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Ultrawide band gap amorphous oxide semiconductor, Ga–Zn–O

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ABSTRACT

We fabricated amorphous oxide semiconductor films, a-$(Ga_{1-x}Zn_x)O_y$, at room temperature on glass, which have widely tunable band gaps (E_g) ranging from 3.47–4.12 eV. The highest electron Hall mobility ~7 $cm^2 V^{-1} s^{-1}$ was obtained for E_g = ~3.8 eV. Ultraviolet photoemission spectroscopy revealed that the increase in E_g with increasing the Ga content comes mostly from the deepening of the valence band maximum level while the conduction band minimum level remains almost unchanged. These characteristics are explained by their electronic structures. As these films can be fabricated at room temperature on plastic, this achievement extends the applications of flexible electronics to opto-electronic integrated circuits associated with deep ultraviolet region.

1. Introduction

Amorphous oxide semiconductor (AOS) thin-film transistor was firstly reported in 2004 [1] and has attracted much attention due to their promising properties such as high transparency, high electron mobility, and low-temperature process compatibility. In ionic oxide materials like AOS, conduction band (CB) minimum (CBM) is formed mainly by unoccupied metal *n*s orbitals (n = principal quantum number), while fully-occupied O 2p orbitals contribute mainly to the valence band maximum (VBM) [2–4]. Therefore, large overlap between the *n*s-orbitals of next neighboring cations intervening an oxygen leads to large CB dispersion and high electron mobility even in an amorphous structure as demonstrated for amorphous In–Ga–Zn–O (a-IGZO) [1,2]. However, these materials including a-IGZO suffer from instability against visible light illumination although their band gaps (E_g) are typically larger than 3.0 eV. It is due to defect states just above VBM (near-VBM states), [5,6] which cause subgap optical responses from the photon energy ~2.4 eV [7]. To overcome this issue, we here propose ultrawide band gap AOS with significantly large band gaps ≫3.0 eV, where even subgap states do not cause the visible light absorption. To date, a variety of crystalline transparent conductive oxides (TCOs) have been reported; however, most of them contain the representative TCOs of ZnO, In_2O_3, SnO_2, and Ga_2O_3 as major constituents. Development of AOSs has followed a similar manner, leading to a-In–Zn–O, a-Zn–Sn–O, a-In–Ga–O, a-In–Sn–Zn–O, a-Sn–Ga–Zn–O, a-Hf–In–Zn–O, a-Ga–Cd–O [1,8–11], etc. Among the crystalline TCOs, pure β-Ga_2O_3 has the largest E_g of 4.9 eV [12]; however, electron conduction in pure amorphous Ga_2O_3 (a-Ga_2O_3) has not yet been reported.

In this work, we investigated amorphous thin films in the $(Ga_{1-x}Zn_x)O_y$ system, and obtained semiconducting amorphous films from x = 0 to 0.65, where E_g ranged from 3.47–4.12 eV and the highest mobility of ~7 $cm^2 V^{-1} s^{-1}$ was obtained for E_g = 3.8 eV.

2. Experimental details

All thin films were fabricated by pulsed laser deposition using a KrF excimer laser (wavelength: 248 nm) in an O_2 gas flow at room temperature on silica glass substrates. We synthesized polycrystalline ceramic targets with four different chemical compositions, ZnO, $(Ga_{0.35}Zn_{0.65})O_y$, $(Ga_{0.7}Zn_{0.3})O_y$, and Ga_2O_3. The targets were prepared from powders of ZnO (purity, 99.999%) and Ga_2O_3 (purity, 99.99%), which were sintered at 1500 °C for 5 h in air. Oxygen pressure (PO_2) during deposition and laser fluence were varied with 1–4 Pa and 1–4.5 J/cm^2, respectively. Pulse repetition was fixed at 10 Hz. Some films were subjected to post-disposition thermal annealing at T_a = 200–600 °C in vacuum.

Film structures, densities, and thickness were characterized and determined by high-resolution X-ray diffraction (HR-XRD) and grazing-incidence X-ray reflectivity (GIXRR), respectively. Optical band gap values were estimated by Tauc plots for amorphous films while that of crystalline ZnO was taken from a literature. Electrical properties were measured by Hall effect with the van der Pauw configuration. Desorption of constituents was measured by thermal desorption spectroscopy (TDS). Chemical composition was analyzed by X-ray fluorescence (XRF) spectroscopy, where the chemical compositions were

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calibrated using the results of inductively coupled plasma atomic emission spectroscopy.

The energy levels of CBM and VBM were measured by ultraviolet photoemission spectroscopy (UPS, excited by He I and II light sources). To prepare chemically pure surfaces, Ar ion sputtering was conducted for 1 h at an acceleration voltage of 1 kV in a vacuum chamber connected to the UPS measurement chamber. Work function was determined from the cut-off energy of secondary electrons, and ionization potential (I_p) was estimated by combining the work function and the measured VBM level [13]. Electron affinity (χ, *i.e., CBM level*) was speculated using the band gap by $\chi = I_p - E_g$.

3. Results and discussion

3.1. Deposition condition to obtain amorphous $(Ga_{0.35}Zn_{0.65})O_y$

We first investigated effects of laser fluence and T_a on $(Ga_{0.35}Zn_{0.65})O_y$ thin films. As shown in Fig. 1(a), the thin film deposited at a low laser fluence (1.0 J/cm^2) exhibited only broad halos centered at ~35° and ~63° (the halo around 22° comes from the silica glass substrate), which indicates that the film is an amorphous phase. As the laser fluence increased, a sharp peak appeared at 32.62°, and the halos became sharper, suggesting formation and growth of crystallites. The full width at half maximum value of the halo at 32.2° for the highest laser fluence (4.5 J/cm^2) film was 1.93°, which corresponds to the crystallite size of 4.5 nm by the Scherrer equation. On the other hand, this peak position (32.2°) differs significantly from those of crystalline ZnO and β-Ga_2O_3; i.e., at 31.8°, 34.4°, and 33.5° for $10\bar{1}0_{ZnO}$, 0002_{ZnO}, and $111_{\beta\text{-}Ga_2O_3}$ diffractions, respectively. Thus, it is possible that nanocrystals of solid-solution (Ga,Zn)O were deposited in these films at high laser fluences.

Then, we measured their chemical compositions and film densities using XRF and GIXRR, respectively. As summarized in Table 1, the film density was low, 5.27 g/cm^3, for the low laser fluence of 1 J/cm^2, but increased to 5.69 g/cm^3 with increasing laser fluence to 4.5 J/cm^2. On the other hand, the chemical composition ratio Ga:Zn was almost unchanged at ~65:35.

TDS spectra for H_2O (Fig. 1(c)) show that the low-density film deposited at the low laser fluence (1.0 J/cm^2) exhibited high-density desorption of H_2O molecules from 200–330 °C, while, the high-density film deposited at 4.5 J/cm^2 exhibited much less H_2O desorption. It is known that high-density impurity hydrogen >10^{20} cm^{-3} is contained in usual AOS such as a-IGZO deposited by conventional pulsed laser deposition and sputtering, which comes from the residual gas in the deposition chamber and/or supplied gases [14]. These results suggest that the low densities of the lower laser fluence films are related partly to the incorporation of more H-related impurities such as H, H_2O, and OH. The incorporation of the impurities is enhanced at a lower deposition rate because the incorporation rate of hydrogen (i.e., number of hydrogen atoms per second) should be constant and determined by their densities in the residual/supplied gases, while a lower deposition rate requires a longer deposition time and consequently incorporate

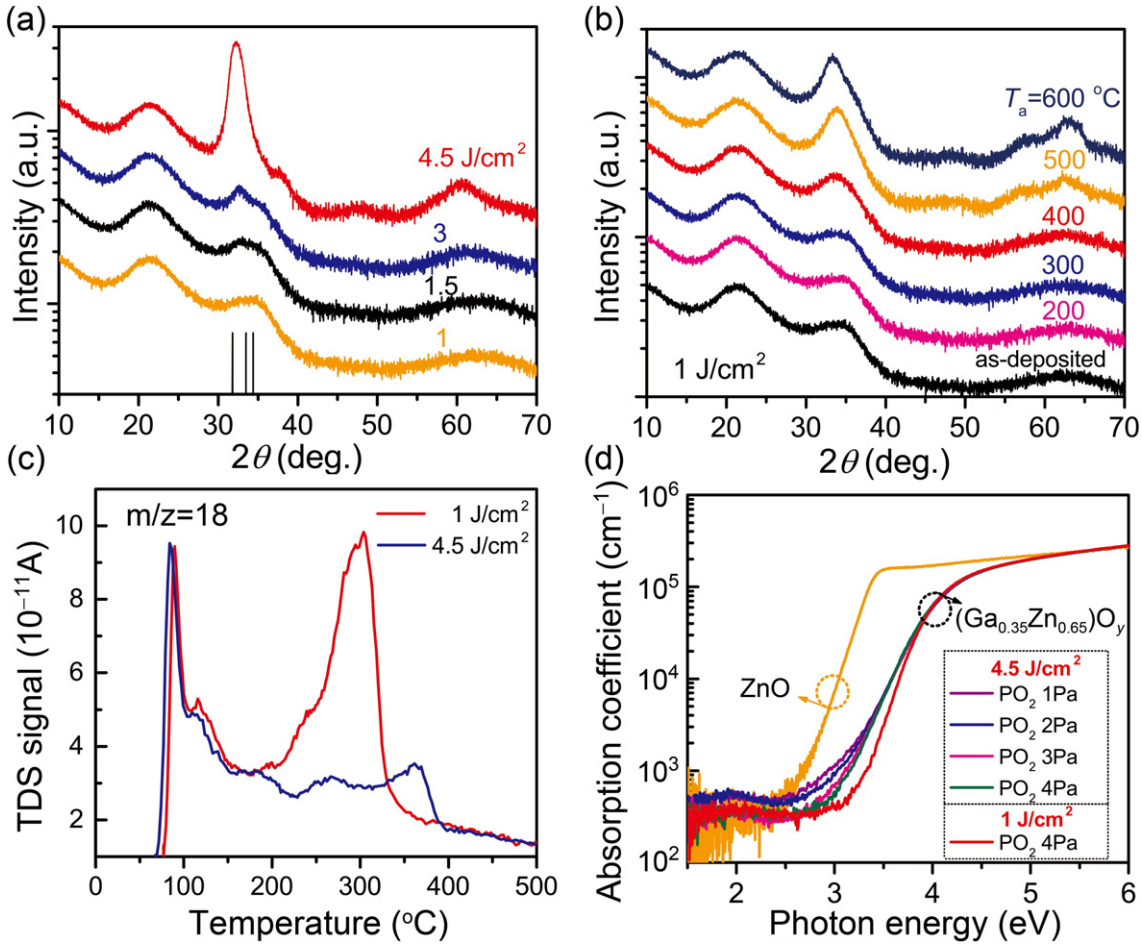

Fig. 1. Structures and optical properties of $(Ga_{0.35}Zn_{0.65})O_y$ thin films. XRD patterns of (a) as-deposited thin films deposited at laser fluences between 1.0 and 4.5 J/cm^2 and (b) annealed thin films, deposited at laser fluence 1.0 J/cm^2, at T_a = 200–600 °C. (Vertical bars show diffraction peak positions for $10\bar{1}0_{ZnO}$, 0002_{ZnO}, and $111_{\beta\text{-}Ga_2O_3}$). (c) TDS spectra for m/z = 18 (H_2O) of thin films deposited at laser fluences of 1.0 and 4.5 J/cm^2. (d) Optical absorption spectra of thin films deposited at fluences of 1.0 and 4.5 J/cm^2 and PO_2 = 1–4 Pa. That of a polycrystalline ZnO thin film is shown for comparison.