OPENING MINDS:
RESEARCH FOR SUSTAINABLE
DEVELOPMENT

Nano Structures of Tin (iv) Oxide Coated with Thin Layer of Silica Using Silicic Acid Synthesised from Rice Husk Ash

N.F. Ajward*, J.C.N. Rajendra and V.P.S. Perera

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

**Corresponding author: Email: nf2010.ajward@gmail.com*

1 INTRODUCTION

The nano structures of composite materials contribute to many device applications due to their novel physical and chemical properties when compared with pure materials. At some specific ratios these materials exhibit unusual characteristics that are not to be seen in pure form (Nupearachchi and Perera, 2014). There is much research done regarding this fact and composite films of semiconductors have been employed even in Dye Sensitized Solar Cells (DSSC) to improve their efficiency. One of the technological developments that took place in DSSCs during the past decades is the replacement of nano-crystalline TiO_2 photo of these cells with composite semiconductor materials where composite happen to consist of either mixtures of two semiconductor materials or semiconductor with some dielectric material as a core shell structure. The study of mixtures of nano crystalline of SnO_2 and ZnO for photo anodes of DSSCs have shown that the efficiency of the composite film of SnO_2/ZnO at 50 % by mass is higher than the films of pure SnO_2 or ZnO (Tennakone *et al.,* 2001). Also SnO_2 and Al_2O_3 were used in various compositions and the research has concluded that the composite film of SnO_2 crystallites coated with ultrafine particles of Al_2O_3 generates an exceptionally high open-circuit voltage when compared to a cell made only from SnO_2 (Kumara *et al.,* 2001). The research on composite of SnO_2 and MgO demonstrated that the cell fabricated with SnO_2 film only delivered very low photocurrent and photovoltage, while the cell made of SnO_2 and MgO composite delivered a short circuit photocurrent of $\sim$ 2.5 mA cm^{-2} with an open circuit voltage of $\sim$ 500 mV (Tennakone *et al.,* 2001).

In our previous research study, through the Impedance Spectroscopic (IS) analysis we found that impedance of the film made of 30% of SiO2 in the SnO2 and SiO2 composite exhibited the maximum impedance, which was one order of magnitude higher than the impedance of the SiO2 film. Even the dielectric loss of the film was minimal at this composition. Therefore, we concluded that the permittivity of the composite reaches a maximum value at this specific ratio of SiO2 and SnO2 (Ajward *et al.,* 2016). Even the dielectric loss of these films was minimal at this composition. In that study, nano silica was extracted through the reaction of Rice Husk Ash (RHA) with NaOH followed by acidification. Rice husk is an agricultural waste rich in silica that comprises more than 20%. The carbonaceous compounds in the rice husk can be easily eliminated by burning them to produce RHA which contain more than 90% of silica.

Here we report on the extraction of silica in RHA by using Sodium hypochlorite (NaClO). NaClO reacts with silica in RHA and Silicic acid could be obtained. Silicic acid is a compound that contains silicon, oxygen and hydroxyl groups. The general formula of silicic acid is $[SiO_x(OH)_{4-2x}]_n$. In our study, orthosilicic acid has been used to coat a thin film of SiO_2 on nano crystalline films of SnO_2 which will be a prospective photo anode for DSSCs. The composite films were characterized with impedance spectroscopy and Mott-Schottky measurements.

2 METHODOLOGY

2.1 Preparation of RHA and Synthesis of silicic acid

Rice husks collected from a rice mill were washed thoroughly with tap water followed by distilled water and dried in an oven at 120 °C. 100 g of dried rice husks was burnt at 700 °C to obtain RHA. 20 g of RHA was stirred 2 hours with 250 ml of sodium hypochlorite solution at temperature of 80 °C. Then it was left to cool down to room temperature and filtered. The filtrate was crystalized by using the rotary evaporator. The crystals were grinded using agate mortar and pestle. 1.20 g of this powder containing Silicic acid was dissolved in 100 ml of distilled water.

2.2 Deposition of SnO_2 films on CTO glass plates

2.6 g of SnO_2 (particle size 20 nm, Alpha Acer) was mixed with 1.5 g of ethyl cellulose and 5.9 g of α-terpineol. The mixture was grinded 20 minutes using a mortar and pestle. The paste was spread by doctor blade method on the Conducting Tin Oxide (CTO) glass plates cut into the size of 1.5cm × 3cm which were cleaned in an ultrasonic bath using detergent and distilled water prior to the deposition. After that the SnO_2 coated films were dried on a hot plate and sintered in a furnace at 450 °C for 30 minutes.

2.3 Coating thin SiO_2 layer on SnO_2 films

The prepared SnO_2 films were dipped in 10 ml of silicic acid solution for 30 minutes and the plates were kept on a hotplate at a temperature of 70 °C for drying and they were sintered in a furnace at 450 °C for 30 minutes.

2.4 Characterization techniques of the films

Deposited films were electrochemically characterized by impedance spectroscopic measurement techniques. The shift in the flat band potential of the SnO_2 films after coating SiO_2 layer was determined with Mott-Schotky measurements. The charge transfer resistance of the films was calculated by potentiostatic measurement of impedance in the frequency range 0.1 Hz to 1 MHz using Auto Lab FRA 32.

3 RESULTS AND DISCUSSION

3.1 Reaction chemistry

When RHA is reacted with sodium hypochlorite, sodium silicate is produced dissolving silica in RHA according to the following reaction.

$SiO_2 + 2\,NaClO + H_2O = Na_2SiO_3 + 2HClO$ (1)

Hypochlorous acid formed in this reaction bring down the pH of the medium to a lower value. Since hypocaloric acid is a weak acid, sodium silicate produced in equation (1) converts into orthosilicic acid as in the following reaction.

$Na_2SiO_3 + 2HClO = H_2SiO_3 + 2NaClO$ (2)

But when we consider both the reactions together, overall reaction is to produce orthosilicic acid according to the following reaction by hydrogenation of silica which is the natural occurring process of silicic acid in the earth's crust.

$SiO_2 + H_2O = H_2SiO_3$ (3)

Although silicic acid can be produced by acidification of sodium silicate, it readily loses water to form polymeric silica gel. But that is avoided here because Hypochlorous acid is a weak acid. But if we keep this aqueous solution exposed to air for several days, precipitation of SiO_2 at the bottom of the container could be noticed. Therefore, immediately after the dissolution of silica, water has to be removed to obtain the white powder containing orthosilicic acid. This powder completely dissolved in water, indicating that the removal of water does not convert the silicic acid in the powder to silica. However, there can be unreacted sodium hypochlorite contained in this white powder.

3.2 Determination of flat band potential

The shift in the flat band potential of the SnO_2 films after coating SiO_2 layer was determined with Mott-Schottky measurements. Figure 1 shows the flat band potential of SnO_2 film and SnO_2 film after coating a thin layer of Silica by dipping the SnO_2 coated films in a solution containing orthosilicic acid. Measurements were taken changing the biasing voltage for two frequencies of 1000 Hz and 2000 Hz.

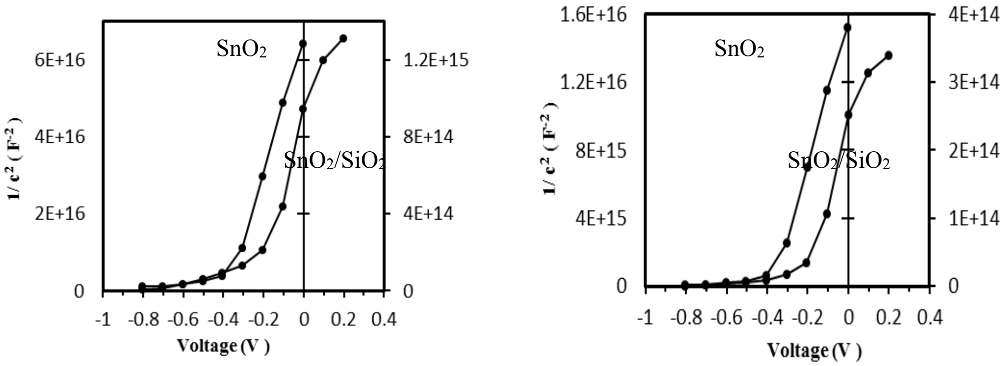

Figure 1: Mott-Schottky plots of SnO_2 films and SnO_2 films coated with SiO_2 layer measured with (a) 1000 Hz and (b) 2000 Hz frequencies.

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. It can be clearly seen that the flat band potential of SnO_2 films after coating a thin layer of SiO_2 shifts towards more positive potentials with respect to the Ag/AgCl reference electrode. The flat band potential of SnO_2 film is at -0.32 V and it is at -0.28 V when thin layer of SiO_2 was coated. These values are same for the both frequencies, i.e. for 1000 Hz and 2000 Hz used in this measurement.

3.3 Charge transfer resistance

Nyquist plots for SnO_2 films and SnO_2 films coated with SiO_2 layer are shown in figure 2. It is obvious that the charge transfer resistance of the film at the electrolyte interface increase after coating a thin layer of SiO_2.

The impedance of the SnO_2 film alone is about 40 KΩ and it is about 100 KΩ when thin layer of SiO_2 was coated on SnO_2 film. By coating a thin layer of SiO_2 on the films of SnO_2 supposed to suppress recombination of electrons in conduction band of SnO_2 with the reducing agents in the electrolyte. Therefore, these films could be employed in DSSCs as prospective photo anodes to increase their efficiency.

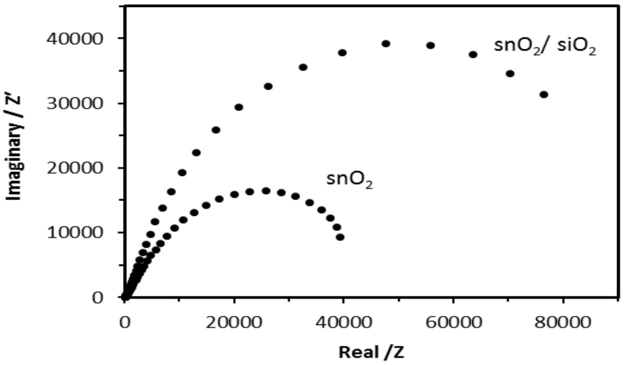

Figure 2: Nyquist plot of (a) SnO_2 films and (b) SnO_2 films coated with SiO_2 layer

4 CONCLUSIONS

Orthosilicic acid was synthesized reacting rice husk ash with sodium hypochlorite. A thin layer of silica is coated on nano crystalline SnO_2 films by dip coating silicic acid on SnO_2 films. Coating thin layer of SiO_2 on SnO_2 nano crystallites films shift the band gap of SnO_2 films by 0.04 mV. The Nyquist plots of the films reveal that the charge transfer resistance of the film is also increased two-fold. These surface modified films are prospective candidates for photo electrodes of DSSCs.

Acknowledgments

The authors wish to thank the faculty of Natural Sciences of the Open University of Sri Lanka for the financial support.

REFERENCES

.

Ajward, N.F., N.R.A.M. Ruwangika, G.M.L.P. Aponsu, D.L.N. Jayathilaka, J.C.N. Rajendra and V.P.S. Perera, (2016) Analysis of Composite Films Made of Tin (IV) Oxide and Silica using Electrochemical Techniques, *Proceedings of the Technical Sessions*, 32, 9-15.

Kumara, G.R.R.A., K. Tennakone, V.P.S. Perera, A. Konno, S. Kaneko, M.T.O. Kuya (2001) Suppression of Recombinations in a Dye-Sensitized Photo electrochemical Cell made from a Film of Tin (iv) Oxide Crystallites Coated with a thin Layer of aluminium Oxide, *J. phys. D: Appl. Phys.* 34 868-873.

Nupearachchi, C.N. and V.P.S. Perera (2014). Analysis of the behaviour of SnO_2 composites of ZnO and TiO_2 using impedance spectroscopy, *J. Natn. Sci. Foundation Sri Lanka*, *42* (1) 17-22. Tennakone, K., G.R.R.A. Kumara, I.R.M. Kottegoda, V.P.S. Perera (1999) An efficient dye-sensitized solar cell made from oxides of tin and zinc, *Chem. Commu*., 15-16

Tennakone, K J Bandara, P.K.M. Bandaranayake, GRA Kumara and A Kono, (2001) Enhanced efficiency of a dye sensitized solar cells made from MgO coated nanocrystalline SnO_2, *Jpn. J. Appl. Phy.* 40, 732-734.