Transparent heaters made by ultrasonic spray pyrolysis of SnO₂ on soda-lime glass substrates

Mohammad Ansari, Mehdi Akbari-Saatloo and Mohsen Gharesi

Electronic Materials Laboratory, Electrical Engineering Department, K. N. Toosi University of Technology, Tehran 16317-14191, Iran.

mohammad.ansari1371@gmail.com akbari@email.kntu.ac.ir m.gharesi@gmail.com

Abstract. Transparent heaters have become important owing to the increasing demand in automotive and display device manufacturing industries. Indium tin oxide (ITO) is the most commonly used material for production of transparent heaters, but the fabrication cost is high as the indium resources are diminishing fast. This has been the driving force behind the intense research for discovering more durable and cost-effective alternatives. Tin oxide, with its high temperature stability and coexisting high levels of conductivity and transparency, can replace expensive ITO in the fabrication of transparent heaters. Here, we propose tin oxide films deposited using ultrasonic spray pyrolysis as the raw material for the fabrication of transparent heaters. Silver contacts are paste printed on the deposited SnO₂ layers, which provide the necessary connections to the external circuitry. Deposition of films having sheet resistance in the 150 Ω/sq range takes only ~5 minutes and the utilized methods are fully scalable to mass production level. Durability tests, carried out for weeks of continuous operation at different elevated temperatures, demonstrated the long load life of the produced heaters.

1. Introduction

Transparent conducting films (TCFs) are extensively employed as the heating element in numerous device structures. Fabrication of heaters for lab-on-a-chip applications and defogger systems for outdoor display panels, vehicle windows, and camera lenses are just a few of many fields where high-power TCFs are required [1-3]. Indium tin oxide (ITO) has been conventionally the major material used for the production of transparent heaters. High fabrication cost due to rare indium resources, brittleness, and poor temperature stability, have raised questions on ITO’s suitability for the sustainable use in industrial applications [4, 5]. Carbon nanotubes, graphene layers, and metallic nanowires were recently proposed as ITO alternatives [6-8]. Despite their superior optical properties, long-term stability of these heaters is yet questionable and more has to be done on large-area fabrication methods.

Figure of merit for TCFs is defined as the ratio of electrical conductivity (σ) to visible light absorption coefficient (α) [9]. Assuming equal α values, this definition leads to higher figure of merit for more conducting layers. This is a practical guideline for transparent electrodes fabrication, but a transparent material for on-chip heater applications should be selected more carefully. Doped metal oxides utilized for fabrication of TCFs have low resistivities of ~10⁻¹ Ω.cm. In order to obtain durable operational characteristics at elevated temperatures, the metal oxide deposits have micrometric thicknesses and thus sheet resistances in the 1-4 Ω/sq range [10, 11]. These values are too low for...
heater fabrication and cause excessive power consumption in the metal electrodes and wirings. Geometries with high length-to-width aspect ratios are usually regarded as possible solutions, although, the method complicates the fabrication process and results in extra costs.

Tin oxide, an n-type wide-bandgap semiconductor, is mostly known for its widespread application as the sensing element of gas sensors. Exceptional high-temperature stability and remarkable sensitivity to a wide variety of analyte molecules have led to its popularity in the field of chemical sensors [12-16]. Doped tin oxide films with transparency in the whole visible spectrum have been widely suggested for utilization as electrodes in optoelectronic devices [17]. The undoped material is also a promising candidate for TCF fabrication. Low formation energy of oxygen vacancies causes significant nonstoichiometry in the SnO structure even at room temperature. Oxygen vacancies donate electrons to the conduction band resulting in metal-like conductivity in SnO films while not changing their optical absorption characteristics in comparison with stoichiometric SnO [18].

Here, transparent tin oxide heaters are fabricated on standard soda-lime glasses using a homemade ultrasonic spray pyrolysis (USP) system. USP technique is chosen due to its simplicity, cost effectiveness and suitability for mass production [19, 20]. The method is optimized to result in dense polycrystalline films at deposition temperatures as low as 300 °C. Ohmic Ag/SnO contacts are formed on the grown films [21]. The load life of the fabricated samples is investigated over weeks of continuous operation at temperatures in the 80-150 °C range.

2. Experimental

Standard 1-mm thick soda-lime glass slides are washed with absolute acetone, rinsed with distilled water, and dried on a hot plate at 150 °C for 10 min. These are laser cut into 5 mm x 5 mm chips and subjected to the same washing procedure. The utilized USP deposition system was previously described in ref. [22]. The precursor solution is prepared by dissolving 0.2 moles of SnCl₂H₂O (Merck Millipore, 107815) in 1.0 litre of absolute ethanol (99.5% v/v). Piezoelectric transducers working at 1.7 MHz frequency are embedded in a water filled tank. A polymer container is placed on top of the water tank which prevents the solution-caused corrosion of the vaporization system. The precursor solution is poured into the polymer container through a flow control valve with ~30 mL/h rate. Continuous flow of air with an average rate of 3 L/min carries the generated aerosol droplets to the deposition chamber. The aerosol strikes the substrate surface which is heated to 300 °C by an underlying resistive heater. The substrate temperature is monitored using a fine S-type thermocouple and controlled by the voltage applied to the heater.

Some of the samples were annealed at 400 °C in air for half an hour. Lateral silver electrodes are paste-printed on the films followed by field-assisted heat treatments at 300 °C to ensure ohmicity of the connections [21, 23]. Durability tests are performed by continuously applying AC heating voltages to the fabricated samples. Device resistances are measured with 24 h time intervals while controlling the heating voltages to keep the operating temperatures constant. The utilized experimental setup is schematically illustrated in figure 1.

3. Results

Owing to the lower growth temperature compared to the previously reported USP depositions [9], the method is applicable for production of tin oxide films on soda-lime glasses, as well. The planar scanning electron microscopy (SEM) image of the surface of an as-deposited sample is shown in figure 2a. The polycrystalline film has a dense morphological structure. The average grain size, measured using the line averaging method, is ~70 nm. The cross-sectional micrograph shown in figure 2b illustrates a 400 nm-thick homogeneously deposited film on the glass substrate. The average sheet resistance of the samples is around ~150 Ω/sq at room temperature. Considering the sample geometry, the resistivity of the deposited material is calculated to be ~6×10⁻⁵ Ω.cm.
Figure 1. The schematic presentation of the sample structure and the experimental setup utilized for the durability tests.

Figure 2. SEM micrographs from the tin oxide layer grown on a soda-lime glass substrate; (a) the plan-view and (b) the cross-section.

Photographs of as-deposited and annealed tin oxide samples are represented in figure 3. The annealed tin oxide films have a clearly enhanced visible transparency which is induced by their improved stoichiometric composition relative to the as-grown ones. This is consistent with a rise of ~20% in layers sheet resistance occurred after the annealing process; the increase in resistance is attributed to the decrease in the oxygen vacancy concentration in the layer.

Resistance-temperature diagram of a fabricated sample is shown in figure 4.a. Clearly, the device shows negative temperature coefficient of resistance (TCR) in the investigated temperature range which originates from both the increased oxygen vacancy concentration and the enhanced ionization mechanism at higher temperatures [24, 25]. Negative TCR heaters are known for their resistance to hot-spot generation and, hence, excellent reliability for long-term operations [26]. As shown in figure 4.b, the resistance values show negligible variation in a 2-week test period; only 0.9, 1.0 and 2.5% increase was recorded for the devices operating continuously at 80, 100 and 150 °C, respectively. The annealed devices offer even better long run stability; no resistance change was recorded during a similar experimental session.
4. Conclusions

Tin oxide films were grown on soda-lime glass substrates using a homemade USP system. The deposition temperature is 300 °C which is safe for the glass substrates. Layers with sheet resistances of ~150 Ω/sq are grown in deposition times as low as 5 minutes. SEM micrographs revealed the polycrystalline nature of the deposits and a homogenous layer thickness of ~400 nm across the substrate. The samples exhibited fine optical transparency in visible spectrum. Ohmic silver contacts were formed on the films, and the reliability of the resistor samples for long-term use as on-chip transparent heaters was investigated. The devices showed negligible resistance variation after a 2-week of continuous operation at the 80-150 °C temperature range. The results show that undoped tin oxide layers are promising alternatives to the expensive ITO device components.

References

[1] Im K, Cho K, Kim J and Kim S 2010 Transparent heaters based on solution-processed indium tin oxide nanoparticles Thin Solid Films 518 3960-3.
[2] Kang J, Kim H, Kim K S, Lee S K, Bae S, Ahn JH, Kim YJ, Choi JB and Hong BH 2011 High-performance graphene-based transparent flexible heaters Nano Lett. 11 5154-8.
[3] Zhang X, Yan X, Chen J and Zhao J 2014 Large-size graphene microsheets as a protective layer for transparent conductive silver nanowire film heaters Carbon 69 437-43.
[4] Jung D, Kim D, Lee K H, Overzet L J and Lee G S 2013 Transparent film heaters using multi-walled carbon nanotube sheets Sens. Actuators, A 199 176-80.
[5] Rao K D and Kulkarni G U 2014 A highly crystalline single Au wire network as a high temperature transparent heater Nanoscale 6 5645-51.

[6] Yoon Y H, Song J W, Kim D, Kim J, Park J K, Oh S K and Han C S 2007 Transparent Film Heater Using Single-Walled Carbon Nanotubes Adv. Mater. 19 4284-7.

[7] Kang J, Kim H, Kim K S, Lee S K, Bae S, Ahn J H, Kim Y J, Choi J B and Hong B H 2011 High-performance graphene-based transparent flexible heaters Nano lett. 11 5154-8.

[8] Bob B, Machness A, Song T B, Zhou H, Chung C H and Yang Y 2016 Silver nanowires with semiconducting ligands for low-temperature transparent conductors Nano Res. 9 392-400.

[9] Gordon R G 2000 Criteria for choosing transparent conductors MRS Bull. 25 52-7.

[10] Gupta R, Rao K D, Kiruthika S and Kulkarni G U 2016 Visibly Transparent Heaters ACS Appl. Mater. Interfaces 8 12559-75.

[11] Gao K H, Lin T, Liu X D, Zhang X H, Li X N, Wu J, Liu Y F, Wang X F, Chen Y W, Ni B and Dai N 2013 Low temperature electrical transport properties of F-doped SnO$_2$ films Solid State Commun. 157 49-53.

[12] Hossein-Babaei F and Amini A 2014 Recognition of complex odors with a single generic tin oxide gas sensor Sens. Actuators, B 194 156-63.

[13] Wang C, Yin L, Zhang L, Xiang D and Gao R 2010 Metal oxide gas sensors: sensitivity and influencing factors Sensors 10 2088-106.

[14] Hossein-Babaei F, Zare A H, Ghafarinia V and Erfantalab S 2015 Identifying volatile organic compounds by determining their diffusion and surface adsorption parameters in microfluidic channels Sens. Actuators, B 220 607-13.

[15] Hossein-Babaei F, Paknahad M and Ghafarinia V 2012 A miniature gas analyzer made by integrating a chemoresistor with a microchannel Lab Chip 12 1874-80.

[16] Hossein-Golgoo S M and Hossein-Babaei F 2011 Assessing the diagnostic information in the response patterns of a temperature-modulated tin oxide gas sensor Meas. Sci. Technol. 22 035201.

[17] Elangovan E and Ramamurthi K 2003 Optoelectronic properties of spray deposited SnO$_2$: F thin films for window materials in solar cells J. Optoelectron. Adv. Mater. 5 45-54.

[18] Kılıç Ç and Zunger A 2002 Origins of coexistence of conductivity and transparency in SnO$_2$, Phys. Rev. Lett. 88 095501.

[19] Jadsadapattarakul D, Euvananont C, Thanachayanont C, Nukeaw J and Sooknoi T 2008 Tin oxide thin films deposited by ultrasonic spray pyrolysis Ceram. Int. 34 1051-4.

[20] Lee S Y and Park B O 2006 Structural, electrical and optical characteristics of SnO$_2$: Sb thin films by ultrasonic spray pyrolysis Thin solid films 510 154-8.

[21] Hossein-Babaei F, Moghadam S and Masoumi S 2015 Forming ohmic Ag/SnO$_2$ contacts Mater. Lett. 141 141-4.

[22] Gharesi M and Ansari M 2016 Tin Oxide Microheater for Chemical Sensors IOP Conf. Ser.: Mater. Sci. Eng. Vol. 108 012018.

[23] Hossein-Babaei F, Lajvardi M M and Alaei Sheini N 2015 The energy barrier at noble metal/TiO$_2$ junctions Appl. Phys. Lett. 106 083503.

[24] Gurlo A 2006 Interplay between O, and SnO$_2$: oxygen ionosorption and spectroscopic evidence for adsorbed oxygen ChemPhysChem 7 2041-52.

[25] Hossein-Babaei F and Alaei Sheini N 2016 Electronic conduction in Ti/Poly-TiO$_2$/Ti structures Sci. Rep. 6 29624.

[26] Simon I, Bârsan N, Bauer M and Weimar U 2001 Micromachined metal oxide gas sensors: opportunities to improve sensor performance Sens. Actuators, B 73 1-26.