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Effect of Mg addition on the electrical characteristics of solution-processed amorphous Mg–Zn–Sn–O thin film transistors

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ABSTRACT

Solution-processed thin film transistors (TFTs) using a magnesium zinc tin oxide (MZTO, Ma–Zn–Sn–O) channel layer were fabricated and bias-stress stability during device operation was evaluated. The cause of the bias-stress instability was investigated through comparison with zinc tin oxide (ZTO, Zn–Sn–O) TFTs. The MZTO layers had a significantly lower oxygen vacancy concentration than the ZTO layer, which affected the electrical characteristics as well as bias-stress stability of MZTO TFTs. When 2 mol% Mg was added, a more stable transistor was attained, showing a typical semiconductor behavior with a saturation mobility of 0.27 $cm^2/V \cdot s$, on/off ratio of 3.3×10^6, off-current of 5.3×10^{-12}A, and threshold voltage of 5.4 V.

1. Introduction

Oxide semiconductors have emerged as a substitute for amorphous silicon (a-Si) used as a channel layer of thin film transistors (TFTs) since they exhibit outstanding characteristics in terms of optical transparency and mobility compared with a-Si [1–3]. In-based oxide semiconductors such as InGaZnO [4, 5] and InZnO [6, 7] have been extensively studied. However, indium is a rare and expensive material. Thus, the development of In-free oxide semiconductors is needed. Sn-based ZnSnO (ZTO) semiconductor has been considered as an alternative channel layer [8–10].

In order to improve the electrical performance of ZTO TFTs, an appropriate metal has been added to a ternary Zn–Sn–O system as a carrier suppressor. In particular, quaternary systems such as GaZnSnO [11], AlZnSnO [12], ZrZnSnO [13], and TiZnSnO [14] have been studied. The choice of appropriate element for carrier suppression depends on various factors such as the electronegativity of the metal atom and the bandgap energy of the metal oxide [15, 16]. When the difference of the electronegativity between two atoms is large, the bonding between them becomes stronger. The atom with relatively low electronegativity has a tendency to bond with oxygen, resulting in decreasing oxygen vacancies, which are carrier sources in a lot of oxide semiconductors. Also, the incorporation of constitutive elements of metal oxide with a wide bandgap may influence a carrier concentration by increasing the activation energy for carrier generation. Mg has a low electronegativity of 1.31 and its oxide (MgO) has a wide bandgap of 7.8 eV. Therefore, it is expected that the electrical performance of ZTO TFTs could be improved by incorporating Mg as a carrier suppressor [17].

An oxide semiconductor could be fabricated by using a solution process, which is simple and cost-effective. Recently, solution-processed high performance TFTs using ZnO [18], InZnO [19], ZnSnO [20], and InGaZnO [21] have been reported. However, solution-processed TFTs exhibit an intrinsic instability of devices under gate bias stress and illumination condition, which limits a practical use on account of the lack of reproducibility and reliability [22]. Under positive bias stress (PBS) condition, the threshold voltage of ZTO-based TFTs was significantly shifted to a positive bias direction without a step change in field-effect mobility and subthreshold swing [23]. Thus, it is suggested that the instability of ZTO-based TFTs might be attributed to the transient charge trapping in a ZTO channel or interface between a ZTO channel layer and a dielectric material [11]. It is considered that oxygen vacancies in most oxide TFTs act as major trap sites. For this reason, the defect states including oxygen vacancies must be decreased to improve the bias-stress instability of solution-processed TFTs. This can be attained by varying the chemical composition of solution-processed oxide semiconductors. In particular, Mg has an important role in the control of the concentration of oxygen vacancies in solution-processed oxide semiconductors as described above.

In this paper, we report the bias-stress stability and device performance of solution-processed Mg–Zn–Sn–O (MZTO) TFTs. The presence of Mg ions suppresses the generation of oxygen vacancies, resulting in decreasing the number of electron trap sites and charge carrier concentration. TFTs with Mg-doped ZTO channel layers exhibited a better device performance than those with an undoped ZTO channel layer.

2. Experimental details

A Mg–Zn–Sn solution was prepared by combining various amounts of anhydrous magnesium chloride ($MgCl_2$) with 0.1 M of zinc acetate

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($Zn(CH_3COO)_2$) and 0.2 M of tin chloride dihydrate ($SnCl_2 \cdot 2H_2O$) dissolved in 2-methoxyethanol solvent of 5 mL. To make the solution stable, the precursor solution was mixed with ethanolamine (C_2H_7NO) of 0.2 mL. The solution was stirred with a magnetic bar at 60 °C for 2 h. The molar ratio of Zn:Sn was fixed at 1:2 and the Mg content was varied as follows: [Mg] / ([Zn] + [Sn]) = 0 (0%), 0.01 (1%), and 0.02 (2%). This nominal composition represents atomic percent. A heavily doped p-type Si wafer was used as a gate electrode, and a 100-nm thick SiO_2 used as a gate dielectric was fabricated by thermal oxidation on the p^+-Si wafer. The 25-nm thick channel layer of MgZnSnO was prepared by spin-coating the stock solution at 4000 rpm for 30 s. After the deposition of MZTO thin films, the spin-coated sample was prebaked at 150 °C for 1 h, and then annealed at 400 °C for 1 h. The 150-nm thick Al film was deposited as a source and drain electrode by using an e-beam evaporator. The width and length of the TFT were 100 and 500 μm, respectively. The performance of the solution-processed MZTO TFTs was measured in dark room temperature with a semiconductor parameter analyzer HP 4156C. Positive bias stress tests were carried out for 3600 s with a gate bias voltage of + 20 V.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements were performed to investigate the crystal structure and microstructural evolution. The composition and chemical state of the deposited films were characterized by X-ray photoelectron spectroscopy (XPS). The optical properties of ZTO and MZTO films were also characterized by ultraviolet–visible (UV–VIS) spectroscopy.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of MZTO films with different Mg contents annealed at 400 °C in ambient air. They exhibited no remarkable peaks, indicative of formation of amorphous MZTO films irrespective of the Mg content. This is also confirmed by high-resolution TEM (HRTEM) measurement. Fig. 1(b) is a bright-field TEM micrograph of a MZTO film with 2 mol% Mg. It showed that the uniform MZTO thin film of about 25 nm was deposited on a SiO_2/Si substrate. The inset is a HRTEM micrograph corresponding to the MZTO layer. No lattice fringes were observed.

Fig. 2 shows the transfer characteristics of MZTO TFTs as a function of Mg content at a drain voltage of 30 V. The electrical characteristics of the MZTO TFTs were summarized in Table 1. With increasing Mg content from 0 to 2 mol%, the off current of the TFTs decreased by around four orders of magnitude from 1.1×10^{-8} to 5.3×10^{-12} A and the on-current decreased slightly from 2.7×10^{-5} to 1.8×10^{-5} A. The threshold voltage of TFTs increased slightly from 3.5 to 5.4 V. This might be attributed to reduction of carrier concentration caused by the addition of Mg charge carrier suppressors and the resulting increase of electrical resistivity of the channel layer. If the electrical resistivity of the channel layer increases, more voltage is required to obtain the same current quantity, inducing the positive shift of transfer curves. As described in the following, the increase of bandgap with Mg content could influence the conductivity of the channel layer. The addition of Mg in ZTO brought about the widening of the energy bandgap, inducing the increase of the activation energy by deepening the donor energy level in the energy bandgap. As a result, the addition of Mg in ZTO decreased the carrier concentration and increased the resistivity of the channel layer. It was found that with increasing Mg content, saturation mobility μ_{sat} and subthreshold swing SS were reduced and then increased slightly but on/off current ratios were increased and then decreased slightly.

The bias-stress stability of MZTO TFTs as a function of Mg content was investigated. Fig. 3 exhibits the transfer curves and the square root of the drain current (I_D) of MZTO TFTs after applying a positive gate bias of 20 V for 500–3600 s. ZTO TFTs without Mg content showed a significantly large threshold shift of ΔV_T = 19.1 V, while MZTO TFTs with 1 and 2 mol% Mg exhibited a relatively small threshold shift of

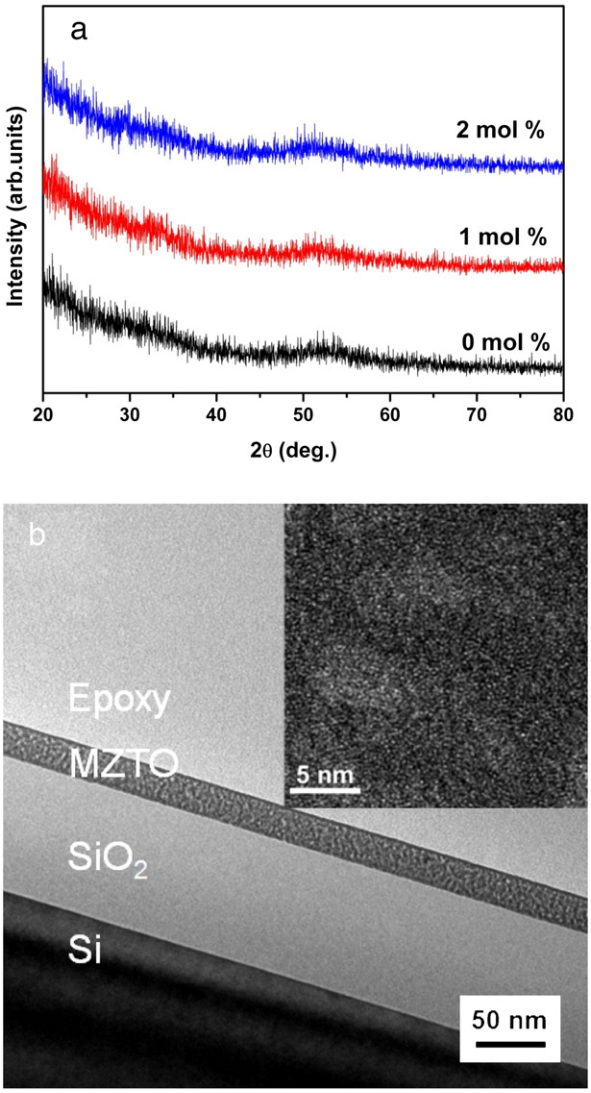

Fig. 1. (a) XRD patterns of MZTO films with different Mg contents annealed at 400 °C in ambient air. (b) A bright-field TEM micrograph of a MZTO film with 2 mol% Mg. The inset is a HRTEM micrograph corresponding to the MZTO layer.

ΔV_T = 17.9 and 16.8 V, respectively. These results indicated that MZTO TFTs had better bias-stress stability than ZTO TFTs. Thus, it is considered that the Mg atoms incorporated into the ZTO films contributed

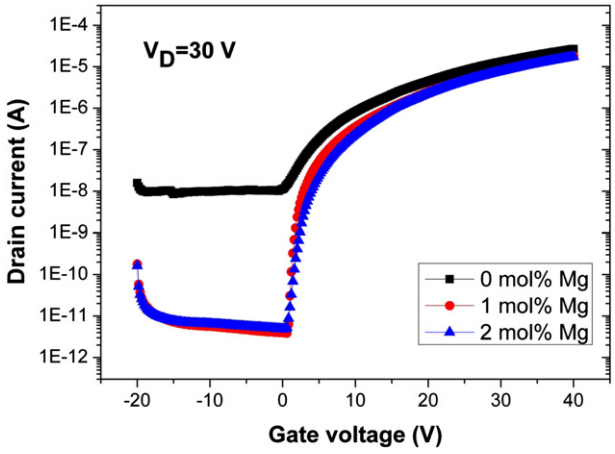

Fig. 2. Transfer characteristics of MZTO TFTs as a function of Mg content at a drain voltage of 30 V.