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Solution-processed semiconducting aluminum-zinc-tin-oxide thin films and their thin-film transistor applications

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Abstract

We prepared aluminum-zinc-tin-oxide (AZTO) thin films by the solution spin-coating method and investigated their physical and electrical properties according to different incorporated amounts of Al. AZTO films annealed at 400 °C were amorphous. Though SnO_2 crystallites were detected in films annealed at temperatures higher than 500 °C, the number of crystallites decreased as the Al content increased. Thin films had a smooth and uniform surface morphology with an optical transmittance value higher than 92% in the visible range. Electrical conductivity and its temperature dependence varied markedly according to the amount of Al incorporated in the film. We therefore systematically investigated activation energies for carrier transport for each film composition. Thin-film transistors (TFTs) were fabricated using solution-processed AZTO as an active channel layer. The effects of the amount of Al incorporated in the thin film on TFT characteristics were also evaluated. The best device performance was observed for a TFT with a 5 mol%-Al-incorporated AZTO channel. Field effect mobility, subthreshold swing, and on/off ratio were approximately 0.24 $cm^2\ V^{-1}\ s^{-1}$, 0.69 V/dec, and 1.03×10^6, respectively.

Keywords: Oxide semiconductor; Solution process; Al-Zn-Sn-O; Thin-film transistor

1. Introduction

Recent days, some urgent requirements, such as larger size and higher resolution, are still pending for the flat-panel display (FPD) industries. To realize next-generation FDPs with these characteristics, thin-film transistors (TFTs), which comprise the backplanes of FPDs, should have high mobility, good uniformity, and excellent stability. Although conventional amorphous silicon TFTs can provide features of good uniformity and low-cost process, their field-effect mobility and device stability are not optimal for next-generation FPDs [1]. Low-temperature poly-silicon TFTs have the advantages of high mobility and good stability. However, their poor uniformity and expensive process are critical problems, especially for larger-size applications [2]. From these backgrounds, oxide semiconductor TFTs are considered promising candidates for the backplane of next-generation FPDs. The choice of oxide semiconducting active channel layer is critical to obtain excellent TFT characteristics. Thus far, various materials, such as ZnO [3,4], Zn-Sn-O (ZTO) [5,6], In-Zn-O [7,8], In-Zn-Sn-O [9], In-Ga-O [10], and In-Ga-Zn-O (IGZO) [11-13] have been employed to fabricate oxide TFTs and have been reported to show acceptable device performance for FPD backplane applications. In particular, amorphous IGZO is one of the best compositions due to its relatively high carrier mobility, good uniformity, and a wide process window. LG Displays (Korea) recently (2013) released a 55-in. full-high-definition (FHD) organic light-emitting diode TV that employs an IGZO oxide TFT active matrix [14]. Despite these technological advancements, however, new oxide compositions with higher carrier mobility and better device stability than current oxide compositions are still in demand. When exploring new oxide compositions for future electronic system applications, two main factors should be taken into consideration. The first factor is that indium- and gallium-free compositions would be ideal from the perspectives of resource depletion and eco-friendliness. Another consideration is the solution process compatibility of the oxides; simpler processes and higher throughput than those required using vacuum deposition methods would be of great benefit [15-17]. If these two factors are taken into consideration, fabrication costs could be reduced, which is important in the FPD industry. Although oxide semiconductors prepared by solution processes

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require thermal treatment at high temperature to guarantee the electrical properties of the semiconducting thin films, new methodologies to effectively reduce process temperature have been developed [18-20].

In this work, we propose solution-processed Al-Zn-Sn-O (AZTO) thin film as the active channel for oxide TFT applications, and we investigate device feasibility with regard to the two above-mentioned considerations. Some reports demonstrated the device characteristics of oxide TFTs with an AZTO channel deposited by the sputtering method [21–23]. However, there are no systematic studies on the material properties of solution-processed semiconducting AZTO thin films and the dependence of these properties on the amount of Al incorporated into the thin films. We investigated the physical and electrical characteristics of spin-coated AZTO thin films with different Al contents of source solutions. Furthermore, we fabricated and characterized top-gate oxide TFTs with a gate-stack structure of an atomic-layer deposited Al_2O_3 gate insulator and solution-processed AZTO channel layer to investigate device feasibility.

2. Experimental details

AZTO precursor solutions were prepared by diluting and blending commercial metal-organic solutions (synthesized by Kojundo Chemical Laboratory, Japan) of ZnO (SYM-ZN20), SnO_2 (SYM-SN05), and $AlO_{1.5}$ (SYM-AL04). Initial concentration of each solution was 2.0, 0.5, and 0.4 M. In order to adjust the concentration of all solutions to 0.2 M, solutions were diluted with n-butyl acetate [$CH_3COO(CH_2)_3CH_3$, CAS no. 123-86-4]. This final concentration was chosen by considering the viscosity of the solutions and the wettability on glass substrates, which are important factors to take into consideration to obtain coated thin films with a smooth and uniform morphology. First, ZTO precursor with a Zn/Sn atomic ratio of 50/50 was prepared by blending the diluted solutions. Then, other three types of AZTO solutions with Al contents of 2, 5, and 10 mol% were prepared. All blended solutions were stirred at 60 °C for more than 1 h to enhance their stability and homogeneity. AZTO solutions with various amounts of Al were spin-coated on substrates at 2000 rpm for 30 s and dried at 250 °C for 10 min to remove solvent. Film thickness obtained by one coating process was approximately 25 nm. Crystallinity and surface roughness of the coated films were investigated by X-ray diffraction (XRD, Rigaku DCC-300) and atomic force microscopy (AFM), respectively. Diffraction patterns were measured with Cu Kα radiation (40 kV/60 mA) at a scan rate of 2°/min. Optical transmittance in the visible range was measured by a UV spectrophotometer (U-3501). Sheet resistances of the prepared AZTO films were evaluated by the four-point probe method as a function of temperature in the range from 50 to 400 °C. Compositions of the prepared AZTO thin films were also analyzed by Auger electron spectroscopy (AES).

AZTO TFTs were fabricated with a top-gate-bottom-contact structure. Indium-tin oxide (ITO)-coated glass was prepared as a substrate. The ITO layer was patterned into the source/drain (S/D) electrodes using a wet etching process. AZTO active channel layers with different Al amounts were spin-coated onto the S/D patterned substrates using the prepared precursor solutions. Coating processes were repeated twice with an interval of drying process at 250 °C for 10 min to control film thickness. Thermal annealing was performed at 500 °C for 1 h in oxygen ambient. Then, a thin protection layer (PL) of Al_2O_3 with a thickness of 12 nm was deposited by atomic layer deposition (ALD) on the AZTO layers before the patterning process of active regions. This PL protected the solution-processed AZTO channel layers during the lithography process for channel formation. Active channels of AZTO were patterned by a diluted hydrofluoric acid-base wet etchant at room temperature. 100-nm-thick Al_2O_3 films were deposited by ALD at 150 °C as gate insulators. Metal contacts were opened by wet etching the given areas of Al_2O_3 gate insulators with phosphoric acid at 120 °C. Gate electrodes and S/D pads were finally formed by deposition and patterning of Al film. The device characteristics of the fabricated AZTO TFTs were evaluated using a semiconductor parameter analyzer (Keithley 4200SCS) in a dark box at room temperature. Channel width and length of measured TFTs were 40 and 20 μm, respectively.

3. Results and discussion

3.1. Material properties of solution-processed AZTO thin films

In order to investigate the crystallinity of spin-coated AZTO films with different amounts of Al, XRD patterns were obtained according to changes in annealing temperature for the AZTO films. For these measurements, the film thickness of each film was increased to approximately 100 nm to clearly confirm crystallization and/or second phase formation. Fig. 1(a) shows the XRD peaks of ZTO film (Zn/Sn = 50/50) treated at various temperatures of 250, 400, 500, and 600 °C. Feasible peaks can be picked up to be $ZnSnO_3$ at $2\theta = 22.7°$, 32.4°, and 52.4° (JCPDS file no. 11-0274). While these peaks were not detected for all films, some peaks representing SnO_2 (110), (101), and (211) planes appeared at $2\theta = 26.6°$, 33.9°, and 51.8° (JCPDS file no. 41-1445), respectively, for the film annealed at 600 °C. SnO_2 (101) peak was also detected even for the film annealed at 500 °C. However, no distinct peaks were detected for the films annealed at 400 °C, although a broad peak remained around 34°. These results indicate that phase separation and segregation of SnO_2 crystallites occurred preferentially rather than formation of ZTO crystallites, starting at an annealing temperature of 400 °C. Crystallinities of the ZTO films changed as the Al content of the AZTO films increased. Fig. 1(b)–(d) shows XRD patterns for AZTO films with Al amounts of 2, 5, 10 mol%, respectively, for annealing temperatures of 250–400, 500, and 600 °C. Peak intensities of the SnO_2 phases decreased with increasing Al content. Actually, for AZTO films with 10-mol% Al, only a small peak corresponding to the SnO_2 (101) plane was detected, even at the annealing temperature of 600 °C. These results indicated that incorporation of Al into ZTO effectively suppressed the appearance of segregated SnO_2 phases from the ZTO lattice. Amorphous phases of the solution-processed AZTO films could essentially be obtained by incorporation of more than 5 mol% Al even when thermal treatment was performed at 500 °C. Consequently, it can be expected that film composition