

# Hybrid-Phase Microstructure in ITO-stabilized ZnO Thin Films and Its Application to High-Performance Thin-film Transistors

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## Abstract

*ITO-stabilized ZnO thin films with a novel hybrid-phase microstructure are introduced, where a number of nanocrystals are embedded in an amorphous matrix. Following the study on microstructural and electrical properties of thin films, the corresponding staggered bottom- and top-gate thin-film transistors with optimal channels are both fabricated and exhibit a fairly high and uniform electrical performance, especially in field-effect mobility and subthreshold swing. In addition, such devices are also proven to be air-stable owing to in situ passivation of hybrid-phase microstructural ITO-stabilized ZnO channels.*

## 1. Introduction

Recently, metal oxide (MO) semiconductors have drawn great attention as TFT channels, and these MO thin-film transistors (TFTs) possess many promising advantages, such as reasonable electrical performance and high optical transparency, low processing temperature and production costs as well [1,2]. Since reported by Hosono *et al.* in 2004 [3], amorphous indium-gallium-zinc oxide (a-IGZO) promptly became the most prevalent multicomponent MO material, and its electrical properties are not deteriorated too much in spite of the atomic disorder. However, with the advancement of next-generation active-matrix (AM) displays towards large area, ultra-high definition (UHD) display, and system on panel (SoP), a-IGZO seems still insufficient to fulfill the requirements of TFTs for higher mobility [4-5]. As the fundamental binary MO material, ZnO is attractive with medium electrical performance, and its earth-abundance offers potential opportunities in low-cost applications. But, the pristine polycrystalline ZnO (pc-ZnO) TFTs always suffer from native defects (such as oxygen vacancies ( $V_O$ ), dangling states) and grain boundaries (GBs), which result in severe instability issues and required further modifications [1]. On the other hand, it is always controversial on whether the amorphous phase overweighs the nanocrystalline phase in MO semiconductors, in particular after the amorphous oxide semiconductors (AOS) mobility limits are proposed [5]. For most MO TFTs, their best performance is actually obtained at the boundary between the amorphous and crystalline phases.

In this paper, a novel hybrid-phase microstructure with nanocrystals blended in amorphous phase was introduced into ITO-stabilized ZnO thin films for the first time. Then, the corresponding bottom- and top-gate TFTs were both

successfully fabricated and exhibited remarkable electrical performance with device uniformity comparable to AOS TFTs. Moreover, the devices even without any passivation were found to be air-stable, and in-situ passivation of channels is given to explain such phenomenon.

## 2. Deposition and Properties of Films

As known, the sputtered ITO and ZnO thin films are generally polycrystalline. When ITO and ZnO are blended together using dc and rf sputtering power, respectively, a novel hybrid-phase microstructure is found in the deposited thin films, where parts of ITO/ZnO grains survive in nanocrystalline phase and are embedded in an amorphous matrix. In Fig. 1a, the X-ray diffraction (XRD) spectra display a quite weak and wide peak between ITO (222) peak and ZnO (002) peak. According to Scherrer's equation, the grain size derived is about 1.5 nm, indicating the existence of nanocrystals inside the co-sputtered thin films. The microstructure was further probed using a high resolution transmission electron microscope (HRTEM). It can be seen that the columnar nanocrystals with clear lattice fringes are sparsely distributed in the amorphous matrix, so the grain boundaries are diluted (Fig. 1b). Different from other amorphous InSnZnO films, it is believe that the inherent hybrid-phase microstructure will also make a great contribution to TFTs with high electrical performance and stability especially in comparison with the pc-ZnO and a-IGZO TFTs. Thus, the ITO/ZnO co-sputtered thin films proposed in this paper is named as hybrid-phase microstructural ITO-stabilized ZnO thin films.

Since the conductivity of ITO and ZnO are both sensitive to the amount of  $V_O$  inside thin films, the oxygen partial pressure ratio ( $P_{O_2}=O_2/(Ar+O_2)$ ) is regarded as one of most important parameters to affect the electrical properties of co-sputtered films. To understand the relationship more clearly, X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical states of oxygen in the deposited thin films. As shown in Fig. 2a-2d, the XPS spectra of O 1s peak can be divided into three peaks  $O_I$ ,  $O_{II}$ ,  $O_{III}$ , and further fitted as a Gaussian distribution. Theoretically, the  $O_I$ ,  $O_{II}$  and  $O_{III}$  peak are relevant to the oxygen bonded in oxide lattices (In-O, Sn-O and Zn-O), oxygen deficiencies in lattices (such as  $V_O$ ) and chemisorbed oxygen (such as the bonded oxygen in hydroxyl groups), respectively. These peaks are correspondingly centered in the vicinity of 530.2 eV, 531.6 eV and 532.2 eV. The symmetric variations in Fig.

2(e) imply that  $P_{O_2}$  can regulate the amount of  $V_O$  and indirectly manipulate the electrical conduction of ITO-stabilized ZnO thin films. When  $P_{O_2}$  rises from 10% to 60%, the relative area ratio of  $V_O$  decreases to only 6.58%, and the resistivity differs by nearly two orders of magnitude when oxygen is in insufficient and excess status.

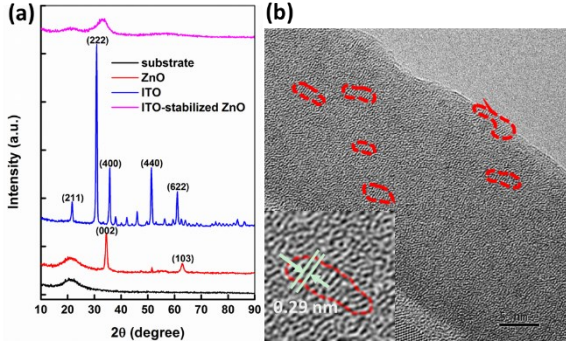


Fig. 1. (a) XRD spectra and (b) HRTEM cross-sectional image of hybrid-phase microstructural ITO-stabilized ZnO thin films.

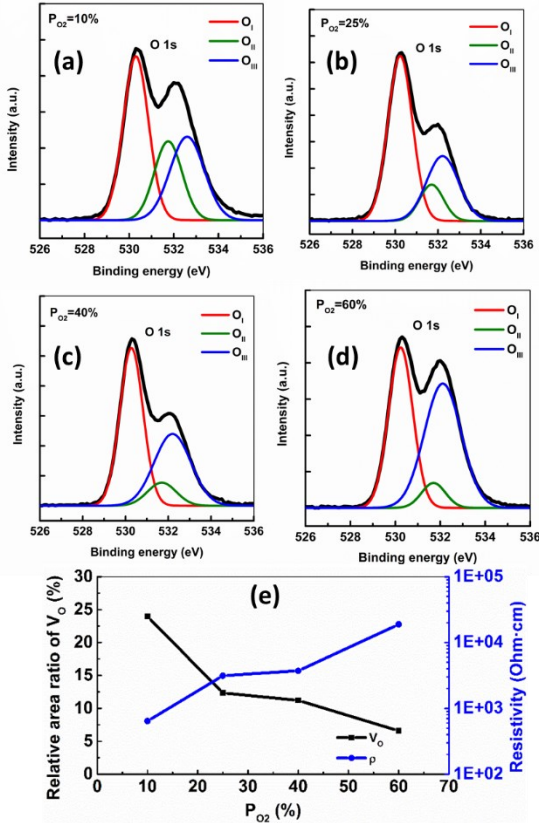


Fig. 2. XPS O 1s spectra of hybrid-phase microstructural ITO-stabilized ZnO thin films co-sputtered with  $P_{O_2}$  of (a) 10%, (b) 25%, (c) 40% and (d) 60%; (e) the relative area ratio of  $V_O$  and resistivity of thin films as a function of  $P_{O_2}$ ;

### 3. Device Fabrication

With hybrid-phase microstructural ITO-stabilized ZnO channels, both staggered bottom-gate and top-gate TFTs were fabricated. The bottom-gate device started on 4-inch heavily doped n-type silicon wafers, which were coated by 120-nm-thick thermal oxide on the front surface. 50-nm-thick ITO-stabilized ZnO channels were deposited on

$SiO_2/Si$  substrates using magnetron co-sputtering the ITO (90 wt%  $In_2O_3$  and 10 wt%  $SnO_2$ ) and ZnO target at room temperature. In order to obtain TFTs with optimal electrical performance, various sputtering conditions including  $P_{O_2}$  and dc power ( $P_{DC}$ ) are attempted. Next, the active channels were patterned using conventional photolithography and etched in diluted hydrofluoric acid. The channel width and length were 90  $\mu m$  and 45  $\mu m$ , respectively. After photoresist stripping and drying, a lift-off method was performed to form Al source and drain (S/D) electrodes, which was deposited by DC magnetron sputtering. Finally, the devices were subjected to thermal annealing at 300°C in air. The electrical characteristics of devices were measured in the probe station using a semiconductor parameter analyzer (Agilent 4156C).

Based on the co-sputtering conditions employed in the optimal bottom-gate TFTs, the staggered top-gate TFTs were then fabricated. The substrates were 4-inch p-type silicon wafers coated with 500-nm-thick thermal oxide. 80-nm-thick ITO was formed as S/D electrodes by lift-off technique at first. The ITO-stabilized ZnO channels were then deposited with  $P_{O_2}$  of 40% and  $P_{DC}$  of 120 W, and patterned into active islands by wet etch. Next, 150-nm-thick PECVD- $SiO_2$  gate dielectric and 200-nm-thick Al gate electrode deposition was performed in sequence, followed by dry etch processes. The devices were also annealed at 300°C in air, and the whole processes were conducted within 300°C.

### 4. Results and Discussion

Fig. 3(a) reveals the transfer curves with various sputtering  $P_{O_2}$  under a constant dc and rf power (120W dc and 150W rf). It is noted that there exists a dramatic threshold voltage ( $V_{th}$ ) shifts from -35.85 V to -0.75 V when  $P_{O_2}$  initially rises. This is consistent with the sharp decrease in relative area ratio of  $V_O$  (Fig. 2). However, the field-effect mobility ( $\mu_{fe}$ ) always maintains at relatively high values ( $>20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ). According to Adler's percolation conduction model,  $\mu_{fe}$  generally increases with the rise of carrier concentration, because more carriers can reduce the potential difference between Fermi level and percolation potential barriers. On the other hand, if the intrinsic height of percolation potential barriers is low, carriers can also transport with less impedance. For the ITO-stabilized ZnO thin films with hybrid-phase microstructure, the height reduction of percolation barriers is possibly provided by the ordered atomic arrangement within nanocrystals, diluted grain boundary density, and 5s orbital overlaps of In/Sn cations in the amorphous matrix. Fig. 3(b) shows an obvious change in electrical performance of devices when  $P_{DC}$  climbs beyond 60 W. One plausible explanation is that the channels are dominated by pc-ZnO and fail to exhibit the advantages in hybrid-phase microstructural ITO-stabilized ZnO thin films. Above all, the optimal devices are obtained when  $P_{O_2}$  and  $P_{DC}$  are set as 40% and 120 W, respectively. The key electrical parameters of corresponding bottom- and top-gate TFTs are listed in Table 1, and their transfer and output curves are plotted in Fig. 4.

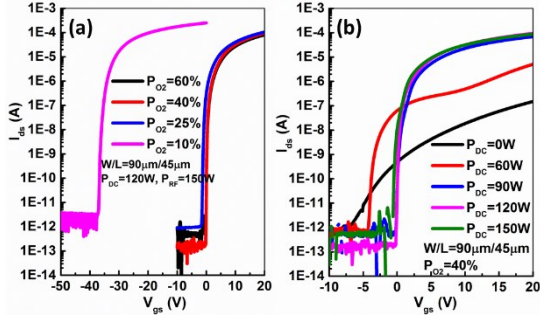


Fig. 3. Transfer curves of hybrid-phase microstructural ITO-stabilized ZnO TFTs with various (a)  $P_{O_2}$  and (b)  $P_{DC}$ .

Table 1. Key electrical performance of bottom- and top-gate TFTs with the optimal hybrid-phase microstructural ITO-stabilized ZnO channels

	Bottom-gate	Top-gate
$V_{th}$ (V)	0.46	-0.65
$\mu_{fe}$ ( $cm^2/Vs$ )	26.08	19.10
On-off ratio ( $\times 10^8$ )	10.9	1.61
SS (V/decade)	0.089	0.115

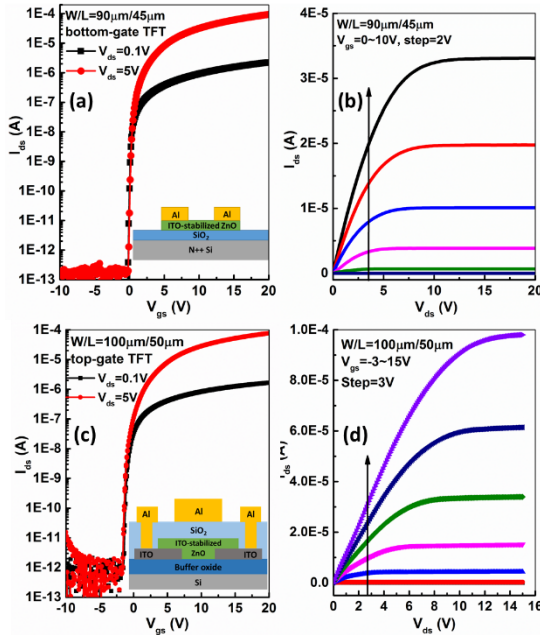


Fig. 4. The transfer curves of (a) bottom- and (c) top-gate TFTs; the output curve of (b) bottom- and (d) top-gate TFTs.

Fig. 5 shows the spatially uniformity of bottom-gate TFTs over a 4-inch silicon wafer, which was comparable to AOS TFTs. Apart from the enhanced device behaviors, it is clearly seen that all the transfer curves shift within a rather narrow range. This is because the grain size of nanocrystals inside is no more than 2 nm. When involved in TFTs with micrometer scaled channel length, these nanocrystals look quite small and sparse, and the diluted grain boundaries can be almost negligible.

Furthermore, Fig. 6 illustrate the excellent environment stability of TFTs, even for the unpassivated bottom-gate devices with backsurface exposed in air. The  $V_{th}$  of unpassivated bottom-gate devices only drops from about

0.5 V to below zero within the first day, then achieves a dynamic equilibrium for a long period, which are much air-stable than those pristine pc-ZnO and a-IGZO TFTs. Such phenomenon can be explained by in situ passivation of channels. Specifically, ZnO nanocrystals inside can be encapsulated by the amorphous ITO/ZnO matrix, which is less sensitive to the ambient. Therefore, it suppresses the ambient chemisorption effects at the backsurface and grain boundaries of ZnO.

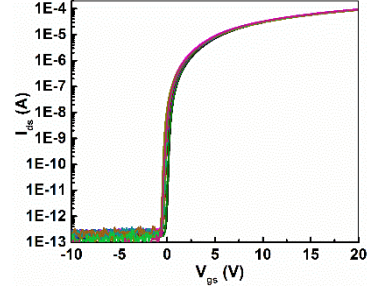


Fig. 5. Transfer curves of 15 bottom-gate hybrid-phase microstructural ITO-stabilized ZnO TFTs, which are uniformly distributed over a 4-inch silicon wafer.

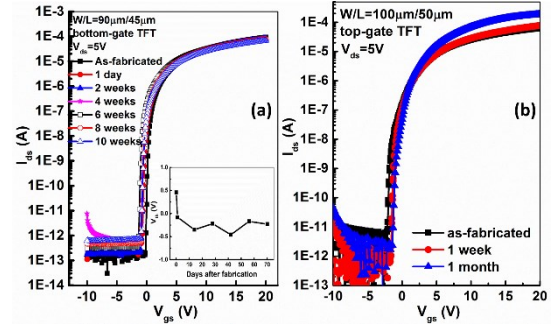


Fig. 6. The air stability of (a) unpassivated bottom- and (b) top-gate TFTs with hybrid-phase microstructural ITO-stabilized ZnO channels.

## 5. Conclusions

A novel hybrid-phase microstructure was introduced in ITO-stabilized ZnO thin films for the first time, where nanocrystals were embedded in an amorphous matrix. The microstructural and electrical properties of thin films were then studied. Afterwards, both corresponding bottom- and top-gate TFTs were fabricated and exhibited remarkable electrical performance and uniformity. At last, as a unique merit of the hybrid-phase microstructure, in situ passivation of channels was pointed out to explain the excellent environment stability of devices.

## References

- [1] E. Fortunato, P. Barquinha, R. Martins, *Adv. Mater.* Vol. 24, p. 2945 (2012).
- [2] P. Carcia, R. McLean, M. Reilly, G. Nunes Jr, *Appl. Phys. Lett.* Vol. 82, p. 1117 (2003).
- [3] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, *Nature* Vol. 432, p. 488 (2004).
- [4] T. Kamiya, K. Nomura, H. Hosono, *Sci. Technol. Adv. Mater.* Vol. 11, p. 044305 (2010).
- [5] K. A. Stewart, B.-S. Yeh, J. F. Wager, *J. Non. Cryst. Solids* Vol. 432, p. 196 (2016).