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Dielectric Properties of Composite Films Made from Tin(IV) Oxide and Magnesium Oxide

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Abstract

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. 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 a considerable use of these equivalent circuits.

Films made from SnO_2 and MgO have been taken into consideration and analyzed using IS to find the dielectric properties. Analyzing the Nyquist plots, the sheet resistance of the CTO glass was found to be around 610 Ω. But the parallel resistance of the film varied dramatically while altering the composition.

10% of MgO in the SnO_2/MgO composite showed a high impedance which is in two orders of magnitude higher than pure MgO. This is due to the confinement of electrons in quantum well structure formed by layer of MgO around SnO_2 particles. The dielectric loss is also found to be minimal at this composition. The variation of real and imaginary parts of permittivity of the composite films of SnO_2 and MgO are being discussed for different compositions in this study. SnO_2 and MgO composite films of 10% MgO could find applications in devices such as capacitors and thin film transistors to be used as a novel dielectric.

Introduction

Small signal measurement of linear electrical response of a material including electrode effects and the subsequent analysis are considered in impedance spectroscopy (IS) to yield useful information about physicochemical properties of the systems of interest (Macdonald, 1992). Furthermore, the response due to the

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different processes is recorded in a single frequency sweep, according to 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 such as resistance, capacitance and loss tangent of materials to extract the available information and characterize the dielectric properties.

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 a considerable use of equivalent circuits and shows a more complex behavior depending on the frequency range used in the complex impedance analysis.

Physical characteristics including the dielectric properties dramatically change in composite materials rather than in the individual constituent. Therefore, in this study, composite porous films made of SnO_2 and MgO have been taken into account and the characteristics of these films were analyzed using IS to describe the variation of dielectric properties of different compositions.

Methodology

Series of nanocrystalline SnO_2 and MgO composite films with area 1 cm^2 were prepared by different mass percentages keeping the total mass at 0.5 g. Films of thickness 10 μm (estimated gravimetrically) were prepared using doctor blade method on conducting tin oxide (CTO) glass plates (15 Ωcm^{-2}) which was made by grinding SnO_2 and MgO powder (Aldrich) 15 minutes with 1 ml of acetic acid and two drops of Triton X-100 in ethyl alcohol. These films were sintered at 450 ^0C 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 MgO 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.

Results and Discussion

A characteristic semicircle Nyquist plots (where real impedance is plotted against the imaginary impedance) were observed for all of the SnO_2 and MgO composite films. Composite SnO_2 and MgO films deposited on CTO glass model a cell where the sheet resistance (Z_1) of the CTO glass is in series with the parallel combination of capacitance and resistance of the composite film (Z_2). (Figure 1)

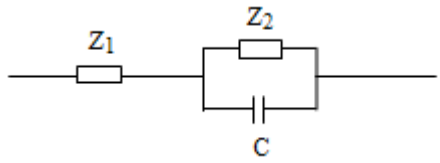

Figure 1. Equivalent circuit for MgO and SnO_2 composite films

It was noted that Z_1 value did not vary significantly in all the compositions because it represents the sheet resistance of the CTO glass which was found to be around 610 Ω. But Z_2 value which is the parallel resistance of the film varied dramatically while altering the composition (Figure 2).

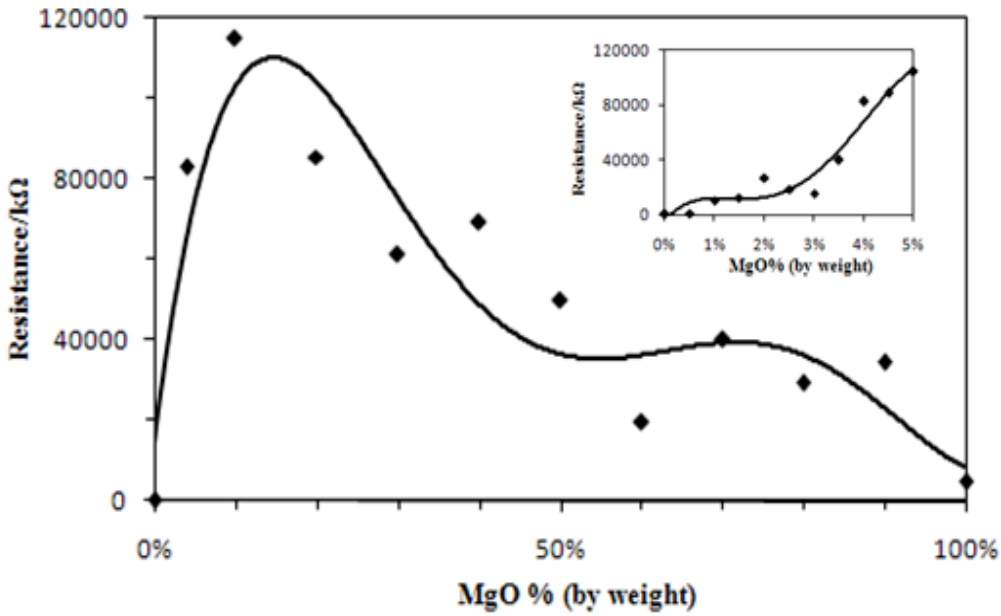

Figure 2. Variation of the resistance vs MgO % (by weight) of SnO_2/MgO composite films

As evident from insertion of Figure 2, dramatic increment of the resistance in the composite film initially observed up to 10% of MgO in the composite film. This value is in two orders of magnitude higher than the resistance of 100% MgO film of the same thickness. Further addition of MgO to the composite decreased the resistance of the film rapidly and remains nearly constant from 40% to 80% of MgO in the film. Again after 80%, resistance reduces further until 100% of MgO is reached.

This behaviour of the SnO_2 and MgO composite film could be explained considering the band structure of SnO_2 and MgO. Figure 3 depicts the energy positions of conduction band and valence band of SnO_2 and MgO. The band gap of SnO_2 is ~ 3.8 eV and it is 7.8 eV for MgO. SnO_2 and MgO make a type 1 hetero-structure at the interface as can be seen from the band diagram. According to the experimental procedure some of the MgO added to the paste dissolve in acetic acid as magnesium acetate and MgO is formed again at the sintering of the film at 450 ^{0}C around SnO_2 particles.

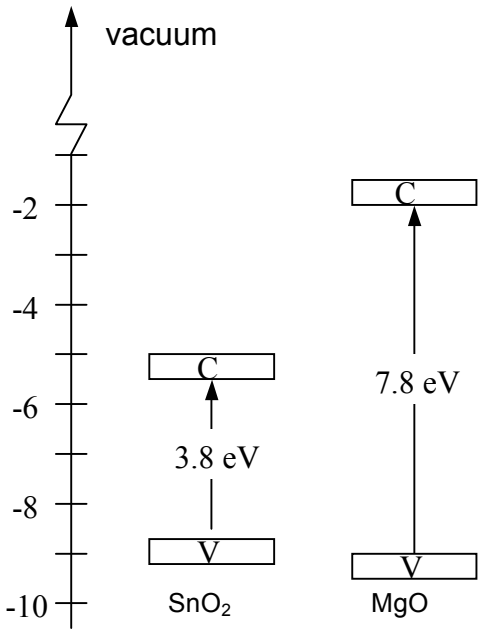

Figure 3. Energy level diagram of SnO_2 and MgO

At low percentages of MgO the thickness of the MgO shell formed around the SnO_2 particles can be calculated from the formula

$T = \frac{r}{3} \times \frac{W_S}{W_C} \frac{\rho_S}{\rho_C}$ 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. The particle size of SnO_2 is known to be around 200 nm from SEM measurement. Substituting the density of SnO_2 (6.95 x 10^3 kg m^{-3}) and MgO (3.58 x 10^3 kg m^{-3}) in the above formula, thickness of the MgO shell at different percentages of MgO was calculated and is given in Table 1.

Table 1. Thickness of MgO shell on SnO_2 particles at different MgO %

MgO%	1%	2%	3%	5%	10%
T (nm)	0.2	0.4	0.5	1.0	2.0

When the percentage of MgO is less than 3% (T < 0.5 nm) the resistance of the film is only slightly higher than the pure SnO_2 film. This can be clearly seen in the inset of Figure 2. At this thickness of the MgO shell (<0.5 nm) electrons can tunnel across it when an ac signal is applied. So, that the resistance of the film is considerably low (Figure 4a). But when the MgO percentage is further increased (~10%) the composite structure becomes more like a multiple quantum well structure where electrons in SnO_2 particles have to traverse to the subsequent SnO_2 particle across deep trap states of MgO following a trapping and detrapping mechanism (Figure 4b).

It can be found in the literature that MgO has trap states at 1.8 eV, 2.4 eV and 3.2 eV below the conduction band measured by UV/visible reflectance spectroscopy (Berger *et al.*, 2004). When the MgO percentage is further increased the electron transport merely takes place across the shallow traps of MgO, so that the resistance of the film is reduced again because now the electrons confined in SnO_2 particles of quantum well structure have disappeared (Figure 4c).

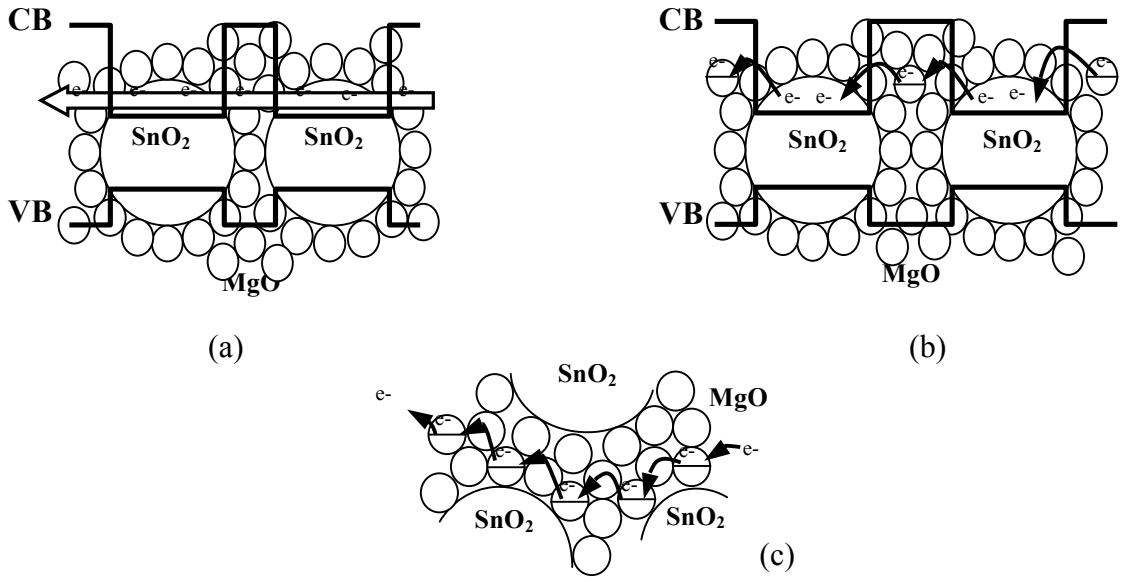

Figure 4. Mechanisms of electron transport in SnO_2/MgO composite at different MgO% (a) MgO< 3% (b) MgO~10% (c) MgO> 40%

Since we have carried out the impedance spectroscopic measurements on SnO_2 and MgO composite films as a parallel plate capacitor, the capacitance, *C* and loss tangent, *tan δ* were measured for different compositions of the films to find out the real and imaginary parts of permittivity. The relative complex permittivity, *ε** relate to the real permittivity *ε* and imaginary permittivity *έ* as,

$$\varepsilon^* = \varepsilon - j\varepsilon' \text{where, } j = \sqrt{-1}.$$

The real (*ε*) and imaginary (*έ*) part of permittivity can be calculated from the measured capacitance and loss tangent as,

$$\varepsilon = \frac{Cd}{\varepsilon_0 A} \text{ and } \varepsilon' = \varepsilon \tan\delta, \text{ where } d \text{ is the thickness of the}$$

film, *A* area of the film and ε_o is permittivity of free space (ε_o = 8.85 x 10^{-12} $C^2N^{-1}m^{-2}$).

Figure 5 shows the variation of real part of permittivity with MgO % in the composite films of SnO_2 and MgO. Similar to the variation of film resistance, the real part of the permittivity also got the highest value at 10% of MgO in the composite films. The insertion of Figure 5 is the variation of capacitance of the films at different compositions which follows the same pattern.

The imaginary part of the permittivity of the composite films is depicted in Figure 6. It is noticeable that the $\acute{\varepsilon}$ has lower value at 10% of MgO in the composite film. The imaginary part of permittivity is responsible for the dielectric losses.

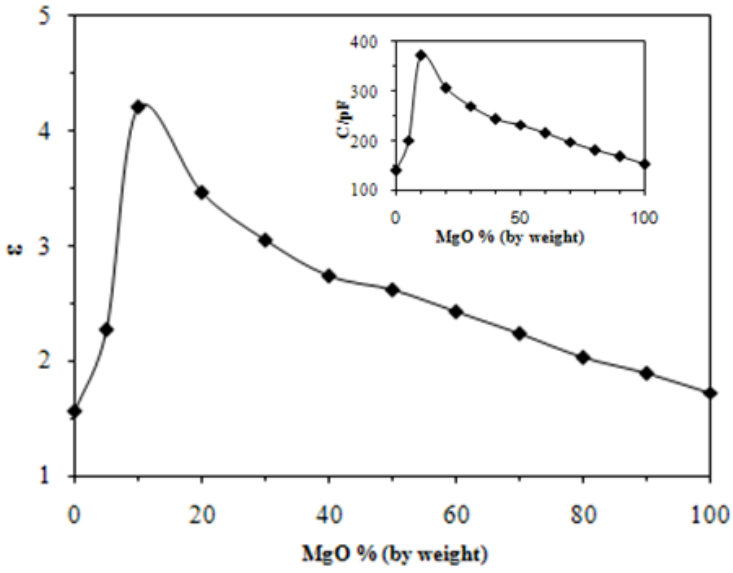

Figure 5. Variation of real part of permittivity (ε) with MgO %

Therefore the dielectric loss has a minimum at 10% MgO which lies in between the dielectric losses of SnO_2 and MgO.

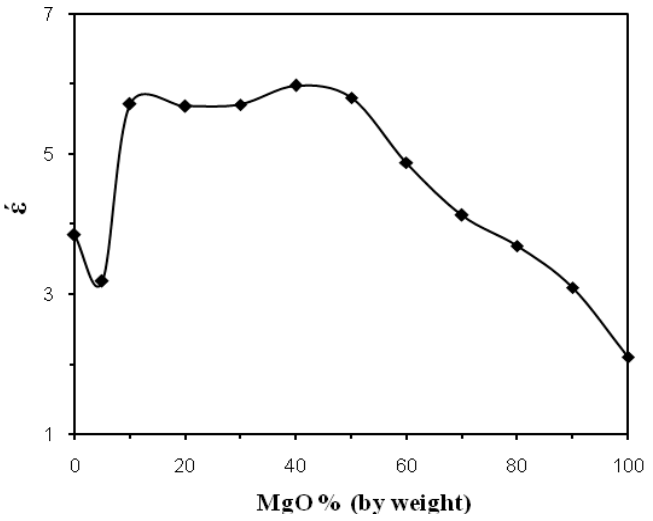

Figure 6. Variation of imaginary part of permittivity (έ) with MgO%

Figure 7 compares the dielectric loss of pure SnO_2, MgO and composite film of 10% MgO at different frequencies. Flattening the curves after 10 Hz, the composite film of 10% of MgO has the lowest dielectric loss. This observation further verifies the behaviour of έ of the composite at 10% of MgO.

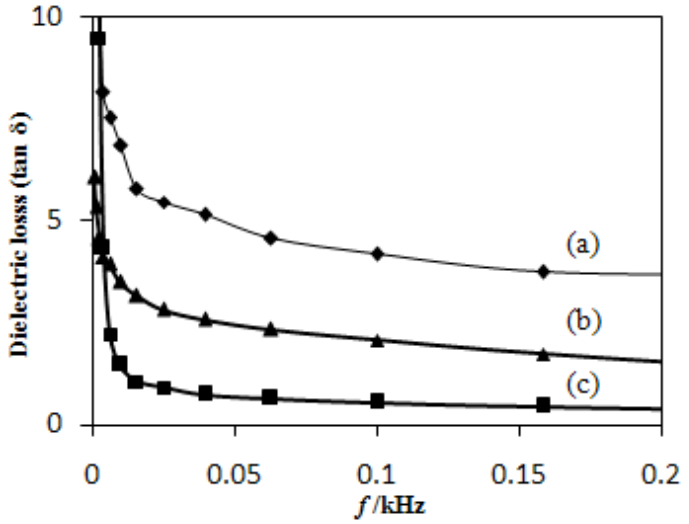

Figure 7. Dielectric losses of (a) SnO_2 (b) MgO and (c) SnO_2 and MgO film with 10% of MgO

Conclusion

The resistance and capacitance of composite films made of SnO_2 and MgO were measured by impedance spectroscopy. The real and imaginary parts of the permittivity of the composites were calculated measuring capacitance and loss tangent. Addition of 10% MgO to the composite showed a high impedance which is in two orders of magnitude higher than pure MgO. This can be explained by electron confinement in quantum well structures formed due to MgO thin shell around SnO_2 particles. The loss tangent is also found to be minimal at this composition. Therefore, 10% of MgO in the SnO_2 and MgO composite could be applicable in devices such as capacitors and thin film transistors to function as a good dielectric material.

References

Bisquert, J. (2002).Theory of the Impedance of Electron Diffusion and Recombination in a Thin Layer. *J. Phys. Chem. B*, 106, 325-333.

Berger, T.; Sterrer, M.; Diwald, O.; Knözinger, (2004) E. *J. Phys. Chem. B*, *108*, 7280-7285.

Macdonald, J .R. (1992). Impedance Spectroscopy. *Annals of Biomedical Engineering*, 20, 289-305