A 22% EFFICIENT SEMICONDUCTOR/ LIQUID JUNCTION SOLAR CELL — THE PHOTOELECTROCHEMICAL BEHAVIOR OF n-WSe₂ ELECTRODES IN THE PRESENCE OF I₂/I⁻ IN AQUEOUS ELECTROLYTE

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One of the most efficient semiconductor/liquid-junction photoelectrochemical cells (PEC) reported to date is presented. It consists of a SeCl₄-grown n-WSe₂ single crystal anode, with a $3.10^{16} \text{ cm}^{-3}$ conduction-band electronic density, and a platinum cathode. Both electrodes are immersed in a 2M KI + 0.005M I₂ aqueous electrolyte. The calculations of the main physical parameters determining the high value (22%) of the visible light-to-electrical energy conversion efficiency have been carried out. We particularly show that the lifetime of the photogenerated holes is larger than their transit time across the space-charge so that the carriers reach the semiconductor surface, where they can react with the electrolyte, without recombining.

1.0 INTRODUCTION

Photoelectrochemical cells are highly attractive devices for visible light-to-electrical energy conversion. The layered dichalcogenide n-WSe₂ is among the most promising electrode materials. Kline and al.^{1,2} obtained 9% and 17% visible light-to-electrical power conversion efficiencies respectively for monochromatic (647 nm) and polychromatic irradiations. In fact, the attainment of such high efficiencies implies the use of both:

- i) a single crystalline sample with a step free Van der Waals surface exposed to the incident light^{1–11}.
- ii) a 0.005M I₂ + 2M KI aqueous electrolyte².

All n-WSe₂ crystals investigated to date have been grown by chemical vapor transport using Cl₂ and Br₂ as transport agents¹⁻¹¹. However, none of these previous studies correlated the influence of the transport agent upon the photocurrent-voltage characteristics and, thus, upon the photoconversion-efficiency. Such correlation will be investigated here and the choice of the transport agents will be justified below.

The following physical parameters determining the photoconversion efficiency have never been reported for n-WSe₂:

1°) the space charge layer thickness (W); W must be large enough to ensure efficient separation of most of the photogenerated electron-hole pairs,

2°) the recombination-time (Tr) or life-time of the photogenerated holes; Tr must be larger than (or equal to) the hole transit time (Tt) across the space charge so that the carriers can reach the semiconductor surface without recombining.

In addition, the flat band potential V_{fb} , the bulk-hole diffusion length L_p and the ionized donor density N_D used to determine W and estimate the Tr/Tt ratio, are evaluated.

2.0 CHOICE OF THE TRANSPORT AGENTS

In WSe₂ the carrier transport in the perpendicular direction of the VdW surface is determined by randomly distributed stacking faults (Se vacancies and W in excess)²⁻¹². These defects probably act as recombination (trap) centres for the photogenerated carriers and, thus, affect the electrode-efficiency.

Consequently it can reasonably be assumed that if Cl₂ or Br₂¹⁻¹¹ as well as Se or Te are present in the transport agent, the concentration of stacking faults, i.e. the concentration of anionic vacancies, should be diminished if Se and Te occupy anionic positions. Thus, the carrier transport would be less affected by the recombination centers and the semiconductor efficiency would be enhanced.

The following transport agents were chosen: SeCl₄; TeCl₄; Br₂ + 20% Se. Crystals of n-WSe₂ grown using only Br₂ as a transport agent will also be considered and serve as a standard reference².

3.0 EXPERIMENTAL

3.1 Sample preparation

The conditions for the growth of the crystalline samples by chemical vapor transport are summarized in Table I. Step free VdW surfaces, examined with the help of a Siemens Autoscan microscope, are obtained by pressing pieces of adhesive tape onto the crystal and peeling off thin layers. Final thicknesses ($1\text{--}3 \times 10^{13}$ mm) are measured perpendicularly to the VdW surface using a precision screw gauge.

TABLE I
Experimental crystal-growth conditions

Sample	Transport agent	Temperatures (°C)	
		source	growth
A	Br ₂	985	975
B	Br ₂ + 20% Se	930	900
C	SeCl ₄	987	967
D	TeCl ₄	930	920

3.2 Electrode fabrication

The electrodes for the PEC are made as follows: an electrical contact is made with an In-Ga eutectic and a copper wire on the VdW surface at the back side of the crystal; then the back of the semiconductor is covered with an epoxy resin leaving a light-exposed VdW surface area of about 2–5 mm².

3.3 Photoelectrochemical measurements

Photoelectrochemical measurements are performed under potentiostatic conditions using a conventional three-electrode electrochemical cell with a platinum electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. A 2M KI + 0.005M I₂ aqueous electrolyte is used.

The electrode is illuminated through a quartz window in the cell wall using a 150 W high pressure Xe lamp (ORIEL) as light source whose output is passed through either

- a visible (MTO Photovex) band-pass filter absorbing wavelengths smaller than 520 nm; the resulting visible-light irradiance is then 26 mW/cm²,
- a monochromator (ORIEL: model 7240).

The light intensity is measured through a calibrated thermopile (KIPP: model 754324) placed at the same position as the n-WSe₂ electrode.

Optical absorption spectra are recorded with a CARRY 17 ratio-recording spectrophotometer.

4.0 RESULTS AND DISCUSSION

4.1 Output-power characteristics

Fig. 1 shows the variation of the photocurrent (I_{ph}) versus voltage ($\Delta V = V_{cathode} - V_{anode}$, i.e., spontaneous working conditions) for the different electrodes (A–D). Polychromatic visible light is used.

As expected, the efficiency observed for sample A (11%) is close to that obtained by Kline and al² under polychromatic irradiation with no Se present in the transport agent.

The much higher efficiencies observed for samples B and C (17% and 22%) should be correlated, as expected, to the predominant role of Se and Cl₂ in the crystal growth. On the other hand, the lowest quantum yield occurring for sample D (4%) will be interpreted below.

The 22% efficiency value, together with the reasonably large open circuit potential (close to 0.6 v) places the corresponding semiconductor among the most efficient electrodes reported for visible light-to-electrical energy conversion.

4.2 V_{fb} , L_p , N_d determination

These parameters can be determined from the photocurrent efficiency (η' -voltage V semiconductor measured vs. SCE) characteristics of the electrodes. For the sake of clarity the most and less efficient electrodes (C and D respectively) will be considered.

η' is calculated from:

FIGURE 1 Output-power characteristics: variation of the photocurrent vs. potential (V anode-V cathode). Exp. cond.: 0.005M I₂ + 2M KI aqueous electrolyte; visible-light irradiance: 26 mW/cm².

$$\eta' = \frac{I_{ph}}{q\phi} \quad (1)$$

where ϕ is the photon flux absorbed by the electrode.

The η' -V characteristics are given in Fig. 2 at $\lambda = 920$ nm and -0.6 V < V < +0.8 V (corrosion occurs above 0.8 V).

4.2.1 V_{fb} In the vicinity of -0.5 V the light is chopped (Fig. 2) in order to accurately determine the transient-photocurrent onset potential, V_{on} , which is approximately equal to V_{fb} :

$$V_{on} = V_{fb} = -0.5 \text{ V}$$

4.2.2 N_d and L_p The shape of the η' -V curves, and particularly the smooth increase of the photocurrent with potential above 0 V, can be described using Gartner theory¹⁴:

$$\text{Ln}(1 - \eta') = -\alpha W - \text{Ln}(1 + \alpha L_p) \quad (2)$$

where α , whose dependence vs. wavelength is given in Fig. 3, is the semiconductor absorption coefficient corresponding to incident light normal to the VdW surface. W is given by¹⁴:

$$W = \left(\frac{2\varepsilon'_r \cdot \varepsilon_o}{q \cdot N_d} \right)^{\frac{1}{2}} (V - V_{fb})^{\frac{1}{2}} \quad (3)$$

where ε'_r , ε'_o and q have their usual meaning and $\varepsilon'_r = 13$ for WSe₂ when measured perpendicularly to the VdW planes¹⁵.

Combination of Eq. (2) and Eq. (3) gives:

$$-\text{Ln}(1 - \eta') = \alpha \left(\frac{2\varepsilon'_r \cdot \varepsilon_o}{q \cdot N_D} \right)^{\frac{1}{2}} (V - V_{fb})^{\frac{1}{2}} + \text{Ln}(1 + \alpha L_p) \quad (4)$$

According to Eq. (4) a graph of $-\text{Ln}(1 - \eta')$ vs. $(V - V_{fb})^{\frac{1}{2}}$ is linear as shown in Fig. 4. The slope and the intercept allow the determination of N_d and L_p for sample C, $N_d = 3.20^{16} \text{ cm}^{-3}$ and $L_p = 3.10^{-6} \text{ cm}$. For sample D, $N_d = 9.10^{15} \text{ cm}^{-3}$ and $L_p = 3.10^{-7} \text{ cm}$.

4.3 W determination and Tr/Tt ratio evaluation

W , which can now be determined from Eq. (3), is slightly lower for sample C ($2.2 \cdot 10^{-5} \text{ cm}$ for 1 volt band-bending) than for sample D ($4.0 \cdot 10^{-5} \text{ cm}$ for 1 volt band-bending).

Consequently, for the former electrode a larger part of the electron-hole pairs are photogenerated in the visible beyond the space-charge and, thus, are likely to recombine.

Although the power conversion efficiency should be higher for

FIGURE 2 Photocurrent efficiency — voltage (V anode vs. SCE) characteristics plotted for $\lambda = 920$ nm.

FIGURE 3 Wavelength variation of the absorption coefficient: incident light normal to the VdW surface. Similar characteristics occur for samples C and D.

sample D, this does not occur (Fig. 1). It is probable that the Tr/Tt ratio is lower than unity, for sample D only, at least for $\Delta V \leq 0.6$ v.

As mentioned above the condition $Tr/Tt \geq 1$ is necessary to get absence of electron-hole recombination within the space charge and thus get high photoconversion efficiency.

According to Salvador¹⁶, the Tr/Tt ratio can be written:

FIGURE 4 Determination of N_d and L_p from $-\ln(1 - \eta')$ vs. $(V - V_{fb})^{1/2}$ plots. The straight lines are obtained by minimum least squares fitting of the experimental points with a correlation factor of 0.999.

$$\frac{Tr}{Tt} = \frac{L_p'^2 \cdot q^2 \cdot N_d}{2 \cdot \epsilon_r \epsilon_o \cdot kT} \geq 1 \quad (5)$$

where L_p' is the hole diffusion length within the space charge layer and must not be misunderstood with the bulk-hole diffusion length

L_p . As the electrode potential increases from V_{fb} , L'_p increases ($L'_p \geq L_p$)¹⁶.

One obtains the lowest Tr/Tt limits by inserting L_p values in Eq. (5):

$$(Tr/Tt)_{min} = 0.99 \quad \text{for sample C}$$

and

$$(Tr/Tt)_{min} = 2.10^{-3} \ll 1 \quad \text{for sample D}$$

Consequently electron-hole recombinations occur inside the depletion layer for sample D only, and obviously predominate within the potential range given in Fig. 1. Thus, the observed efficiency is low.

Since the size of Te anions is much larger than that of Se anions (2.21 Å and 1.98 Å in Pauling's scale respectively), important distortions probably occur when Te anions enter the lattice. They would give rise to additional recombination centers which drastically inhibit the formation of the photocurrent.

5.0 CONCLUSION

It thus appears that single-crystalline n-WSe₂ electrode, having donor density and bulk-hole diffusion length close to $3.10^{16} \text{ cm}^{-3}$ and $3.2 \cdot 10^{-6} \text{ cm}$, respectively, give rise to high solar-to-electrical energy conversion efficiency.

In fact, single-crystalline n-WSe₂ films having such characteristics are highly desirable from the practical viewpoint of future development of large scale energy converters. These types of films are presently under investigation in this laboratory.

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