PHOTOELECTROCHEMICAL STUDIES ON P-InP / SnO$_2$ HETEROJUNCTIONS

Y RAMPRAKASH

Central Electrochemical Research Institute, Karaikudi - 623006

S BASU and D N BOSE

Semiconductors Division, Materials Science Centre Indian Institute of Technology, Kharagpur 721302

ABSTRACT

Transparent and conducting films of SnO$_2$ were deposited by spray pyrolysis technique from solution containing stannous chloride, HCl, ethanol and water onto heated glass and p-InP substrates kept at 450°C in air. The P-InP/SnO$_2$ heterojunctions thus formed were used as photoelectrodes in 0.5 M H$_2$SO$_4$-0.1 M Fe$^{2+/3+}$ redox electrolytes. Current-voltage characteristics in dark showed rectifying behaviour while Mott-Schottky plots in an indifferent electrolyte confirmed a negative band-bending. The flat-band potential (V$_{fb}$) was thus found to be -0.27 V vs SCE. Spectral response over the wavelength range 0.4 to 0.8 μm was characteristic of absorption in InP. On illuminating with a tungsten-halogen lamp providing approximately AM 1 intensity at the photoelectrode, the photoelectrochemical (PEC) cell produced an open-circuit voltage, V$_{oc}$ = 0.15 V, and a short-circuit current density, J$_{sc}$ = 87 μA/cm^2. These results are discussed with the help of a band diagram.

Key words : Photoelectrode, photoelectrochemical cells, P-InP / SnO$_2$

INTRODUCTION

One of the methods of protecting the surfaces of semiconductors prone to anodic or cathodic dissolution is to coat them with thin layers of stable wide band-gap oxide materials. This approach has been employed [1] to achieve stable surfaces of Si, n-InP, GaAs and n-CdS. The protective front layer was a thin film of n-TiO$_2$ formed by chemical vapour deposition. Otherr workers [2,3] have used n-CdS thin films as optical windows over n-GaAs and n-InP surfaces for obtaining stability and enhancement in efficiency of the photoelectrochemical (PEC) cells. The cell based on n-GaAs as expected was found to yield higher solar conversion efficiency while the n-InP based PEC cell [3] showed improvement in stability only.

Indium phosphide, a direct band-gap material (E$_g$ = 1.34 eV at 300°C) of the III-V group of semiconductors, is a promising material for photovoltaic [4] and PEC [5] solar energy conversion. Transparent and conducting tin-oxide layers are important because of their increasing applications in optoelectronic devices such as heterojunction solar cells, display and image storage devices. In solar energy conversion field it forms efficient heterojunctions with Si, InP, GaAs and other suitable semiconductors wherein it acts mainly as an optical window because of its high band-gap (E$_{g, SnO2}$ = 3.5 eV). In the present experiments, its importance also arises because of its good chemical stability in alkaline and acid electrolytes.

EXPERIMENTAL

Single crystals of p-InP, obtained from Metals Research, UK, have the following specifications: hole concentration, p = 1.8 x 10^{18} cm^{-3}, resistivity, ϱ = 0.055 ohm-cm and hole-mobility, μ_h = 66 cm^{-2} V^{-1} Sec^{-1}. The specimens (approximately 0.06 cm^2 in area) were mechanically polished using diamond paste and were ultrasonically cleaned in trichloroethylene, acetone and methanol. The samples were then etched in 1 % bromine in methanol and rinsed in triple distilled water. Ohmic contact to p-InP was done by evaporating In-Zn alloy followed by a short heat-treatment at 400°C in hydrogen atmosphere. The samples were then loaded into the spraying chamber and a solution containing stannous chloride, HCl, ethanol and water was sprayed onto the surfaces of p-InP and cleaned glass substrates, heated to 450°C and maintained at this temperature within ± 10°C. Compressed air at a pressure of 0.4 kg.cm^{-2} was used for atomisation. During the spraying operation, an interval of two to three minutes was allowed to avoid excessive cooling of the substrate and for the temperature to regain its original value. The spraying rate was 5 ml.min^{-1}. After spraying the required volume of solutin (50 ml) the specimens were allowed to cool slowly to room temperature. Subsequently, they were annealed in argon atmosphere at 250°C for about 10 minutes.

The PEC experiments were conducted in a perspex cell with a glass window. The p-InP electrodes with SnO$_2$ on its surface were used as the photoelectrodes. A large area Pt foil was used as the counter electrode while the reference electrode was a saturated calomel electrode. An electrolyte consisting of 0.5 M H$_2$SO$_4$ (pH = 1.3) and 0.1 M Fe$^{2+/3+}$ redox-system was used for the experiments. Current and voltage were measured by means of a Keithley 160-B digital multimeter. Capacitance of the space charge layer was measured at 1 KHz frequency under depletion mode. A d.c. reverse bias varying between 0 and 0.5 volt was applied across the interface and an a.c. signal of 25 mV amplitude was superimposed over it. For C-V measurements, an indifferent electrolyte having the composition: 0.2 M KCl - 25 ml and 0.2 M HCl - 33.6 ml (pH = 1.3) was specially used in order to have a perfect blocking junction. High purity argon was bubbled through the electrolytes before and during the experiments to remove dissolved oxygen. Spectral response measurements were performed with interference filters (bandwidth - 10 nm approx) placed between the source and the PEC cell.

RESULTS AND DISCUSSION

The thickness of the tin oxide layers were found to be approximately 1635Å units from weighing experiments. The resistivity of the films was found to be in the range 0.04 - 0.07 ohm-cm from four-point probe measurements. Optical absorption studies over the wavelength range 0.4 to 0.8 μm indicated that the films were transparent over the region, the transmittance being 90 %. Carrier concentration in tin oxide was found to be 5.6 x 10^{18} cm^{-3}

E_{SnO_2} — 10) from Mott-Schottky plots. The carrier concentration was found to be of the same order as calculated from the resistivity and mobility values.

Figure 1 shows the log-J vs V characteristics in dark under forward and reverse bias. The behaviour under forward bias can be approximated to:
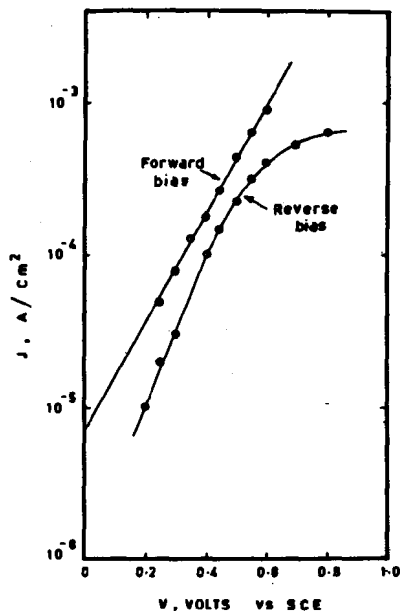

Fig. 1 : Dark J-V characteristics in 0.5 M H2SO4 - 0.1 M Fe$^{2+/3+}$ redox system

$$J = J_o \exp(qV/nkT)$$

where J_o is the reverse saturation density in $A.cm^{-2}$, V the voltage measured against SCE and n the ideality factor. From figure 1, J_o — $7 \times 10^{-6} A.cm^{-2}$ and n — 4.9 were obtained. The ideality factor indicates that there is a large density of surface states at the SnO_2 surface which is in contact with the electrolyte. Although larger values of ideality factors are expected in semiconductor-electrolyte junctions, no satisfactory explanation has been forthcoming. Explanations of larger n factors invoked [6] mechanisms such as internal field emission, generation - recombinations, tunneling through space-charge layer etc. The reverse characteristics showed a tendency to saturate at a current density approximately equal to $10^{-6} A.cm^{-2}$.

The variation of junction capacitance with voltage is shown in figure 2. The linearity of the Mott-Schottky plot suggests uniform distribution of ionized donors within the space-charge layer. The extrapolation of the straight line curve onto the potential axis gave an intercept at $-0.27 V$ vs SCE and is equal to the flat-band potential. From the inverse slope, an acceptor concentration, N_A — $9.2 \times 10^{17} cm^{-3}$ was obtained assuming static dielectric constant of InP to be 12.35.

The normalised response of the PEC cell for various spectral illuminations is shown in figure 3. The response goes through a maximum at λ — $0.5 \mu m$ and showed a sudden decrease at $0.6 \mu m$. At longer wavelengths, the optical absorption in InP play a role in current collection. Thus the spectral response is mainly characterised by absorption of radiation in InP resulting in electron-hole pair production and subsequent charge separation. The role of tin-oxide was to protect the surface of InP apart from being optically transparent for wavelengths greater than its band-gap. Figure 4 depicts the PEC cell output characteristics under 100 mw. cm^{-2} tungsten-halogen illumination. The intensity of light at the photoelectrode was measured by a calibrated 'Suryamapi'. The cell showed $V_{\sim}$ — $0.15 V$, J_{sc} — $87 \mu A. cm^{-2}$ and fill-facotr, F.F. — 0.43.

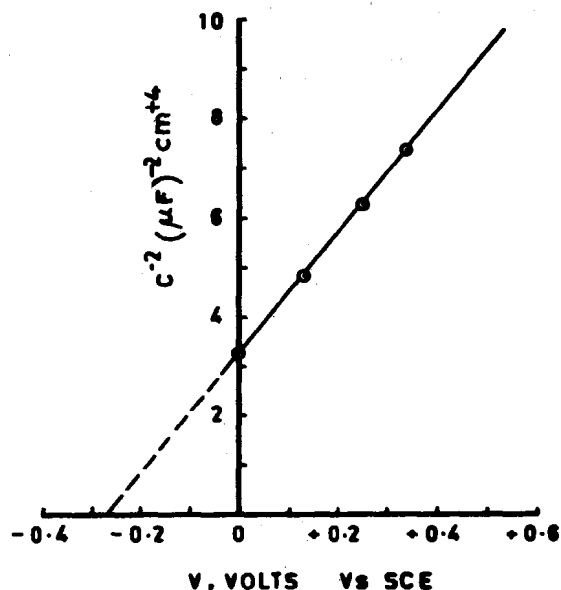The results obtained can be explained with the help of the energy band diagram shown in figure 5.

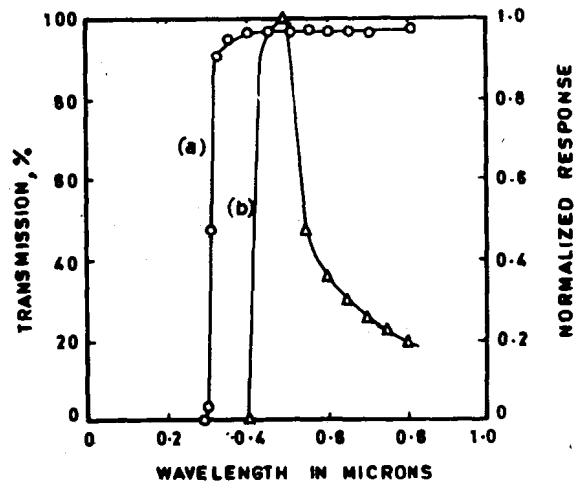Fig. 2 : Mott-Schottky plot in an indifferent electrolyte (pH — 1.3) at frequency f — 1 KHZ

Fig. 3 : (a) Transmittance of SnO2 layer (thickness — 1635Å) on plain glass substrate
(b) Spectral response of the p-InP/SnO2 based photoelectrochemical cell

The band bending at the electrolyte was not indicated for simplicity reasons. The electron affinity (X) and the band-gap (E_g) of SnO_2 and InP were taken from literature. The band energy diagram revealed a potential discontinuity (ΔE_c) of 0.52 eV in the conduction band. The valence band discontinuity (ΔE_V) is 2.65 eV. The electrolyte is in contact with the tin oxide and hence there would be further band bending in dark due to this contact. Under illumination, with energies greater than the band-gap of tin oxide, electron-hole pair production would take place in SnO_2. As the barrier height is reduced at the electrolyte-tin oxide contact, the photogenerated holes in tin oxide are pushed into the electrolyte under the influence of the field where they find suitable energy positions at the $Fe^{2+/3+}$ redox levels. The electrons which move into the bulk of SnO_2 find an energy barrier ΔE_C and hence are prevented from transfer into the bulk of InP. Carrier generation in InP occurs for wavelengths greater than $0.35 \mu m$ as tin oxide acts mainly as a transparent window in this region. The photogenerated minority carriers in InP can travel downhill across the energy separation shown by ΔE_C while holes if any, generated in SnO_2 can also move uphill across the energy barrier ΔE_V and contribute to the current flow.
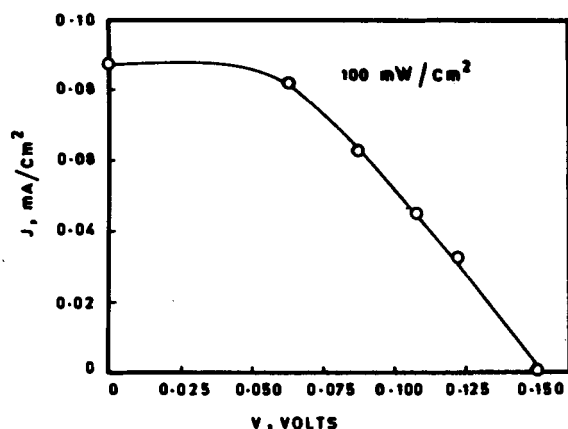
Fig. 4 : Power output characteristics at 100 mW. cm^{-2} tungsten-halogen irradiance
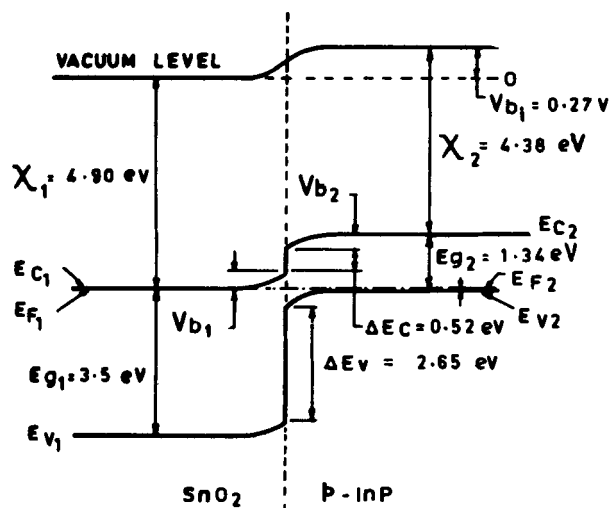
Fig. 5 : Energy band diagram for the SnO$_2$/p-InP heterojunction

The electrons entering tin oxide have to traverse through its thickness which is much larger than the tunneling width for electrons. Since the film resistivity is low, conduction through tin oxide film is by the usual band mechanism. The majority carriers (holes) move into the bulk of p-InP under the influence of the electric field. Hence the external current direction is from p-InP to the Pt counter electrode. The external current resulting from carrier generation (if any) in tin oxide will be from platinum to p-InP. Hence the net current will be the result of the two currents.

CONCLUSIONS

The high values of ideality factor indicated the non-ideal behaviour of the junction. This is partly due to the degradation of the surface of InP subjected to high temperatures during annealing and spray pyrolysis. It is known that phosphorous out-diffusion takes place at such temperatures. Direct evidence for this has been obtained [7] in sub-band gap illumination experiments. The existence of a high density of interface states at p-InP/SnO$_2$ junction would naturally degrade current collection while the diffusion lengths in InP would be adversely affected by the prolonged heat treatment.

The C-V studies and the band diagram justified low open-circuit voltages obtained in the present experiments. The spectral response is mainly determined by absorption and carrier generation in InP. The poor cell output resulting from low V$_{oc}$ and J$_{sc}$ is due to opposing fields in the two junctions, viz electrolyte/SnO$_2$ and SnO$_2$/p-InP. Improvement in heterojunction fabrication technique may result in better junction properties.

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