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Tuning the electrical properties of ZnO thin-film transistors by thermal annealing in different gases

J.D. Jin [a], Y. Luo [a], P. Bao [a], C. Brox-Nilsen [a], R. Potter [b], A.M. Song [a],*

[a] School of Electrical and Electronic Engineering, University of Manchester, Manchester M13 9PL, UK
[b] School of Engineering, University of Liverpool, Liverpool L69 3GH, UK

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ABSTRACT

A method has been developed to tune the electronic property of zinc-oxide thin-film transistors (TFTs) by annealing them in different gases. The experiments show that annealing in air increases the threshold voltage of the TFTs, while annealing in nitrogen gas reduces it. The zero-bias conductivity can be changed by nearly six orders of magnitude. With a combination of annealing in air and nitrogen it is hence possible to tune the threshold voltage over a wide range of pre-determined values to satisfy different circuit applications. The annealed devices also show good stability over a 25-day period in ambient air without encapsulation. The effects on other performance parameters of the TFTs and possible physical mechanisms are discussed.

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1. Introduction

There is a growing interest in zinc-oxide (ZnO) due to a number of desirable properties including the wide band-gap, relatively high electron-mobility, large exciton binding energy, and transparency [1–4]. ZnO thin-films have been grown by various deposition techniques, such as chemical-vapour deposition [5], sputtering [6], pulsed-laser deposition [7], molecular-beam epitaxy [8] and atomic-layer deposition (ALD) [9,10]. The wide range of applications include light-emitting diodes [11], flexible electronics [12], solar cells [13], and driving circuitry for liquid crystal displays (LCDs) and organic light-emitting diode TVs [14]. Much research has hence been carried out to focus on ZnO-based thin-film transistors (TFTs) recently [6,12,15–17].

ZnO films naturally exhibit *n*-type conductivity and its origin has been discussed in terms of native defects, such as oxygen vacancies and zinc interstitials [18], as well as hydrogen impurity [19]. A large number of oxygen deficiencies may occur under metal-rich, oxygen-deficient, high-temperature growth conditions [20]. The exact mechanism for the *n*-type conduction in ZnO has been under debate both experimentally and theoretically [21]. Furthermore, the absorption of oxygen onto the ZnO film surface and/or interface was suggested to induce acceptor-like surface states [22]. Whereas physisorbed molecular oxygen remains electrically neutral, causing little influence to the electrical conduction of the film, chemisorbed surface oxygen involves charge transfer, resulting in a field depletion of surface electrons and conduction band bending [23]. All these factors commonly lead to undesirable or uncontrollable TFT threshold voltages, which is still one of the main problems of ZnO technology for different circuit applications. Moreover, whereas normally-off devices are ideal in many applications such as LCD driver circuits, normally-on transistors with a negative threshold voltage may be desirable in other applications, e.g., as the load transistor in inverters and ring oscillators. It is therefore useful to develop ways to tune and control the threshold voltage of ZnO TFTs to satisfy the requirements of different applications.

It has been reported that the electrical properties of polycrystalline ZnO films could be strongly affected by oxygen adsorption and desorption, resulting in changes in the conductivity [24]. Doping methods have been explored to achieve higher carrier concentrations and in some cases even *p*-type doping was reported [25–28]. The effects of thermal annealing on the conductivity of ZnO have been studied previously [29–33]. Nevertheless, most of the work was carried out in a single gas environment. In this study, the effects of thermal annealing in either air or nitrogen environment have been investigated. We demonstrate that the threshold voltage of ZnO TFTs can be tuned over a wide range of pre-determined values. Films produced by ALD and sputtering were both used as the active layer in our experiments, and they showed similar effects. However, since ALD grown ZnO thin films typically offer better quality than sputtered ZnO films [10], we only present here the ALD ZnO TFT results.

2. Experiments

The polycrystalline ZnO films in this work were grown by ALD with diethylzinc (DEZn) and H_2O using a Cambridge Nanotech Savannah reactor. DEZn and H_2O were both held at room temperature (~20 °C)

* Corresponding author. Tel.: +44 161 3064762.
E-mail address: A.Song@manchester.ac.uk (A.M. Song).

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and dosed into the chamber using 20 ms doses separated by 3 s gas purges with 10 sccm of argon. Several different ZnO growth conditions were employed and the growth temperature ranged from 150 to 250 °C. The films were not intentionally doped and the thickness was from 48 to 60 nm. The substrates were thermally oxidised Si (100) with a 300 nm SiO_2 layer. Only the results obtained using 57-nm-thick ZnO films grown at 200 °C are reported here, but the films grown under other conditions showed similar effects after annealing. Al source/drain contacts with a thickness of 150 nm were deposited by thermal evaporation through a shadow mask, defining a TFT channel width $W = 2$ mm and a channel length $L = 60$ μm. A schematic of the fabricated bottom-gated ZnO TFTs is shown in the inset of Fig. 1. The devices were annealed in either air or nitrogen atmosphere using a Linkam annealer with a TP 94 temperature control unit with 1 °C temperature accuracy. Two types of annealing test were performed, the first a temperature-dependence measurement in which different annealing temperatures were applied to the device in either air or nitrogen environment. The second was a time-dependence measurement in which different annealing times were applied to the device in a single gas environment. Finally, a stability assessment was carried out on a particular sample over a 25 day period. All electrical characterizations were carried out using an Agilent E5270B semiconductor parameter analyser under ambient condition in dark.

3. Results and discussion

3.1. Temperature-dependence assessment

In the temperature-dependence assessment, the annealing in air was performed for 1 h at temperatures ranging from 180 to 280 °C for each individual device. Then, the samples annealed in air at 280 °C were chosen for subsequent annealing in nitrogen at 180, 200, 220, 260 and 280 °C for 1 h.

The effects of the process conditions on the following TFT performance parameters were studied: channel conductivity σ_{CH}, carrier mobility, and threshold voltage shift. The as-deposited films were found to have a very high conductivity with a typical value of about 11,300 S/m. ALD grown ZnO films generally exhibit high conductivity and high carrier concentration at growth temperatures higher than 150 °C, which may be due to metal-rich growth conditions and oxygen deficiencies [10]. Fig. 1 shows the variation of σ_{CH} as a function of the annealing temperature in air and nitrogen atmosphere. The conductivity of the TFT channel decreased by increasing the annealing temperature in air, by nearly six orders of magnitude as the annealing temperature reached 280 °C. In contrast to the decreased conductivity when annealing the TFTs in air, annealing in nitrogen was found to increase the conductivity of the channel layer and also the threshold voltage significantly as shown in Fig. 1. At low annealing temperatures (below 150 °C) in air, the conductance of the TFTs was too high to observe strong field modulation. When the annealing temperature reached 220 °C in air, well-defined transistor behaviour was observed as shown in Fig. 2. Above this temperature, the TFTs always showed good field effect whether the devices were annealed in air or nitrogen.

The field effect mobility in the saturation region and threshold voltage was extracted using the standard equation:

$$I_{DS} = \frac{1}{2}\mu C_i \frac{W}{L}(V_{GS} - V_T)^2,$$

where C_i is the gate capacitance per unit area, μ is the mobility in the saturation region, V_{GS} is the gate voltage referenced to the source and V_T is the threshold voltage. The device performance parameters of each ZnO sample are summarised in Table 1.

The changes in the mobility and threshold voltage as a function of annealing temperature in air and nitrogen atmosphere are displayed in Fig. 3(a) and (b) respectively. After annealing samples in air at higher temperatures, the electron mobility was reduced and the threshold voltage gradually shifted in the positive direction. This change could be subsequently reversed by re-annealing in nitrogen. These results demonstrate that the film conductivity and TFT threshold voltage can be tuned in both directions by annealing the devices in different gases.

3.2. Time-dependence assessment

At a given temperature, samples were also annealed for different lengths of time: 15, 30, 60 and 120 min. As the annealing time exceeded 60 min, relatively little change in the electrical characteristics was observed. Typical results of the mobility and threshold voltage values obtained with different annealing times are displayed in Fig. 4. The comparison of temperature-dependence and time-dependence assessments shows that the amount of threshold voltage shift and mobility change depended mainly on the annealing temperature rather than the annealing time.

3.3. Influence of annealing

To understand the above observations, we first note previous separate studies on ZnO annealing in nitrogen [29,32,33] and oxygen [30]. Initially the as-deposited ZnO TFTs had a highly conductive channel layer, which could hardly be modulated by the gate voltage. This means that the ZnO channel layer had a very high carrier concentration, most likely due to metal-rich growth conditions and oxygen deficiencies at elevated growth temperatures [10]. It was suggested that the

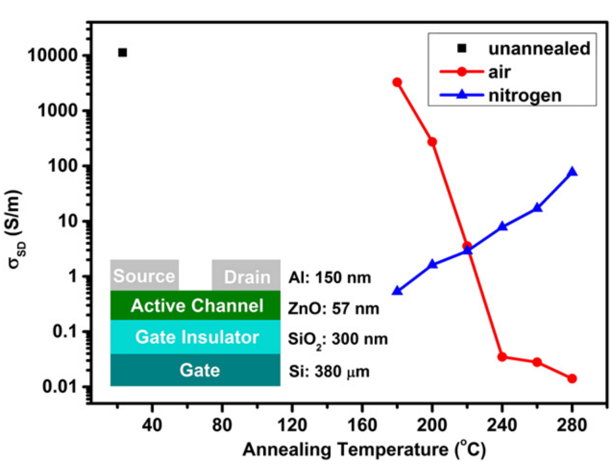

Fig. 1. Conductivity versus annealing temperature. The inset shows a schematic of the fabricated bottom-gated TFT.

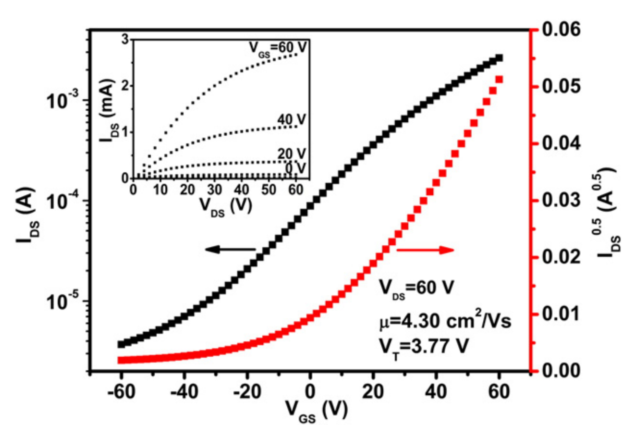

Fig. 2. Transfer characteristic of a ZnO TFT measured after annealing at 220 °C in air. The dashed lines represent experimental data and the solid line is a linear fit to the square root of the source-drain current to extract the mobility and threshold voltage. The inset shows the TFT output characteristic.

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