface crystallization that occurred by high dose on the IGZO surface. However, we concluded that the surface crystallization due to high dose didn't cause the increase of grain sizes inside the HEEBI treated films with a higher dose because IGZO films had an amorphous structure regardless of the dose of irradiation, as evident in Fig. 4.

Conclusions

In this study, we investigated the effects of HEEBI on the electrical, optical, and structural properties of IGZO films grown on the glass substrate with an rf magnetron sputtering technique. Hall, PL spectra, and XPS measurements revealed that the *n*-type conductivity was preserved in HEEBI treated films with a low dose of 10^{14} electrons/cm^2 and converted to *p*-type conductivity with further increase in the amount of dose due to strong reduction of donor-like V_o defects as a result of formation of either O_i (due to in-diffusion of O from the ambient) or V_{zn} (due to out-diffusion of Zn) acceptor defects. XPS and Hall results also indicate that the mobility of IGZO films increases with

increasing the amount of In. XRD results showed that the halo peak at around 34 ° was attributed to IGZO films and the amorphous structure of IGZO films was preserved in HEEBI treated films. It is also concluded from SEM result that the high irradiation dose causes the surface crystallization on the IGZO surface, which results in the rough morphologies on the film surface.

Acknowledgements

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