

RESEARCH ARTICLE

Analysis of the behaviour of SnO₂ composites of ZnO and TiO₂ using impedance spectroscopy

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Abstract: Composite semiconductor nanostructures will contribute in large measure for the future generation of cost effective optoelectronic devices. In order to advance the progress it is important to understand the mechanism of charge injection, transport and recombination in these systems. Impedance spectroscopy (IS) is a relatively old and powerful method for characterizing many of the electrical properties of materials and their interfaces. In this study, the impedance of composite porous films of SnO₂/ZnO and SnO₂/TiO₂ have been taken into consideration and their behaviour in composite films was analyzed using IS to describe the mechanism of charge carrier transportation.

The composites of SnO₂ and ZnO showed higher resistivity than their pure form and when SnO₂ : ZnO is in 1:1 ratio the resistivity of the composite film was the lowest (7.6×10^4 kΩ m). When the percentage of SnO₂ is around 40 % and 90 % the resistivity of the films were higher where each of these cases could be explained by the depletion of electrons in the conduction band of SnO₂ and ZnO at the interface. In contrast to the SnO₂ and ZnO composite films, the minimum resistivity of 5.86×10^5 Ωm was obtained for SnO₂ and TiO₂ composite films when SnO₂ is 33 %, which is lower than when they are in pure form. This low resistivity of both composite films is possibly attributed to the formation of a super structure in the composites where the electrons transport ballistically in mini bands.

Keywords: Composite films, dye sensitized solar cells, impedance spectroscopy.

INTRODUCTION

Composite materials sometimes exhibit rather unusual characteristics that are not prominent in pure materials and they could lead to novel applications

and enhancements in existing devices. One of the fields that has remarkably developed during the past few years by the application of composite materials is the technology in dye sensitized photo electrochemical cells (PECs) where oxides of composite nanocrystalline semiconductor materials replaced the photo electrodes of PECs based on nanocrystalline TiO₂ (Tennakone *et al.*, 1999 ; Kitiyanan *et al.*, 2005; Hamann *et al.*, 2008; Nho & Cuong, 2008). Tennakone *et al.* (1999) had achieved a dramatic enhancement in the conversion efficiency of dye sensitized solar cells (DSSCs) with the application of mixed SnO₂ and ZnO semiconductor particles in the working electrode. An equally important issue in this development is to understand the mechanism of charge injection transport and recombination in these systems (Bisquert, 2002). However, the revelation of the enhancement mechanism is not completely explored. Yet, it can lead to further improvements of conversion efficiency and may contribute to the progress of future generation photovoltaic devices and applications in many other fields.

Intensive work in DSSC research has been devoted to the synthetic chemistry, structural and photovoltaic characterization of mesoporous nano crystalline TiO₂ materials and TiO₂ based DSSCs, which give a photo conversion efficiency of nearly 10 % (Grätzel, 2003). In contrast, other metal oxide semiconductors have gained less attention although they satisfy the necessary photo electrochemical properties similar to TiO₂. In fact SnO₂ has at least two advantageous features compared to TiO₂ for the application in DSSCs. Its higher electron mobility than TiO₂ suggests a faster transport of photo induced electrons by diffusion in SnO₂ than in TiO₂ and its larger

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band gap (3.8 eV) than the anatase phase of TiO_2 would create fewer oxidative holes in the valence band, so as to facilitate the long term stability of DSSCs (Qian *et al.*, 2009). However, SnO_2 based DSSCs were developed with less success and the conversion efficiencies of SnO_2 photo electrodes reported so far are much lower than those of TiO_2 (Chappel & Zaban, 2002).

In this study, the impedance of composite porous films deposited on conducting tin oxide (CTO) glass has been taken into consideration. A series of composite films were made with different mass percentages of SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$. Impedance spectroscopy was used as the measuring tool in their characterization.

METHODS AND MATERIALS

A series of nanocrystalline composite films of SnO_2 were prepared for different mass percentages of SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$ while keeping the total mass at 0.5 g. Films (1 cm $\times$ 1 cm) of thickness 10 μm were prepared using doctor blade method on conducting tin oxide (CTO) glass plates (15 Ωcm^{-2}), by grinding SnO_2 and ZnO (or TiO_2) powder with acetic acid and Triton X-100 in ethyl alcohol. These films were sintered at 450 $^\circ\text{C}$ in a furnace for 30 min.

Complex plane impedance spectra of these films were measured by Solartron 1260 frequency response analyzer using SMART software, which is provided with the instrument. Sweeps were carried out for different mass percentages of SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$ films coated on CTO glass with Pt sputtered glass plate as the counter electrode by setting the AC level at 100 mV in the frequency range of 1 MHz - 1 Hz while measuring the impedance in 1.0 s integrations.

RESULTS AND DISCUSSION

A characteristic Nyquist plot of semi circular shape was observed for all the mass ratios of composites of SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$ where some of them are shown in Figure 1 (a) and (b), respectively. Subsequently, to find the equivalent circuit and the significance of the different components the results were compared with a theoretical model. From the given impedance spectrum, the resistances and capacitance values of components in the equivalent circuit given in Figure 2 were calculated. The composites of SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$ films deposited on CTO glass model a cell where the contact resistance (Z_1) of the CTO glass and the oxide semiconductors is in series with the parallel combination of capacitance (C) and resistance of the composite film (Z_2) as shown in Figure 2.

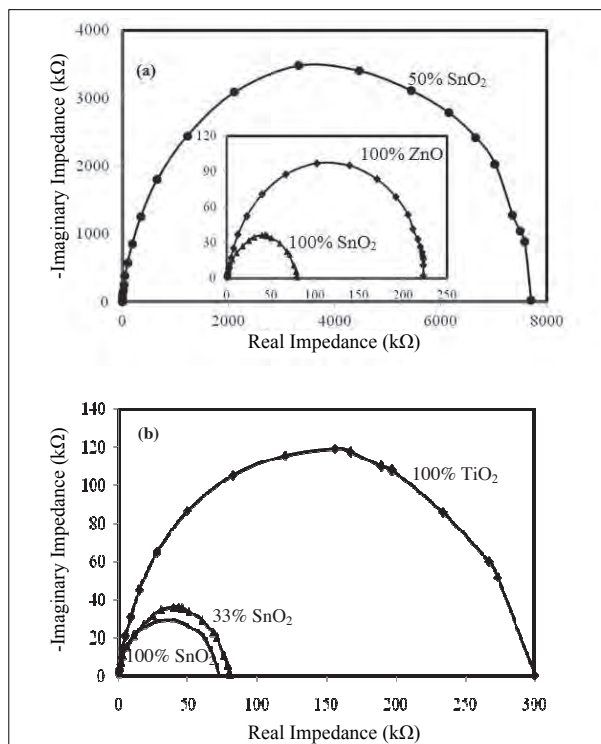


Figure 1: Nyquist plot of composite films made from (a) SnO_2/ZnO and (b) $\text{SnO}_2/\text{TiO}_2$

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

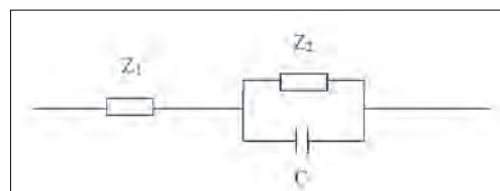


Figure 2: The equivalent circuit for composite SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$ films

The average Z_1 value did not vary significantly in all compositions of SnO_2/ZnO and $\text{SnO}_2/\text{TiO}_2$ because it represents the contact resistance of the CTO glass with the composites, which was found to be around 486 Ω and 665 Ω , respectively.

However, the average Z_2 value, which is the parallel resistance of the films varied dramatically while altering the composition. The observation can be explained as follows for SnO_2/ZnO composite films. Since both the SnO_2 and ZnO are n-type semiconductors, their

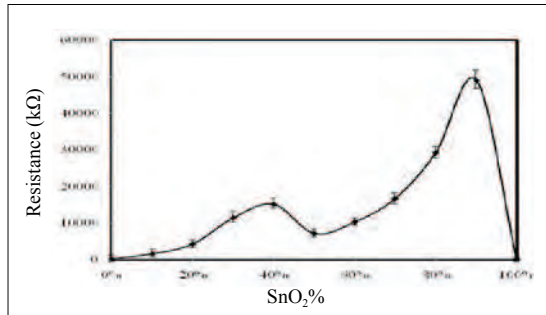


Figure 3: Plot of Z_2 vs SnO₂% (by weight) for SnO₂ and ZnO composite films

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 SnO₂. The peaks correspond to an introduction of 40 % and 90 % of SnO₂ in the composite film. When we consider the first peak, the majority is ZnO particles (~ 60 % of the composite). Due to the space charge layer produced on ZnO by the depletion of electrons to SnO₂ particles (Zheng *et al.*, 2009; Uddin *et al.*, 2012), the conduction band is bent as shown in Figure 4(a).

In a single isolated SnO₂ or ZnO particle, band bending could not be observed because the particle size of both materials is less than 200 nm, where the depletion layer is generally spread out to 1 μm.

Figure 5 shows the scanning electron micrographs of (a) 100 % SnO₂ and (b) 50 % SnO₂ of SnO₂/ZnO composite films from which the particle sizes could be estimated. When the majority is SnO₂ particles as in

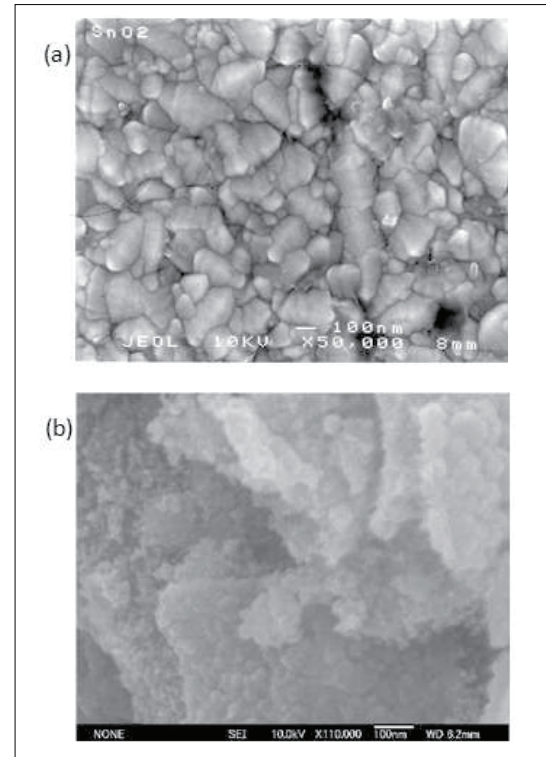


Figure 5: Scanning electron micrographs of (a) 100 % SnO₂ and (b) 50 % SnO₂ of SnO₂/ZnO composite films

Figure 4(b), the electrons may travel through several SnO₂ particles to meet a ZnO particle, which relaxes to the conduction band edge of SnO₂ on its way. Now the electron has a lower energy than the conduction band of ZnO. 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. A very high resistivity of the second peak at the composition of 90 % of SnO₂ is attributed to this reason. When both materials are in 1:1 ratio, transferring electrons have a less tendency to fall into the conduction band edge of the neighbouring SnO₂ particles. Here the electrons travel from one ZnO particle to another, tunnelling through the conduction band of SnO₂ particles as shown in Figure 4(c). Therefore in this situation, resistance of the film decreases to the minimum.

The results of this study correlates with the previous results of fabrication of dye-sensitized solar cells with composite of SnO₂ and ZnO (Kumara *et al.*, 2003). In the study the authors have clearly reported that the solar cells made with the 1:1 ratio of SnO₂ and ZnO has the highest efficiency.

In contrast to the SnO₂/ZnO composite films, the Z_2 value rapidly decreased in the composite film of

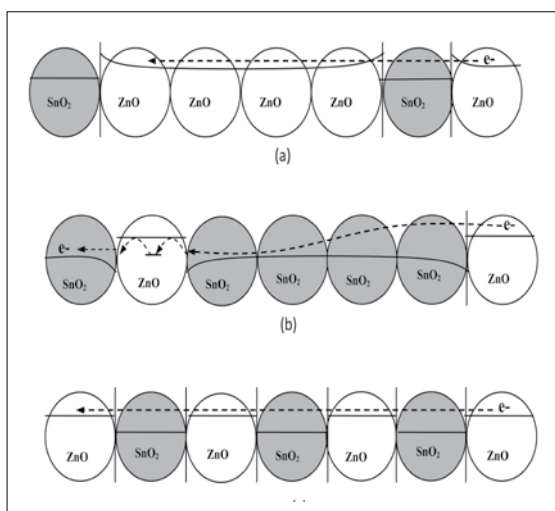


Figure 4: The mechanisms of electron transport in SnO₂ and ZnO composites at different mixing ratios (a) 40 % SnO₂ (b) 90 % SnO₂ and (c) 50 % SnO₂

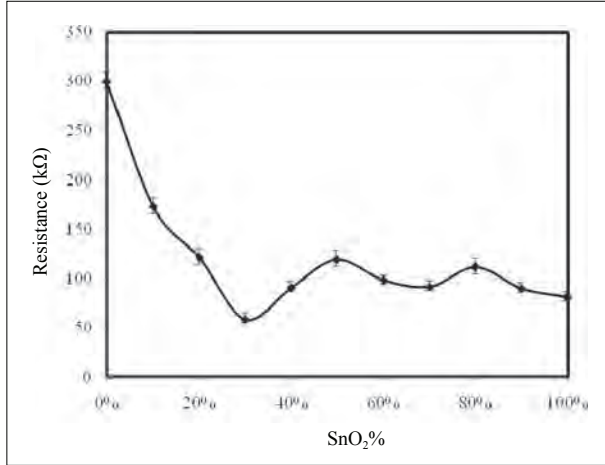


Figure 6: Plot of Z_2 vs SnO_2 % (by weight) for SnO_2 and TiO_2 composite films

$\text{SnO}_2/\text{TiO}_2$ while altering the composition (Figure 6). The wavy nature of the variation of impedance with the composition of the film is an interesting observation made in this study.

The average particle size of TiO_2 (Degussa P-25) and SnO_2 used in this study has been estimated with the particle size analyzer and scanning electron micrographs (SEM) and are in the order of 10 nm and 200 nm, respectively. Therefore at the preparation of the films, small TiO_2 particles tend to deposit on large SnO_2 particles, making a shell around it.

The thickness, T of a shell around a core particle of average radius r of this nature can be estimated using the formula

$$T = \frac{r}{3} \times \frac{W_s \rho_s}{W_c \rho_c} \quad \dots(1)$$

where W_s : weight of shell material, W_c : weight of core material, ρ_s : density of shell material and ρ_c : density of core material (Bandaranayake *et al.*, 2004).

The thickness can also be related to the roughness factor R by the relation

$$T = \frac{W_c}{\rho_s R A} \quad \dots(2)$$

where A is the surface area of the film.

The thicknesses of the TiO_2 shell calculated using the above formula at the points which gave maximum and minimum resistivity of the film at different compositions is given in Table 1. In these calculations the density of TiO_2 and SnO_2 is taken as $4.23 \times 10^3 \text{ kg m}^{-3}$ and $6.25 \times 10^3 \text{ kg m}^{-3}$, respectively. The number of TiO_2 particles, N that resides in between two consecutive SnO_2 particles in the composite is also estimated with the knowledge of the thickness of TiO_2 shell and the particle size of TiO_2 considering $r \gg T$.

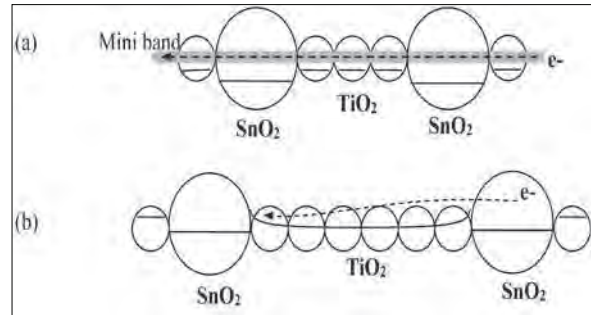


Figure 7: Electron transport in (a) mini bands and (b) hetero structures of SnO_2 and TiO_2 composites

The resistivity of pure SnO_2 ($0.9 \times 10^6 \Omega\text{m}$) is very much less compared to the resistivity of pure TiO_2 ($3.0 \times 10^6 \Omega\text{m}$) as evident from Figure 6. It also requires at least 20 % of TiO_2 in the composite film for monolayer coverage of SnO_2 particle according to Table 1. Therefore when the direct contacts of SnO_2 particles are forbidden by the inclusion of high resistive TiO_2 particles in between SnO_2 particles, it is obvious that the resistivity of the composite increases. This was prominent above 20 % of TiO_2 in the composite film. It is not clear why the resistivity decreases at 65 % and increases again at 50 % of SnO_2 in the composite film. This ambiguous behaviour has to be studied further to explain it meaningfully. The important finding of this study is that the resistivity of the composite film becomes lesser than the resistivity of both individuals when the film consists of 33 % of SnO_2 . In this composition the average number of TiO_2 particles in between two SnO_2 particles is found to be 8. This kind of reduction of resistivity in a composite nanostructure

Table 1: Thickness of TiO_2 shell on SnO_2 particles and average number of TiO_2 particles resides in between two SnO_2 particles at different SnO_2 % of the composite films.

SnO_2 %	33 %	50 %	65 %	80 %
T (nm)	41.19	20.28	10.14	5.07
N	8	4	2	1

could only happen due to the formation of a super structure where electrons move ballistically (Figure 7a). The electron confining Bohr radius, α of a nanoparticle is given by

$$\alpha = \frac{\hbar}{(2m^* E)^{1/2}} \quad \dots(3)$$

where m^* is the electron effective mass.

The formation of a super structure with SnO₂ and TiO₂ seems possible, when the effective mass of electrons in SnO₂ and TiO₂ are considered, which are $0.1m_e$ and $10m_e$, respectively (m_e : rest mass of electron). The small effective mass of electrons in SnO₂ makes a longer length for electron confinement in SnO₂. Therefore, even 200 nm particles of SnO₂ could contribute to form a super structure in this composite film. On the other hand although the calculations indicate that there are 8 particles of TiO₂ in between two SnO₂ particles at this composition, in practice, it can vary from place to place.

Therefore the reason for the other compositions greater than 33 % of SnO₂ are unable to work as super structures is possibly because of the direct contacts of SnO₂ at high SnO₂ percentage levels, which do not support the formation of super structures. When the SnO₂ composition further reduces, the super structure disappears and band bending occurs in the TiO₂ phase (Figure 7b). At this stage a rapid increment of the resistivity of the composite could be observed as seen in Figure 6.

CONCLUSION

The composites made by mixing SnO₂ and ZnO particles showed a high resistivity compared to each of them in pure form. However, compared to other mixing ratios, when SnO₂ and ZnO are in 1:1 ratio the resistivity of the composite film was the lowest (7.6×10^4 kΩm). Again when the percentage of SnO₂ is around 40 % and 90 % the resistivity of the films were higher. Each of these cases can be explained by the depletion of electrons in the conduction band of SnO₂ and ZnO at the interface and the formation of a space charge layer. The analysis of impedance spectroscopic measurements of SnO₂ and ZnO composite films showed that the suggested approach is capable of describing the optimum mixing ratio of 1:1 in a frequency resolved measurement domain.

In contrast to the SnO₂ and ZnO composite films, a minimum resistivity of 5.86×10^5 Ωm was obtained for

SnO₂ and TiO₂ composite films when the percentage of SnO₂ is 33 %, which is lower than when they are in pure form. This low resistivity of the film is possibly attributed to the formation of a super structure in the composite where the electrons transport ballistically in mini bands. These structures could be preliminary tested in the future for optoelectronic devices such as solar cells to optimize their efficiencies.

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