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Effects of yttrium additions on the microstructure and charge transport properties of indium tin oxide semiconductors

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ABSTRACT

The effects of yttrium (Y) additions (x=0, 0.05, 0.1, and 0.2) on the microstructure, chemical structure, and electrical properties of Y_xInSnO_y (YITO) thin films, prepared using a sol-gel process were examined. The transmission electron microscopy (TEM) observations showed that the undoped InSnO (ITO) film consisted of an amorphous structure with local crystalline domains on the film surface, whereas the Y additions (x=0.05, 0.1, and 0.2) to ITO suppressed the formation of the crystalline phase. X-ray photoelectron spectroscopy (XPS) analysis showed that the Y content decreased the concentration of oxygen vacancies owing to the strong incorporation of Y with oxygen. As a result of the Y incorporation, the carrier concentration of ITO films decreased. The saturation mobility (μ_{sat}), the on-off ratios ($I_{on/off}$), and the sub-threshold swing (S.S) of YITO films were 1.1 $cm^2 V^{-1} s^{-1}$, ~10^6, and ~0.5 V $decade^{-1}$, respectively, which are comparable with 1.7 $cm^2 V^{-1} s^{-1}$, ~10^5, and ~1.17 V $decade^{-1}$ of ITO film. Additionally, the initial threshold voltage (V_{TH}) was positive shift with increased of Y addition and V_{TH} shift (ΔV_{TH}) under the positive bias stress (PBS) results decreased by Y addition.

1. Introduction

Indium tin oxide (ITO)-based thin films have been studied as next generation semiconducting device materials in the electronics industry because of their excellent conducting and transparent characteristics. Specifically, both In and Sn have the same $[Kr]4d^{10}5s^0$ electronic configuration and the same overlap between the adjacent spherical *ns* orbitals, which can provide high conductivity. However, the high conductivity of ITO associated with the high carrier concentration via oxygen vacancies is a problem that needs to be overcome for practical semiconductor applications. Therefore, the oxygen vacancy concentration should be controlled to an optimum level for use in a semiconductor.

Over the past few year, a considerable number of studies have been conducted to reduce the oxygen vacancies by adding material with a strong oxygen affinity such as Ga, Hf, Mg, Zr, La_2O_3, MgO, ZrO_2, and SrO to the InZnO and ZnSnO systems. The oxygen affinity can be explained in terms of Gibbs free energy of additives, ΔG_f^o. Until now, to the best of the author's knowledge, no systematic study has been performed on oxide addition with stable ΔG_f^o for ITO systems. Especially, study on the effect of the yttrium (Y) addition has not been carried out. It is expected that Y could control the carrier concentration more effectively than indium or tin because of the stable ΔG_f^o of Y [1]. Moreover, the oxide semiconductors with the Y addition appear to be more stable in high electric fields because of the band gap energy (E_g,~5.6 eV) of Y_2O_3 [2]. Therefore, the Y incorporation with the oxide films might control the electrical characteristics of the films through the control of the oxygen vacancy and E_g.

In most oxide semiconductors, vacuum techniques are used such as magnetron sputtering, pulse laser deposition (PLD), and atomic layer deposition (ALD), due to their high reliability and reproducibility. In comparison, the solution processed oxide semiconductors as a channel of TFTs is currently attracting attention as the upcoming future display, because the solution process does not require the vacuum process and provides cost-effectiveness and precise control ability of the composition. Solution based deposition methods such as spin coating [3], inkjet [4], and spray [5] have been used over the past few years for the fabrication of oxide semiconductors TFTs.

In this paper, amorphous YInSnO (YITO) TFTs were prepared using a sol-gel solution chemical process. The ratio of Y to ITO was varied with the aim of controlling the carrier concentration of the ITO films and the electrical characteristics of TFT. The microstructure,

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chemical structure, and electrical properties of the sol-gel processed YITO films were then examined.

2. Experimental

The precursor solution for YITO was synthesized using a sol-gel reaction. Yttrium (III) nitrate hexahydrate [$Y(NO_3)_3{\cdot}6H_2O$], Indium (III) nitrate hydrate [$In(NO_3)_3{\cdot}xH_2O$, Aldrich], and Tin (II) chloride dehydrate [$SnCl_2{\cdot}2H_2O$] were used as precursor materials. The precursor materials were dissolved in 2-methoxyethanol and ethanol at 60°C for 2 h to produce 0.1 M of concentration. The precursor solution with atomic ratios of Y: In: Sn=x: 1:1 (x=0, 0.05, 0.1, and 0.2, hereafter denoted as the 0-, 0.05-, 0.1-, and 0.2-samples, respectively) were prepared to understand the effect of the Y addition. Mono-ethanolamine (MEA) was added to the solutions as a stabilizer. The YITO precursor solutions were spin-coated on SiO_2/Si substrates and then dried at 150 °C for 10 min. The coated YITO gel-films were heated at 400 °C for 1 h in air. Finally, the aluminum source and the drain electrode with a thickness of 100 nm were deposited on the YITO films by thermal evaporation using a shadow mask. The channel width and the length were 100 μm and 50 μm, respectively.

The thermal behavior of the solution processed YITO solution were evaluated by thermogravimetric and differential thermal analysis (TG/DTA, Seiko Exstar) in the range from room temperature to 1000 °C. The chemical variation in the YITO thin films was examined using X-ray photoelectron spectroscopy (XPS). The microstructure of the YITO films was investigated using high resolution transmission electron microscopy (HRTEM, JEM3010, JEOL). The electrical properties of YITO TFTs at room temperature were estimated using a semiconductor parameter analyzer (HP4145B). The saturation mobility (μ_{sat}) and sub-threshold swing (S.S) are calculated from the following formulas (1) and (2)

$$S.S=\left[\frac{d(\log_{10}I_{DS})}{dV_{GS}}\right]^{-1} \quad (1)$$

$$I_{DS}=\left(\frac{C_i\mu_{sat}W}{2L}\right)(V_{GS}-V_{th})^2 \quad (2)$$

where $W$and L are the width and the length of the transistor, respectively, and C_i is the capacitance per unit area of the gate insulator. To evaluate the device stability of the YITO TFTs, a positive bias stress (PBS) test was performed for 3000 s at a drain voltage of 20 V. All bias-stress measurements were carried out at room temperature in air and the threshold voltage (V_{TH}) value is measured by drawing a straight line at 10^{-9}. The gate bias was interrupted at predetermined times to measure the transfer characteristics.

3. Results and discussion

In order to evaluate the effect of Y additive on the thermal behavior of the precursor solution and to determine the heat treatment temperature of the gel film, we performed a thermal analysis of the precursor solutions with a composition of In: Sn=1:1 and Y: In: Sn=0.05: 1:1 using TG/DTA, as shown in Fig. 1. The TG curve of the ITO & YITO precursor solution shows significant weight loss with an endothermic peak of the DTA curve at around 100°C. The weight reduction in the solution is due to thermal decompositions of both the complex ligands originating from the stabilizing agent and the organic groups associated with the metal salts [6]. For the ITO (0-sample) precursor solution, the last stage in the range of 329–376 °C could be attributed to the crystallization of ITO; the crystallization behaviors of these ITO thin films will be described again in the TEM section. After this stage, significant weight loss was not observed. While the large exothermic peak from the DTA of YITO solution observed at around 242 °C could be related to the dehydroxylation of M-OH and the

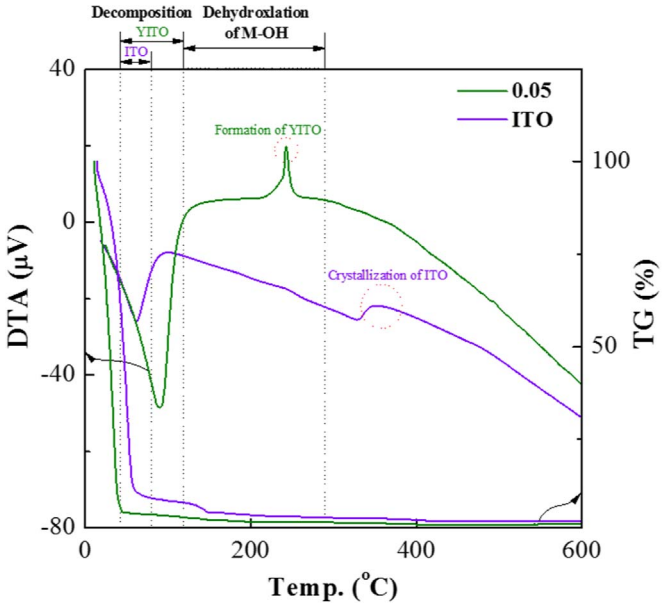

Fig. 1. TG/DTA curves of the ITO and YITO precursor solutions.

polycondensation ($MO+xH_2O\uparrow$) [7,8], the weight loss that accompanies this exothermic peak confirms that the large exothermic peak was due to the dehydration of M-OH [8]. The thermal analysis of the YITO solution indicates that the amorphous thin film would be discernible after heat treatment at temperatures over 250 °C [6]. In order to eliminate any residual solvent, impurities, and unnecessary anion groups, the heat treatment temperature of 400 °C was selected.

The microstructure of the YITO thin films was investigated by HR-TEM. Fig. 2 shows a cross-section view of the YITO film on a SiO_2/Si substrate with Fig. 2(a)–(d) showing the 0-, 0.05-, 0.1-, and 0.2-samples, with the inset showing the fast Fourier transform (FFT) pattern. All films have uniform thickness in the range of 9.0–11 nm. Fig. 2(a) shows the partially crystalline region of the ITO thin film. Also, the lattice distance of crystalline was measured to be 2.6 Å. Accordingly, the crystal grown orientation was calculated as ITO (400) from the JCPDS card [9,10]; this result was confirmed by the *fast Fourier transform* (FFT) patterns. On the other hand, the YITO (0.05-, 0.1-, and 0.2-) films have an amorphous phase as shown in Fig. 2(b)–(d), respectively, and no differences are observed between these samples. This suggests that the crystal grain growth in YITO is strongly related to the Y element. Usually, some additional elements need to be incorporated into the thin films to make an amorphous phase or to prevent their crystal growth [9]. This is explained as the result of Y being incorporated into the ITO lattice, and the consequent disturbance of crystalline growth due to the larger atomic radius (180 pm) of Y than In (167 pm) and Sn (140 pm) [11]. In order to investigate the effect of the Y contents on chemical changes, XPS was used to analyze the metal-oxygen (M-O) bonding in the YITO film. Fig. 3(a) presents the O1s XPS spectra of the YITO films. The XPS spectra of the YITO O1s peak around 530 eV corresponds to the O1s core level. The XPS oxygen peak was deconvoluted into three peaks by Gaussian fitting. According to the XPS spectra, the peak on the low energy side of the O1s spectrum (O_I) (which is the peak located at 529.9–530.1 eV), corresponds to O^{2-} ion bonded with the In, Sn, and Y atoms in YITO [12–14]. The features at around 531.3–531.4 eV (O_{II}) and around 532.5 eV (O_{III}) are related to oxygen vacancies (oxygen deficiency region) and chemisorbed hydroxide (M-OH) or physisorbed H_2O and CO_2, respectively [12–14]. The ratios of O_I/O_{TOT}, O_{II}/O_{TOT}, and O_{III}/O_{TOT} were calculated from peak areas and are shown in Fig. 3(b). O_I/O_{TOT} was increased and the O_{II}/O_{TOT} and O_{III}/O_{TOT} decreased with increasing Y content. The O_I/O_{TOT} ratio for the 0-, 0.05-, 0.1-, and 0.2-samples linearly increased to 55.9%, 58.4%, 61.3%, and 63.5%,

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