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Comparative studies on the physical and electronic properties of reactively sputtered ZnO and ZnON semiconductors

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Abstract

Thin film transistors were fabricated using ZnO and ZnON semiconductors grown by DC reactive sputtering. After low vacuum annealing at 250 °C, ZnON devices exhibit superior electrical performance ($\mu_{sat}=56.3$ cm^2/Vs, $V_{th}=-1.59$ V, and SS = 0.51 V/dec) in comparison with ZnO devices ($\mu_{sat}=0.99$ cm2/Vs, $V_{th}=3.28$ V, and SS = 1.22 V/dec). The physical and electronic structures in both materials were analyzed by X-ray diffraction and X-ray absorption spectroscopy, respectively. The chemical bonding states were also examined by X-ray photoelectron spectroscopy. Consequently, nitrogen incorporation in DC reactive sputtering is found to suppress crystallization and enhance electron transport by the formation of Zn–N bonds.

Keywords: D. ZnO; ZnON; Oxide semiconductor; X-ray absorption; Thin film transistor

1. Introduction

High performance active matrix devices based on amorphous oxide thin film transistors (a-OxTFTs) have been investigated intensively, for liquid crystal display (LCD) and organic light-emitted diode (OLED) applications owing to their high field effect mobility (~10 cm^2/Vs) and large area uniformity [1]. Studies on In and Zn-based multi-component metal oxides such as InGaZnO [2], InZnO [3], HfInZnO [4] and InZnSnO [5] have been constantly reported, focusing mainly on high field effect mobility and high stability with respect to bias, temperature and illumination stress. Since Ye et al. reported on zinc oxynitride (ZnON) semiconductors in 2009 [6], semiconductors based on this compound have drawn attention due to several advantages such as high field effect mobility (~100 cm^2/Vs) and device stability with respect to illumination [7–10]. Recently, studies on nitrogen-doped ZnO have gained attention for various applications such as photo-electrochemical devices and photo-sensors involving the design of the material's optical band structure [10–13]. Especially, nitrogen plays important roles when zinc oxynitride is formed. The low electron effective mass (m_e^*/m_e=0.19) in nitrogen-rich ZnON results in high electron mobility. Also, the nitrogen related states in the band-gap effectively screen the oxygen related defect states by allowing fast electron–hole recombination after exposure to light, which suppresses photo-induced device degradation by the occurrence of persistent photoconductivity (PPC). Despite the above advantages, the electrical transition between as-deposited ZnON and post-annealed ZnON has not been examined in detail yet. In order to understand the effect of heat treatment to the material and device characteristics, a thorough investigation on the physical, chemical and electronic properties induced by nitrogen in ZnON should be carried out. In this study, the electrical properties of TFT devices based on ZnO and ZnON semiconductors are investigated, with respect to the physical and electronic structures, along with the chemical bonding states.

2. Experimental

Bottom gate ZnO and ZnON TFTs with an inverted staggered structure were fabricated on heavily doped p-type

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Si wafers. Thermally grown 100 nm-thick SiO_2 was used as the gate insulator. A 3-in Zn metal (99.999%) target was used to perform reactive DC sputtering. Two different gas mixtures, namely Ar/O_2 (5/5 sccm) and Ar/O_2/N_2 (5/1.2/40 sccm) were adopted to deposit ZnO and ZnON films, respectively. The DC power and process pressure were kept at 100 W and 5 mTorr, respectively. Semiconductor layers with 30 nm thickness were then grown and patterned by fine metal shadow masks, and subsequent post annealing was conducted in a low vacuum furnace ($\sim 10^{-1}$ Torr) at 250 °C. After annealing, 100 nm-thick indium tin oxide (ITO) films were sputter deposited as source-drain electrodes, also patterned by shadow masks. The channel width and length of the devices under consideration were 800 and 200 μm, respectively. In order to investigate the physical and chemical properties of the films, separate layers of ZnO and ZnON were prepared on bare Si wafers using the aforementioned growth methods.

The electrical properties of the TFTs were measured using a HP 4145B semiconductor analyzer and an evacuated probe station ($\sim 10^{-3}$ Torr) to exclude environmental effects. The crystal structure was analyzed by X-ray diffraction (XRD) method using the 3D-XRS line at the Pohang accelerator laboratory (PAL). The chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS). The electronic structure was analyzed by X-ray absorption near edge spectroscopy (XANES) using the 10D-XAS line at the Pohang accelerator laboratory (PAL).

3. Results and discussion

Initially, devices with ZnO and ZnON films in the as-deposited state exhibited highly insulating and metallic properties, respectively (not shown). After post annealing in low vacuum at 250 °C for 1 h, semiconducting behavior was obtained in both devices. The representative parameters such as saturation mobility (μ_{sat}), threshold voltage (V_{th}), and subthreshold swing (SS) were then extracted, as shown in Fig. 1 (a). Superior device performance is observed in ZnON devices ($\mu_{sat} = 56.3$ cm^2/Vs, $V_{th} = -1.59$ V, and SS = 0.51 V/dec) in comparison with ZnO TFTs ($\mu_{sat} = 0.99$ cm^2/Vs, $V_{th} = 3.28$ V, and SS = 1.22 V/dec). Especially, the saturation mobility of ZnON TFTs is higher than that of ZnO TFTs by several orders of magnitude as shown in Fig. 1 (b).

Fig. 2 shows X-ray diffractograms of ZnO and ZnON films, where the 002 peak of hexagonal ZnO becomes more intense in the vacuum-annealed ZnO film. On the other hand, ZnON films exhibit amorphous phases regardless of thermal treatment. It was previously suggested in a former publication [8] that the presence of nitrogen may suppress the crystallization of ZnON films due to the structural disparity between hexagonal ZnO and cubic Zn_3N_2 that tend to form simultaneously within the material. Also, because of the different ionic radii of oxygen (O^{2-}, 126 pm) and nitrogen (N^{3-}, 132 pm) ions, lattice distortion is anticipated to occur in the oxynitride, which may also inhibit the formation of a particular microstructure.

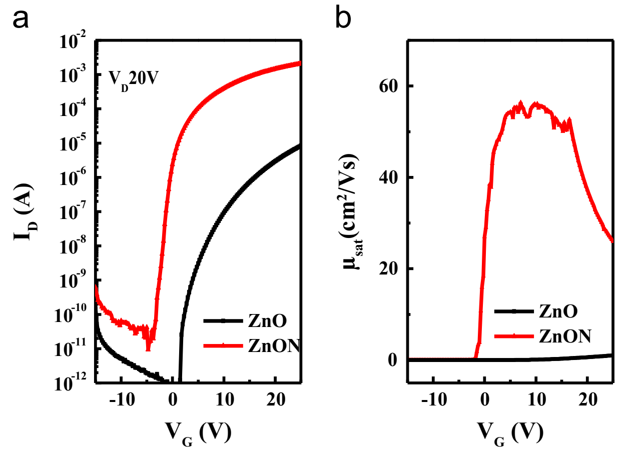

Fig. 1. (a) Representative transfer curves (I_D vs V_G) of ZnON and ZnO TFT device annealed at 250 °C for 1 h and (b) saturation mobility (μ_{sat}) values as functions of gate voltage for ZnON and ZnO TFT devices.

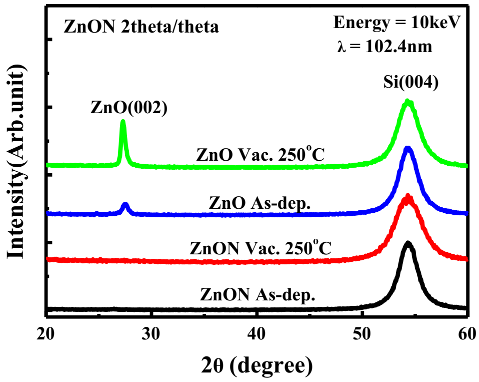

Fig. 2. X-ray diffractograms of ZnON and ZnO thin films obtained with the 3D-line XRS at the Pohang accelerator laboratory (PAL).

Fig. 3 (a) and (b) shows the O K-edge and N K-edge X-ray absorption spectra of the ZnO and ZnON films. X-ray absorption near edge spectroscopy (XANES) is useful at investigating the electronic structure based on molecular orbital theory [14]. The relative intensities of the featured peaks (P1–P7) reflect the quantitative changes in the molecular orbital bond symmetry [15–17]. The peaks labeled P1, P2, P3 and P4 are attributed to electron excitation from the O 1 s orbital to the O 2pσ (along the plane of the film) and the O 2pπ orbitals (along the vertical *c*-axis). The energetic order of O K-edge can be sorted as P1 (Zn 4s-O 2pσ) > P2 (Zn 4sp-O 2pπ) > P3, P4 (Zn 4d-O 2p). On the other hand, the positions of featured peaks P5, P6 and P7 in the N K-edge are related to the Zn 3d-N 2pσ state, the Zn 3d-N 2pπ in a phase mixed with N_2 molecules (due to vibration mode), and the N–O state, respectively.

The above O K-edge spectra in the ZnO films exhibit characteristics similar to former studies related with their crystal orientation [15]. From the O and N K-edge spectra, it may be deduced that the as-deposited ZnON film exhibits rather weak Zn–O bonding properties, which may result in metallic conductivity due to non-bonding Zn metal. After post annealing, different shapes of bonding symmetry are obtained, which are highly likely to occur by the stabilized Zn–O bonds and the substitution of oxygen sites by nitrogen resulting in the formation of O–Zn–N bonds [15–18]. Since the as-deposited ZnON films exhibit mainly