Effect of Firing Temperature on Electrical and Structural Characteristics of Screen Printed In$_2$O$_3$ Thick Films

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Abstract. In$_2$O$_3$ thick films were prepared on porous alumina (Al$_2$O$_3$) substrate by using standard screen printing technique and fired at different temperatures from 750°C to 950°C in air atmosphere. The DC resistance of film was measured by half bridge method in air atmosphere at different temperatures. The films were showing decrease in resistance with increase in temperature indicating semiconductor behavior. The resistivity ($\rho$), activation energy ($\Delta E$) and temperature coefficient of resistance (TCR) are evaluated at different firing temperatures. Samples were characterized by X-ray diffraction (XRD) technique, scanning electron Microscopy (SEM)), Energy Dispersive Spectroscopy (EDX) and Atomic force microscopy (AFM) technique, for compositional, phase confirmation and surface growth and morphology study.

Introduction

Indium oxide (In$_2$O$_3$) belongs to class of wide band gap metal oxides (Eg = 3.6 eV) and is of interest for many device applications and fundamental research [1]. It has interesting properties such as high transparency to visible light, high electrical conductance. In$_2$O$_3$ has been widely used in microelectronic field as gas detectors, window heaters, solar cells, memory devices, and flat panel materials. In the last years the gas sensing and properties of In$_2$O$_3$ as semiconductor gas sensor have been investigated [2]. Several deposition methods have been used to grow In$_2$O$_3$ films such as spray pyrolysis, evaporation, chemical vapour deposition, magnetron sputtering, pulsed laser deposition, a sol-gel technique and a screen printing technique [3]. The screen printing technique was introduced in the later part of the 1950’s to produce compact, robust and relatively inexpensive hybrid circuits for many purposes. Later on a thick film technique has attracted attention for the sensor field. Screen printing is a viable and economical method to produce thick films of various materials [4].

In this paper, preparation of In$_2$O$_3$ thick films by standard screen printing technique and their electrical and structural properties at different firing temperatures have been investigated.

Experimental

Thick Films Fabrication

The Commercially available yellowish In$_2$O$_3$ powder (Loba Chem. purity 99.99%) was weighed and calcined in air at 300°C for 2 hour. Thick films of calcined powder were fabricated using standard screen printing method. Paste for thick film printing consists of two parts (i) solid phase and (ii) liquid phase. A ratio of 70 to 30 was taken for solid and liquid phase. Solid phase is of functional material (powder and glass frit) whereas liquid phase is of organic vehicle which are temporary binders. Calcined indium oxide powder was used a functional materials along with 5% (by weight) of locally prepared glass frit based on lead borosilicate composition. Ethyl cellulose (EC, Aldrich) and Butyl Carbitol Acetate (BCA, Aldrich) were used as temporary binders. These binders are known to give thixotropic property to the paste. The paste for the thick film printing was prepared by finely grinding the calcined powder in agate-mortar and pestle. Then EC was added and well mixed with powder. Then BCA was added drop by drop and mixed well until the required viscosity was achieved, suitable for screen printing. Viscosity of the paste was controlled in a way
that it passes easily through the screen and does smear on the substrate too. The paste was then screen-printed (nylon mesh) onto alumina substrate (96% pure, Kyocera). After screen printing films were dried under IR lamp (250W, Philips) for 30 minutes to remove organic vehicle and then samples were fired at the temperature of 750°C, 850°C, 950°C with firing cycle of 45 minutes with a soaking time of 15 min at peak temperature. Thickness of the fired films was measured by using Taylor-Hobson (Taly-step UK) system, which was observed in range of 12 µm to 15 µm, from sample to sample.

**Electrical Characterization**

The D.C. resistance of the film was measured using half bridge method as function of temperature described elsewhere[4]. The films were set in temperature controlled atmosphere. The fixed DC voltage was applied to circuit and external resistance RL was connected in series with thick film. The resistances of the film were obtained by measuring output voltage using digital multimeter (Classic5175 DM,±0.5%) across resistance RL. Digital Temperature controller with chromel–alumel thermocouple was used to indicate operating temperature. The resistance of thick film (Rs) was calculated by relation,

\[ R_s = R_L \left[ \frac{V_{app}}{V_o} - 1 \right] \]

where \( V_{app} \) is applied voltage and \( V_o \) is Voltage across external Resistor \( R_L \).

The resistivity value of each film was calculated from dimensions of the film. TCR and Activation energy were evaluated from observed data in the temperature range 30°C to 250°C.

**Structural and Morphological Studies**

After firing at different temperatures, the bulk XRD analysis of TFRs was carried out using a X-ray diffraction (D8 Advance BRUCKER AXS diffractometer) for the Bragg angle (2θ) from 20° to 80° using cuKα radiations (\( \lambda = 0.1542 \text{ nm} \)) was carried out to examine final composition of indium oxide thick film samples. The average grain size of indium oxide thick film samples were calculated by using Scherrer formula.

The surface morphology and chemical composition of films were analyzed using scanning electron microscope [SEM model JEOL 6300(LA) Germany] coupled with an energy dispersive spectrometer (EDS JEOL, JED-2300, Germany). Surface Topography and Morphology of film is done by Atomic Force Microscopy (AFM, Metris-2001A-NC).

**Results and Discussions**

**X-ray Diffraction Analysis**

The XRD pattern of \( \text{In}_2\text{O}_3 \) film samples at different firing temperatures from 750°C to 950°C is shown in Figure 1. As firing temperature increases from 750°C to 950°C, several sharp and intense peaks appear in XRD profiles, indicating a high degree of crystallinity and increased grain size. It is observed that as firing temperature increases, the major contribution towards cubic phase also increases. The higher peak intensities of XRD pattern is due to the better crystallinity and bigger grain size can be attributed to agglomeration of particles. The average crystallite size was calculated using Scherrer formula and was estimated to be 29.10nm, 31.13nm and 35.14nm for 750°C, 850°C and 950°C respectively. Thus the grain size increases with an increase in firing temperature which is in good agreement with the previous reported work [4]. Some peaks of \( \text{Al}_2\text{O}_3 \) are due to alumina substrate [4].

**Surface Morphology Analysis**

Scanning electron microscopy is convenient technique to study the microstructure of \( \text{In}_2\text{O}_3 \) thick film samples. Figure 2. (a), (b), (c) shows the surface morphology of \( \text{In}_2\text{O}_3 \) films fired at different temperatures observed by Scanning Electron Microscopy. The micrograph of these samples shows voids between the particles are basically due to evaporation of the organic solvent during the firing
of the films. The In$_2$O$_3$ films show increase in grain size and decrease in porosity with increase in firing temperature.

![Figure 1. XRD pattern of In$_2$O$_3$ films fired at (a) 750°C (b) 850°C (c) 950°C.](image)

![Figure 2. SEM images of In$_2$O$_3$ thick films fired at (a) 750°C (a) 850°C (a) 950°C.](image)

**Elemental Analysis**

The EDX analysis was used to examine the composition of the film materials. Table 1. Shows the composition of the elements of the In$_2$O$_3$ films fired at different temperatures. It is evident from Table1. that the EDX analysis shows the major peaks of In and O and no other impurity elements are presents in the composition. The EDX analysis also shows that by firing at higher temperatures, excess oxygen is released. From the analysis it was found that In$_2$O$_3$ films are non-stoichiometric.

<table>
<thead>
<tr>
<th>Firing Temperature</th>
<th>Element</th>
<th>At. wt %</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>750°C</td>
<td>In</td>
<td>82.94</td>
<td>88.97</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>17.06</td>
<td>6.58</td>
</tr>
<tr>
<td>850°C</td>
<td>In</td>
<td>83.35</td>
<td>89.18</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>16.65</td>
<td>6.40</td>
</tr>
<tr>
<td>950°C</td>
<td>In</td>
<td>85.04</td>
<td>90.01</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>14.96</td>
<td>5.65</td>
</tr>
</tbody>
</table>

The Surface topography, growth and surface roughness properties of film were studied with help of atomic force microscopy. The surface topography of film fired at 750°C was measured by the AFM (Metris-2001A-NC, manufactured by Burleigh Instruments Inc). All AFM measurements were carried out in the contact mode at the ambient atmosphere and at room temperature. Scans were made over areas 1 × 1 μm, 2.5 × 2.5μm, 5 × 5 μm and 10 × 10 μm with resolution 512 × 512 pixels. In$_2$O$_3$ showed rectangular as well as triangular grain growth on alumina substrate with
average grain size ~ 200 nm and rms surface roughness ~400 nm per micron. High roughness is due to screen printing technique.

Figure 3. AFM images of In$_2$O$_3$ on Al$_2$O$_3$.

**Electrical Characteristics**

Figure 4 shows variation of resistance with Temperature for In$_2$O$_3$ thick films fired at temperature 750, 850, 950°C respectively in air. Figure 5. Shows Arrhenius plot of Log Rs versus 1/T for In$_2$O$_3$ thick films. The variation of grain size, resistivity, TCR, and activation energy of In$_2$O$_3$ thick films with firing temperature is summarized in Table 2. It is observed that the resistivity, activation energy decreases where TCR and grain size increases with increasing firing temperature. These results may be attributed to increase in degree of crystallinity with the firing temperature.

<table>
<thead>
<tr>
<th>Firing Temp (°C)</th>
<th>Avg grain size (D nm)</th>
<th>TCR (/°C) at const. temp.</th>
<th>Resistivity (Ω m)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>L.T. Region</td>
</tr>
<tr>
<td>750</td>
<td>30</td>
<td>0.004814</td>
<td>0.526</td>
<td>0.114</td>
</tr>
<tr>
<td>850</td>
<td>32</td>
<td>0.00597</td>
<td>0.400</td>
<td>0.100</td>
</tr>
<tr>
<td>950</td>
<td>36</td>
<td>0.00833</td>
<td>0.293</td>
<td>0.091</td>
</tr>
</tbody>
</table>

**Conclusions**

In$_2$O$_3$ thick films were deposited on alumina substrate using standard screen printing technique and fired at different temperatures were showing semiconductor behavior. It is found that film fired at 950°C offer low resistivity, low activation energy, high TCR, high grain size. XRD and SEM studies have revealed polycrystalline morphology of In$_2$O$_3$ thick films. It also shows voids between the particles basically due to evaporation of organic solvents during the firing of the films. The
grain size increases with firing temperature of the films. AFM revealed that In$_2$O$_3$ showed rectangular as well as triangular grain growth on alumina substrate with average grain size ~ 200 nm and rms surface roughness ~400 nm per micron.

References


