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

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ABSTRACT

Much research has been done focusing on the different kinds of mixed phase porous films of nanostructured semiconductors as they play a vital role in catalysis, optoelectronics, energy conversion and storage. Small signal frequency resolved techniques such as impedance spectroscopy (IS) has been used as a tool to resolve the mechanisms of carrier transport, trapping and their interactions in these films. IS measurements yield useful information about physicochemical properties of a system that can be represented by a network of resistances and capacitances in an equivalent circuit. In this study, impedance of composite porous films made from SnO_2 and Al_2O_3 which have energy band gaps of 3.8 eV and 8.3 eV respectively has been taken into consideration and their behaviour is analyzed using IS to describe the mechanism of charge carrier transportation. It was found out that the composite films have the highest resistance when the Al_2O_3 composition is 70%.

1. INTRODUCTION

Impedance Spectroscopy (IS) is a novel and powerful method for characterizing many of the electrical properties of materials and their interfaces. It may be used to investigate the dynamics of bound or mobile charges in the bulk or interfacial regions of any kind of solid or liquid materials. Thus, it is studied in many fields including photoelectrochemistry, solid state electronics and solid state ionics. IS is becoming an analytical tool in material research and development as it involves a relatively simple electrical measurement that can be readily be automated and whose results may often be correlated with many complex material variables, from mass transport, rates of chemical reactions, corrosion and dielectric properties to defects, microstructures and the compositional influences on the conductance of solids. It can predict aspects of the performances of chemical sensors and fuel cells and has been used extensively to investigate membrane behaviour in living cells. It is useful as an empirical quality control procedure. Yet, it can contribute to the interpretation of fundamental electrochemical and electronic processes [1].

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 [2]. This technique is widely used due to its sensitivity and its ability to separate the different processes involved in the materials and devices [3]. 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. One of the authors of this paper has previously reported such an analysis done on composite films of MgO and SnO_2 using IS [4].

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In this study, the behaviour of composite films made from Al_2O_3 and SnO_2 were analyzed using IS to describe the mechanism of charge carrier transportation.

2. METHODOLOGY

Series of nanocrystalline Al_2O_3 and SnO_2 composite films were prepared by different mass percentages keeping the total mass at 0.5 g. Films of surface area 1 cm^2 and thickness 10 μm were prepared using doctor blade method on conducting tin oxide (CTO) glass plates (15 Ωcm^{-2}) which was made by grinding Al_2O_3 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 Al_2O_3 and SnO_2 films coated on CTO glass with Pt sputtered glass plate as the counter electrode by setting AC level at 100 mV in the frequency range from 1 MHz to 1 Hz while measuring the impedance in 1.0 s integrations.

Dye sensitized solar cells (DSSC) were also fabricated using these films by immersing them in ethanolic dye solution containing Ruthenium N719 dye for 12 hours. A Pt sputtered CTO glass plate on the top of the dye coated electrode was attached as the counter electrode. The capillary space in between was filled with an electrolyte containing tetra propyl ammonium iodide 0.738 g and I_2 0.060 g which was dissolved in 3.6 ml of ethylene carbonate and 1.0 ml of acetonitrile. Cells were characterized by illuminating with tungsten filament light (100 mWm^{-2}) and a source meter coupled to a computer.

3. RESULTS AND DISCUSSION

A characteristic semi circle Nyquist plots (where real impedance is plotted against the imaginary impedance) were observed for all of the Al_2O_3 and SnO_2 composite films. 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 equivalent circuit were calculated.

Composite Al_2O_3 and SnO_2 films deposited on CTO glass modelled a cell where the contact resistance (Z_1) of the CTO glass and the oxide of semiconductor is in series with the parallel combination of capacitance and resistance of the composite film (Z_2). The values of these parameters were found with the proper interpretation of the Nyquist plots using SMART software.

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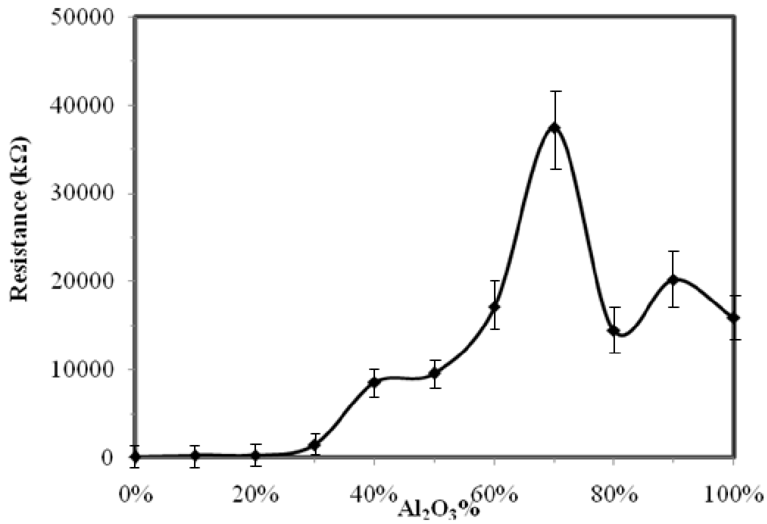

Fig. 1: Resistivity vs Al_2O_3% by weight of Al_2O_3 and SnO_2composite films

It was noted that Z_1 value did not vary significantly in all the Al_2O_3 and SnO_2 compositions because it represents the contact resistance of the CTO glass and the oxide of semiconductor which was found to be around 1013 Ω. But Z_2 value which is the parallel resistance of the film varied dramatically while altering the composition (Fig. 1). When the Al_2O_3 percentage is increased in the Al_2O_3 and SnO_2 composite, impedance of the film continuously increased and reached the maximum at 70% of Al_2O_3. Further increment of Al_2O_3 decreased the impedance again. The observation can be explained as follows.

When the percentage of Al_2O_3 is less than 30% the resistance of the film is only slightly higher than pure SnO_2 film. In this case electron transport occurs mainly across interconnected SnO_2 particles (Fig. 2a). But when the percentage is further increased, Al_2O_3 particles come in between the SnO_2 particles, so that resistance of the films increases rapidly. At 70% the composite structure probably become like a multiple quantum well structure where electrons trap in SnO_2 particles. After relaxation of electrons in the conduction band of SnO_2 particles, they have to acquire sufficient thermal energy to jump into the surface states of adjacent Al_2O_3 particles to transport across Al_2O_3 particles following trapping and detrapping mechanism to the next SnO_2 particle (Fig. 2b). It is evident with the data that the resistance of the film become low again when electrons transport merely via trap states of Al_2O_3 as shown in Fig. 2c. In this case resistance of the film is reduced because now the probability of electrons confined in SnO_2 particles of quantum well structure vanishes.

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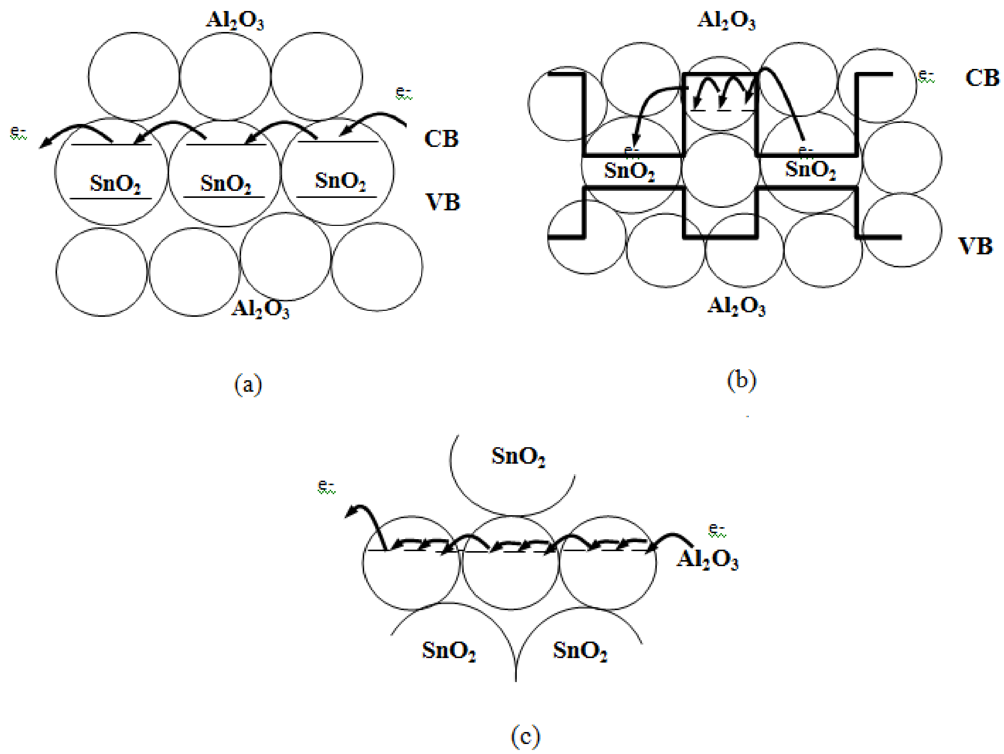

Fig. 2: Mechanisms of electron transport in SnO_2/Al_2O_3 composite at different Al_2O_3% (a) $Al_2O_3 < 30\%$ (b) Al_2O_3 ~70% (c) $Al_2O_3 > 80\%$

The I-V characteristics of the cells were measured under the simulated sun light of 100 $mWcm^{-2}$. (Table 1)

Table 1: Photo electric properties dye sensitized solar cells made from SnO_2/ Al_2O_3 composite films

Composition	Current Density $J_{sc}(mAcm^{-2})$	Open Circuit Voltage V_{oc} (mV)	Fill Factor FF (%)	Efficiency η (%)
100% SnO_2	1.888	116.5	30.7	0.068
100% Al_2O_3	0.936	166.9	38.0	0.059
70% Al_2O_3	0.272	218.7	50.9	0.030

Although the solar cells did not show any significant photocurrents and photovoltages, I-V characteristics of these cells supported to validate the previous results. Since the particle size of SnO_2 and Al_2O_3 are relatively large (SnO_2~200 nm and Al_2O_3~100 nm) photocurrents and voltages are lower than the previously reported values [5] because

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effective surface area of the film for dye adsorption is less. The lowest photocurrent was observed for the composite film with 70% of Al_2O_3 although it has the highest photovoltage. The reason for low photocurrent can be ascribed as high resistance of the composite film than pure Al_2O_3 where photocurrent is higher than this composition. The highest photocurrent with lowest photovoltage is observed for pure SnO_2 film as depicted in Fig. 3 because of its lowest film resistance.

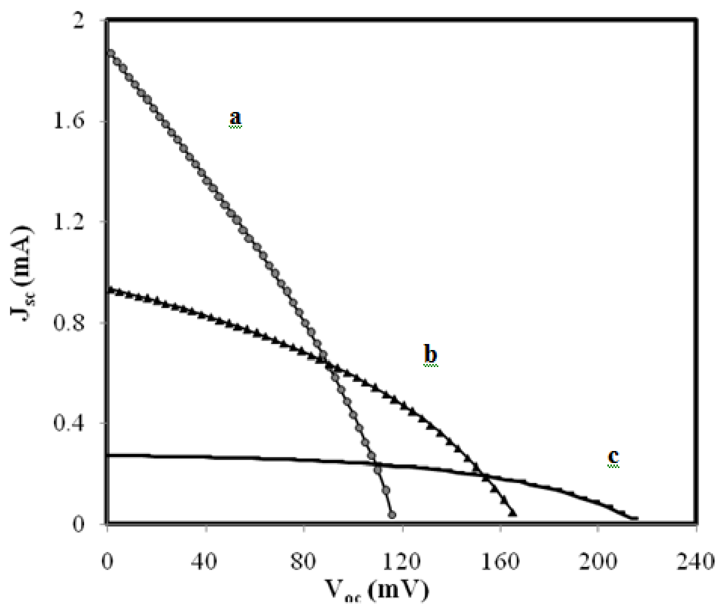

Fig. 3: I-V characteristics of SnO_2/ Al_2O_3 composite films

a) 100% SnO_2 b) 100% Al_2O_3c) 70% Al_2O_3

4. CONCLUSION

The resistance of composite films made of SnO_2 and Al_2O_3 were measured with impedance spectroscopy. The addition of 70% Al_2O_3 to the composite showed the highest impedance. The charge transport mechanisms at different levels of Al_2O_3 in the composite films were discussed. Various compositions of Al_2O_3 in the SnO_2/ Al_2O_3 composite structures were tested also for dye sensitized solar cells and found that the photocurrent is lowest when the film resistance is highest at 70% of Al_2O_3 in the film. This composition may vary depending on the particle sizes of SnO_2 and Al_2O_3 which need further investigation to properly understand this behaviour.

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