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Characterization of Pb_3O_4 films by electrochemical techniques

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Abstract. The band gap of semiconductor is determined by photovoltage spectrum. The photovoltage sign shows the semiconductor to be of *n*-type conductivity. Mott-Schottky plot gives the position of Fermi level, the approximate position of band edges, donor density in the semiconductor and space charge layer thickness. The results agree with other reported values.

Keywords. Electrochemistry; photovoltage; photoelectrochemical

1. Introduction

The practical application of the concepts of semiconductor electrochemistry is still not a sufficiently developed field, although sufficient information regarding its characteristics is available since the last two decades. In many semiconductors, electrochemical characterization has been used successfully (Faktor *et al* 1980) to determine band gap, donor density, space charge layer width, absorption coefficient, type of conductivity, carrier concentration, composition, diffusion length etc. In the present investigations, the semiconductor Pb_3O_4 is characterized by photovoltage spectrum and capacitance-voltage characteristics.

2. Experimental details

The Pb_3O_4 films (thickness 6·3 μm) were obtained by annealing the electrodeposited β-PbO_2 films on nickel substrates for 24 hr at 450°C (Sharon *et al* 1984c). These films exhibited low conductivity ($\sim 10^{-4}$ ohm^{-1} cm^{-1}). The photovoltage spectrum was obtained by measuring the open circuit photovoltage between Pb_3O_4 electrode and platinum counterelectrode dipped in redox electrolyte IO_3^-/I^- (0·2 M) at different wavelengths of light (200–800 nm). The semiconductor electrode was illuminated by xenon arc lamp (Oriel, 500 W) through a monochromator (Oriel) keeping the cell 7·8 cm away from the latter. Capacitance-voltage characteristics were studied with the three electrode system i.e. semiconductor, platinum and saturated calomel electrode (SCE) as reference dipped in buffer solution (pH = 7). The capacitance was measured by LCR bridge (Systronics) at various electrode potentials (vs SCE) of semiconductor electrode. AnalaR grade of chemicals were used in all the experiments without any further purification. All the solutions were prepared in triple distilled water.

3. Results and discussion

The criteria for electrolyte selection, validity of photovoltage spectrum for band-gap determination and interpretation of Mott-Schottky plot are discussed below.

3.1 *Electrolyte selection*

The criteria for the most suitable electrolyte in contact with semiconductor are that it should not react chemically with the semiconductor and should produce sufficient band bending. Based on earlier studies (Sharon *et al* 1984c), the redox couple IO_3^-/I^- (0·2 M, pH = 7) satisfies both the conditions. Therefore, IO_3^-/I^- was selected for further studies.

3.2 *Photovoltage spectrum*

Open-circuit photovoltages of the photoelectrochemical (PEC) system Pb_3O_4/IO_3^-, I^-/Pt were measured at various wavelengths of light. The photovoltage sign gives conductivity type of semiconductor (Peter 1983; Faktor *et al* 1980). In this system anodic behaviour of photovoltage of the semiconductor was observed which indicates its *n*-type of conductivity.

A plot of photovoltage against the wavelength of light is shown in figure 1. The absorption edge of the spectrum gives the band-gap value 2·12 eV which is in good agreement with the value of 2·18 eV reported earlier (Pamfilov *et al* 1967). This value is also comparable with that measured earlier by photocurrent method (E_g = 2·0 eV) (Sharon *et al* 1984a) and reflectance spectrum (Sharon *et al* 1984b) (E_g = 2·1 eV). The exact explanation of photovoltage spectrum is not available till date. However, Williams

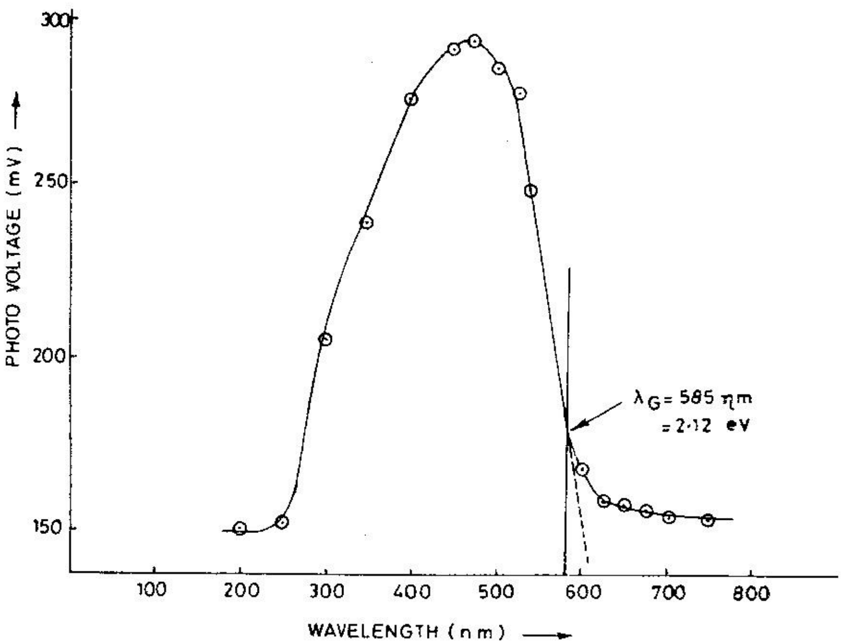

Figure 1. Photovoltage vs wavelength of light for the system n-Pb_3O_4/IO_3^-, I^-/Pt to determine the band gap of Pb_3O_4.

(1959) observed that the photovoltage spectra of ZnO and CdSe exactly behave as optical density vs wavelength plot and give similar absorption edge. This can be explained as follows:

Based on the equation for the generation rate $g_p(x)$ as a function of depth (x) for the semiconductor electrolyte junction (Myamlin and Plaskov 1967)

$$g_p(x) = P(1-R)\alpha \exp(-\alpha x),$$

an expression for small signal photovoltage is given as (Faktor *et al* 1980),

$$KP\left[\frac{(1-R)\alpha L_p}{1+L_p}\right]$$

where K is the constant for the given material; P, the photon flux; R, the surface reflectivity; α, the absorption coefficient and L_p = hole diffusion length. In the above expression, if $\alpha \cdot L_p \ll 1$ which is always true when band gap is not too low, $V_{ph} = KP(1-R)L_p \times \alpha$. At constant photon flux $KP(1-R)L_p = A$ = constant $V_{ph} = A\alpha$. Hence, V_{ph} is directly related to α and consequently shows the same spectral distribution.

3.3. *Capacitance-voltage characteristics*

The capacitance-voltage characteristics were studied by using the well-established Mott-Schottky plot for semi-conductor-electrolyte junction (Gerischer 1979). The $(\text{capacitance})^{-2}$ vs electrode potential plot for the electrochemical system Pb_3O_4/buffer solution (pH = 7)/Pt is given in figure 2. The condition when electrode potential is equal to zero gives the flat-band potential. The value of flat-band potential (V_{fb}) as obtained from this plot is $-0{\cdot}405$ V vs SCE which is comparable to that reported

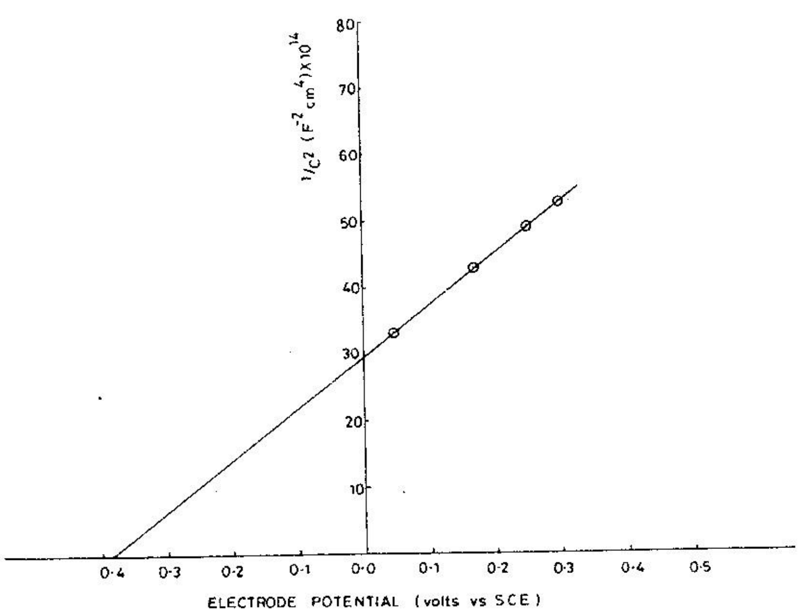

Figure 2. Mott-Schottky plot for the system n-Pb_3O_4/Buffer solution (pH = 7)/Pt to study capacitance voltage characteristics. Electrode potential is measured with respect to saturated calomel electrode (SCE).

earlier (i.e. -0.31 V vs SCE) using photocurrent method (Sharon *et al* 1984a) for polycrystalline Pb_3O_4 pellets.

The flat band potential gives the position of Fermi-level in semiconductors. The position of Fermi-level with respect to vacuum level is given by

$$E_F = e V_{fb}\,(\text{vs SCE}) - 4.781\ \text{eV (Gerischer 1975)}$$
$$= 4.376\ \text{eV}$$

In highly doped semiconductors the Fermi level position lies 0·1 eV below that of conduction band edge (Scaife 1980). However, these Pb_3O_4 films have low conductivity. Therefore, if we assume this difference as 0·2 eV, the approximate positions of conduction and valence band edges can be given as -4.176 eV and -6.356 eV respectively. The donor density in the semiconductor is calculated from the slope of Mott-Schottky plot (figure 2). Using the reported value of dielectric constant ($\varepsilon = 15$) of Pb_3O_4 (Oehme 1964) the donor density is calculated to be 1.19×10^{-16} cm^{-3}. Putting the appropriate values of donor density, dielectric constant and flat band potential, the space charge layer width in semiconductor was calculated to be 7.80×10^{-5} cm.

4. Conclusions

The electrochemical characterization methods are fast and much less complicated. Specially the band gap measurement is very simple and reliable. The value of V_{fb} (-0.405 V vs SCE) is also in good agreement with that of determined by photocurrent method (-0.31 V vs SCE). However, detailed studies are needed to explain the exact behaviour of photovoltage spectrum and this is now in progress.

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