

Mott-Schottky Analysis of SnO₂ Nanoparticles by Impedance Measurements under Ultrahigh Pressure

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In this study, the SnO₂ nanoparticle powders were compacted into a disk shape form of under a ultrahigh pressure up to 49.6 GPa. Complex impedance analysis of nano-SnO₂ thick film/electrode system was studied as a function of applied potential. A calculated Mott-Schottky plot for the film is presented. Both flat-band potential and donor concentration were estimated from the space charge capacitance at a definite frequency. The film can be described as an n-type semiconductor with a high concentration of donors.

Keywords: SnO₂ Nanoparticles, Mott-Schottky, Impedance Spectroscopy.

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1. INTRODUCTION

Nanostructured tin dioxide has attracted increasing interests owing to its outstanding electrical and electrochemical properties and is a material with versatile applicability in a wide range of processes such as gas sensors, solar cell and optoelectronic devices [1, 2]. It is interesting to study its properties under hydrostatic pressure. The high-pressure behaviors of bulk SnO₂ have been investigated both in experiments and in theories [3, 4]. The ac impedance technique can be used to evaluate the film capacitance at different voltage. Mahmoudi Chenari et al. [5, 6] have reported the dielectric properties and impedance spectroscopy studies of SnO₂ nanoparticles with different grain sizes at different pressure. Mott-Schottky model have been used extensively to determine the carrier concentration and flat band potential [7]. The method was extended to many n and p-type semiconductors.

In the present work, the Mott-Schottky plot of nano-SnO₂ thick layer was investigated using electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL DETAILS

SnO₂ nanoparticles were synthesized by a simple sol-gel method which its details reported elsewhere [8]. Pellet of 11.6 mm in diameter and 0.8 mm in thickness were made by applying an ultra- high pressure up to 49.6 GPa on the powder sample. The sample was mounted on a conductive holder, which consisted of copper electrodes. Impedance measurements were performed on Cu/nano-SnO₂ thick film/Cu arrangement with using a computer-controlled AUTOLAB potentiostat and galvanostat as a function of frequency ranging from 1 Hz to 1 MHz at room temperature.

3. RESULTS AND DISCUSSION

3.1 Impedance Study

Impedance analysis has been well known to resolve the contribution from various microscopic elements

such as the grain, grain boundary, and electrodes to the total dielectric response. The high and low frequency semicircle can be attributed to the grain and grain boundary properties of the material. Each region can be realistically described by a parallel combination of a capacitor and a resistor [5, 6]. The corresponding equivalent circuit of SnO₂ nanoparticle is illustrated in Fig. 1 (inset). The Fig. 1 shows the complex impedance plots of the Cu/nano-SnO₂/Cu arrangement at ultra high pressure. As shown in Fig. 1, two semicircles present corresponding different transition mechanisms. High impedance value is observed at low frequency side due to the space charge polarization. The frequency dependence of the magnitude $|Z|$ at different applied potentials is shown in Fig. 2. At higher frequency, decreasing of the impedance is caused by the increasing conductivity of sample. In comparison to the impedance measurement at lower pressure [5, 6], a higher value for magnitude $|Z|$ was obtained at 49.6 GPa, which can be ascribed to the more induced deep defect state in film.

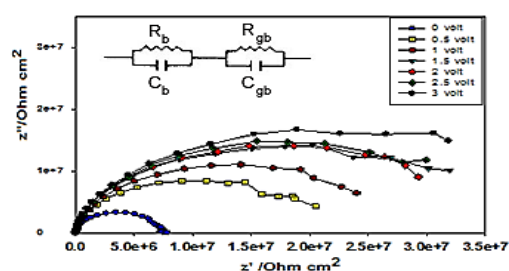
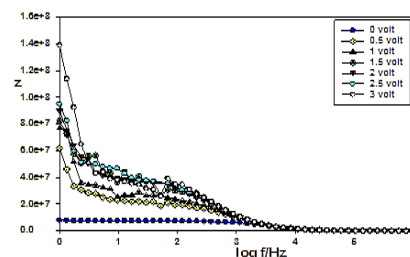


Fig. 1 – Nyquist plot of SnO₂ nano particles at high pressure



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Fig. 2 – Magnitude plot of SnO₂ nanoparticles

3.2 Mott–Schottky Analysis

The Mott–Schottky model is based on the following equation [9]:

$$C_{SC}^{-2} = \frac{2}{eN_D\epsilon\epsilon_0} \left(|V - V_{fb}| - \frac{kT}{e} \right) \quad (1)$$

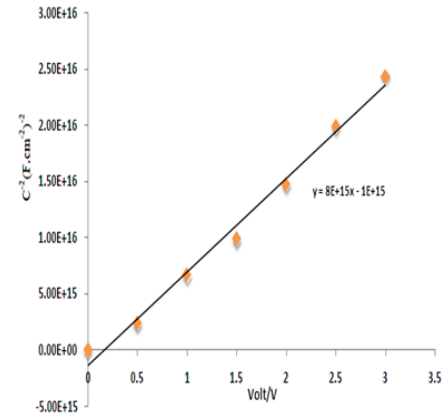
Which expresses the applied potential dependence of the capacitance of the space charge-layer (C_{SC}). In equation (1), ϵ is the dielectric constant for SnO₂, ϵ_0 the permittivity of space, e is the electron charge, V the applied potential (V), V_{fb} the flat band potential (V), k the Boltzmann constant equal to 8.16×10^{-5} eV/K, T the absolute temperature (K) and N_D is the carrier concentration (cm^{-3}). A calculated Mott-Schottky plot is presented in Fig. 3. The charge carrier concentration were determined from the slop of $1/C^2$ vs. V plots as $N_D = 5.4 \times 10^{23} \text{ cm}^{-3}$ and from the extrapolated intercept on voltage axis, flat band potential (V_{fb}) was estimated as $V_{fb} = 0.125$ V. The thickness of the space-charge layer was evaluated based on the following equation [10]:

$$L_{SC} = \left\{ \frac{2\epsilon\epsilon_0}{eN_D} (V_{fb} - V) \right\}^{1/2} \quad (2)$$

For a potential of 0(V), the value calculated is 1.6×10^{-9} Cm.

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Fig. 3 – Mott–Schottky plot of the SnO₂ nanoparticles

4. CONCLUSION

There are two components to the impedance, grain interior resistance (R_{gi}) and grain boundary resistance (R_{gb}). The high-frequency semicircle has been attributed to the grain interior resistance and the low-frequency semicircle is due to grain boundary resistance corresponding different transition mechanisms. From the Mott–Schottky plot the film was found to be a highly disordered n-type semiconductor with a charge carrier concentration in order of 10^{23} cm^{-3} and flat band potential of about 0.125 V.