Annual Academic Sessions 2011
ISSN 2012-9912; ©2011 Open University of Sri Lanka

CHARACTERIZATION OF COMPOSITE FILMS MADE FROM TIN (IV) OXIDE AND TITANIUM (IV) OXIDE WITH IMPEDANCE SPECTROSCOPY

C. N. Nupearachchi* and V. P. S Perera

Department of Physics, The Open University of Sri Lanka, Nawala, Nugegoda

INTRODUCTION

Different kinds of mixed phase porous films of nanostructured semiconductors have been extensively used in many devices nowadays and much research has been done focusing on the use of these materials in technical applications such as catalysis, optoelectronics, energy storage and production. 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 (Macdonald, 1992). Furthermore, the response due to the different processes is recorded in a single frequency sweep, according various frequencies existing in the system. This technique is widely used due to its sensitivity and its ability to separate the different processes involved in the materials and devices (Bisquert, 2002). 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 nano-structured 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, impedance of composite porous films has been taken into consideration and the behaviour of composite films made from SnO_2 and TiO_2 which have energy band gaps of 3.8 eV and 3.2 eV respectively were analyzed using IS to describe the mechanism of charge carrier transportation.

METHODOLOGY

Series of nanocrystalline SnO_2 and TiO_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 SnO_2 and TiO_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. A sweep was carried out for different mass percentages of SnO_2 and TiO_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.

RESULTS AND DISCUSSION

A characteristic Nyquist plots (where real impedance is plotted against the imaginary impedance) as shown in Figure 1 was observed for all of the SnO_2 and TiO_2 composite films.

* All correspondence should be addressed to Miss. C. N. Nupearachchi, Department of Physics, Open University of Sri Lanka (email: chathunilnupe@gmail.com)

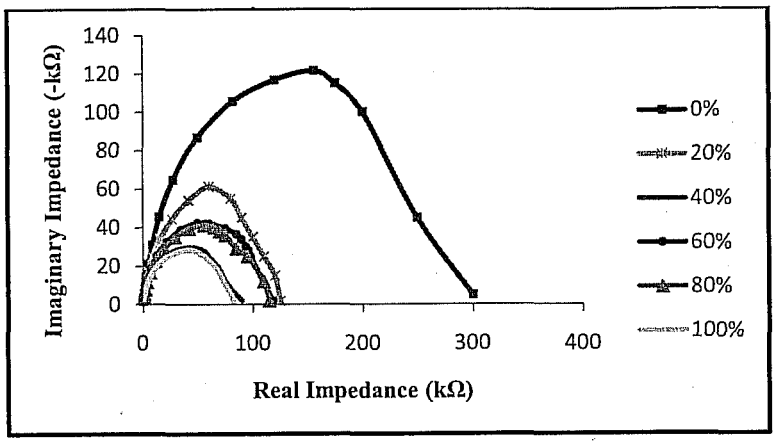

Figure 1. Nyquist plots of samples made from 0% SnO_2 to 100% SnO_2

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.

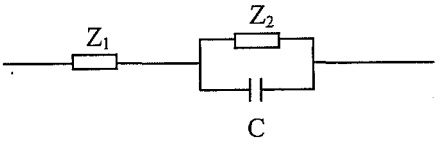

Figure 2. Equivalent circuit for TiO_2 and SnO_2 composite films

Composite SnO_2 and TiO_2 films deposited on CTO glass model a cell where the sheet resistance of the CTC 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.

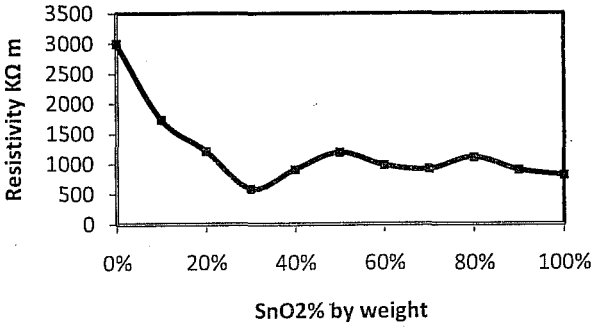

Figure 3. Resistivity vs SnO_2% by weight of TiO_2 and SnO_2 composite films

It was noted that Z_1 value did not vary significantly in all the SnO_2 and TiO_2 compositions because it represents the sheet resistance of the CTO glass which was found to be around 665.94 Ω. But Z_2 value which is the parallel resistance of the film varied dramatically while altering the composition (Figure 3).

The wavy nature of the variation of impedance with the composition of the film is an interesting observation made in this study. It has been reported earlier that the average particle size of TiO_2 and SnO_2 used in this study are in the order of 10 nm and 200 nm respectively measured with particle size analyzer and also estimated by scanning electron micrograms (SEM). Therefore at the film preparation, 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

$$T = \frac{r}{3} \times \frac{W_S \rho_S}{W_C \rho_C}$$ 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

$$T = \frac{W_C}{\rho_S R A}$$ 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 density of TiO_2 is taken as (4.23×10^3) kg m^{-3} and density of SnO_2 is taken as (6.95×10^3) kg m^{-3}. The number of TiO_2 particles, N that resides in between two consecutive SnO_2 particles in the composite is also calculated with the knowledge of the thickness of the TiO_2 shell and particle size of TiO_2 considering $r >> T$.

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

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

The resistivity of pure SnO_2 (0.9×10^6 Ω m) is very much less compared to the resistivity of pure TiO_2 (3.0×10^6 Ω m) as evident from Figure 3. It also requires at least 20% of TiO_2 in the composite film for monolayer coverage of SnO_2 particle according to the Table 1. Therefore when the direct contacts of SnO_2 particles are forbidden by 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 the 20% of TiO_2 presence in the composite film. It is not clear why the resistivity decreases at 65% of SnO_2 and increases again at 50% of SnO_2 in the composite film This ambiguous behaviour has to be studied further to explain it meaningfully. But anyway, the remarkable discovery of this study is resistivity of the composite film become lesser than the resistivity of both the 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 could only happen due to formation of super structure where electrons move ballistically (Figure 4a). The electron confining Bohr radius, α of a nanoparticle is given by

$$\alpha = \frac{\hbar}{(2m^* E)^{1/2}}$$ where m^* is the electron effective mass.

Formation of super structure with SnO_2 and TiO_2 seems possible, when the effective mass of electrons in SnO_2 and effective mass of electrons in TiO_2 are considered, which are $0.1m_e$ and $10m_e$ respectively. (m_e: rest mass of electron) The small effective mass of electron in SnO_2 makes longer length for electron confinement in SnO_2. Therefore even 200 nm particles of SnO_2 could contribute to form a super structure in this composite film. On the other hand though the calculations state that there are 8 particles of TiO_2 in between two SnO_2 particles at this composition, it can vary in place to place in practice. Therefore the reason why the other compositions greater than 33% of SnO_2 won't work as super structures is possibly because of direct contacts of SnO_2 at high SnO_2 % levels which do not support the formation of super structures. When SnO_2 composition further reduces the super structure vanishes and band bending occurs in the TiO_2 phase (Figure 4b). At this stage rapid increment of the resistivity of composite could be observed as seen in Figure 3.

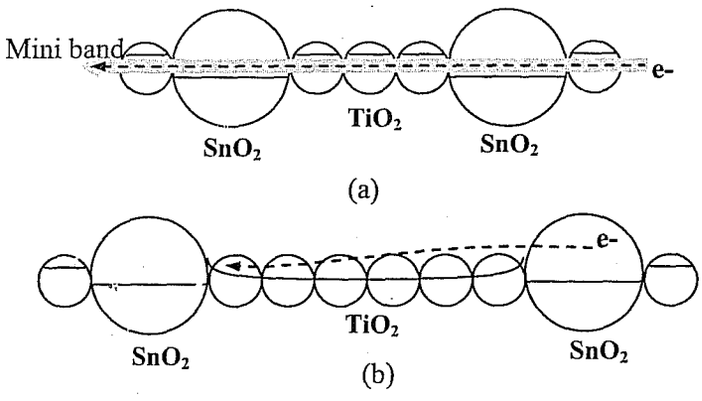

Figure 4. Electron transport in (a) mini bands and (b) hetero structures of SnO_2 and TiO_2 composites.

CONCLUSION

A composite film deposited on CTO glass can be represented by a simple configuration of a single resistor in series with a RC transfer circuit in impedance spectroscopic measurements. A minimum resistivity of 5.86×10^5 Ω m (or conductivity of 1.7×10^{-6} S m^{-1}) was obtained for these films when SnO_2 is 33%. This low resistivity of the film is possibly attributed to formation of super structure in the composite where electrons transport ballistically in mini bands. These structures could be tested in future for optoelectronic devices such as solar cells to optimize their efficiencies.

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