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Analysis of Composite Films Made of Tin (IV) Oxide and Silica using Electrochemical Techniques

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ABSTRACT

Impedance Spectroscopy and Mott-Schottky measurements are powerful tools used to investigate the dynamics of mobile charges in solid materials to characterize their electrical properties. Composite films made with different compositions of SnO_2 and, SiO_2 extracted from rice husk were characterized using the above techniques. Impedance of the films varied significantly with the composition and had the maximum impedance when SiO_2 was 30%, which was one order of magnitude higher than the impedance of the SiO_2 films. Dielectric loss of the film was also found to be minimum at this composition. These results were attributed due to the enhancement of the permittivity of the composite at the above mixing ratio of SiO_2 and SnO_2. The flat band potential of the composite films at different compositions showed no significant difference, so that the two materials seems to remain unbound after sintering at 450 °C.

1. INTRODUCTION

Techniques such as Impedance Spectroscopy (IS), Mott-Schottky measurements, cyclic voltametry are used to investigate the dynamics of mobile charges in the bulk or interfacial regions of any kind of solid or liquid as they are considered powerful tools for characterization of electrical properties [1]. Measurements taken using these techniques may often be correlated with many complex material variables, from mass transport, rates of chemical reactions, corrosion and dielectric properties to defects. Thus, they are used in many fields including solid state electronics, photoelectrochemistry and solid state ionics. They can predict aspects of the performances of devices such as chemical sensors, rechargeable batteries, solar cells, fuel cells and have been used extensively to investigate membrane behaviour in living cells as well [2].

In the majority of cases, the nano-structured films embody complicated networks consisting of resistances and capacitances that can be represented by an equivalent circuit. In this regard IS analysis generally makes considerable use of equivalent circuits and shows complex behaviour depending on the frequency range used in the impedance plane. It also requires consideration of additional aspects such as resistance, capacitance and loss tangent of materials to extract the available information and characterize the dielectric properties.

Conversely, Mott-Shottky measurement is a popular method to find the flat band potential and doping density of semiconductor materials.

In this study, a series of composite films made with different compositions of Tin (IV) Oxide (SnO_2) and Silica (SiO_2) were characterized with impedance spectroscopy and Mott-Schottky measurements. The silica used was extracted from rice husk because they were reported to be of high purity in nano range [3].

2. METHODOLOGY

Rice Husk (RH) of BG 300 rice variety was collected and washed with distilled water and dried at 120 °C. The dried RH was fully burnt to white ash at around 700 °C in a muffle furnace and the Rice Husk Ash (RHA) was collected.

2.1 Extraction of Silica

The RHA obtained was refluxed with 2M HCl and washed thoroughly with distilled water and dried. 10 g of the sample was stirred in 80 ml of 2.5 N sodium hydroxide solution. It was then boiled in a covered 250 ml Erlenmeyer flask for 3 hours and the solution was filtered using a Whatman No. 41 filter paper. Filtrate was allowed to cool down to room temperature and 5 N H_2SO_4 was added to the filtrate until it reached pH 2. Then NH_4OH was added to the suspension until it reached pH 8.5 and allowed to be at room temperature for 3 hours. The precipitated SiO_2 was separated by filtration and washed thoroughly with distilled water. The silica obtained was oven dried at 120 °C for 12 hours and cooled down to room temperature.

2.2 Preparation of SnO_2 Particles

Tin (IV) chloride was dissolved in distilled water to obtain 0.5 M solution and ammonia was added while stirring the solution to obtain fine particles of SnO_2. The SnO_2 particles were washed thoroughly with distilled water to remove chlorine ions. Then the particles were suspended in a diluted ammonium solution for some time and washed and dried at 120 °C for 12 hours in a drying oven.

2.3 Preparation of SnO_2 and SiO_2 Composite Films

Series of nano-crystalline SnO_2 and SiO_2 composite films were prepared by different mass ratios by grinding SnO_2 and SiO_2 powder 15 minutes with 1 ml of acetic acid and two drops of Triton X-100 in ethyl alcohol keeping the total mass at 0.5 g. Films (1 cm × 1 cm) of thickness 10 μm (estimated gravimetrically) were prepared using doctor blade method on conducting tin oxide (CTO) glass plates (15 Ωcm^{-2}). These films were then sintered at 450 °C in a furnace for 30 minutes.

2.4 Characterization Techniques

Complex plane impedance spectra of these films were measured using LCR meter (GW Instek-8101) connected to a computer. A sweep was carried out to measure the impedance and phase angle of the films coated on CTO glass with different mass percentages of SnO_2 and SiO_2 using Pt counter electrode. Measurements were made in the frequency range of 1 MHz to 20 Hz setting the ac level at 100 mV. The capacitance of the films was also measured under different dc biased conditions to obtain Mott-Schottky plots using the same instrument.

3. RESULTS AND DISCUSSION

In IS analysis, real impedance of a sample was plotted against the imaginary impedance that was measured in a frequency range to obtain Nyquist plots. Characteristic semi-circles were observed for the Nyquist plots of the SnO_2 and SiO_2 composite films prepared on ITO glass as depicted in Figure 1. The diagonal line with positive slope at low frequency end of the semicircles indicated polarization of the composite films due to kinetic or diffusion control process which represents by Warburg impedance. This behaviour was prominent even in the pure SnO_2 sample of the film. This nature is dominated in other compositions as well because of the addition of SnO_2 into the composites. It is not clear at the moment that the Warburg impedance appears in these composite films due to polarization of SnO_2 particles or some ionic diffusion.

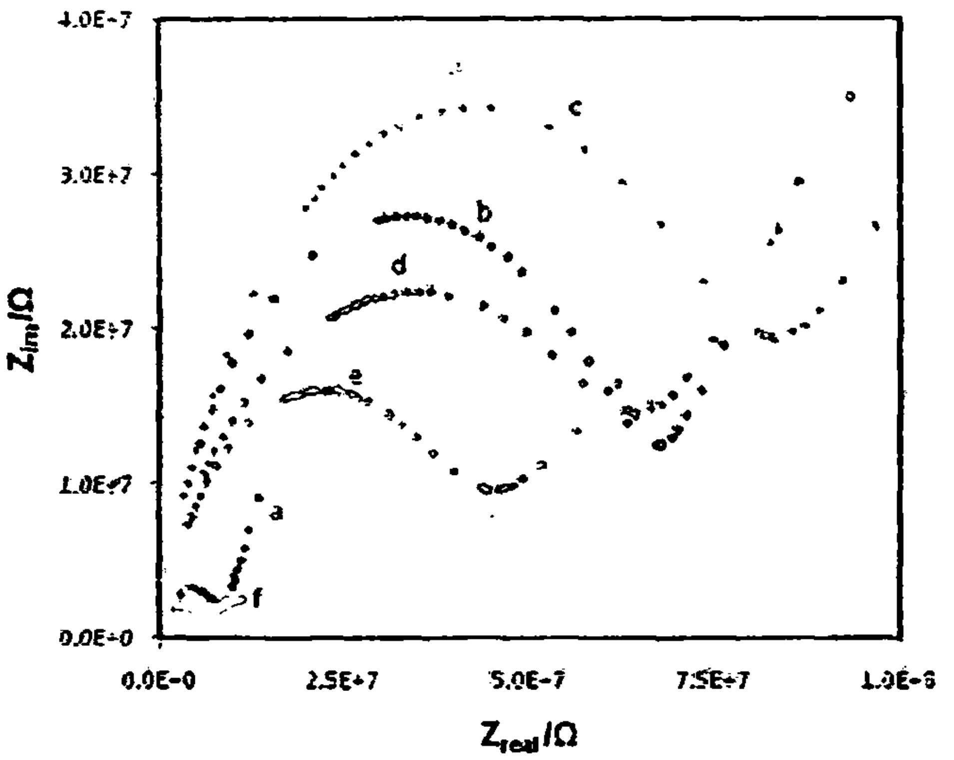

Figure 1: Nyquist plots of composite films of SnO_2 and SiO_2 (a) 0% SiO_2 (b) 10% SiO_2 (c) 30% SiO_2 (d) 40% SiO_2 (e) 70% SiO_2 (f) 90% SiO_2

Composite SnO_2 and SiO_2 films deposited on CTO glass model an equivalent circuit where the contact sheet resistance (R_s) of the film with CTO glass is in series with the parallel combination of capacitance and resistance of the composite films. Adding the double layer capacitance and charge transfer impedance, we usually obtain the equivalent circuit of a Randles cell. Since there is no simple element to model Warburg impedance (W), it is not possible to construct a dummy cell, so that Figure 2 models an equivalent circuit for blend of electronic and ionic charge transfer in the composite films.

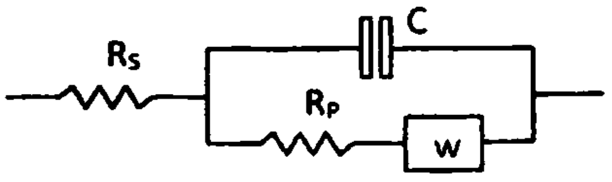

Figure 2: Equivalent circuit for blend of electronic and ionic charge transfer in composite films of SnO_2 and SiO_2.

The contact sheet resistance, R_s of the films with CTO glass was more or less the same for all the compositions. This could be obtained by extrapolating the semicircles at the high frequency end that tend to reach the real impedance (Z_{real}) axis of the plot which seems to be a low value. But R_P value, which is the parallel resistance of the films, varies dramatically while altering the composition.This was calculated by determining the distance between the intersection points of the semicircirles with the real impedance axis. Variation of R_P against SiO_2% of the composite film is plotted in Figure 3.

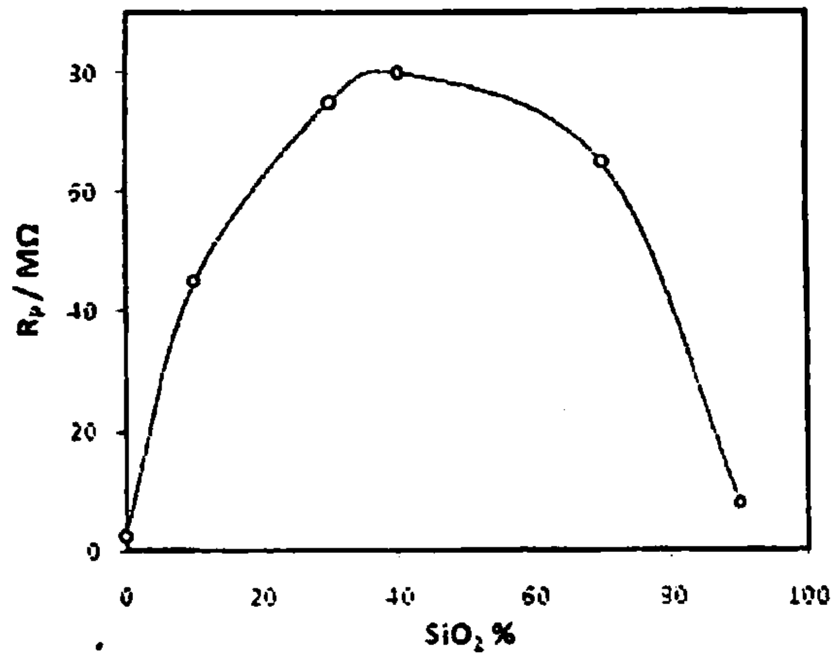

Figure 3: Resistance (R_P) vs SiO_2% (by weight) of SnO_2 and SiO_2 composite films.

According to the above graph addition of SiO_2 rapidly increases the resistance of the composite films initially and the maximum resistance of 80 MΩ is reached when the film has ~ 30% of SiO_2 by weight. Further addition of SiO_2 to the composite decreases the resistance of the film again. The significant observation made in this investigation is that the impedance of the composite film with 30% of SiO_2 is one order of magnitude higher than pure SiO_2. This may be a consequence of polarization of SnO_2 particles and maximum impedance may be dominated when SiO_2 particles are distributed distinctively in SnO_2 matrix at that ratio.

The relative complex permittivity, ε^* defines with real part of the permittivity ε and imaginary part of the permittivity (or complex permittivity) ε' as, $\varepsilon^* = \varepsilon - j\varepsilon'$ where, $j = \sqrt{-1}$.

The complex permittivity, $\varepsilon^{/}$ attributes to the bound charge and dipole relaxation phenomena that gives rise to energy loss in addition to the loss due to the free charge conduction, σ. Thus the loss tangent (*tanδ*) is defined as the ratio between the loss reactions to the lossless reactions as,

$$tan\delta = \frac{\omega\varepsilon^{/}+\sigma}{\omega\varepsilon} \quad \text{where } \omega \text{ is the angular frequency.}$$

In a dielectric, either the conduction electrons or the dipole relaxation, typically dominates the loss. For the case of the conduction electrons being the dominant loss, $tan\delta = \frac{\sigma}{\omega\varepsilon}$. Otherwise the dipole relaxation phenomena be the dominant so that $tan\delta = \frac{\varepsilon^{/}}{\varepsilon}$.

Since we have carried out the impedance spectroscopic measurements of SnO_2 and SiO_2 composite films configured as a parallel plate capacitor, dielectric loss or loss tangent was calculated for different compositions of the films.

Figure 4 compares the dielectric loss of pure SnO_2, SiO_2 and composite film of 30% SiO_2 measured at different frequencies. SnO_2 has the highest dielectric loss attributed due to high conduction of electrons. The composite film of 30% of SnO_2 has the lowest dielectric loss. This could possibly result due to increase of the real permittivity of the composite film at 30% of SiO_2 irrespective of the contribution from conduction electrons or the dipole relaxation.

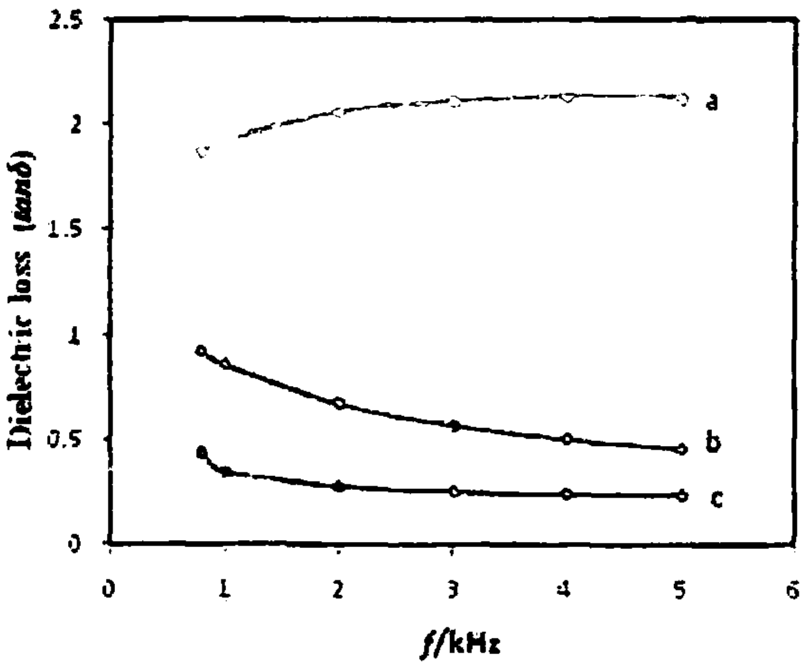

Figure 4: Dielectric loss of (a) SnO_2, (b) SiO_2 and (c) composite film with 30% of SiO_2

The Mott-Schottky relationship involves the apparent capacitance measurement as a function of potential under depletion condition given by the equation,

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 e N_d}\left[(V - V_{FB}) - \frac{kT}{e}\right]$$

where, C is the capacitance of the space charge region, ε is the dielectric constant of the semiconductor, ε_0 is the permittivity of free space, N_d is the donor density, V is the applied potential, V_{FB} is the flat band potential, k is the Boltzmann Constant, and T is the absolute temperature. The donor density can be calculated from the slope of the $1/C^2$ vs. V curve, and the flat band potential can be determined by the intersection point of the graph with the voltage axis.

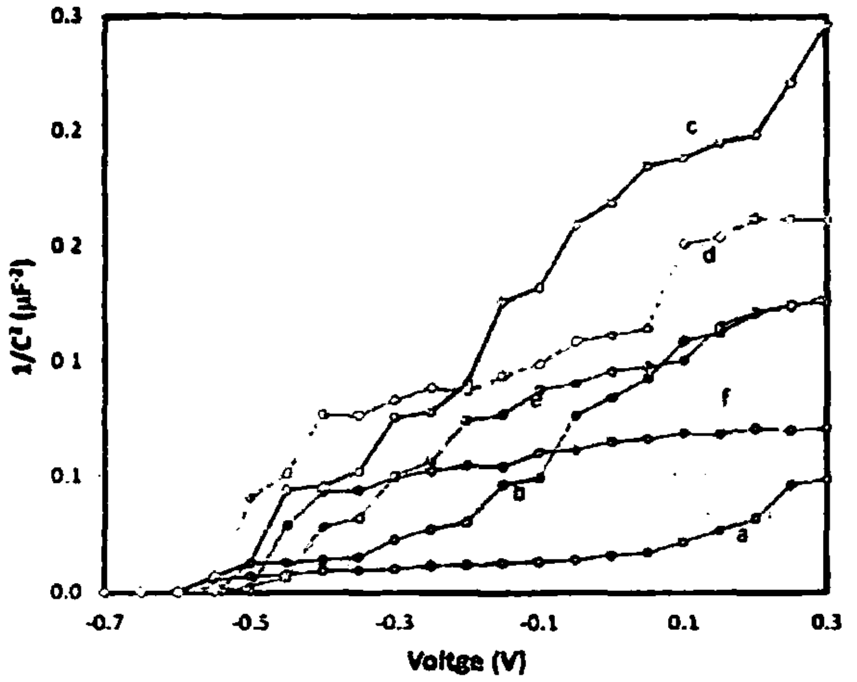

Figure 5. Mott-Schottky measurements of composite films of SnO_2 and SiO_2. (a) SnO_2 (b) 10% SiO_2 (c) 20% SiO_2 (d) 30% SiO_2 (e) 40% SiO_2 (f) 50% SiO_2

Figure 5 shows the Mott-Schottky measurements of composite films of SnO_2 and SiO_2measured under different dc biased conditions with an ac signal of 100 mV and 500 Hz for various compositions. All the compositions seem to cut the voltage axis at arround ~ -0.55V indicating that the addition of SiO_2 to the composite has not affected significantly to change the flat band potential of SnO_2. But the gradient of the plots varies with the composition of the films indicating that the donor density of the films change with SiO_2 addition. This indicates that SiO_2 particles were not sintered to the surface of SnO_2 particles during the heating at 450 °C. Thus formation of a junction between the two materials has not taken place enabling electrons to transfer from one material to the other, which could affect the flat band potential of SnO_2.

4. CONCLUSION

Composite films made of different compositions of SnO_2 and SiO_2 were characterized using impedance spectroscopy and Mott-Schottky measurements. Impedance of the film made of 30% of SiO_2 in the SnO_2 and SiO_2 composite exhibited the maximum impedance, which was one order of magnitude higher than the impedance of the SiO_2 film. Even the dielectric loss of the film was minimal at this composition. Therefore it could be concluded that the permittivity of the composite reach a maximum value at this specific ratio of SiO_2 and SnO_2. Since the flat band potential of the composite films at different compositions showed no significant difference, it was evident that two materials remain independently in the composite without sintering to each other. Thus, this material at the optimized condition could be applicable in devices such as super capacitors and thin film transistors to function as a dielectric with high permittivity.

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