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In memoriam prof. dr. Liviu Oniciu

MOTT-SCHOTTKY ANALYSIS OF ELECTRODEPOSITED ZnS THIN FILMS

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ABSTRACT. Some semiconductor properties, flat band potential and donor density, of electrodeposited ZnS thin films were evaluated by Mott-Schottky analysis. To this aim the depletion region capacitance of semiconductor/ solution interface was determined by analysis of impedance spectrums.

Keywords: *ZnS, thin film, semiconductor, impedance spectroscopy.*

INTRODUCTION

In recent years, extensive studies have been carried out on preparation and characterization of large band gap semiconductors, such as TiO_2, ZnS, ZnO, SnO_2, due to their application in photovoltaic-photoelectrochemical energy conversion and photoconductors [1-4]. Devices based on these materials require obtaining of thin films, usually by the means of vacuum deposition techniques (i.e., molecular beam epitaxy, vapour phase epitaxy or metal-organic chemical vapour deposition) or spray pyrolysis [5-7]. However, chemical and electrochemical depositions are attractive alternatives, mainly due to their lower cost and to advantages related to the use of ambient temperature and pressure. The electrodeposition is further advantaged by an easier control of the film growth, by using electric charge as process advance variable, and by higher yields, restricting the film formation on the electrode interface [8-10].

The properties of electrodeposited thin films can be obtained by examining electronic structures of the semiconductor/solution interface. Electrochemical and electrophotochemical techniques of investigation are well-suited for obtaining of some important properties of the semiconductor, namely donor density and flat-band potential, both factors influencing the efficiency of photoelectrical and photochemical application of semiconductors. There are a number of such techniques used for measuring these properties;

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the flat-band potential (E_{fb}) can be determined either by measuring the photopotential or the onset of the photocurrent as a function of radiation intensity, or by measuring the capacitance of the space charge region into semiconductor [1, 11, 12]. The latter technique, employed in this work, allows the determination avoiding the use of controlled level of electromagnetic radiation that would have requested a more sophisticated instrumental setup.

The selected determination method of a semiconductor/electrolyte interface flat-band potential was performed using a correlation between capacitance of the semiconductor depletion layer and applied voltage bias, correlation common known as Mott-Schottky analysis. Several methods of capacitance measurement are described in literature, among which a.c. voltammetry, capacitive reactance and impedance spectroscopy measurements are the most utilized [13].

The aim of present work is to perform a Mott-Schottky analysis on semiconductor ZnS thin film electrodes by means of impedance spectroscopy.

RESULTS AND DISCUSSION

A common approach in describing the response of a system to an a.c. perturbation is the recourse to an electrical equivalent circuit, composed by resistances, R, and capacitances, C.

The most complex equivalent circuit takes into account the behaviour of all the elementary steps that accompany the charge transfer across the semiconductor/solution interface. It uses elements for solution phase (R_s), depletion region (R_{dep} and C_{dep}), electric double-layer (C_{dl}), and for the charge transfer (R_{ct}) and mass transport (R_{dif} and C_{dif}). These electric elements describe the charge transport into solution and semiconductor phases, charge accumulation on semiconductor/solution interface and elementary steps of the faradaic process, respectively. Solely depletion region capacitance is of interest in present investigation.

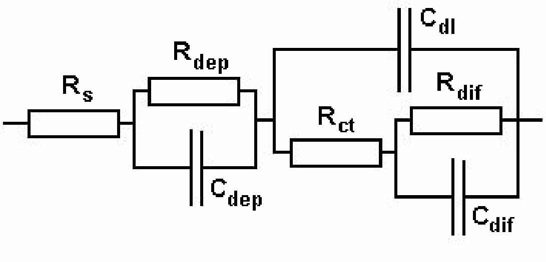


Figure 1. General equivalent circuit of a metal/semiconductor/solution system.

Depending on the experimental conditions employed, the contribution of some elementary steps can be neglected, as summarised in ref. [13]. In present study, by using a reasonable high concentration of electrolyte solution which increases C_{dl}, one can set aside not only the faradaic terms (R_{ct}, R_{dif} and C_{dif}) as the low reactance of C_{dl} acts as a shunt, but also the C_{dl} itself as it is connected in series with another capacitance of lower value. Accordingly, a simplified equivalent circuit that retains only R_s, R_{dep} and C_{dep} is further discussed and utilised.

It is now at hand to discuss about choosing the method of capacitance measurement. When using a.c. voltammetry or capacitive reactance (X_C) measurements of pulsation ω, the presence of R_s and R_{dep} resistance will cause an under-evaluation of measured capacitance (C_{meas}):

$$C_{meas} = \frac{1}{\omega X_C} = \frac{C_{dep} R_{dep} + 1/\omega}{R_{dep} + R_s + \omega C_{dep} R_{dep} R_s} \tag{1}$$

Eq. 1 evidences the conditions necessary for accurate capacitance determination, namely $\omega >> 1/C_{dep} R_{dep}$ and $R_s << R_{dep} / (1 + \omega C_{dep} R_{dep})$, which are often difficult to fulfil. Nevertheless, taking into account the advantages of measuring into a frequency domain, impedance spectroscopy measurements allow calculation of every element of equivalent circuit.

The impedance spectroscopy measurements were performed on aluminium electrode uncovered or covered by ZnS thin layers obtained by electrodeposition on potential controlled conditions at -1.25 or -1.45 V vs. SCE, see ref. [14]. Impedance spectrums are measured for dc bias values (E_{cc}) in the range of -0.5 to -1.7 V vs. SCE, avoiding, as possible, sulphide oxidation or zinc ion reduction, both reactions compromising the semiconductor properties.

Obtained spectrums of both electrodes exhibit only one depressed semi-circular loop as predicted by the simplified equivalent circuit. Fig. 2 presents measured spectrum, as Nyquist plots, for the film deposited at -1.25 V vs. SCE for selected d.c. biases presented in legend.

A critical part of any attempt to use impedance spectroscopy to measure capacitance is the numerical correlation between the measured data and a selected equivalent circuit. In present work, a complex non-linear least squares (CNLS) fitting procedure was selected, which involves minimizing of:

$$S(\theta) = \sum_{i=1}^{n} \left[\left(Z_{re,i} + jZ_{im,i} \right)\Big|_{measured} - Z_M(f_i, \theta) \right]^2 = \sum_{i=1}^{n} [\varepsilon_i]^2 \tag{2}$$

and uses the measured impedance and the model impedance:

$$Z_M(f_i,\theta) = Z_{M,re,i}(f_i,\theta) + jZ_{M,im,i}(f_i,\theta) \tag{3}$$

where f is the frequency, j is the complex operator, θ is here a 4-element real vector of (R_s; R_{dep}; C_{dep}; α), and ε_i is an identically distribution complex error term, with the real and imaginary components being independent on each other [15].

It is known that on polycrystalline electrodes the double-layer capacitance is often frequency dependent. Whatever of atomic scale (i.e., steps, kinks and dislocations) or larger (i.e., scratches, pits and grooves), surface irregularities cause this capacitance dispersion phenomenon. To characterize this phenomenon, the response of the capacitance can be approximated to a constant phase element; in other words $C(f) \propto (j\ 2\pi f)^{1-\alpha}$, with exponent α value between 0.7 and 0.9 is common with solid electrodes [16]. On these bases, the components of the model impedance are:

$$Z_{M,re,i}(f_i,\theta) = R_s + \frac{R_{dep}\left[1 + 2\pi f_i R_{dep} C_{dep}\sin(\alpha)\right]}{1 + 4\pi f_i R_{dep} C_{dep}\sin(\alpha) + (2\pi f_i R_{dep} C_{dep})^2} \tag{4}$$

$$Z_{M,im,i}(f_i,\theta) = -\frac{2\pi f_i R_{dep}^2 C_{dep}\cos(\alpha)}{1 + 4\pi f_i R_{dep} C_{dep}\sin(\alpha) + (2\pi f_i R_{dep} C_{dep})^2} \tag{5}$$

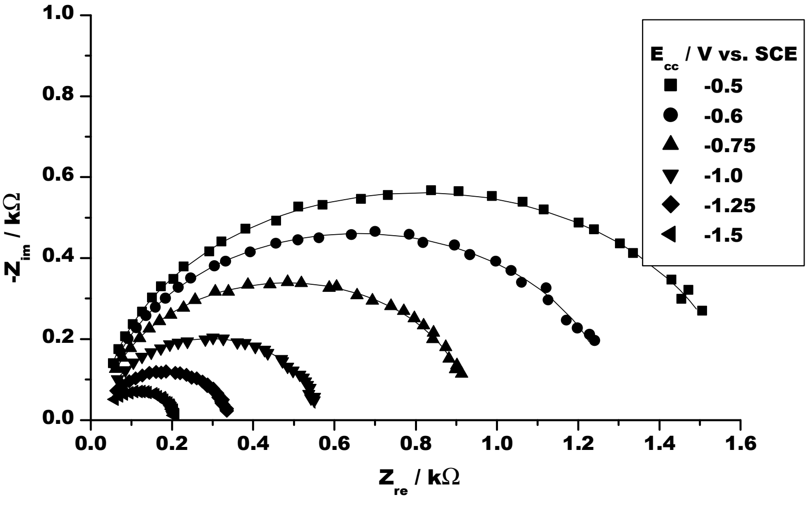
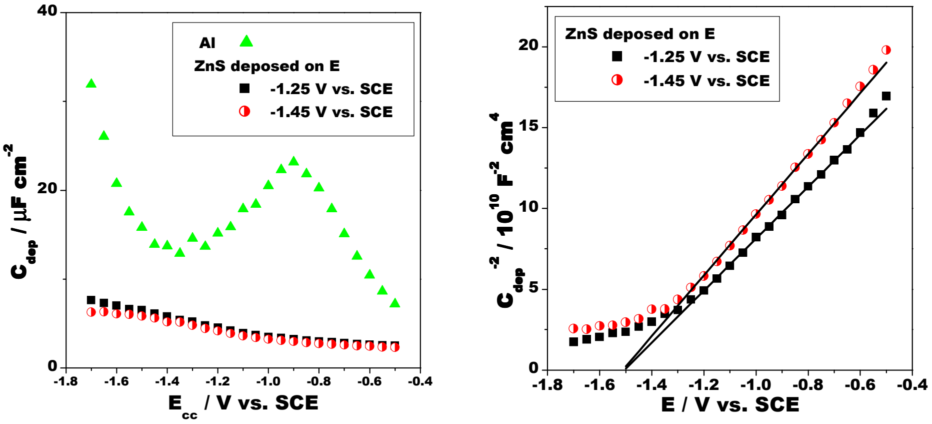


Figure 2. Influence of applied dc potential (for selected values presented in the legend) on Nyquist plot of measured impedance spectra for the ZnS film obtained at -1.25V vs. SCE. Continuous lines denote the fitted spectrums.

The fittings were performed in Microcal Origin 5.0 using the simplex algorithm. The results of the fitting procedure are the components of θ. To evaluate graphically the fitting goodness, corresponding fitted curves are also presented in fig. 2. From the components of fitted vector, analysis is restricted to depletion region capacitance C_{dep}. Fig. 3a depicts the influence of applied dc bias on the capacitance values of the three investigated electrodes. The significantly higher values are obtained for the uncovered electrode; in this case, due to absence of semiconductor film, the determined capacitance corresponds to the electric double-layer.



(a) **(b)**

Figure 3. Influence of applied dc potential on calculated C_{dep} (fig. 2a) and Mott-Schottky linearization (fig. 2b). Presented data correspond to Al electrode uncovered and covered with a ZnS film electrodeposited as indicated in legend.

The flat-band potential of a semiconductor/solution junction can be calculated from the Mott-Schottky equation [17]:

$$1/C_{dep}^2 = \frac{2}{e_o N_d \varepsilon A^2}(E - E_{fb}) \qquad (6)$$

where A is the interfacial area, e_o the elementary charge, N_d the donor density and ε the dielectric constant of the semiconductor. Accordingly, a plot of $1/C_{dep}^2$ vs. E should give a straight line with the flat-band potential as x-axis intercept and the slope allowing calculation of donor density.

It is clear from the data presented in fig. 3b that Mott-Schottky equation is valid within a wide potential range, of about 0.7V, which indicates a well-defined electronic surface state of deposited film. Wider linear potential range, that exceeds 1V, can be obtained only for high organised solids, namely single crystals. Furthermore a positive slope is an indication of an n-type semiconductor.

At negative potentials (roughly for E< -1.2 V vs. SCE) a significant deviation from linearity is observed. This deviation is very likely related to the presence of surface states because an electronic structure change, as a result of elementary zinc formation by reduction, would have decreased the depletion region capacitance dramatically. Accordingly, at lowest investigated potentials the reduction process corresponds to sulphur or polysulphide reduction, since a 1:1.1 Zn:S molar ratio for the obtained film was previously establish [14].

When the data in fig. 3b are fitted using equation (6), a value for the flat-band potential of (-1.51 ± 0.02) V vs. SCE was calculated. This value is in good agreement with that found in the literature (-1.54 V vs. SCE) for a single crystal ZnS [18]. The donor density was estimated to be (7.4 10^{18} and 6.9 10^{18}) cm^{-3} for the films obtained by electrodeposition at -1.25 and -1.45 V vs. SCE, respectively. The donor density values should be regarded with caution because the surface area of the irregularly crystallites contained by the semiconductor thin film could only be estimated with a rather poor accuracy. But, assuming potential independence of surface area, on basis of increasing the slope of Mott-Schottky plot when electrodeposition takes place at a more negative potential, one can discuss about the nature of reaction causing the excess of sulphur in electrodeposited film. Because elementary sulphur has no implication into charge transport, reduction of thiosulphate takes place more likely to polysulphide than to elementary sulphur.

CONCLUSIONS

Impedance spectroscopy was employed in order to obtain information about the electric charge depletion in a semiconductor thin film of ZnS obtained from electrodeposition from acidified thiosulphate solution containing zinc ion. The investigation of two ZnS films, obtained by electrodeposition at -1.25 and -1.45 V vs. SCE, allowed calculation of the flat-band potential of (-1.51 ± 0.02) V vs. SCE and the donor density was estimated to be (7.4 10^{18} and 6.9 10^{18}) cm^{-3}, respectively.

In a previous paper electrodeposition of ZnS thin films was investigated by cyclic voltammetry and electrochemical quartz crystal microbalance allowed the estimation of an 1:1.1 Zn:S stoechiometric ratio. The present Mott-Schottky analysis suggested that the excess sulphur of ZnS films is caused by the presence of zinc polysulphide, excluding the presence of elementary sulphur, as the donor density of semiconductor is potential dependent.

EXPERIMENTAL SECTION

The impedance spectroscopy measurements were performed using a computer controlled potentiostat (Elektroflex EF-451, Hungary) by means of a customised Turbo Pascal^{TM} software application. A 10mV ac perturbation, with frequencies in range of 0.3 to 10 KHz, was superimposed to the imposed voltage bias.

A standard three-electrode electrochemical cell configuration was employed for the measurements. The reference electrode was a double-junction saturated calomel electrode (SCE) and the counter electrode was a spiralled Pt wire. The working electrode was obtained by electrodeposing a 1μm thin film of ZnS onto an Al (refined, 99.5% purity) disk electrode (A=0.032 cm^2). Electrodeposition details are presented elsewhere [14]. The electrolyte solution employed was Na_2SO_4 0.2 M (p.a. Riedel de Haen), being prepared using distilled water.

All measurements were performed with the cell introduced into a dark casket and kept at 20 ± 1 ^{o}C.

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