Electrical Performance Enhancement of Al–Zn–Sn–O Thin Film Transistor by Supercritical Fluid Treatment

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Abstract—In this letter, a low-temperature supercritical fluid (SCF) treatment was employed to enhance the electrical and optical properties of amorphous Al–Zn–Sn–O thin film transistors (a-AZTO TFTs) for flat-panel displays. The carrier mobility and threshold voltage of a-AZTO TFT were improved significantly after SCF process because of the reduction of trap density in the a-AZTO active layer. In addition, the SCF-treated a-AZTO TFT exhibited superior electrical reliability and less degradation after negative gate bias illumination stress. X-ray photoelectron spectroscopy analysis confirmed that the proposed SCF treatment could effectively oxidize a-AZTO film and change the oxidation states of Sn, resulting in the improvement of a-AZTO TFT device characteristics.

Index Terms—Al–Zn–Sn–O thin film transistor (Al–Zn–Sn–O TFT), supercritical fluid (SCF), transparent amorphous oxide semiconductor (TAOS).

I. INTRODUCTION

THIN film transistors (TFTs) using transparent amorphous oxide semiconductor (TAOS) have attracted great attentions for the backplane technology of a large-sized liquid-crystal displays and active matrix organic light-emitting diode displays because of its superior characteristics of high mobility, room temperature deposited, good uniformity, and compatibility with present display industry [1]–[3]. Transparent metal oxide TFTs using In–Zn–O [4], Hf–In–Zn–O [5], In–Zn–Sn–O [6], and In–Ga–Zn–O [7] as an active channel layer have been widely studied in the recent years. Although those TFTs performed good electrical performance, containing the rare-dispersive elements will be a critical issue for the long-term applications [8]. Therefore, rare elements-free transparent metal oxide semiconductors are considered to be the promising candidates for the next generation display technologies [9]. In this letter, a TAOS material, Al–Zn–Sn–O (AZTO), is employed as active channel layer of TFTs. All components in AZTO are plenty and universal in the earth. Some previous literatures reported AZTO active layer could be deposited at room temperature and the TFTs exhibit prominent electrical

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performance [10]. In this letter, a supercritical fluid (SCF) technology is proposed at 150 °C to enhance the electrical performance and reliability of AZTO TFTs. The SCF provides good liquid-like solvency and high gas-like diffusivity, giving it excellent transport capacity [11], [12]. The oxidant is also easily dissolved in SCF with specific surfactants. It is thereby allowed for the SCF to transport the oxidant and penetrates the active layer for trap passivation and interface oxidation at low temperature for promoting the electrical characteristics of AZTO TFT. Photoreaction of the SCF-treated AZTO TFT also is discussed to further examine the potential of AZTO TFT for flat-panel display backplane technologies.

II. DEVICE FABRICATION

TFT devices were fabricated on the silicon wafer with a bottom-gated inverted-staggered structure. First, a 100-nm-thick thermal oxide was thermally grown on n^+ heavily doped (100) silicon substrate, which acted as a gate electrode. The active channel layer of a 25-nm-thick AZTO layer was formed by RF reactive sputtering with a power of 80 W at room temperature in a mixture of argon and oxygen with target of 3:67:30 mol% (Al_2O_3:ZnO:SnO_2). The flow rates of argon and oxygen gases were 10 and 2 SCCM, respectively. Then, a 100-nm-thick indium tin oxide was formed serving as source/drain electrodes by RF sputtering system and all the layers were defined by shadow masks. Both the channel width and length of AZTO TFTs were varied from 1000 to 200 μm. Sequentially, all samples were thermally annealed at 450 °C for 1 h in a furnace with N_2 gas flow rate of 10L/h under atmosphere pressure, and denoted as the standard samples. It was followed that the samples were posttreated and divided into two groups for study in this letter. In the first group, the sample was placed in a SCF system at 150 °C for 1 h, where it was injected with 2000–3000 psi of super-critical CO_2 (SCCO$_2$) fluid that were mixed with 5 vol% of propyl alcohol and 5 vol% of pure H_2O. The propyl alcohol acts as a surfactant between nonpolar-SCCO$_2$ fluid and polar-H_2O molecules, such that the H_2O molecules are uniformly distributed in supercritical CO_2 fluid. The SCCO$_2$ fluid acted as a transporter to carry the H_2O molecules into metal oxide films [13]. In the second group, samples were immersed in pure H_2O vapor at 150 °C for 1 h for comparison to clarify the effects of H_2O vapor. All electrical measurements were carried out by using the semiconductor parameter analyzer, Keithley 4200. The material analysis of X-ray photoelectron
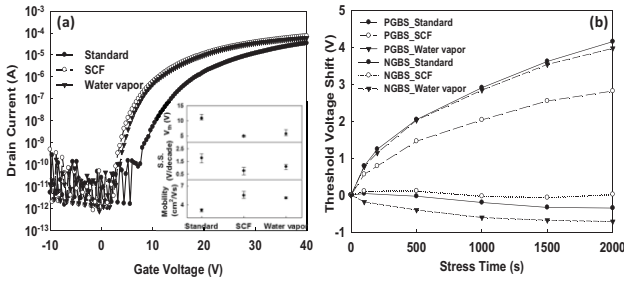
Fig. 1. (a) Drain current (I_D) versus gate voltage (V_G) curves of a-AZTO TFT devices with different posttreatments at a drain-to-source voltage of 11 V. Inset: device parameters, including threshold voltage (V_{th}), subthreshold swing (SS), and mobility (μ). (b) Threshold voltage shifts of a-AZTO TFT devices with different posttreatments as a function of gate bias stress. The conditions of GBS test were under the positive and negative gate bias with an electrical field of 2.5 MV/cm and source/drain were grounded for 2000 s.

Fig. 2. XPS analysis of Sn $3d_{5/2}$ spectrum for the a-AZTO thin films after (a) standard process, (b) SCF posttreatment, and (c) water vapor treatment.

spectroscopy (XPS) was also performed to examine the evolution of chemical bondings for 25 nm-thick AZTO thin films with different posttreatments.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows the transfer characteristics of AZTO TFTs with different posttreatments. The drain-to-source voltage (V_{DS}) was 11 V. The extracted threshold voltage (V_{th}), subthreshold swing (SS), and carrier mobility of each AZTO TFT are also compared in the inset. The mobility was extracted by the slope of $|I_D|^{1/2} - V_G$ plot as equation, $\mu = 2L/WC_{OX}(\partial|I_D|^{1/2}/\partial V_G)^2$. It is clearly observed that after SCF process, the threshold voltage of AZTO TFT decreased from 10.84 to 4.93 V, and the value of SS also was improved from 1.76 to 0.77 V/decade. In addition, the mobility was enhanced significantly from 3.16 to 5.51 cm²/Vs. Trap densities (N_t) can be estimated from SS value with the following formula. $SS = \log_e 10 \times (k_B T/e)[1 + e(tN_t + D_{it})/C_i]$, where k_B is the Boltzmann constant, T is the temperature, e is the elementary electric charge, t is the thickness of the AZTO active layer, and D_{it} is the interface trap density, assuming the trap tN_t dominated and D_{it} is negligible [14], [15].
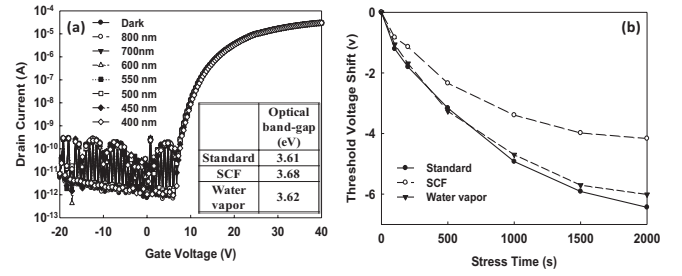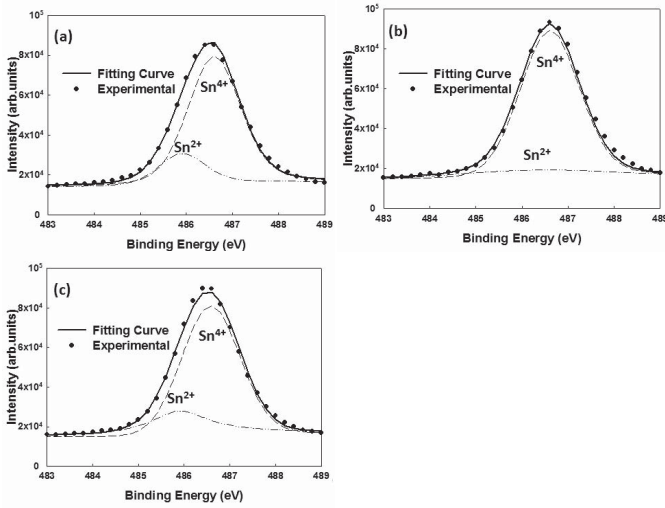

Fig. 3. (a) Transfer characteristics of the a-AZTO TFTs without any posttreatments under light radiation. Inset: corresponding values of optical energy bandgap (E_g) of a-AZTO films after different posttreatments. (b) Threshold voltage shifts of a-AZTO TFT devices with different posttreatments as a function of negative GBS under light illumination.

The N_t value of a-AZTO TFT for the standard, SCF-treated, and the water vapor process was 1.02×10^{18}, 2.48×10^{18}, and 1.49×10^{18} cm⁻³, respectively. This indicated that the proposed SCF treatment effectively decreased the trap density of AZTO active layer and improved the electrical performance of AZTO TFTs. In contrast, the performance of AZTO TFTs with H_2O vapor treatment was also improved. Chen *et al.* [11] reported that the H_2O absorbed in metal oxide thin films was dissociated into H and OH groups. The hydrogen atoms could be incorporated into metal oxide thin film to form hydrogen-related donors, whereas the dangling bonds or traps in the metal oxide thin film could be passivated by OH and form M–OH bonds (M is a metal cation). The passivation effect of OH on the amorphous AZTO film with large amount of dangling bonds will be more significant. In addition, Nomura *et al.* [14] reported that the OH bonds in metal oxide film would react with neighboring hydrogen and generate H_2O molecules by the following equation: $M-OH + M-OH \rightarrow V_{\ddot{o}} + M - O - M + H_2O \uparrow + 2e^-$, where M is a metal cation and $V_{\ddot{o}}$ is an ionized oxygen vacancy. It was also consisted with the experiment results, both SCF and H_2O vapor could improve the electrical performance of AZTO TFTs. The results of gate bias stress (GBS) are shown in Fig. 1(b). In this measurement, an electric field of 2.5 MV/cm was applied to gate electrode and source/drain electrodes were grounded. The instability of SCF treated a-AZTO TFT was improved effectively, and the value of V_{th} shift after positive GBS testing was 2.81 V, whereas it was 4.15 V for the a-AZTO TFT without SCF treatment. Comparatively, the improvement in V_{th} shift was not observed for the H_2O vapor-treated one. It indicated that the effects of SCF treatment were different from the H_2O vapor treatment. The XPS analysis was used further to identify the physical mechanism for electrical enhancement of a-AZTO TFTs. Fig. 2 shows the XPS of Sn $3d_{5/2}$ spectrum for the a-AZTO thin film with different posttreatments. The peak of Sn $3d_{5/2}$ signal has two components with binding energies of 486.6 and 485.9 eV, respectively, which were fitted by Gaussian–Lorentzian deconvolution. The higher binding energy centered at 486.6 is originated from the Sn⁴⁺ bonding state, whereas the lower binding energy centered at 485.9 is attributed to the Sn²⁺ binding state [16]. The ratio of Sn⁴⁺ component, which was defined as Sn⁴⁺/(Sn⁴⁺+Sn²⁺) were 81.1%, 89.1%, and 82.6% for the a-AZTO film with the standard

process, SCF treatment, and H_2O treatment, respectively. The performance of a-AZTO TFTs was strongly dominated by Sn^{4+}, because the field-effect carrier mobility of amorphous oxides was controlled by heavy metal cations with $(n-1)d^{10}ns^0(n\geq4)$ electronic configurations. In the a-AZTO thin film, Sn^{4+} with the electron configuration of $4d^{10}5s^0$ dominated the mobility owing to $5s^0$ orbital of Sn^{4+} being larger than $4s^0$ orbital of Zn^{2+} [10]. After SCF treatment, the ratio of Sn^{4+} increased from initial 81.1% to 89.1%. This indicated SCF process could effectively oxidize the a-AZTO thin film and transform Sn^{2+} to Sn^{4+}. The $SCCO_2$ fluid owns superior capability to transport H_2O molecules into metal oxide film, even arriving the interface and causing oxidation reaction [13]. This treatment has superior ability for oxidation and changes the Sn^{2+} into Sn^{4+}. The improvement of interface could explain the enhancement of GBS test. The modification on the oxidation state of Sn ion enhanced the electrical performance and stability of a-AZTO TFTs. The electrical characteristics of standard a-AZTO TFTs under light radiation with wavelengths ranging from 800 to 400 nm were studied. Fig. 3(a) shows the V_{th} value kept intact under visible-light illumination. The same phenomenon was also observed for the case of a-AZTO TFTs with SCF process or H_2O vapor treatments (not shown). This inset of Fig. 3(a) extracted the optical band gap (E_g) of a-AZTO films with different posttreatments by using Tauc's model [17]. All the a-AZTO thin films performed E_g larger than 3.62 eV, explaining that electrical characteristics of a-AZTO TFTs were not affected by visible-light illumination because of the large band gap of active layer. Therefore, a-AZTO films would not easily absorb the light with wavelengths ranging from 800 to 400 nm. The negative gate-bias illumination stress (NGBIS) was also examined further for the consideration of TFT-backplane technology as shown in Fig. 3(b). In the stress testing, source/drain electrodes were grounded and 25 V was applied to gate electrode. The light illumination with the intensity of 740 mW/cm^2 and wavelength of 546 nm was employed as radiation source. The V_{th} shift of the SCF-treated a-AZTO TFT was only -4.17 V, whereas it was -6.44 and -6.01 V for the standard and H_2O-vapor treated ones, respectively. Although the a-AZTO layer has no optical absorption at 546 nm, the light illumination would effectively excite the oxygen vacancies (V_o) to become the charged oxygen vacancy (V_o^{2+}) [18]. The generated V_o^{2+} states act as the positive fixed charges, which were trapped at the interface by negative gate bias. Therefore, the effective gate bias was changed by those trapped charges resulting in a negative shift in transfer characteristics of a-AZTO TFT. The V_{th} shift of SCF-treated a-AZTO TFT after NGBIS for 2000 s was less than the others because of the less trap density in the active a-AZTO layer. These above results indicated that the SCF process not only improved the electrical performance and stability of a-ATZO TFTs, but also reduced the electrical degradation after negative gate bias illumination stress.

IV. CONCLUSION

In summary, this letter has demonstrated the effects of low-temperature SCF on the a-AZTO TFTs. The SCF process

could effectively oxidize the a-AZTO thin film and modify the oxidation states of Sn, resulting in the improvement of electrical performance and stability of a-AZTO TFTs. In addition, the optical band gap increased after SCF process. After NGBIS, the V_{th} shift of the SCF treated a-AZTO TFT was reduced significantly than the one without SCF posttreatment. Owing to its low process temperature and efficient trap passivation in active layer, the SCF posttreatment is highly promising for emerging amorphous oxide TFT manufacturing.

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