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# Characterization of Composite Films Made from Tin (IV) Oxide and Zinc Oxide with Impedance Spectroscopy

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## ABSTRACT

In this study, impedance of composite porous films has been taken into consideration. A series of composite films were made with different mass percentages of $SnO_2$ and ZnO which have energy band gaps of 3.8 eV and 3.2 eV respectively. Impedance spectroscopy was used as the observing tool in their characterization. A simple configuration of a single resistance in series with a RC transfer circuit of the composite film is discussed. Such models can be extended in order to describe porous electrodes where the interfacial polarization displays complex properties such as frequency dispersion. A minimum resistivity of $7.6 \times 10^{4}$ kΩ m (or conductivity of $1.3 \times 10^{-5}$ mS $m^{-1}$) was obtained for these films when $SnO_2$ and ZnO mixing ratio was 1:1. The analysis of impedance spectroscopic measurements of $SnO_2$ and ZnO composite films showed that the suggested approach is capable of identifying the optimum mixing ratio in a frequency resolved measurement domain.

## 1. INTRODUCTION

Different kinds of porous and mixed phase films such as nanostructured semiconductors have been extensively used in many devices nowadays. Considering the small scale nature of the constituents of the porous network, charge carriers of transit are always close to the surface implying that transfer processes are strongly coupled in these systems. Small signal frequency resolved techniques appear as a major tool for resolving the mechanisms of carrier transport, trapping and their interactions. Impedance spectroscopy (IS) subsumes the small signal measurement of the linear electrical response of a material of interest including electrode effects and the subsequent analysis of the response to yield useful information about physicochemical properties of the systems [1]. IS is studied in many fields including photoelectrochemistry, solid state electronics and solid state ionics. This technique is widely used due to its sensitivity and its ability to separate the different processes involved in the materials and devices [2]. However impedance analysis of systems requires consideration of additional aspects to characterize the transport mechanisms and extract the available information. In the majority of cases, the nanostructured films are better represented by a more complicated network of resistances and capacitances, so-called equivalent circuit. IS analysis generally makes considerable use of equivalent circuits and shows a more complex behaviour depending on the frequency range used in the complex impedance plane.

In this study, the behaviour of composite films made from ZnO and $SnO_2$ were analyzed using IS to describe the mechanism of charge carrier transportation.

## 2. METHODOLOGY

Series of nanocrystalline ZnO and $SnO_2$ composite films were prepared by different mass percentages keeping the total mass at 0.5 g. Films (1 cm × 1 cm) of thickness 10 μm were prepared using doctor blade method on conducting tin oxide (CTO) glass plates (15 Ω $cm^{-2}$) which was made by grinding ZnO and $SnO_2$ powder with acetic acid and Triton X-100 in ethyl alcohol. These films were sintered at 450 $^0$C in a furnace for 30 minutes.

Complex plane impedance spectra of these films were measured by Solartron 1260 frequency response analyser using SMART software which is provided with the instrument. Their associated equivalent circuits were synthesized with different combinations of resistors and capacitors.

A sweep was carried out for different mass percentages of ZnO and $SnO_2$ films coated on CTO glass with Pt sputtered glass plate as the counter electrode by setting AC level at 500 mV in the frequency range from 1 MHz to 1 Hz while measuring the impedance in 1.0 s integrations.

## 3. RESULTS AND DISCUSSION

A characteristic Nyquist plot (where real impedance is plotted against the imaginary impedance) of the shape as shown in figure 1 was observed for all of the ZnO and $SnO_2$ composite films.

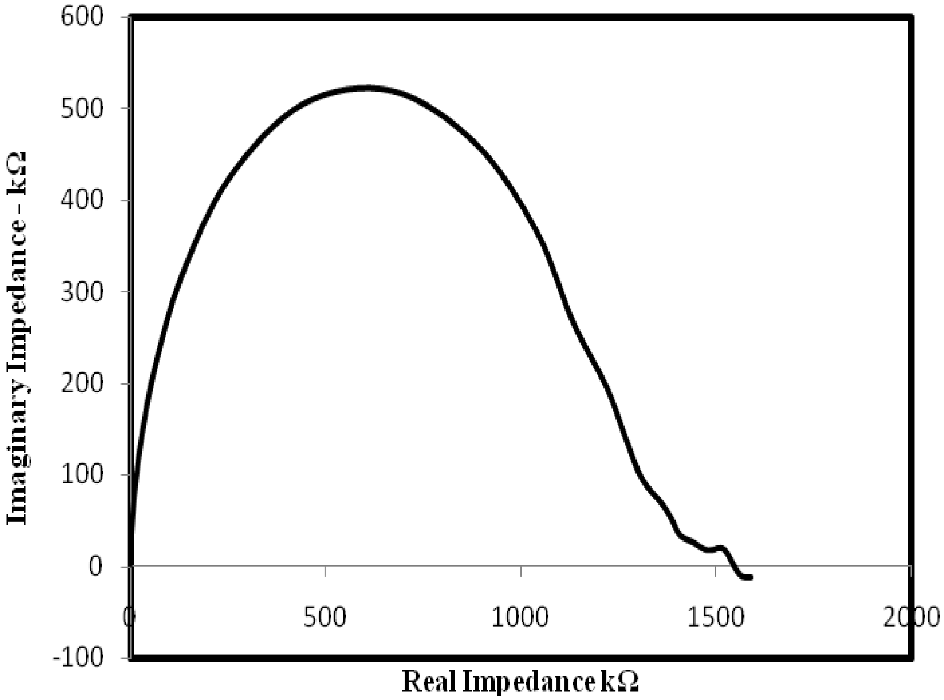


Figure 1.Nyquist plot of a sample made from 90% ZnO and 10% $SnO_2$

On the Nyquist plot, the impedance is represented by a vector of amplitude Z and phase angle Φ. Series and parallel resistances and capacitances of the film can be found out with a Nyquist plot. Subsequently, it is possible to find the equivalent circuit and the significance of the different components. It was carried out by comparing the results with a theoretical model.

From the given impedance spectrum, resistances and capacitance values of components in the following equivalent circuit were calculated.

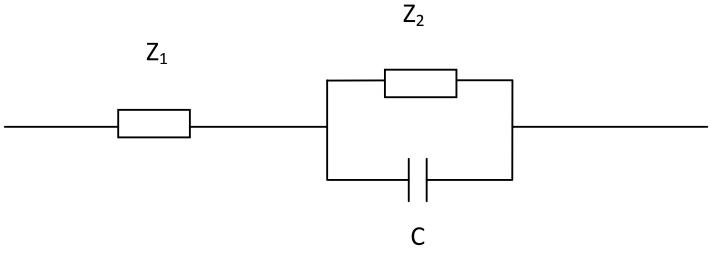


Figure 2. Equivalent circuit for ZnO and $SnO_2$ composite films

Composite ZnO and $SnO_2$ films deposited on CTO glass model a cell where the sheet resistance of the CTO glass is in series with the parallel combination of capacitance and resistance of the composite film (Figure 2).

The values of the above parameters were found with the proper interpretation of the Nyquist plots using SMART software. For example, capacitance was determined by examination of the maximum data point of the curve on the real axis. The lowest intercept point of the curve with real axis gave value for $Z_1$ and the second intercept gave the value of total resistance $Z_1$ and $Z_2$.

It was noted that $Z_1$ value did not vary significantly in all the ZnO and $SnO_2$ compositions because it represents the sheet resistance of the CTO glass which was found to be around 486 Ω. But $Z_2$ value which is the parallel resistance of the film varied dramatically while altering the composition. The observation can be explained as follows. Since both the ZnO and $SnO_2$ are n-type semiconductors, their resistances are at low values when they are in pure form compared to other mixing ratios. In Figure 3, two peaks can be observed with minima at 50% of $SnO_2$. The peaks correspond to an introduction of 40% and 90% of $SnO_2$ in the composite film. When consider the first peak, the majority is ZnO particles (~ 60%) of the composite.

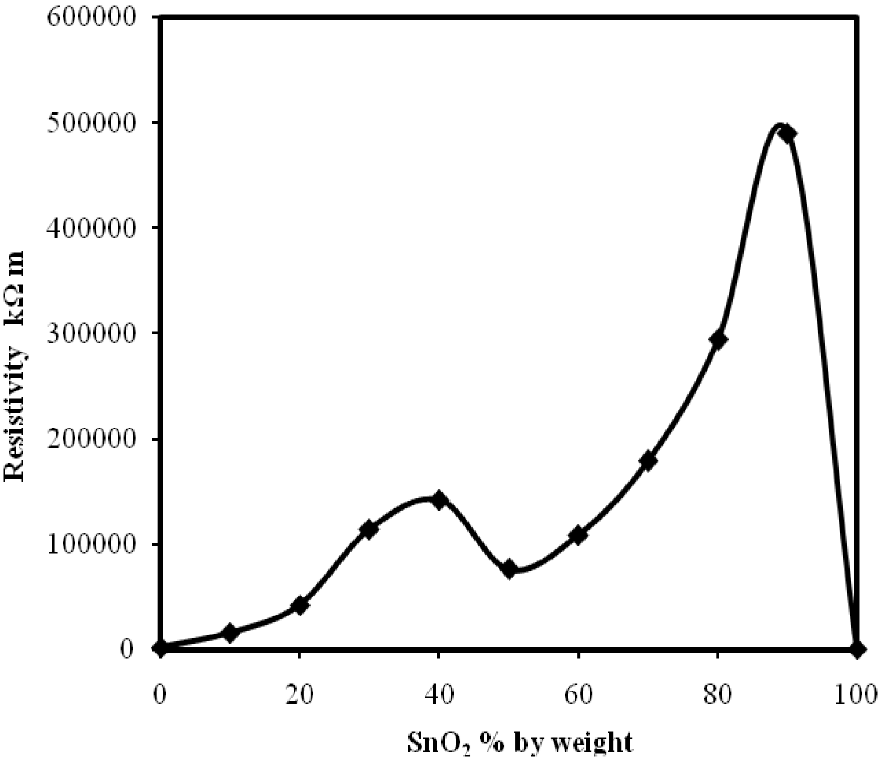
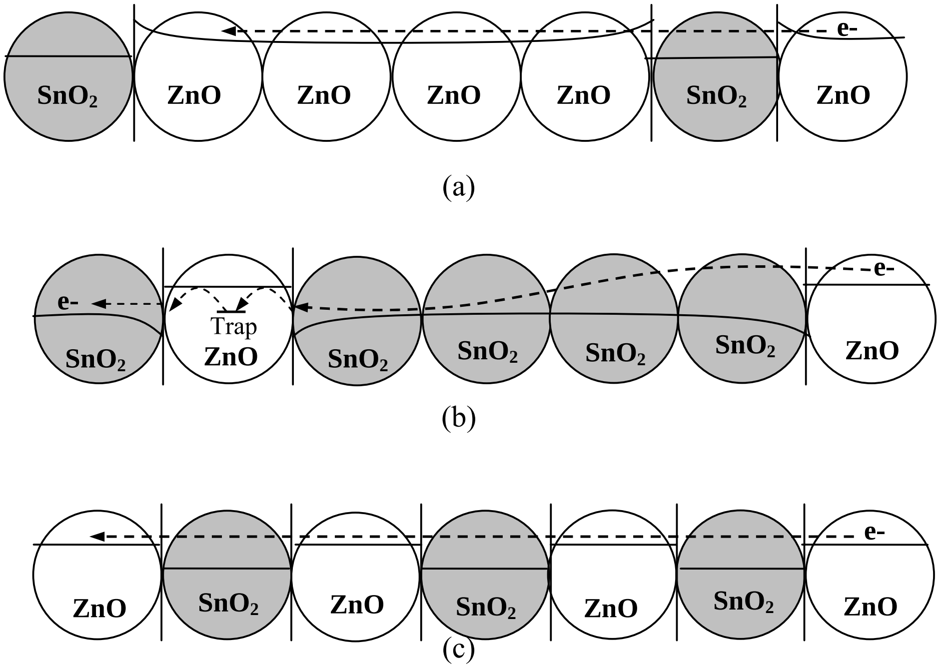


Figure 3. Resistivity vs ZnO % by weight of ZnO and $SnO_2$ composite films

Due to the space charge layer created on ZnO by depletion of electrons to $SnO_2$ particles, the conduction band is bent as shown in Figure 4(a). The space charge layer prohibits the electrons to transport across the conduction band of $SnO_2$ which in turn increases the resistivity.

In a single isolated $SnO_2$ or ZnO particle, band bending could not be observed because the particle size of both the materials are less than 500 nm, where depletion layer is generally spread out to 1 μm. On the other hand, when the majority is $SnO_2$ particles as in Figure 4(b), the electrons may travel through several $SnO_2$ particles to meet a ZnO particle which relaxes to the conduction band edge of $SnO_2$ on its way. Now the electron has a lower energy than the conduction band of ZnO. So, the only possible path for the electron to travel through the ZnO particle is hopping through the shallow traps in the ZnO particles which will increase the resistance very much. Very high resistivity of the second peak at the composition of 90% of $SnO_2$ is attributed due to this reason.

When both the materials are in 1:1 ratio, transferring electrons have a less tendency to fall into the conduction band of neighbouring $SnO_2$ particles. Here the electrons travel from one ZnO particle to another ZnO particle tunnelling through the conduction band of $SnO_2$ particles as shown in Figure 4(c). Therefore in this situation, resistance of the film decreases to the minimum.



(a)

(b)

(c)

Figure 4. The mechanisms of electron transport in $SnO_2$ and ZnO composites at different mixing ratios (a) 40% $SnO_2$ (b) 90% $SnO_2$ (c) 50% $SnO_2$

The results of this study correlates with the previous studies of fabrication of dye-sensitized solar cells with composite of $SnO_2$ and ZnO [3]. There also the authors have clearly indicated that the solar cells made with the 1:1 ratio of $SnO_2$ and ZnO has the highest efficiency. Therefore, our study justifies the previous work of use of this composite material in solar cells in 1:1 ratio of $SnO_2$ and ZnO for the optimum performance.

## 4. CONCLUSION

The composites made mixing $SnO_2$ and ZnO particles showed less conductivity compared to each of them in pure form. But compared to other mixing ratios, when $SnO_2$ and ZnO are in 1:1 ratio the resistivity of the composite film was the lowest. Again when the percentage of $SnO_2$ is around 40% and 90% the resistivity of the films were higher. Each of these cases is explained by depletion of electrons in the conduction band of $SnO_2$ and ZnO at the interface and formation of space charge layer. Because of the space charge layer, recombination processes could be eliminated when this composite material is used in opto-electronic devices.

## ACKNOWLEDGEMENT

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