

Combinatorial study of zinc tin oxide thin-film transistors

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Groups of thin-film transistors using a zinc tin oxide semiconductor layer have been fabricated via a combinatorial rf sputtering technique. The ZnO:SnO₂ ratio of the film varies as a function of position on the sample, from pure ZnO to SnO₂, allowing for a study of zinc tin oxide transistor performance as a function of channel stoichiometry. The devices were found to have mobilities ranging from 2 to 12 cm²/V s, with two peaks in mobility in devices at ZnO fractions of 0.80±0.03 and 0.25±0.05, and on/off ratios as high as 10⁷. Transistors composed predominantly of SnO₂ were found to exhibit light sensitivity which affected both the on/off ratios and threshold voltages of these devices. © 2008 American Institute of Physics. [DOI: 10.1063/1.2828862]

Modern technology is demanding that consumer electronics such as displays be optimized not only for performance and power consumption, but for weight, flexibility, and durability as well. Transistors in light-weight, flexible displays must have relatively high carrier mobility and, in order to be compatible with a large area, flexible substrate, must be insensitive to bending. There are various semiconductors that are well suited to these requirements. Amorphous silicon (*a*-Si) is already widely employed in various large area applications, most notably in liquid crystal displays and large area photovoltaics.

Organics such as pentacene are also being explored. However, both *a*-Si and organic devices are limited to mobilities of ~1 cm²/V s,¹⁻³ have relatively low on currents and are opaque. On the other hand, amorphous metal oxides have been shown⁴⁻⁷ to have high mobilities (up to 50 cm²/V s) and on currents while also having the benefit of being largely transparent. For these reasons, zinc tin oxide (ZTO) has attracted attention, due to its high mobility and optical transmittance,^{6,8} which offer the possibility of high-performance transparent electronics for applications such as displays. Thus far, transistors fabricated via sputtering of ZTO have achieved mobilities as high as 50 cm²/V s and on/off ratios of 10⁷.^{6,9} These devices were primarily fabricated using premade sputtering targets, usually of a ZnO:SnO₂ mixture of 1:1 or 2:1. Due to the impracticality of fabricating separate targets for a large variety of different stoichiometries, only a limited number of these ratios have been explored. ZTO is known to be crystalline in the forms ZnSnO₃ (Ref. 10) and Zn₂SnO₄ (Ref. 11), making the 1:1 and 2:1 ratios that are most commonly tested seem to be the obvious choices, as it is often the case that the crystalline forms of a material have higher carrier mobilities. Despite this, the electronic properties of these films are not particularly well understood and a combinatorial study of ZTO-based thin-film transistor performance is necessary. A previous study¹² was conducted for pure ZnO and SnO₂ devices, plus (ZnO)_x(SnO₂)_{1-x} devices at three ratios of $x=0.33, 0.50,$ and $0.67,$ examining mobility as a function of stoichiometry and annealing conditions. Devices of each stoichiometry were fabricated in separate runs, with different sputtering targets, introducing a degree of experimental uncertainty in comparing the results.

This experiment used a combinatorial rf sputtering technique that yields a range of ZnO:SnO₂ ratios whose composition varies as a function of position on a substrate. Additionally, multiple samples were fabricated under the same conditions to facilitate optimization of annealing conditions. Our technique makes no assumptions about the preference of one composition over another, and allows for a fine-grained systematic study of performance as a function of stoichiometry.

Top contact thin film transistors were fabricated on 100 mm heavily *n*-doped (arsenic, <0.005 Ω cm) <100> prime grade silicon wafers with a 1000±20 Å thermally grown SiO₂ layer, acquired from Silicon Quest International. The doped silicon acted as a common gate for all devices on the wafer, while the oxide acted as the dielectric. Each experiment consisted of four of these wafers. Prior to being placed in the sputtering chamber, each wafer was oxygen-plasma cleaned in a reactive ion etcher at a power density of 0.08 W/cm² in 150 mTorr of O₂. 50 mm ZnO (99.999%) and SnO₂ (99.9%) targets were purchased from Kurt J. Lesker and Williams Advanced Materials, respectively. The ZnO and SnO₂ targets were sputtered at powers of 43 and 108 W, respectively, with a sputter gas pressure of 5 mTorr consisting of 90% Ar and 10% O₂. The substrates were nominally at room temperature. The combinatorial technique¹³ used to create these samples involved sputtering both targets simultaneously at the same fixed radial distance from the center of a rotating table to which the wafers were fixed. This resulted in a toroidal “track” of sputtered film on the table and wafers. The sources were masked such that ZnO had a deposition rate of ~4 Å/s at the outer edge of the track and this rate decreased linearly to 0 at the inner edge of the track, while the SnO₂ target had approximately the same rates, but decreasing from the inner to the outer edge. The table was rotated quickly with respect to the deposition rate (15 rpm) such that the thickness of ZnO deposited per rotation was less than a monolayer, varying between 0 and 0.4 Å. This resulted in intimate mixing of the sputtered materials and, ideally, a continuum of stoichiometries of the form (ZnO)_x(SnO₂)_{1-x} ranging approximately linearly from $x=0$ at the inner edge to $x=1$ at the outer edge.

To avoid large leakage currents resulting from the increased sensitivity to pinholes and fringing effects inherent in samples having many transistors using a single, large area semiconductor layer, the deposited metal oxides on each wafer were patterned using a stainless steel shadow mask dur-

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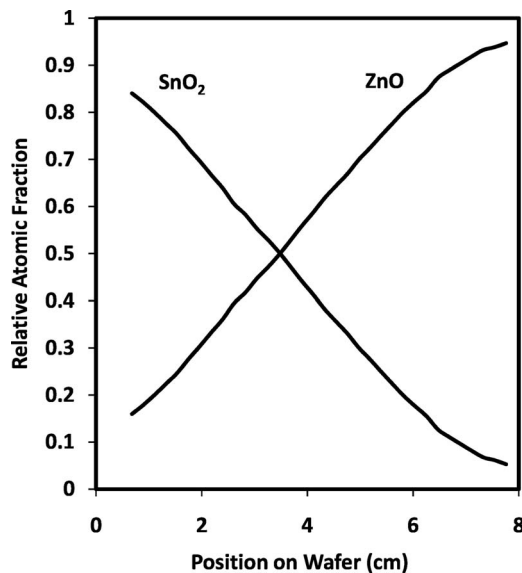


FIG. 1. Atomic fraction of ZnO and SnO₂ as a function of position on the wafers.

ing the sputtering process, such that each transistor had an electrically isolated active channel. To eliminate possible unintentional doping of the semiconductor due to oxygen deficiencies, the wafers were postannealed in O₂ for 30 min at temperatures of 550, 600, 650, and 700 °C. Aluminum source and drain contacts were then vacuum vapor deposited through a shadow mask. Devices had width/length ratios varying from 4 to 16, with channel lengths varying from 125 to 500 μm and there were a total of 256 devices per wafer.

A JEOL JXA-8200 Electron Probe Microanalyzer was used in wavelength dispersive spectroscopy mode to examine the stoichiometry of the resulting film. The sputtered semiconductor layer was revealed to have a relative atomic fraction of 85% Sn, 15% Zn at one extreme and 5% Sn, 95% Zn at the other (Fig. 1), varying approximately linearly between the two. The ratio of oxygen to zinc and tin signals is consistent with a film consisting primarily of ZnO and SnO₂ [tin (IV) oxide], as opposed to SnO [tin (II) oxide]. There was some initial concern that the use of shadow masks in direct contact with the wafer would result in contamination of the deposited film due to secondary sputtering of the stainless steel mask. However, the wafers yielded no iron signal when tested using the electron probe.

Using a Dektak profilometer, the deposited film was found to be ~500 Å thick at all positions within the sputtered track. Initial test samples were annealed under argon,⁸ but these were found to be highly conductive while off, exhibiting poor on/off ratios particularly in regions of high SnO₂ concentration. However, another set of devices that were annealed under O₂ had vastly improved on/off ratios compared to this original set. This difference in off current is consistent with as-deposited films containing a high density of oxygen vacancies that heavily dope the semiconductor and limit gate-induced modulation of active channel conductivity. Of the four annealing temperatures studied, devices annealed at 600 °C exhibited the highest performance and lowest rate of defects.

Testing of electrical transport characteristics was done in a dark, grounded box, in atmosphere and at room temperature. A single common gate contact was made by scratching

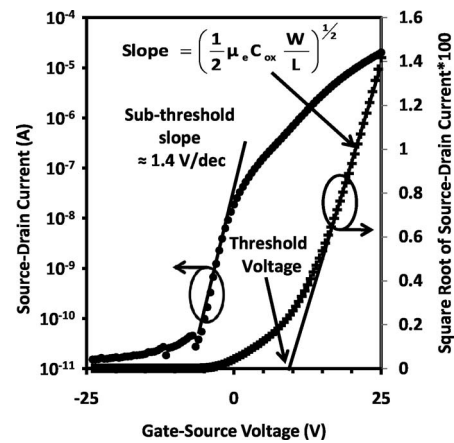


FIG. 2. A saturation transfer curve ($V_{DS}=+25$ V) demonstrating the method used to find carrier mobility, threshold voltage and subthreshold slope. The device in this figure has a composition of (ZnO)_{0.84}(SnO₂)_{0.16}.

through the oxide to the heavily doped silicon. All contact was made using tungsten probes under a microscope. Each *n* type device was characterized using its saturation transfer curve, acquired by sweeping the gate voltage from on to off to on ($V_{GS}=V_{DS}$ to $-V_{DS}$ and back). Typically, V_{DS} was set to +25 V. Voltages were supplied and currents recorded using a pair of Keithley 237 Source Measure Units. Ideal field effect transistor equations were used to determine the mobility and threshold voltages,

$$i_{DS} = \frac{1}{2} \mu_e C_{ox} \frac{W}{L} (V_{GS} - V_T)^2 \quad \text{or}$$

$$i_{DS}^{1/2} = \alpha (V_{GS} - V_T),$$

where

$$\alpha = \left(\frac{1}{2} \mu_e C_{ox} \frac{W}{L} \right)^{1/2} \quad \text{for } V_{DS} > V_{GS} - V_T.$$

Here, μ_e is the electron mobility, i_D is the source-drain current, V_{GS} is the gate-source voltage, V_T is the threshold voltage, W is the channel width, L is the channel length, and C_{ox} is the capacitance per unit area of the oxide dielectric. The mobility was found by taking the slope of the linear portion of the square root of the source-drain current as a function of gate-source voltage (α), and the threshold voltage was found by determining the V_{GS} intercept of this linear portion (Fig. 2). The on/off ratio was simply taken to be the ratio of the maximum to minimum measured source-drain currents.

Using the saturation transfer curves (see Fig. 2 for a typical device) and electron probe data, electron mobilities were found to vary from 2 to 12 cm²/V s across the available range of stoichiometries. While mobilities for sputtered ZTO devices have been reported to be as high as 50 cm²/V s⁶, these were reported for devices fabricated using indium tin oxide (ITO) instead of aluminum for the source and drain contacts. It is likely that the higher contact resistance for devices with Al source and drain contacts limits the observed mobilities in our devices.⁹ Two peaks in mobility are obvious in the data (Fig. 3), with one at a ZnO fraction of 0.25±0.03 and another at 0.80±0.05. The first of these peaks exhibits the highest mobility at 10–12 cm²/V s, while the second is slightly lower at 8–11 cm²/V s. A trough is also visible, centered around the 1:1 point. Threshold volt-

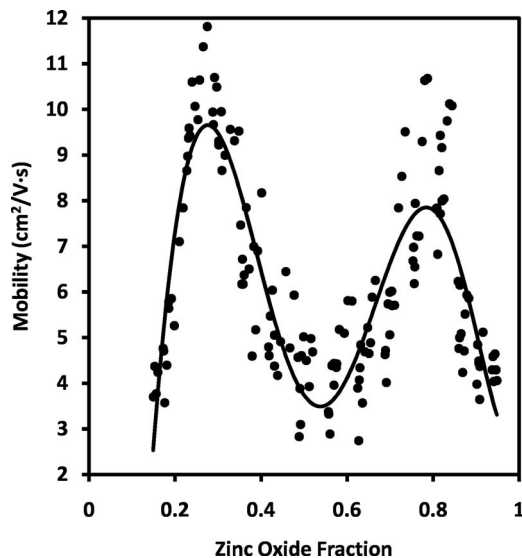


FIG. 3. Mobility as a function of zinc oxide fraction across an entire wafer of devices. Note that the line serves as a guide to the eye only.

ages varied from -8 to $+18$ V (Fig. 4), with the largest of these in the regions of lowest mobility. These data suggest that the electrical properties of these films are quite sensitive to stoichiometry and are not optimized at the 1:1 or 2:1 stoichiometries. No significant hysteresis was visible between the on-to-off and off-to-on sweeps. On/off ratios were on the order of 10^6 (Figs. 2 and 4) and the best subthreshold slopes were 1.4 V/decade (Fig. 2) independent of stoichiometry, when tested with no prior light exposure. However, ZnO fractions ≤ 0.33 were found to be highly light-sensitive, exhibiting changes in on/off ratio of as much as 10^5 for light versus dark conditions. Mobility was not affected by light exposure. This effect will be the subject of an upcoming paper.

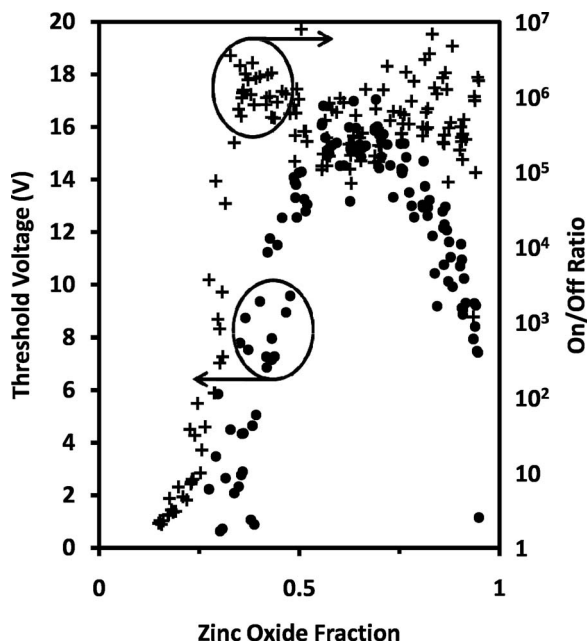


FIG. 4. Threshold voltage and on/off ratio as a function of zinc oxide fraction across an entire wafer of devices. The sudden decrease in both threshold voltage and on/off ratio is due to the light sensitivity of these devices.

These results contradict the conclusions of previous work,¹² showing what appears to be a minimum in mobility at $x=0.50$, which was previously found to be a stoichiometry for peak mobility. It should be noted that with the exception of the mobility measured at one stoichiometry in the previous work, the data otherwise coincide with the data presented here. For example, the relationship between threshold voltage and stoichiometry and the poor subthreshold behaviour in devices with high SnO₂ content are both consistent with previous results. We note the following differences between the two experiments. In this study, devices covering the range of compositions were fabricated at the same time, in the same deposition run, and on the same substrate using the same sputtering targets. In the previous study, devices of each stoichiometry were fabricated separately using different sputtering targets for each ratio. We report saturation mobilities, effectively averaged over the range of voltages well above threshold, while the previous study examines differential linear mobilities. In addition, the previously reported mobilities were found to be monotonically increasing with increasing $V_{GS}-V_t$ and the largest mobilities (at the highest V_{GS}) were reported, thus, favoring devices with the most negative threshold voltages.

In conclusion, $(\text{ZnO})_x(\text{SnO}_2)_{1-x}$ transistors were fabricated combinatorially for $0.15 \leq x \leq 0.95$. The highest electron mobilities were observed at $x \approx 0.25 \pm 0.05$ and 0.80 ± 0.03 , which contradicts earlier predictions of 0.50 and 0.67 (Ref. 6) and an earlier experimental report of a broad peak around 0.50.¹² Ongoing efforts are being made to understand the origin of the improved mobility at these stoichiometries. Additionally, some film compositions were shown to be light sensitive, which may limit the usefulness of these films in transparent devices for display applications. Future work will investigate the origin, nature and wavelength dependence of this effect.

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