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A low-temperature method, supercritical CO_2 ($SCCO_2$) fluid technology, is employed to improve the device properties of ZnO TFT at 150 °C. In this work, the undoped ZnO films were deposited by sputter at room temperature and treated by $SCCO_2$ fluid which is mixed with 5 ml pure H_2O. After $SCCO_2$ treatment, the on/off current ratios and threshold voltage of the device were improved significantly. From x-ray photoelectron spectroscopy analyses, the enhancements were attributed to the stronger Zn–O bonds, the hydrogen-related donors, and the reduction in dangling bonds at the grain boundary by OH passivation. © *2009 American Institute of Physics*.
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In recent years, ZnO-based thin-film transistors (TFTs) have attracted much attention for the application in flexible displays or transparent active matrix organic light-emitting diode displays,[1–3] which is due to their excellent uniformity and great transparency to the visible light of a wide band gap (3.2–3.3 eV). Many deposition methods have been used to prepare the ZnO films, such as sputtering,[4,5] pulsed laser deposition,[6] and chemical vapor deposition.[7] The sputter deposition is more favorable among these methods because the fabrication of ZnO TFT is comparable to the conventional amorphous-Si TFT. However, the ZnO thin films, deposited at room temperature, without doping usually exhibit an insulating property.[8,9] In order to improve the quality of ZnO films, a high-temperature postdeposition-annealing[10] or a high deposition temperature[8] is necessary. Nevertheless, high-temperature process is not suitable to substrates with low glass transition temperatures (T_g), such as glasses and plastics. Therefore, finding a low-temperature method to enhance the quality of ZnO thin film is required.

In our previous works, supercritical CO_2 ($SCCO_2$) fluid technology has been proposed to improve the dielectric properties of sputter-deposited hafnium oxide films and passivate the defect states in hydrogenated amorphous-silicon TFTs (*a*-Si:H TFTs).[11,12] In this study, we also employed the supercritical CO_2 ($SCCO_2$) fluid technology at 150 °C to enhance the performance of sputtered ZnO TFT. The $SCCO_2$ fluid exhibits liquidlike property, which has excellent transport ability. Furthermore, the $SCCO_2$ fluid has gaslike and high-pressure properties to diffuse into the nanoscale structures without damage. Hence, the $SCCO_2$ fluid can carry the H_2O molecule effectively into the ZnO films at low temperature and passivate traps by H_2O molecule at low temperature. The experimental results focus on material analyses and

electrical characteristics of the sputter deposited undoped ZnO film to investigate the efficacy of the $SCCO_2$ treatment.

The undoped ZnO TFT is the bottom-gate and bottom-contact type structures. The channel width (*W*) and length (*L*) of the TFTs were 50 and 8 μm, respectively. The device was fabricated by the following deposition procedure. First, a 300-nm-thick MoW gate electrode was deposited and patterned on the glass substrate. For the gate insulator, a 300-nm-thick silicon nitride (SiN_x) was deposited by plasma enhanced chemical vapor deposition. Then, a 100-nm-thick indium tin oxide film was deposited and patterned in forming the source/drain electrodes. Finally, a 100-nm-thick undoped ZnO film was formed by rf magnetron sputtering system at room temperature. The active layer was defined using photolithography and wet etching. To optimize the device characteristics, two different post-treatments were performed on the ZnO film. For the first method, device labeled as "H_2O vapor" was placed in a pressure-proof stainless steel chamber, and a pure H_2O vapor was immersed into ambience at 150 °C for 1 h. For the second method, device labeled as "$SCCO_2$" was performed on a supercritical fluid system full of 3000 psi $SCCO_2$ fluids which was mixed with 5 ml pure H_2O at 150 °C for 1 h. Finally, we define a control sample without any treatment marked as "standard." After these different treatments, the electrical characteristics of the device were measured in the dark environment at room temperature using Agilent 4156-C semiconductor analyzer. In addition, x-ray photoelectron spectroscopy (XPS) was used to determine the chemical functional bonds of the ZnO films.

Figure 1 shows the typical transfer curves I_{DS}-V_{GS} at V_{DS}=20 V. The threshold voltage (V_t) was defined as the gate voltage at which the drain current reaches 10^{10} A. The sub-threshold slope (SS) was extracted from drain current in the sub-threshold region (the drain current from 10^{-12} to 10^{-10} A) under saturation operation. As shown in the figure, the characteristics of undoped ZnO TFTs were much affected

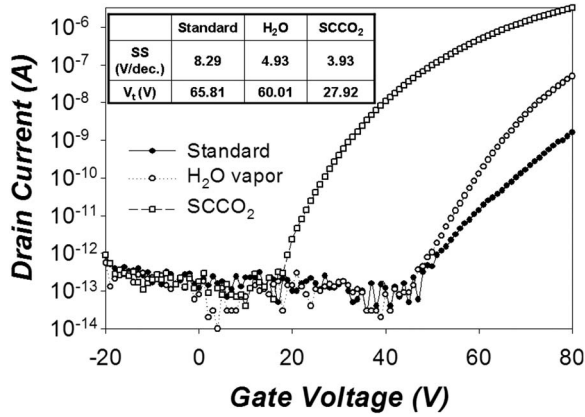a)Electronic mail: tcchang@mail.phys.nsysu.edu.tw.

FIG. 1. Transfer curves of undoped ZnO TFT after different treatment conditions.

by the post-treatment. For the standard ZnO TFT, the device characteristics exhibit the largest V_t of 65.81 V and the lowest current. The result indicated that the standard device with undoped ZnO film as an active channel does not show acceptable transistor characteristics. However, because the as-deposited ZnO film is consisted of numbers of ZnO grains, the carriers have to transport from source to drain via the grain boundaries as the device is operated. Therefore, the traps in grain boundaries may cause the potential barrier resulting in a low drain current and a high V_t. After H_2O vapor treatment, the device exhibits a slightly improved drain current ($\Delta I_{on} \sim 1$ order) and SS (Δ SS ~ 3.36 V/decade). However, a large V_t still existed, and it means that only partial traps were passivated by the H_2O vapor treatment. Clearly, for the $SCCO_2$ treatment, V_t, drain current, and on/off current ration (I_{on}/I_{off}) were significantly enhanced compared to the two devices. It exhibited the V_t of 27.92 V, the SS of 3.93 V/decade, and I_{on}/I_{off} of 10^6. The field-effect mobility was extracted by standard method ($I_{DS}{}^{0.5}$ versus V_{GS} plot etc.), the corresponding mobility values for three devices were 2.82E-5, 1.01E-3, and 2.6E-2. From the above results, $SCCO_2$ treatment is the most effective method to improve the device property because the most traps at grain boundaries were passivated.

In order to analyze the composition of the ZnO film after post-treatment, the XPS analysis is performed, and the binding energies have been calibrated by taking the carbon C $1s$ peak (285.0 eV) as reference. The Zn $2p_{3/2}$ peaks of ZnO thin films after different treatments are shown in Fig. 2, and
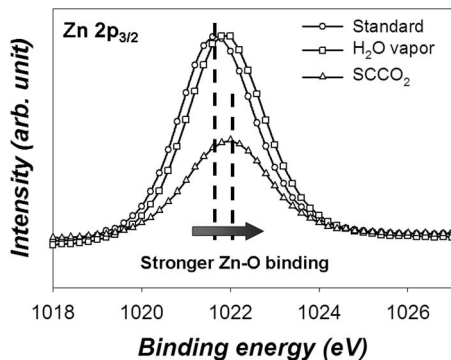

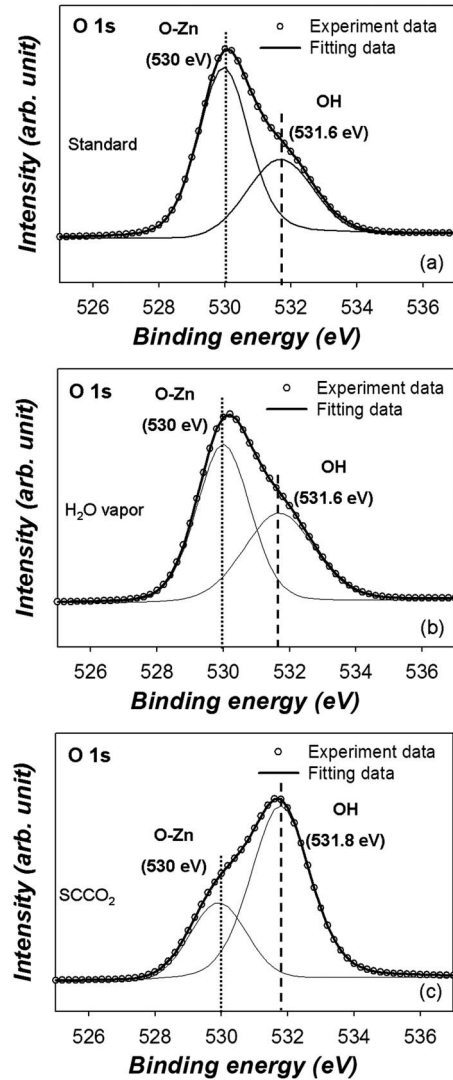FIG. 2. XPS of Zn $2p_{3/2}$ spectra for the ZnO thin films after different treatment conditions.

FIG. 3. XPS of O $1s$ spectra with two resolved O bonding components for the ZnO thin films after various treatment conditions, including (a) standard, (b) H_2O vapor, and (c) $SCCO_2$.

the energy state of standard sample at about 1021.6 eV corresponds to Zn–O bonding.[13] After the treatment of H_2O vapor and $SCCO_2$ treatment, the binding energy shifts to 1021.9 and 1022.1 eV, respectively. The stronger Zn–O bonding indicates that Zn atoms in ZnO film have been oxidized more completely with the H_2O molecules. In addition, the $SCCO_2$ treatment is more efficient than H_2O vapor treatment in transporting H_2O molecules into the ZnO film.

The O $1s$ peaks of various treatments ZnO thin films are shown in Fig. 3. The O $1s$ peaks have a shoulder at higher binding energy, and it increases obviously after the treatment of H_2O vapor and $SCCO_2$. The lower energy peak detected at 530.0 eV corresponds to O–Zn bonding, and the higher energy peak detected at 531.6 eV is attributed to O–H bonding, which can be due to the H_2O molecules adsorption in the ZnO films.[14] However, the standard sample without any post-treatment also exhibit the high-energy peak of O–H bonding, which originated from the surface of ZnO films with adsorbed H_2O molecules as it is exposed to the air. In addition, the H_2O absorbed in ZnO thin films was dissociated into H and OH groups, and rapidly diffused into the ZnO film.[15] As previous study reported, the hydrogen atoms can be incorporated into ZnO to form hydrogen-related donors, such as the

TABLE I. Atomic concentrations calculated from XPS of the ZnO films after various treatment conditions.

	Zn $2p_{3/2}$ (%)	O–Zn (%)	OH (%)
Standard	55.32	29.66	15.02
H_2O vapor	53.98	26.83	16.36
$SCCO_2$	36.21	17.66	46.13

substitutional hydrogen bound to zinc atoms and the interstitial hydrogen bound to oxygen atoms, and improve the electrical conductivity of ZnO film.[16] Otherwise, the dangling bonds (or traps) in the grain boundaries can be passivated by OH and form Zn–OH bonds. Therefore, the dangling bonds (or traps) induced potential barrier can be suppressed. By using the integrated peak area with the sensitivity factors, the atomic concentrations of Zn and O were listed in Table I. The O–H bonding for the standard sample and the ZnO film after H_2O vapor are 15.02% and 16.36%, while the O–H bonding after $SCCO_2$ treatment rapidly increases to 46.13%. The results of the O $1s$ spectra indicate that H_2O molecules can be effectively carried into the ZnO film by the highly diffusing $SCCO_2$ fluid and passivate the traps.

In summary, the significant improvement of electrical characteristics for ZnO TFTs by low-temperature $SCCO_2$ treatment was demonstrated. After the treatment of $SCCO_2$ fluid mixed with pure H_2O, the OH concentration of ZnO films rapidly increased, indicating that the dangling bonds (or traps) within the ZnO films are passivated by forming Zn–OH bonds. It was verified that the $SCCO_2$ fluid is an effective transporter to carry the H_2O molecules into sputter-deposited ZnO films and enhances the device's electrical properties.

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