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Transparent Heater Based on Al,Ga Co-doped ZnO Thin Films

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Abstract

Al, Ga co-doped ZnO thin films were deposited on to glass substrates by aerosol assisted chemical transport (AACT) and were studied for application as transparent thin film heaters. The film thickness was around 400 nm after 60 min of AACT deposition; this gave a sheet resistance of 142.5 Ω /sq, which corresponded to a resistivity of $5.7 \times 10^{-3} \Omega\cdot\text{cm}$. The thin films exhibited a maximum transmittance of 90% in the visible region. A mean temperature of 132.3 $^{\circ}\text{C}$ was reached after applying a voltage of 18 V for 10 min, giving a power consumption of 2.11 W. These results could provide a possibility to use Al, Ga co-doped ZnO thin films as transparent heaters to replace the more expensive indium tin oxide.

Keywords: Transparent conducting oxides; thin film heater; microwave synthesis

1. Introduction

Transparent thin film heaters are useful for clearing automobile windows, mirrors and outdoor displays under extreme environmental conditions.[1,2] They tend to outperform hydrophobic coatings for defrosting and anti-icing applications due to poor mechanical and chemical stability of the hydrophobic coatings in extreme weather conditions.[3] Emerging uses of thin film heaters are for lab-on-chip applications and for wearable body heaters for personalized heating.[4,5] The latter requires coating of the transparent conducting material on to a flexible and stretchable substrate – introducing new material demands such as high mechanical flexibility and stretchability.[5] Transparent and smart windows are also considered key components for next generation energy efficient buildings.[6]

The ideal properties for a transparent thin film heater are low sheet resistance, high thermal stability and high transmittance. Also, excellent areal uniformity is required to achieve even heating from the thin film coating.[7] Indium tin oxide (ITO) has been widely used as a transparent thin film heater as it highly transparent (~90%) and conducting (10 Ω /sq),[7] however, it exhibits a slow thermal response and fails to perform in certain applications that require flexibility and robustness.[7]

Low-cost doped ZnO materials have been widely investigated for transparent conducting oxide (TCO) applications due to the higher natural abundance of Zn compared with In and Sn, and due to its large direct band gap and low resistivity.[8,9] Typically, group III elements such as Al, Ga and In have been investigated as n-type dopants for ZnO.[8] Previous work in our group has shown that co-doped Al, Ga:ZnO shows significantly reduced resistivity compared with singly doped Al:ZnO and Ga:ZnO.[10]

There are not many reports on the use of doped ZnO in transparent heating applications[11] and to the best of our knowledge, there are no reports for the use of Al, Ga co-doped ZnO for this application. In this study, we prepared thin films of Al, Ga co-doped ZnO by aerosol assisted chemical transport (AACT)[10] and studied their application in transparent thin film heaters.

2. Experimental

2.1 Synthesis of AGZO powder and thin film fabrication

AGZO powder was synthesised, suspended and was then used to deposit thin film on glass substrates according to a recently published method using AACT[10]. AGZO powder was synthesised in a microwave reactor from a precursor solution containing $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.00 g), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.0165 g) and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (0.0175 g) dissolved in diethylene glycol (DEG) (45 mL) and deionized water (5 mL). The precursor solution was heated to 200°C for 30 mins at a ramp rate of 20°C, resulting in an opaque suspension. Upon cooling, the AGZO powder was collected by centrifuging and was washed several times with ethanol and was allowed to dry.

For thin film fabrication by AACT, the AGZO powder (0.2 g) was dispersed in methanol (50 ml). Formic acid (0.05 ml) was added to the suspension in order to obtain a better dispersion and ethyl cellulose (0.01g) was added as a binder. The suspension was sonicated for 5 min using a sonicator probe. In the deposition, an ultrasonically produced aerosol of the AGZO suspension was directed via an N_2 gas flow at a flow rate of 323.27 ml min^{-1} towards a glass substrate, which was held at 400 °C in a glass tube in a tube furnace. The deposition was carried out for 60 minutes.

2.2 Material characterisation

X-ray diffraction (XRD) measurements were conducted on a Bruker AXS Advance X-ray diffractometer with primary monochromatic high intensity $\text{Cu K}\alpha$ ($\lambda = 1.541 \text{ \AA}$) radiation and a position sensitive detector. The electrical properties were measured by a four-point probe conductivity meter (Jandel, HM20, Jandel Engineering Ltd., Linslade, UK). The surface and cross-sectional morphology of the thin films were investigated using a Leo 1530 VP field emission gun scanning

electron microscope (FEG-SEM) at an accelerating voltage of 5 kV and a working distance of 5 mm. Optical transmittance measurements of the thin films were conducted using a dual beam Perkin-Elmer Lambda 35 UV-Vis spectrometer over the wavelength range of 300 nm – 800 nm.

2.3 Thin film heater characterisation

Conducting silver paint was used to make electrical connections either side of the AGZO thin film. Silver paint was applied such that an active area of 1.5 x 1 cm was exposed. The resistance across the two silver terminals was 126.7 Ω . Crocodile clips were used to connect the terminals to a DC power supply. A thermal imaging camera (Micro-Epsilon TIM 400T1500 with 13° optics) was used to measure the heating and cooling temperature profiles. Voltage was applied for 600 seconds and then was turned off and the sample was allowed to cool to room temperature (~600 seconds). Heating and cooling profiles were recorded at voltages of 6, 9, 12 and 18 V. The reported temperatures are the average over the active area.

3. Results and Discussion

3.1 Material properties

The AGZO thin films deposited by AACT on glass substrates were analysed by XRD (figure 1a), which showed that the thin films were polycrystalline with a preferred orientation in the (002) direction. The AGZO thin film also showed reflections in the (100), (101), (102), (103), (112) and (004) orientations. The transmittance spectrum in figure 1b shows that the AGZO thin film exhibits a maximum transmittance of around 90% at 575 nm. Figure 1c-d shows the surface and cross-sectional SEM images for AGZO thin film. The SEM image shows excellent thin film coverage with uniform features which consist of sintered AGZO particles. The film thickness after 60 min deposition time was around 400 nm, indicating an average growth rate of ~6.7 nm/min.

Figure 1. (a) X-ray diffraction pattern, (b) optical transmission spectrum, (c) surface SEM image (d) cross-sectional FEG-SEM image of an AGZO thin film deposited by AACT.

3.2 Thin film heater properties

The most important factor for a thin film heater is the sheet resistance of the material, the lower the value, the better its power efficiency. The sheet resistance of the AGZO thin film was $142.5 \, \Omega/\text{sq}$ at a thickness of 400 nm, giving a resistivity of $5.7 \times 10^{-3} \, \Omega\cdot\text{cm}$. Temperature-time profiles of the AGZO thin film (with an active area of $1.5 \, \text{cm}^2$) for different input voltages of 6, 9, 12, 15 and 18 V were measured using a thermal imaging camera. The thin films were allowed to heat for 10 mins and then cool back to room temperature as shown in figure 2a. The average temperature of the thin film after 10 min of heating is plotted as a function of applied voltage in figure 2b. The power consumption, P , and the resistance, R , of the AGZO thin film heater can be determined from equations 1 and 2, where I is the current passing through the AGZO thin film, ρ is the resistivity, L is the distance separation between the electrodes, A is the area of the AGZO thin film, δ is the film thickness and W is the width.

$$P = I^2 R \quad \text{Eq. 1}$$

$$R = \rho \frac{L}{A} = \rho \frac{L}{\delta W} \quad \text{Eq. 2}$$

The current passing through the AGZO heater plotted as a function of applied voltage is also shown in figure 2b. The resistance between the two electrodes was calculated to be $95\ \Omega$. The power consumption of the AGZO heater was 0.267, 0.578, 0.950, 1.56 and 2.11 W for applied voltages of 6, 9, 12, 15 and 18 V, respectively. The thermal stability of the AGZO thin film heater was tested by switching the applied voltage from 0 to 18 V for 18 cycles (figure 2c). A voltage of 18 V was applied for 5 min, followed by 0 V for 5 min. Average temperatures of around 130°C were attained when 18 V was applied for 5 min. The sheet resistance of the heater remained the same before and after the stability measurements, which suggests that the AGZO heater is stable for rapid temperature switching for long periods of time without degradation.

Whilst the thermal properties of the thin film heater depend on the electrical and thermal conductivity and specific heat capacity of the active material, to a large extent, the heating performance is ultimately decided by the substrate properties (substrate type and thickness).[7] More specifically, the response time of the heater depends on the additional mass which can be the substrate or the encapsulating material which is covering the heater.[7] Different substrates and thicknesses are used depending on the application; therefore it is difficult to compare the material like-for-like with other materials which use different substrates and thicknesses in the literature. The thicker the substrate, the longer the response time of the heater will be, due to heat loss to the substrate by conduction. Therefore, thicker substrates will take longer to reach a temperature plateau compared with thinner substrates. In this study, we have used the 3 mm glass substrate, which is the typical thickness of glass used for glazing applications. It, therefore, gives a more realistic insight into the response time of heated windows if our material was to be used.

Figure 2. (a) Heating and cooling temperature profiles of the AGZO thin film heater at various voltages. (b) Average temperature and current as a function of applied voltage. (c) Switching cycles of the AGZO thin film heater between 0 and 18 V.

A thermal image of the AGZO heater is shown in figure 3a along with a histogram of the temperature distribution after 10 min of heating at an applied voltage of 18 V (figure 3b). The mean thin film temperature was 132.3 °C with a standard deviation of 9.7 °C. There were some hotspots on the film which reached high temperatures of 156.7 °C and some cooler areas which were around 100 °C, however, these areas accounted for less than 0.2 % of the film area. The broad temperature distribution is likely to stem from variation in the AGZO thin film thickness.

Figure 3. (a) Thermal image and (b) histogram of temperature distribution of the AZGO thin film heater at an applied voltage of 18 V after 600 seconds of heating.

4. Conclusions

AACT was used to prepare Al, Ga co-doped ZnO thin films on to glass substrates. The thin films exhibited a sheet resistance of 142.5 Ω/sq at a thickness of 400 nm, which corresponded to a resistivity of $5.7 \times 10^{-3} \Omega\cdot\text{cm}$. The films were investigated for use as transparent thin film heaters; average temperatures of 46.6, 58.6, 79.3, 104.0 and 132.3°C were reached after applying 6, 9, 12, 15 and 18 V, respectively, for 10 min. The power consumption of the heater at 18 V was 2.11 W. The results show that the Al, Ga co-doped ZnO thin film can be used as an alternative material for indium in oxide in transparent thin heaters.

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References

- [1] J. Kang, H. Kim, K.S. Kim, S.-K. Lee, S. Bae, J.-H. Ahn, Y.-J. Kim, J.-B. Choi, B.H. Hong, High-Performance Graphene-Based Transparent Flexible Heaters, *Nano Lett.* 11 (2011) 5154–5158. doi:10.1021/nl202311v.
- [2] D. Sui, Y. Huang, L. Huang, J. Liang, Y. Ma, Y. Chen, Flexible and Transparent Electrothermal Film Heaters Based on Graphene Materials, *Small.* 7 (2011) 3186–3192. doi:10.1002/smll.201101305.
- [3] J. Lv, Y. Song, L. Jiang, J. Wang, Bio-Inspired Strategies for Anti-Icing, *ACS Nano.* 8 (2014) 3152–3169. doi:10.1021/nn406522n.
- [4] G. Petrucci, D. Caputo, A. Nascetti, N. Lovecchio, E. Parisi, S. Alameddine, G. de Cesare, A. Zahra, Thermal characterization of thin film heater for lab-on-chip application, in: 2015 XVIII AISEM Annu. Conf., IEEE, 2015: pp. 1–4. doi:10.1109/AISEM.2015.7066835.
- [5] B.W. An, E.-J. Gwak, K. Kim, Y.-C. Kim, J. Jang, J.-Y. Kim, J.-U. Park, Stretchable, Transparent Electrodes as Wearable Heaters Using Nanotrough Networks of Metallic Glasses with Superior Mechanical Properties and Thermal Stability, *Nano Lett.* 16 (2016) 471–478. doi:10.1021/acs.nanolett.5b04134.
- [6] S.-H. Park, S.-M. Lee, E.-H. Ko, T.-H. Kim, Y.-C. Nah, S.-J. Lee, J.H. Lee, H.-K. Kim, Roll-to-Roll sputtered ITO/Cu/ITO multilayer electrode for flexible, transparent thin film heaters and electrochromic applications., *Sci. Rep.* 6 (2016) 33868. doi:10.1038/srep33868.
- [7] R. Gupta, K.D.M. Rao, S. Kiruthika, G.U. Kulkarni, Visibly Transparent Heaters, *ACS Appl. Mater. Interfaces.* 8 (2016) 12559–12575. doi:10.1021/acsami.5b11026.
- [8] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, H. Morkoç, A comprehensive review of ZnO materials and devices, *J. Appl. Phys.* 98 (2005) 41301. doi:10.1063/1.1992666.
- [9] Y. Liu, Y. Li, H. Zeng, ZnO-Based Transparent Conductive Thin Films: Doping, Performance, and Processing, *J. Nanomater.* 2013 (2013) 1–9. doi:10.1155/2013/196521.
- [10] D.S.Y. Jayathilake, T.A.N. Peiris, J.S. Sagu, D.B. Potter, K.G.U. Wijayantha, C.J. Carmalt, D.J. Southey, Microwave Assisted Synthesis and Processing of Al, Ga and Al,Ga Co-doped ZnO for the Pursuit of Optimal Conductivity for Transparent Conducting Film Fabrication, *ACS Sustain. Chem. Eng.* (2017) acssuschemeng.7b00263. doi:10.1021/acssuschemeng.7b00263.
- [11] J.H. Kim, B. Du Ahn, C.H. Kim, K.A. Jeon, H.S. Kang, S.Y. Lee, Heat generation properties of Ga doped ZnO thin films prepared by rf-magnetron sputtering for transparent heaters, *Thin Solid Films.* 516 (2008) 1330–1333. doi:10.1016/j.tsf.2007.03.100.