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Improvement of transistor characteristics and stability for solution-processed ultra-thin high-valence niobium doped zinc-tin oxide thin film transistors

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ABSTRACT

Nb-doped Zinc tin oxide (NZTO) channel materials have been prepared by solution process in combination with the spin-coating method. All NZTO thin film transistors (TFTs) are n-type enhancement-mode devices, either without or with Nb additives. High-valence niobium ion (ionic charge = +5) has a larger ionic potential and similar ionic radius to Zn^{2+} and Sn^{4+} ions. As compared with the pure ZTO device, introducing Nb^{5+} ions into the ZTO channel layers can improve the electrical properties and bias stability of TFTs because of the reduction of the oxygen vacancies. This study discusses the connection among the material properties of the NZTO films and the electrical performance and bias stability of NZTO TFTs and how they are influenced by the Nb/(Nb + Sn) molar ratios of NZTO films.

1. Introduction

Indium gallium zinc oxide (IGZO) thin films have received much interest in recent years as channel materials for the thin film transistors (TFTs), which show a large charge carrier mobility, a high on/off current ratio and good environmental stability [1]. However, indium and gallium are relatively rare elements in the world. Therefore, non-indium-based and non-gallium-based channel materials, such as zinc-tin oxide (ZTO), have attracted a great deal of interest. ZTO based semiconductors have been studied intensively these days as active channel materials for TFTs [2,3], because of their high charge carrier mobility in ambient air, good transparency in visible region, and low-cost production compared to amorphous Si and polycrystalline Si TFTs [4].

Compared with conventional vacuum-based techniques, solution-processed deposition techniques have several advantages such as low cost, low-temperature process, simplicity, easily controlled stoichiometry, and high throughput. Therefore, solution-processed ZTO TFTs can meet the requirements of commercial microelectronics. However, the solution-processed ZTO TFTs usually suffer from a severe bias-stress instability for device operation [5]. In order to improve the device performance, ZTO semiconductors are usually introduced metal ions to boost their performance. A number of workers have investigated ZTO channel layers doped with different metal ions, such as Zr-doped ZTO [6], Ga-doped ZTO [7], La-doped ZTO [8] and Al-doped ZTO [9] and their applications in thin film transistors. The ionic radius of Nb^{+5} is 0.69 Å, which is similar to that of Zn^{+2} (0.74 Å) and Sn^{+4} (0.71 Å). According to Hume-Rothery rules [10], the dopant is able to substitute the host ion with similar ionic radius (i.e., ionic radii must differ by less than 15%). In addition, the ionic potential is defined as an ion's charge divided by its radius, implying that niobium ion with high oxidation state (ionic charge = +5) should have a larger ionic potential [11,12]. After estimation, Nb^{+5} has a ionic potential of 7.14 $Å^{-1}$, which is substantially higher than that of Zn^{+2} (2.70 $Å^{-1}$) and Sn^{+4} (5.63 $Å^{-1}$). Therefore, incorporating Nb ions in ZTO can suppress the generation of oxygen vacancies effectively, resulting from stronger bonds between the metal ions and oxygen ions. Based on this, we firstly attempt to introduce Nb ions into the host ZTO semiconductor to improve the device performance and operational stability of the solution-processed ZTO TFTs.

In this work, we report the fabrication of NZTO TFTs with a large on/off current ratio and a small subthreshold swing using a solution process in combination with the spin-coating technique. We attempt to control the oxygen deficiency of the NZTO TFTs using various molar ratios of Nb, and investigate the effect of Nb contents on the threshold voltage shift and field-effect mobility. In addition, the correlation between the Nb-doping concentration and device stability is also investigated in this study.

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2. Material and methods

A NZTO composite film was prepared using a solution process in combination with the spin-coating method. Hydrated Zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hydrated tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) were firstly used as starting materials for preparing the molar ratio of Zn/Sn = 1. For Nb-doping, different amounts of anhydrous niobium chloride ($NbCl_5$) were weighted according to the Nb/Nb + Sn molar ratios of 1%, 3%, and 5%. All the three types of starting materials were mixed with 50 ml ethylene glycol monomethyl ether (EGME), and then stirred with a magnetic stirrer for 20 h at room temperature to ensure chemical homogeneity. The precursor solution was spin-coated onto a heavily doped p^+-type Si wafer with 100 nm thick SiO_2. The spin-coated NZTO layers were rapidly annealed at 480 °C for 1 h under an air atmosphere. The Si substrate, NZTO and SiO_2 function were used as the gate electrode, active layer and gate dielectric, respectively. Afterwards, the Al source and drain electrodes (300 nm thick) were evaporated by e-beam evaporation through a shadow mask to define the TFT channel width (2000 μm) and length (100 μm).

The thickness and chemical bonding states of the NZTO films were characterized using a transmission electron microscope (TEM, PHILIPS CM-200) and x-ray photoelectron spectroscopy (XPS, JEOL JAMP-9500F), respectively. The characteristic crystal phases of the ZTO films with different Nb contents were identified using Cu Kα in glancing-incident angle X-ray diffraction (GIAXRD, Rigaku D/MAX2500) with an incident angle of 2°. In order to obtain well XRD patterns, the thickness of ZTO films doped with different Nb contents is increased. NZTO precursor solution was spin-coated onto a p^+-type Si wafer with 100 nm thick SiO_2 and subsequently heated at 480 °C on a hot-plate in air for 2 min. The process was repeated for 10 times. The spin-coated NZTO layers were rapidly annealed at 480 °C for 1 h under an air atmosphere for X-ray diffraction analysis. The optical transmittance of the NZTO composite films that were deposited on a quartz glass substrate was measured at normal incidence, from 1100 to 300 nm, using a Hitachi U-2001 UV/Visible Spectrophotometer. All of the electrical characteristics of the NZTO TFTs were measured using a semiconductor parameter analyzer (Agilent 4156 C) under ambient atmosphere in a dark box.

3. Results and discussion

Fig. 1 shows the cross-sectional TEM images of the ZTO films without and with 3% Nb-doping concentration. One can see that the thickness of the 0% and 3% Nb-doped ZTO films, as measured from the images, is about 5 nm. The ZTO films with other Nb contents (i.e., 1% and 5%) have almost the same thickness (images are not shown). Inset in Fig. 1 (b) shows the GIAXRD patterns of 10-layers ZTO films with different Nb contents. The diffraction patterns did not show any characteristic peaks and this indicates that the structure of NZTO films is amorphous. From the TEM images, one can see the 0% and 3% Nb-doped ZTO films without showing lattice fringes, implying an amorphous phase of NZTO films, as shown in Fig. 1. In order to determine the optical band gap of the films, the transmittance spectra of the NZTO films (inset, Fig. 2a) were measured at room temperature by UV/Vis spectrometer. From the transmittance spectra, it is clearly observed that all the thin films exhibit good transparency over 98% in the visible region and a sharp UV absorption cut-off at wavelength <400 nm.

The optical bandgap (E_g) of ZTO films with different Nb additives were evaluated by examining the absorption coefficient of the material from the transmittance results by utilizing the following equation:

$$\alpha h\upsilon = \text{constant} \times (h\upsilon - E_g)^n \quad (1)$$

where α, E_g, and hυ are the absorption coefficient, optical energy bandgap of materials, and incident photo energy, respectively; α can be obtained as [13].

$$T\% = \frac{I}{I_0} = e^{-\alpha d} \quad (2)$$

where T% and d represent transmittance and thickness of a thin film, respectively. In Eq. (1), the exponent n depends on the kind of optical material. Because ZnO-based materials are direct band gap semiconductors, we used n = 1/2 in Eq. (1) to derive optical bandgap. Fig. 2a is a Tauc plot from transmittance spectra data, which shows $(\alpha h\upsilon)^2$ versus hυ for the ZTO film with different Nb-doping concentrations. The optical bandgap E_g can be obtained by extrapolating the linear portion of the absorption edge to find the intercept with photo energy axis in the Tauc plot, which is listed in Table 1. From Table 1, the optical band gap (E_g) of the NZTO thin films increases in accordance with an increase of Nb-doping concentration, suggesting that the Nb atoms have successfully doped into the ZTO films. The optical band gap (E_g) of the NZTO thin films

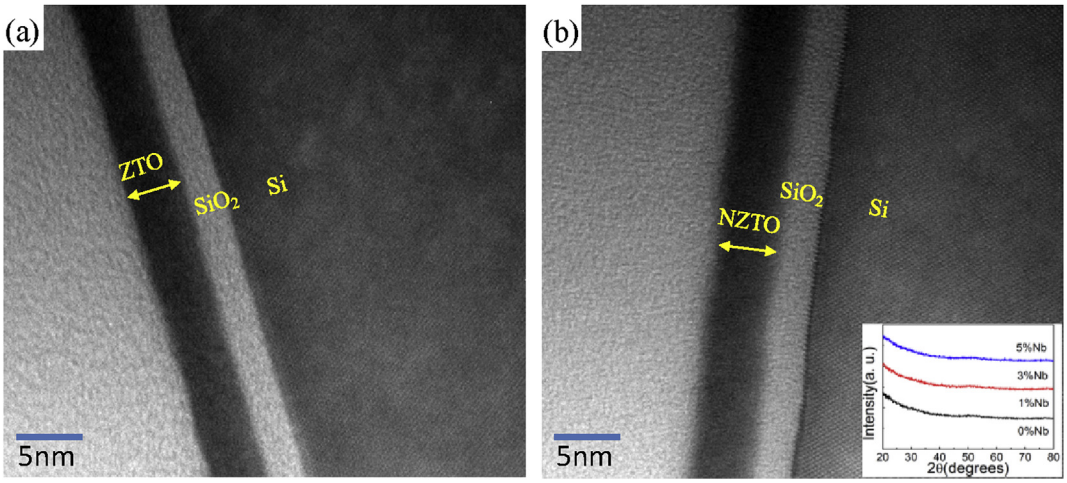

Fig. 1. Cross-sectional TEM image of solution-processed (a) ZTO film and (b) 3% Nb doped ZTO film on SiO_2/p + -Si. Inset in Figure 1 (b) shows the GIAXRD patterns of 10-layers NZTO films with different Nb-doping concentrations.