Field-assisted diffusion of silver in SnO$_2$ thin films

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Abstract. Tin oxide films are known for their wide spread applications in the field of optoelectronics as transparent conductors and as atmosphere sensitive ceramic pellets for chemical sensor fabrication. Forming durable ohmic contacts to these films is vitally necessary for the effective performance and long life of almost all such devices. Silver electrodes are commonly considered as low resistance ohmic contacts to many metal-oxide semiconductors. Particularly in devices operating at elevated temperatures, silver migration can considerably decrease useful device lifetime. Here, we study the performance of silver electrodes paste printed on SnO$_2$ thin films and show that the I-V characteristics of the silver/SnO$_2$ contact changes with operating time at elevated temperatures. SnO$_2$ films are grown on alumina substrates by ultrasonic spray pyrolysis technique. A pair of Ag electrodes are paste-printed on the surface of the grown films followed by a heat-treatment step to stabilize the deposits. The as-fabricated Ag/SnO$_2$ contacts present ohmic characteristics. Continuous application of DC voltages to the samples operating at 350 °C results in a significant drop in the devices’ resistance. The results originate from field-assisted migration of silver ions from the anode to the cathode electrode and formation of Ag micro-filaments in the polycrystalline SnO$_2$ layer.

1. Introduction

Metal oxides, known in the art for their thermal stability, resistance to harsh environs, and unique combination of electrical and optical characteristics, are widely used in sensor technology [1-6]. Furthermore, their promising efficacy in energy harvesting and optoelectronic devices has led to increasing research and investment in the field [7-9]. SnO$_2$ is an n-type wide bandgap semiconductor and the dominant material for the fabrication of chemical sensing pellets [10-13]. Dense polycrystalline tin oxide films have exhibited great potential for utilization as transparent electrodes in optoelectronic devices and as thin film high power resistors in electric heaters [14-16].

Metal oxide devices mostly operate at elevated temperatures and under harsh environmental conditions. Therefore, noble metals with their excellent corrosion resistance are preferred for utilization as the electrode materials. Ohmic contacts are of crucial importance for establishing low-resistance connections to the external circuitry [17-19]. On the other hand, Schottky contacts are advantageous in many device structures including chemical gas sensors, high frequency transistors, and resistive memories [20-23]. Gold and platinum have work functions of 5.1 and 5.65 eV, respectively, which are higher than the SnO$_2$ electron affinity (4.5 eV) [24, 25]. Theoretically, Au and Pt fail to form ohmic connections to tin oxide films. The fabrication method is an important parameter...
influencing the films’ crystallinity and stoichiometry [26]. These parameters, in turn, control the quality of the contacts. It has been reported that Au/ and Pt/SnO₂ contacts may exhibit ohmic characteristics and the ohmicit is attributed to the films polycrystalline nature and the oxygen deficiency at the surface of the tin oxide grains [27, 28].

Silver, with the least price and resistivity among all noble metals, is a favourable material for electrode fabrication on metal oxide semiconductors. With the work function of 4.26 eV, the metal forms a low-resistance ohmic contact with tin oxide layers [17]. In certain cases, silver migration is a prominent factor affecting the device functionality. The phenomenon is observed in many oxides and is considered to be beneficial for attaining switching behaviour in resistive memories [29, 30]. In the case of forming ohmic contacts though, the effect can induce instabilities in the electrical and structural properties of the film.

Here, the field-assisted diffusion of silver in SnO₂ layers is studied at 350 °C. Tin oxide films are grown on alumina substrates by ultrasonic spray pyrolysis (USP). Silver electrodes are paste printed on the deposits. By applying constant external electric fields to the samples operating at elevated temperatures, instabilities in the devices’ current are observed. The recorded phenomena are shown to stem from the electric field-induced movement of the mobile Ag⁺ ions, which result in the formation of conductive paths in the cross-section of the grown oxide layer.

2. Experimental

Standard polycrystalline alumina ceramics with a thickness of 0.5 mm are laser cut into 3×3 mm² squares, washed with acetone and distilled water, and dried on a hot plate at 150 °C. The utilized USP deposition system is a refined form of the system previously described [31]. 0.2 M solution of the precursor (SnCl₂·2H₂O, Merck 107815) in absolute ethanol is poured into a polymer container with an average rate of 30 mL/h. Two piezoelectric transducers working at 1.7 MHz produce the aerosol droplets and a continuous flow of air with 3 L/min average rate transfer them to the deposition chamber. The substrate is placed on a heater and heated to 325 °C. Tin oxide thin films with ~50 kΩ/□ sheet resistance are grown on the substrates in less than 30 seconds. The deposits are annealed at 600 °C for 1 hour in air.

As shown in figure 1, the contacts are asymmetrically configured so that the effective area of the counter electrode is ~10 times more than that of the other. Micron-thick silver layers are deposited on the SnO₂ films using a commercially available silver paste. Ag wires of 0.1 mm diameter are attached to the silver electrodes and provide the connections to the external circuitry. Silver deposits are dried at 110 °C to remove the organic solvent and heat-treated at 400 °C for 15 minutes to ensure the mechanical stability of the connections [17].

![Figure 1. Plan (a) and cross-sectional (b) schematic views of the fabricated Ag/SnO₂ samples.](image-url)
During the I-V tests, device’s voltage is directly monitored; the current is measured by reading the voltage drop on a series resistance. The data is read using a high input impedance operational amplifier and recorded by a 12-bit data acquisition card (Advantech, PCI-1711) with a sampling rate of 50 kilosamples per second. The contact durability tests are performed under continuous application of DC biases to the samples operating at elevated temperatures. Devices’ temperature is monitored by a fine S-type thermocouple and controlled by changing the voltage applied to an underlying resistive heater. The utilized experimental setup is schematically illustrated in figure 2.

3. Results
A biasing of 2.0 V is constantly applied to the samples operating at 350 °C. The variations of the device current are recorded (figure 3). The current is limited to 0.1 A so that the wirings cause negligible error in the measured resistance values. The samples’ resistance has a decreasing trend with time which is attributed to the emergence of conductive pathways in the oxide film. The results are similar to those reported in the silver-based resistive switching devices [29, 30]. There are 2 main mechanisms involved in this process: (a) the production of Ag$^{+}$ ions, and (b) their drift toward the cathode. Owing to high mobility of charged silver species, formation of Ag$^{+}$ ions is believed to be the rate limiting factor [32]. Performing the same experiments under argon atmosphere causes no such change in the device resistances indicating the prominent effect of the atmospheric oxygen on the filament formation process.

The recorded I-V characteristics before and after the forming process at 350 °C are shown in figure 4. The results are obtained using 0.05 Hz triangular voltage waveforms at 25-300 °C. In spite of asymmetric contacts, the I-V curves have an obvious symmetry, indicating ohmic quality of the contacts. At temperatures above 250 °C, hysteresic I-V characteristics emerge, which demonstrate resistive switching. Consecutive formation and collapse cycles of conductive Ag microfilaments has given rise to the observed hysteretic property. Owing to the ionic nature of the phenomenon, the hysteresis loop disappears when the biasing waveform frequency goes above 1 Hz.

![Figure 2](image-url)
Figure 3. Current variation in a tin oxide sample operating at 350 °C under a 2.0 V DC bias.

Figure 4. I-V characteristics of a tin oxide sample in response to a triangular voltage biasing at 0.05 Hz frequency before (a) and after (b, c, and d) the 350 °C-forming process.
4. Conclusions

Ohmic silver contacts were formed on the tin oxide films deposited by spray pyrolysis. The contacts reliability and durability were examined by the continuous application of DC biasing to the samples operating at elevated temperatures. The electric field-induced motion of mobile Ag⁺ ions caused the formation of silver filaments in the oxide layer cross-section, which caused a significant drop in the samples resistance. It was found that oxygen adsorption plays a major role in the ionic migration process. According to the recorded I-V characteristics, the Ag/SnO₂ devices have a potential for utilization as resistance switching devices.

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