PHOTOELECTROCHEMICAL CHARACTERISTICS OF n-InSe SINGLE CRYSTALS

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The photoelectrochemical behaviour of n-InSe single crystals in aqueous solutions has been studied in the presence and absence of several redox systems. Among them, $Ce^{3+/4+}$ and KI/I_2 yielded the highest photocurrents, photovoltages and show the highest stability. The semiconductor energy gap E_g = 1.2 eV, has been calculated from transmittance measurements. The flat band potential U_{FB} = –0.40 V vs NHE and the donor density have been calculated from differential capacity measurements.

Chalcogenides of transition metals with layer structure represent an interesting class of semiconductor materials having potential use in variety of applications such as in the conversion of solar energy, as solid lubricants, in secondary lithium batteries or optoelectronic devices[1–5].

InSe is a semiconductor of the III–VI family and has been the subject of several investigations. The layer structure is characterized by a covalent bond restricted into two dimensions of the layer in the sequence Se–In–In–Se. In the third dimension the adjacent layers are bound together with van der Waals forces.

The band gap energy of 1.3 eV (ref.[6]) and the electronic and optical properties of InSe, similar to those of GaAs or Si, make InSe a very convenient material for photoelectrodes for solar energy conversion as well as for other technological applications[7,8]. The layer structure and the possibility to prepare crystals of p- or n-type semiconductor have predestined InSe also as an interesting material for photointercalation/deintercalation studies[9–11].

In the present study we are reporting optical and photoelectrochemical properties of n-InSe samples doped with Al. Preinvestigation was carried out in aqueous solutions containing redox systems, with the exposed electrode surface parallel to the semiconductor layer.

EXPERIMENTAL

Large InSe single crystals (10 × 10 mm^2) were grown using the Bridgman method. In the first stage, polycrystalline InSe was synthesized at 800 °C from pure 6N In and 6N Se shot in stoichiometric ratio, then placed in a quartz ampoule and evacuated to about 10^{-4} Pa. After the reaction was completed, the compound has been cooled with the temperature gradient of 20 °C cm^{-1}. The samples of crystals grown under the above described conditions showed intrinsic character with high resistivity at a room temperature. The crystals exhibit a typical layer-type structure and mirror-like surfaces. As it was confirmed by X-ray diffraction patterns they crystallize in the γ-3R-polytype structure. In order to produce single crystals with low resistivity and n-type conductivity, Al was introduced as a dopand into the material during the synthesis. Ohmic contacts were created using Ag-paint and Ag-paste[12]. The electrodes were mounted on a copper wire and isolated with an epoxy resin (Scotch–Cast 3MXRR52 41), leaving the surface of the crystal uncovered. The surface area exposed to the solution ranged from 0.030 to 0.080 cm^2.

All solutions were prepared from doubly distilled water and analytical grade chemicals.

Optical properties were studied in the ordinary configuration $\boldsymbol{E} \perp \boldsymbol{C}$, where $\boldsymbol{C}$ is the crystallographic direction perpendicular to the layers and $\boldsymbol{E}$ is the electric field of the incident light. The spectroscopic measurements were performed with a Cary 14 spectrophotometer, using freshly cleaved surfaces 50 μm thick at a room temperature.

Photoelectrochemical measurements were performed using a potentiostat/galvanostat (Princeton Applied Research 170), XY-recorder and a three electrode electrochemical cell with Pt counter and a saturated calomel electrode (SCE) as a reference electrode. A flat quarz window was fitted on to the electrochemical cell for illumination of the semiconductor electrode. A heat absorbing water filter was placed between the light source and the electrochemical cell to minimize the IR radiation. A 150 W tungsten–halogen lamp was used for the experiments, white light 80 mW cm^{-2}.

Impedance measurements were carried out using a PAR 170 electrochemical system consisting of a sine wave generator and a lock-in amplifier. The amplitude of the sinusoidal wave, superimposed on the dc bias, was 0.01 or 0.05 V. The differential capacity values of the semiconductor–electrolyte interface were obtained from admittance measurements as a function of electrode potential in the frequency range from 100 to 1 100 Hz. In all data reported below, the real part of the admittance was small enough, so that, within an experimental error, the imaginary part of the admittance was proportional to the capacity.

All experiments were carried out at a room temperature.

RESULTS AND DISCUSSION

Spectral Response

Figure 1 shows the spectral variation of the absorption coefficient α, extracted from transmittance measurements according to the relation[13]

$$T = (1 - R)^2 \exp(-\alpha d) \ , \qquad (1)$$

where R is the reflectivity constant in the spectral region (R = 0.26, ref.[14]), α is the absorption coefficient and d = 50 μm is the sample thickness.

Figure 2 shows the dependence of $(\alpha h\nu)^2$ on the photon energy of the incident light for InSe. It indicates that α in the spectral region close to the semiconductor absorption edge, matches the relationship $\alpha = A[(h\nu - E_g)^{m/2}]/h\nu$ for $m = 1$, refs[13,15]. From the intercept of the extrapolated straight line, an optical energy gap was found to be equal to 1.197 ≈ 1.2 eV. It corresponds to a direct band gap transition.

Capacity Measurements

In order to determine the flat band potential U_{FB} and the doping level N_D of the n-InSe single crystals, differential capacity measurements as a function of applied potential and frequency were employed. To make sure that the surface of the semiconductor was free of defects, freshly cleaved crystal faces were used.

Figure 3 shows the Mott–Schottky plot[16] for n-InSe/0.1 M H_2SO_4, 2 M KI, 5 . 10^{-2} M I_2 interface in the dark at 0.7 and 1 kHz. Some dispersion was detected, stronger at lower frequency values. The lines converge yielding $U_{FB} = -0.64$ V vs SCE (–0.4 V vs NHE). Similar U_{FB} values have also been reported by Levy-Clement[17] and Fotouhi[18] for n-type crystals.

The energy of Fermi level, E_F, at the flat band potential with respect to vacuum is given by Eq. (*2*), ref.[19]

$$E_F = -(e\, U_{FB} + 4.44)\ , \text{eV}\ . \qquad (2)$$

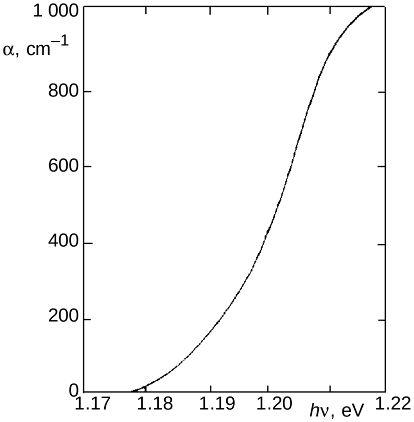

FIG. 1
Spectral variation of the absorption coefficient α for InSe (d = 50 μm) at a room temperature

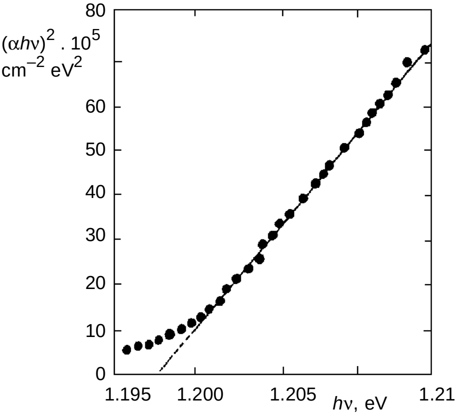

FIG. 2
Plot of $(\alpha h\nu)^2$ vs photon energy

According to Eq. (*2*) and using U_{FB} calculated from the capacity measurements, the energy of the Fermi level is –4.04 eV. Taking into account that the value of the Fermi level is 0.1 V below the bottom of the conduction band edge, E_c, the position of E_c was found to be –3.94 eV. As we can see from the above, $E_g = 1.197 \approx 1.2$ eV, so the valence band edge E_v is estimated to be –5.14 eV. The donor density $N_D = 1.5 \cdot 10^{17}$ cm^{-3} as calculated from the slope of the curve *a* in Fig. 3 for $\varepsilon = 8.8$ (ref.[20]). We report in Table I the values of some physical quantities of n-InSe which have been estimated from the above measurements.

Current–Potential Characteristics

Figure 4 shows the current–potential (*I*–*E*) characteristics of InSe in 0.1 M H_2SO_4, in the absence of any redox system, in the dark and under illumination with concentrated

TABLE I
Photoelectrochemically determined physical quantities of n-InSe in 0.1 M H_2SO_4/2 M KI/5 . 10^{-2} M I_2 at pH 1

Parameter	Value
Flat band potential U_{FB}, V vs NHE	–0.40
Donor density N_D, cm^{-3}	$1.5 \cdot 10^{17}$
Depletion layer width *L* for 1 V, cm	$8.1 \cdot 10^{-4}$
Optical band gap energy (direct), eV	1.2
Conduction band edge E_c, eV	–3.94
Valence band edge E_v, eV	–5.14

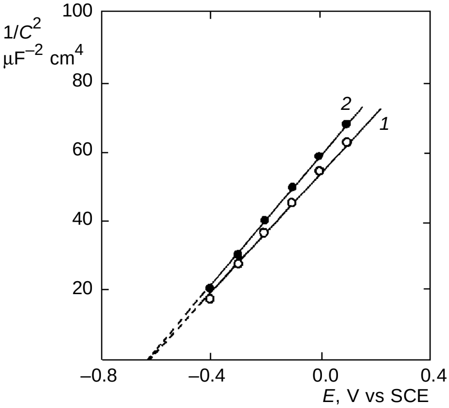

FIG. 3
Mott–Schottky plot of n-InSe in a 0.1 M H_2SO_4/2 M KI/5 . 10^{-2} M I_2 aqueous solution at *1* 0.7 and *2* 1 kHz

white light provided by a 150 W tungsten–halogen lamp. The current–potential curves were obtained at a scan rate of 0.010 V s^{-1}, in the dark and under illumination.

The electrochemical behaviour of the electrode in the dark (background illumination) shows that in the potential range from –0.5 to 1 V vs SCE a very small dark current flows through the semiconductor–electrolyte interface compared to the larger photocurrent. At the potential exceeding the value of 1 V, a dark current appears, as a consequence of the electrode decomposition. Under illumination, an anodic photocurrent which does not become saturated is observed at –0.5 V. Since no redox system has been introduced, we suppose that the photocurrent is caused by the photocorrosion of the semiconductor according to the reaction

$$3\,h\nu \longrightarrow 3\,e^- + 3\,h^+$$

$$InSe + 3\,h^+ \longrightarrow In^{3+} + Se\ ,$$

where h is the Planck constant and e^- and h^+ the photogenerated electrons and holes, respectively. The result was the appearance of a redish Se film on the surface of the electrode causing a decrease of the photocurrent.

In order to use the same crystal again, we had to remove the amorphous Se film by etching in a 2% Br_2–methanol solution. The characteristics of the crystal remained unchanged. In order to observe the effect of pH on the current–voltage characteristics, InSe electrodes were tested in 0.5 M Na_2SO_4 and in 1 M NaOH solutions. The photocurrent–voltage characteristics show no significant displacement of the onset potential be-

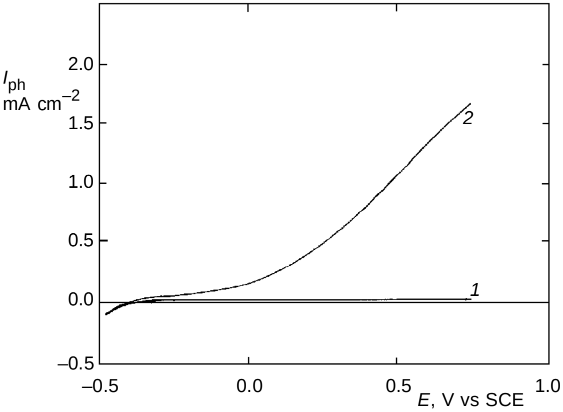

FIG. 4
Potentiostatic current–potential (I–E) curves of n-InSe in the dark *1* and under illumination *2* in 0.1 M H_2SO_4 (pH 1)

tween 0.05–0.2 V with the change of pH. This is in an agreement with the view that in layered semiconductors there is no change of flat band potential with pH or with the type of redox system. In the case of neutral solution the value of I_{ph} was slightly smaller than in the case of acidic solution. On the contrary, photocurrent in the alkaline solution was approximately 10 times smaller and constant at varying potential for the same intensity of illumination. It may be attributed to the creation of a protective In_2O_3 film on the surface of the crystal[21]. The presence of this film is also consistent with the decrease of the photocurrent.

The photoelectrochemical behaviour of InSe was then studied in solutions of various redox systems: 1 . 10^{-2} M Ce^{3+}/Ce^{4+} (1 : 1), 1 . 10^{-2} M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1 : 1), 2 M KI/5 . 10^{-2} M I_2, 1 M $NaOH/Na_2S/S$ (1 : 1 : 1).

In Figure 5 the curves *1*, *2* and *3* represent the first three redox systems in 0.1 M H_2SO_4. The curve for sulfide solution is not provided since this solution did not give any appreciable photocurrent. The dark currents, are very small for a wide range of applied electrode potentials, similar to the currents received in the absence of any redox system.

In order to compare the photoelectrochemical behaviour of n-InSe doped with Cl from the literature[17,22] with our findings, it must be stated here, that the saturation current is recorded at the potential of approximately 0 V. In the case of $Ce^{3+/4+}$ this current can be as high as 40 mA cm^{-2}. Higher concentration of carriers in the InSe crystal in our case (100 times higher than in refs[17,22]) results in a decrease of internal resistance and increase of mobility of minority carriers. Photocurrent appears almost at the same potentials, i.e. between –0.8 to –0.7 V vs SCE, in all three cases. This fact is common

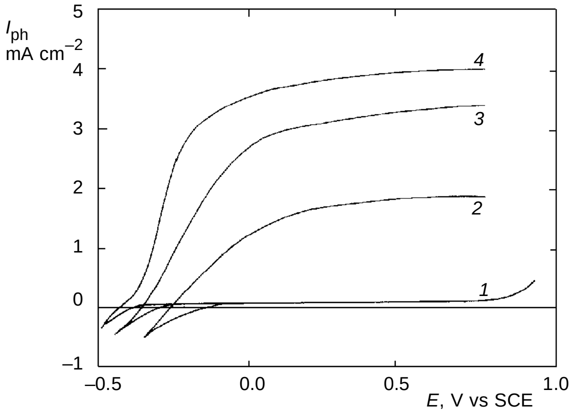

FIG. 5

Potentiostatic current–potential (*I*–*E*) curves of n-InSe in the dark *1* and under illumination in 0.1 M H_2SO_4; *2* 1 . 10^{-2} M $Ce^{3+/4+}$ (1 : 1), *3* 2 M KI/5 . 10^{-2} M I_2, *4* 1 . 10^{-2} M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1 : 1) for layered compounds which do not displace their band edge energies as a result of pH or redox system changes. In the present work we have observed a shift towards negative potentials in the case of $CaI_2/HI/I_2$ and the polysulfide solution.

Since the stability is important for photoelectrochemical applications, we measured I_{ph} as a function of time. Measurements were made in 0.1 M H_2SO_4 solution in the presence of the above systems at the electrode potential of 0.5 V vs SCE, in the region of saturated photocurrent.

Figure 6 shows the I_{ph}/t curves corresponding to the above cases. It can be seen that KI/I_2 insures a more stable behaviour, since after 4 h the decrease of I_{ph} is smaller in comparison to other systems, where larger and more abrupt decrease whithin the same time interval is detected. Generally, the behaviour of InSe under the above conditions can be characterized as not very stable for long time intervals.

Measurements of the photovoltage U_{ph} under open circuit conditions and for various redox systems n-InSe/Redox/Pt are given in Table II. The value of U_{ph} ≈300 mV is

TABLE II
Photopotential values U_{ph} of n-InSe single crystal in the presence of various redox systems

Redox system	U_{ph}, V
1 . 10^{-2} M $Ce^{3+/4+}$(1 : 1)	0.28
1 . 10^{-2} M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1 : 1)	0.33
2 M KI/5 . 10^{-2} M I_2	0.29
1 M $NaOH/Na_2S/S$ (1 : 1 : 1)	0.37

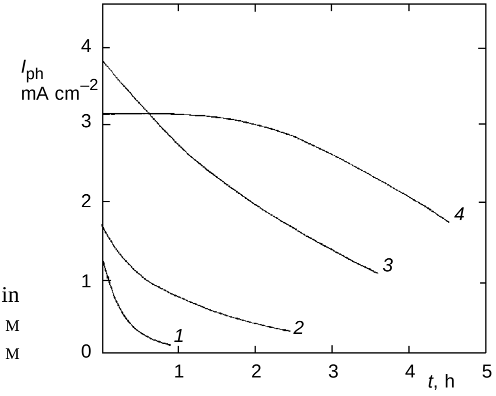

FIG. 6
Output stability of n-InSe at 0.5 V (vs SCE) in 0.1 M H_2SO_4 with *1* blank, *2* 1 . 10^{-2} M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1 : 1), *3* 1 . 10^{-2} M $Ce^{3+/4+}$ (1 : 1), *4* 2 M KI/5 . 10^2 M I_2

comparable to results published by other authors on InSe (ref.[17]). However, it is smaller than U_{ph} measured for solid state solar cells[23,24].

We have also carried out some experiments with undoped crystals. These pure materials had high resistance and exhibited lower photocurrents. The sign of the photovoltage indicates that the crystals are of the n-type but it is remarkable that they can exhibit n- as well as p-type behaviour according to the bias potential. This behaviour as well as the high resistance of these materials indicate a probable intrinsic character, that changes to n-type after doping with Al. Similar observations for InSe have been reported by Levy-Clement[17], who explained this behaviour by photoelectrochemical and photoconductive effects.

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