ZnO:Sn deposition by reactive evaporation: effects of doping on the electrical and optical properties

L. K. Munguti¹, R.J. Musembi² and W.K. Njoroge¹
¹Department of Physics, Kenyatta University, P.O. Box 43844 GPO Nairobi- Kenya.
²Department of Physics, University of Nairobi, P.O. Box 30197- 00100 GPO Nairobi-Kenya.

ABSTRACT
Tin doped zinc oxide thin films have been deposited by reactive evaporation, the deposition has been done at various doping levels ranging from 1% to 8%. The optical properties have been characterized using UV-VIS-NIR spectrophotometer, the data for transmittance has been used for further analysis using scout. The transmittance of doped thin films has been found to be > 75% while for those of as prepared samples has been found to be even higher. The bandgap calculations have shown that the band gap for as prepared and doped thin films ranges between 2.95 – 3.95 eV. The electrical characterization has been done mainly at room temperature using a well calibrated four point probe. The sheet resistivity has been found to range from 24.3-26.7 Ohm cm. The coating have been found to be suitable for antireflectance as well as transparent contacting oxide applications.

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Table 2.1: Tin doping level for Zinc Oxide

<table>
<thead>
<tr>
<th>SAMPLE NAME</th>
<th>TIN DOPING LEVEL FOR ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Undoped</td>
</tr>
<tr>
<td>G</td>
<td>1%</td>
</tr>
<tr>
<td>H</td>
<td>2%</td>
</tr>
<tr>
<td>I</td>
<td>3%</td>
</tr>
<tr>
<td>J</td>
<td>4%</td>
</tr>
<tr>
<td>K</td>
<td>5%</td>
</tr>
<tr>
<td>L</td>
<td>6%</td>
</tr>
<tr>
<td>M</td>
<td>7%</td>
</tr>
<tr>
<td>N</td>
<td>8%</td>
</tr>
</tbody>
</table>

Zinc granules were mixed with tin pellets as per the doping and heated in a sealed glass tube in presence of argon. The resulting alloy was cooled naturally to room temperature. The cooling was done in argon atmosphere for 10 minutes and the cooling time was recorded using a stop watch.

Deposition of the Tin doped Zinc Oxide.

The sealed glass tubes were broken and the compound was removed. A mass of 0.1g of each sample was measured and placed in the boat of the evaporation chamber in the Edward’s Auto 306 Coating unit evaporation system. The chamber was evacuated down to 5.0 x 10⁻⁵ mbar and oxygen was allowed at the rate 20 standard cubic centimetre (sccm). This reduced the chamber pressure to 4.8 x 10⁻⁵ mbar during the deposition period. The current of the heater filament in the chamber was maintained at 3.5A for 3 minutes. Since zinc is more reactive than tin, zinc oxide was formed. Microscope glass slides were used as substrate for all the film deposition. After the deposition...
all the samples were kept in microscope glass slides holder to prevent physical and or environmental damage.

**Optical Properties of Tin Doped Zinc Oxide.**

The raw data for the optical properties of both films were obtained using UV-VIS-NIR Spectrophotometer solid spec DUV at normal incidence. The data for each film was analyzed using the SCOUT software and graphs plotted using OriginPro7 software.

**Electrical Characterization**

The sheet resistivity measurements were carried out using the four point configuration at room temperature (25°C). The four point probe set up usually consists of four equally spaced tungsten metal tips with finite radius. Each tip is supported by springs on the other end to minimize sample damage during probing. The four metal tips are part of an auto-mechanical stage which travels up and down during measurements.

A high impedance current source was used to supply current through the outer two probes and a voltmeter used to measure the voltage across the inner two probes as shown in figure 2. These values of sourced current and measured voltage were used to determine the sample resistivity. Typical probe spacing $S$ was about 1 mm.

**Elemental composition of the films.**

To determine the elemental composition of the films XRF spectroscopy was used. XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis of environmental, geological, biological, industrial and other types of samples. Compared to some competitive techniques such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Spectroscopy (ICPS), and Neutron Activation Analysis (NAA), XRF has the advantage of generally being non destructive, multi-elemental, fast and cost effective.

It also provides fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations, from 100% to few parts per million. A main disadvantage is that analyses are generally restricted to heavier elements than fluorine.

**Results and Discussion**

**Optical spectra of the films.**

The experimental data for transmittance and reflectance was obtained directly from UV VIS NIR Spectrophotometer DUV using the UVprobe software. The data was then converted in to Microsoft Office Excel format from which spectra graphs were plotted. The transmittance spectra for ZnO:Sn is shown in figure 3.1 below.

The films showed high transmittance (>75%) in the visible region (380nm-780nm) showing that tin doped zinc oxide is a suitable window for solar cell applications. The films shows a sharp cut-off in the UV (<380nm) showing strong absorption property of the films. The doped films showed slightly lower transmittance compared with the undoped films in the same range. This can be attributed to the narrowing of the band gap and free charge carrier absorption of photons due increased levels of tin doping. In addition, at high doping levels, there is increased scattering of photons by crystal defects.

The increase in transmittance with wavelength reduces beyond 800 nm. This is caused by increase in reflectance towards the infrared region. The transmittance for undoped films is higher than that of doped due to increased absorption in the doped films.

![Figure 3.1: The transmittance spectra for tin doped zinc oxide](image)

**Zinc Oxide reflectance**

Plots of spectral curves for ZnO:Sn thin films as shown in figure 3.2 shows that in visible spectrum range reflectance is generally low. For incident light of wavelengths above 1000nm, reflectance decreases greatly. This can be attributed to high transmission taking place as a result of low photon energy of incident light.

![Figure 3.2: Optical reflectance of tin doped zinc oxide](image)
Figure 3.3: Simulated versus experimental graph for zinc oxide doped at 4% tin concentration

Figure 3.4: Extrapolation of the linear part of \((\alpha h v)^2\) against energy(eV) for tin doped zinc oxide. The band gap energy was obtained was 2.95 eV for 4% tin concentration

Figure 3.5: Extrapolation of the linear part of \((\alpha h v)^2\) against energy(eV) for tin doped zinc oxide. The band gap energy was obtained was 3.10 eV for 3% tin concentration

Figure 3.6: Variation of band gap with tin doping concentration. The lowest band gap was obtained at 4% tin doping

The graph in figure 3.6 shows that the band gap decreases with increase in tin doping reaching the lowest value at 2.95eV at 4%. Further tin doping leads to increase in band gap at the doping concentration of more than 4%. It is attributed to the fact that the excess tin atoms were segregated into the grain boundaries at the doping concentration of more than 4%. These segregated tin atoms did not act as dopants.

Figure 3.7: Absorption coefficient of tin doped zinc oxide. Low absorption coefficient indicates that zinc oxide is a good window layer for solar cells

**Electrical Resistivity**

Electrical resistivity’s of ZnO and ZnO:Sn for various doping concentrations were measured and presented in graph on figure 3.8. The thickness of the films was of the range 90–150nm.

Figure 3.8: Variation of resistivity with the tin doping levels

Resistivity of undoped ZnO decreases sharply with 1% tin doping. The lowest resistivity was reached at 4% tin doping. The decrease in resistivity may be explained as follows: since the ionic radius of tin (0.38 Å) is smaller than that of the zinc ion (0.6 Å), the tin atoms doped into a ZnO lattice act as donors by supplying two free electrons when the Sn ions occupy Zn ion sites. This in turn increases the free carrier concentration and hence decreases the resistivity. The mechanism of the conduction can be described by the (3.0) below:

\[
\text{SnO}_{22x} \rightarrow \text{Sn}^{2+}_{\text{Zn}} + O^{+} + \frac{1}{2} O_2 + 2e^{-} \tag{3.0}
\]

Sn\(^{4+}\) ions substituted Zn\(^{2+}\) ions in the lattice induce positive Sn\(^{2+}\) charges in the material. In order to maintain electrical neutrality, two negative electrons are induced to compensate the excess positive charges. Hence the resistivity decreases due to increasing free electrons in the film. In the concentrations between 1% and 4% of Sn dopants, little decrease of resistivity is found. However, when more than 4% of Sn was added, the resistivity gradually increased.
At higher concentrations more tin atoms can be effectively incorporated into the lattice of ZnO. On the other hand, the residual stress arises simultaneously as well. The stress field would reflect electric carriers and result in high resistivity. Further more as the doping level is increased, more dopant atoms Zn atoms in the crystal grain and grain boundaries tend to saturation. In this case over high doping concentration will lead to large quantity of ionized impurity. The ionized impurity provide strong scattering centres for charge carriers [4]. According to the Conwell-Weisskoft formula, when degenerate saturation. In this case over high doping concentration will lead to large quantity of ionized impurity. The ionized impurity provide strong scattering centres for charge carriers [4]. According to the Conwell-Weisskoft formula, when degenerate electrons, the energy dependence of ionized impurity scattering mobility \( \mu_i \) is:

\[
\mu_i = \frac{\tau_i(E_F)}{m^*} \left( \frac{\hbar}{m^*} \right) \frac{1}{2} \frac{\epsilon}{\epsilon_F^2} \left( \frac{N_i}{Z_e^2} \right)^{-1} \ln \left( \frac{\epsilon}{\epsilon_F} \right) = \frac{1}{n} \frac{\tau_i(E_F)}{m^*} \left( \frac{\hbar}{m^*} \right) \frac{1}{2} \frac{\epsilon}{\epsilon_F^2} \left( \frac{N_i}{Z_e^2} \right)^{-1} \ln \left( \frac{\epsilon}{\epsilon_F} \right)
\]

(3.1)

Where \( \tau_i(E_F) \) is the relaxation time, which takes into account the scattering events occurring near the Fermi level \( E_F \). \( \epsilon \) is the static dielectric constant of the film, \( m^* \) is the effective mass of electrons, \( Z_e \) is the ion charge and \( N_i \) is the concentration of the scattering centres. From the equation above we can see that a high doping concentration will lead to a large quantity of ionized impurity, resulting to decrease in mobilities of the ZnO:Sn films.

**XRF Spectrum for tin doped Zinc Oxide.**

XRF analysis was carried out using MiniPal2 XRF machine which analyses heavy materials. The analysis was carried out to ascertain the elemental composition of the thin films. The analysis is peak-based where elemental intensities of thin films are calculated and respective spectral background obtained. In figure 3.9, the XRF spectrum for ZnO:Sn shows the peaks of elemental composition of the film.

**Figure 3.9: XRF spectrum of ZnO:Sn thin film with 4% Sn doping concentration.**

The shaded peaks are the elemental composition of the thin film. The elements detected from the XRF analysis are Zn (15%) and Sn (85%) as seen from coloured peaks. For Zn peaks were detected at energies of 1.18 keV, 8.42 keV and 9.6 keV. Peak X is the detector escape which is a spectrum for detector peak. The MiniPal2 XRF machine used filters the detector escape but its spectrum display remains, a reason why it is faint. The faint spectral line Y at the bottom is for the background radiation which is also filtered but remains displayed.

**Conclusion**

Deposition of thin films of ZnO:Sn has been done by reactive thermal evaporation technique. The asprepared and doped thin films have been found to have a high transmittance of over 75%. The optical band gap of the films has been found to range between 2.95 eV and 3.95 eV. The doping level has been found to influence the band gap. An increase in doping level has been found to decrease the band gap which has been attributed to increase in free charge carriers due to high concentration of impurity atoms. The sheet resistance has been found to be around 23.4 ohm cm.

**Acknowledgement**

The authors of this work want to thank the Chief Geologist Department of Mines and Geology Ministry of Environment and Natural Resources for the use XRF spectrometer.

**References**


