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Photovoltages exceeding the band gap observed with WSe_2/I^- solar cells

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Photovoltages ranging between 1.2 and 2.1 V have been observed with single-crystal WSe_2, grown without transport agent, in contact with I^-/I_3^- solutions. This effect is found only with surfaces which have not been renewed by peeling. They show negligible dark currents and both cathodic and anodic photocurrents. The abnormally high photovoltage sometimes disappeared without evident reason but it could nevertheless be used to drive a stable solar cell with an efficiency between 1.5 and 5% for a period of five days. Optical and electrochemical studies show that the phenomenon is due to the presence of two different types of material which coexist at the same surface with different band gaps and flat band potentials. One type shows a compensated behaviour, the other n-type behaviour. High photovoltages are obtained when anodic and cathodic photocurrents, generated simultaneously but at different wavelengths, compensate each other, thus shifting the zero-current point towards more negative potential values. Large photovoltages are therefore only possible while photocurrents are circulating through the two interfaces, thus dissipating energy. The observed phenomenon, though at present fragmentarily understood, could be of some value for the development of semiconductor electrodes with high photovoltages for the decomposition of water.

1. Introduction

Several publications studying the behaviour of WSe_2 as a photoelectrode have recently appeared [1–6]. WSe_2 in contact with I^-/I_3^- solution is characterized by a high stability, and solar energy conversion efficiencies as high as 10.2% have been reported [7]. The maximum photovoltage found for n-type material was 0.71–0.72 V [2, 7]. It is generally agreed that the band gap is an indirect one although its exact value is not yet known. An analysis of the photocurrent drop towards long wavelengths confirmed the indirect nature of the electron transition involved and gave a value of 1.16 eV for the gap [8]. Other estimations of the gap are somewhat higher ($\Delta E_G = 1.35$ eV) [9]. Photocurrents as high as 65 mA cm^{-2} under 150 mW illumination have been reported [5]. p-type WSe_2 also shows considerable photocurrents [1]. In the absence of other oxidizing agents protons are reduced to hydrogen. This is possible since the flat band potential of WSe_2 is slightly more negative than the hydrogen potential. In the presence of redox agents, such as $Fe^{2+/3+}$, photopotentials also exceed 0.5 V.

Samples of WSe_2 studied previously were grown in the presence of transport agents such as I_2 and Br_2. In contrast we studied samples grown directly from the elements without transport agents. The electric contact was made with the silver paste. Such contact was verified to be ohmic. Scotch cast (3M Company) was used to prevent materials other than the WSe_2 being in contact with the solution. Our samples showed both anodic and cathodic photocurrents of variable relative intensity. Such crystals in contact with an electrolyte should show a small photopotential when illuminated. Many samples investigated actually behaved as expected. However, a substantial fraction of these crystals gave a surpri-

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singly high photopotential which reached values between 1.15 and 2.1 V. Such a photoeffect has to be considered abnormal since it reaches and substantially exceeds the value of the forbidden energy gap.

This unusual phenomenon motivated us to search for and analyse the mechanism involved with the hope of understanding and later perhaps controlling such a high voltage output. Its possible implications for photoelectrochemistry could be important since photovoltages exceeding 1.5 V would be sufficient to decompose water for the purpose of hydrogen evolution.

It should be mentioned that photovoltages exceeding the energy gap of a semiconductor have previously been reported in the literature [10, 11]. In most cases polycrystalline samples with preferentially oriented microcrystals seem to be involved. As discussed below we believe that the mechanisms proposed there are not applicable to our phenomenon.

2. Experimental results

The power output characteristic of approximately 70 WSe_2 electrodes has been studied in an electrolyte containing 3 M I^-/0.01 M I_2 during this investigation. Of these electrodes 60% showed a photoeffect which has to be considered as normal: most samples gave photovoltages of less than 300 mV and a few up to 700 mV, a value which has been frequently obtained with n-type WSe_2 prepared in the presence of transport agents [2, 4, 7]. However, 40% of the electrodes prepared yielded a surprisingly high photovoltage varying between 0.7 V and 2.1 V with many samples showing a photopotential higher than the indirect band gap ($\Delta E_G \approx 1.16$ V [8]) of the semiconducting material. These results have been obtained during illumination with white light from a xenon–mercury lamp (maximum light intensities between 100 and 500 mW cm^{-2}). Fig. 1 shows five power output characteristics and gives an idea of the diversity of abnormal electrode behaviour observed. As can be seen, some curves approach the classical pattern observed with normal electrodes, but others show a curious decrease of photocurrent at low photovoltages. We have to emphasize that these abnormally large photovoltages were only observed with the uppermost surface of the WSe_2 crystals as they were grown in the quartz tubes. When this surface was renewed by attaching and removing an adhesive tape, the large effect always disappeared irreversibly.

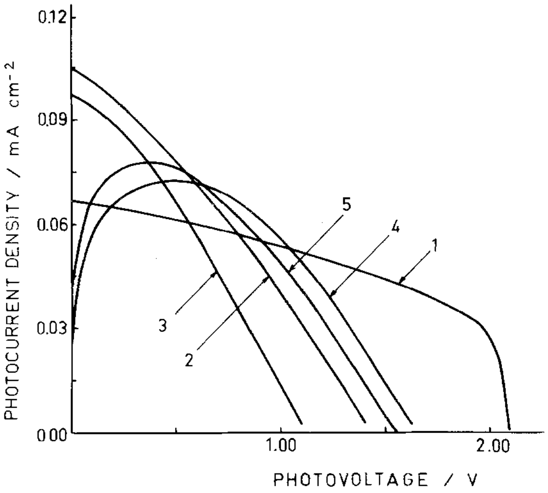

Fig. 1. Power output characteristics of five WSe_2 electrodes showing abnormally high photopotentials (white light from a Xe–Hg lamp; 3 M I^-/0.01 M I_2). The numbers are given as an indication of individual samples in subsequent figures.

Fig. 2 shows the dependence of the photocurrent and the photovoltage on the light intensity. A clear deviation from the classical behaviour is observed. There is no linear dependence of the photocurrent on the light intensity and the photovoltage attains a maximum value at between 2 and 12% of the full illumination. One of the electrodes (other than those presented on Fig. 1) was used for the estimation of the energy conversion efficiency near the maximum photovoltage. It was 1.6 V at an illumination intensity of 4 mW cm^{-2} versus 1.3 V at full light. Two different instruments (a thermopile and a Si photodiode) were used for measuring light intensities and values between 1.5 and 5% were obtained for the solar energy conversion efficiencies.

The electrode stability under high photovoltage output has been tested with one sample for a period of 110 hours. The working output voltage of the solar cell was between 0.9 and 1.0 V and the output photocurrent was approximately 0.11 mA cm^{-2}. No significant degradation of the electrode was observed during the operation (Fig. 3).

Since approximately 40 C cm^{-2} of charge were

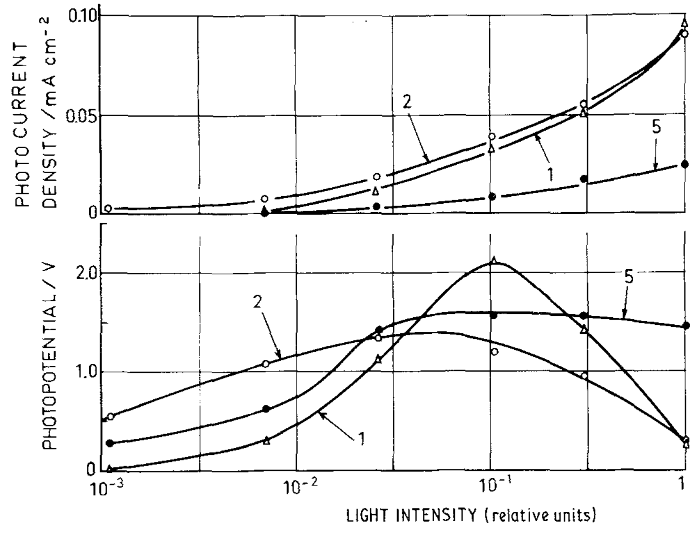

Fig. 2. Dependence of the photocurrents and photovoltages on the intensity of (white) light from a Xe–Hg lamp (logarithmic scale).

passed in this experiment, and since up to 18 holes per molecule of WSe$_2$ could be consumed during its oxidation to selenate, it can be calculated that up to 7000 Se–W–Se sandwich layers might have been consumed. Corrosion could thus have penetrated up to 2000 nm into the material and thus completely destroyed the grown surface of the crystal samples. No change in the crystal could in fact be observed. We conclude therefore that corrosion is not important in this case.

In the course of the investigation of this abnormal photovoltage phenomenon we studied the spectral dependence of photocurrents between wavelengths of 400 and 1100 nm. Both anodic and cathodic photocurrents were observed; however, their spectral dependence was suprisingly different (Fig. 4). When a positive voltage of 0.8 V was applied to the electrode, only anodic photocurrents were observed in the entire spectral region investigated. When a negative voltage of 0.8 V was applied, cathodic photocurrents were generated only by photons with an energy exceeding 1.4 eV. The photocurrents produced by light quanta of smaller energy remained anodic even at such negative electrode potentials. It is obvious from these spectra that different current–voltage characteristics were obtained for different wavelengths of the incident light. The material studied appears to behave as if at least two different semiconductors were coexisting at the same electrode interface.

In order to separate the photoelectrochemical

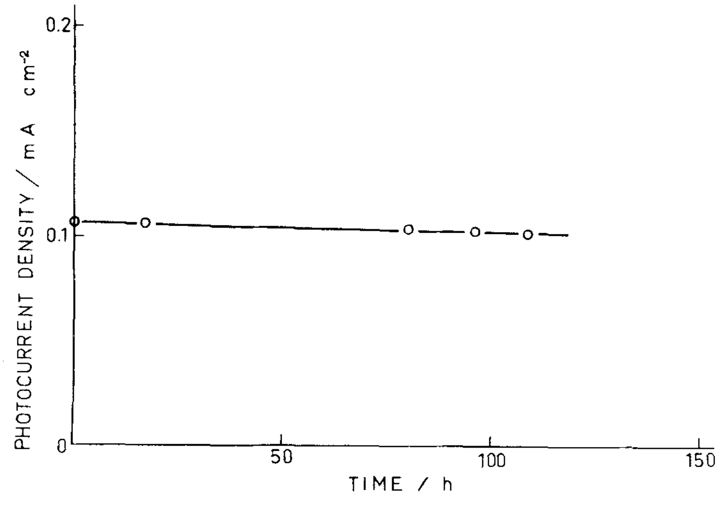

Fig. 3. Long-term experiment with WSe$_2$/I$^-$–I$_3^-$ showing abnormally high photopotential (illumination with white light from a Xe–Hg lamp).

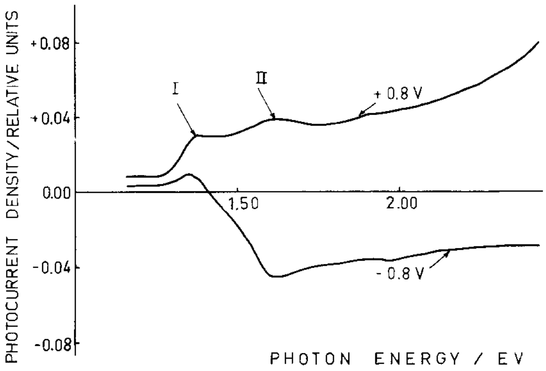

Fig. 4. Spectral dependence and polarity of photocurrents at different electrode potentials: + 0.8 and − 0.8 V/SCE in the presence of 0.1 M H_2SO_4 + 0.05 M K_2SO_4.

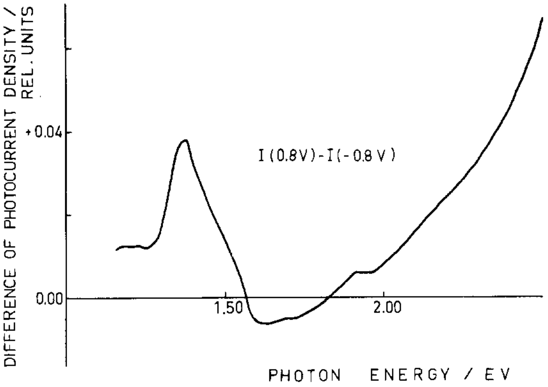

Fig. 5. Difference between photocurrent densities obtained at + 0.8 V and − 0.8 V/SCE.

properties of the supposed different semiconductors more clearly, the spectral difference between the anodic and cathodic response was plotted (Fig. 5). The results show that the semiconductor which generates the anodic currents throughout the current–voltage range studied (semiconductor I) absorbs at longer wavelength and has, consequently, a smaller band gap than the second semiconductor (II) which changes the polarity of its photocurrents. Semiconductor I also shows an increased absorption towards the ultraviolet region. The contribution to the photocurrents by the two different semiconducting surfaces can be easily distinguished by means of the two peaks at 1.27 eV (I) and 1.45 eV (II). It is important to note that the relative intensity is strongly dependent on the applied potential. This is demonstrated in Fig. 6. There are some qualitative differences between different crystal samples but generally the peak corresponding to semiconductor I is only present during anodic polarization while the peak of the second semiconductor (II) is visible during anodic as well as cathodic polarization. For this reason there will be always an intermediate electrode potential at which a cathodic peak II is seen together with an anodic peak I, as in Fig. 4.

Fig. 7 gives photocurrent–voltage dependences taken at two different wavelengths corresponding to the two different peaks. The first curve (I) reflects the behaviour of an n-type semiconductor of moderate electronic qualities characterized by the gradual increase of the photocurrent. Its flat band potential is situated at fairly negative potentials. The second curve (II) characterizes a semi-

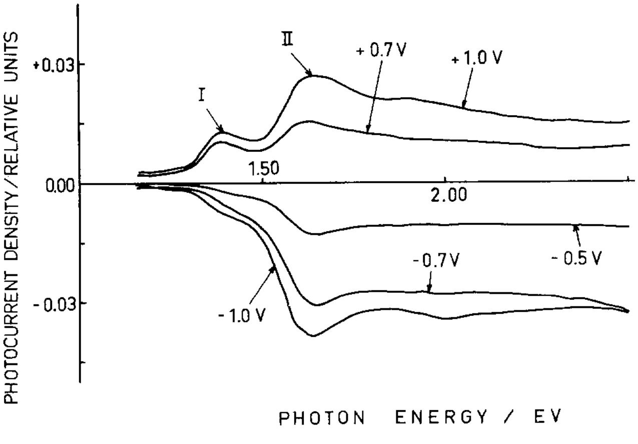

Fig. 6. Photocurrent density as a function of photon energy taken at different electrode potentials in the presence of 0.1 M H_2SO_4 + 0.5 M K_2SO_4 electrolyte.

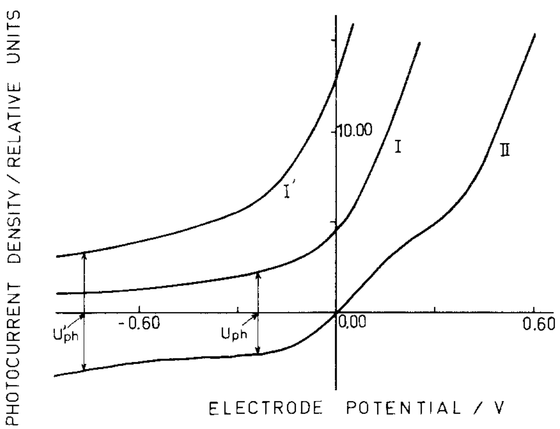

Fig. 7. Photocurrent dependencies taken at different wavelengths, 750 nm (peak I) and 900 nm (peak II). The zero-current potential corresponding to the open-circuit photovoltage is indicated by U_{ph}; the shifted value U'_{ph} obtained when current I is increased threefold (I') is also shown.

conductor which is compensated. Its flat band potential must be situated where the photocurrent crosses the zero current line.

The open-circuit photovoltage of the electrode is defined by the potential at which the total current across the electrode/electrolyte interface vanishes. When anodic and cathodic photocurrents are simultaneously generated they will compensate each other and the open-circuit photovoltage will be a function of the relative contribution of each. Accordingly, the coexistence of currents I and II in Fig. 7 will yield an open-circuit voltage of U_{ph}. To obtain a larger photovoltage U'_{ph} the contribution of photocurrent I has simply to be more important.

It has to be mentioned that photoelectrodes which gave a high photovoltage were frequently destroyed during current–voltage studies. The samples lost their peculiar properties apparently because of a corrosive degradation of the interface at higher electrode potentials. It has repeatedly been observed that the dark current of these electrodes, which was extremely low before the destructive event, became relatively large afterwards. Since it is known that step sites in the crystal surface are responsible for the dark currents [12], we may conclude that defects in the interface which act as recombination centres and adsorption sites are interferring with the observed high-voltage phenomenon. Due to the ease with which the electrode surfaces were destroyed, systematic studies of current–voltage curves in the presence of different redox systems could not be accomplished. This would have been especially interesting in the presence of I^-/I_3^- which is known to produce large photovoltages at n-type WSe_2 [4, 13] but negligible ones at p-type samples [1]. Nevertheless, the results obtained in the absence of I^-/I_3^- and presented in Figs. 4, 6 and 7 and those in the presence of this redox system are compatible in a consistent way.

3. Discussion

The photoelectrochemical phenomenon discussed in this paper would appear to be in contradiction with the conventional well-established theory of semiconductor/electrolyte junctions. According to this theory the maximum obtainable photoeffect should clearly be smaller than the band gap of the semiconducting materials. In contrast we report photovoltages which exceed the size of the band gap and in addition, can even be used to drive solar energy conversion.

The WSe_2 material used was grown in a different way from normal where iodine or bromine is used as a participating transport agent and a doping impurity. Furthermore, macroscopically perfect-looking crystals were used, not asymmetrically grown polycrystalline layers which have occasionally been shown to give rise to abnormally high photovoltages. Our studies of the spectral dependence of photocurrents (Figs. 6 and 7), as well as current–voltage dependences taken at different wavelengths (Fig. 7), give unequivocal evidence of the coexistence of two different semiconductor materials on the same electrode/electrolyte interface. Semiconductor I, which absorbs at a longer wavelength, is an n-type semiconductor. Its band gap obtained by simple extrapolation is approximately 1.27 eV and the existence of photocurrents at a very low polarization indicates a flat band position at a very negative potential. Semiconductor II is compensated and has an energy gap of approximately 1.45 eV and its flat band position can be found near 0 V/SCE, where its photocurrents invert their polarity (Fig. 7). The contribution of each of the semiconductors to the total photocurrent depends on the electrode polarization, which can clearly be recognized in Fig. 6 and which is easily explained in terms of the

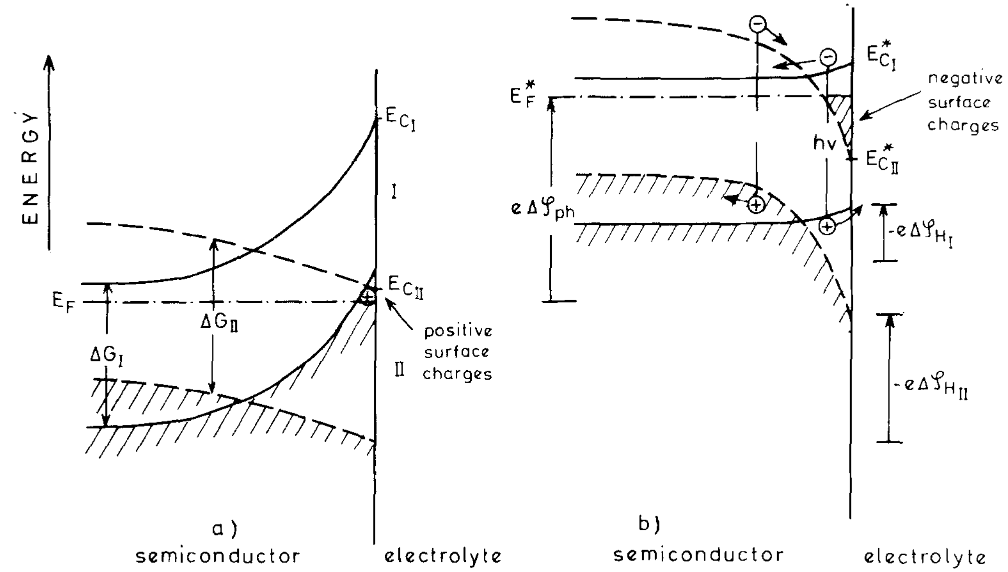

Fig. 8. Energy schemes visualizing the energetic situation resulting from the coexistence of two different semiconductors in the same electrode/electrolyte interface: I (———), II (– – –). (a) In the dark, (b) during illumination while producing a photovoltage exceeding the band gap of each semiconductor.

different material properties of the two semiconductors (Fig. 7). There will consequently always be a potential region in which a photocurrent spectrum of the investigated material shows an inversion of polarity as in Fig. 4.

At equilibrium in the dark, the Fermi level of both coexisting semiconductors must be the same in the interior of the electrode as well as at its surface (Fig. 8a). Taking into consideration the experimentally estimated band gaps and flat band positions, an energy scheme can be proposed in which the energy bands of the two semiconductors are bent in a different way; semiconductor I showing a positive bend and semiconductor II a negative one. In the interior, the common Fermi level is situated in the middle of the forbidden gap of semiconductor II while it is near the conduction band of semiconductor I. Near the interface, the Fermi level should consequently intersect the valence band of semiconductor I. A high concentration of surface charges will therefore have to be taken into account.

The situation in the electrode during illumination under open-circuit conditions is shown in Fig. 8b. The current voltage characteristic shown in Fig. 7 indicates that in the presence of light the anodic photocurrent of semiconductor I compensates the cathodic photocurrent of semiconductor II to produce a vanishing total current. This situation is achieved while semiconductor I has a smaller, positive bending and semiconductor II a larger, negative bending of energy bands (Figs. 7 and 8b). Since the position to the bulk Fermi level remains the same with respect of the energy-band positions of semiconductors I and II, it will have shifted upwards with a displacement proportional to the photovoltages generated. Simultaneously a potential drop in the semiconductor/electrolyte interface is to be taken into consideration to explain the magnitude of the photopotential. As can be seen in Fig. 8b, during illumination the Fermi level will intersect the edge of the conduction band of semiconductor II, thus producing a high concentration of surface charges. It is now well known that the surface position of energy levels in semiconductors is strongly affected under such conditions and considerable shifts are well documented [5, 14]. Important displacements of the energy band have been observed especially with layer-type semiconductors such as WSe_2, both as n-type and p-type [1, 2]. The remarkable dynamics of the interface of these materials as a function of different redox systems (I^-/I_3^-, $Fe(CN)_6^{3-/4-}$, Fe^{2+}/Fe^{3+}) [15, 16], the crystalline quality of the interface [8, 12] and the electrode potential applied [12] is consistent with our proposed model: in the absence of illumination, a Fermi level intersecting the valence band of semi-

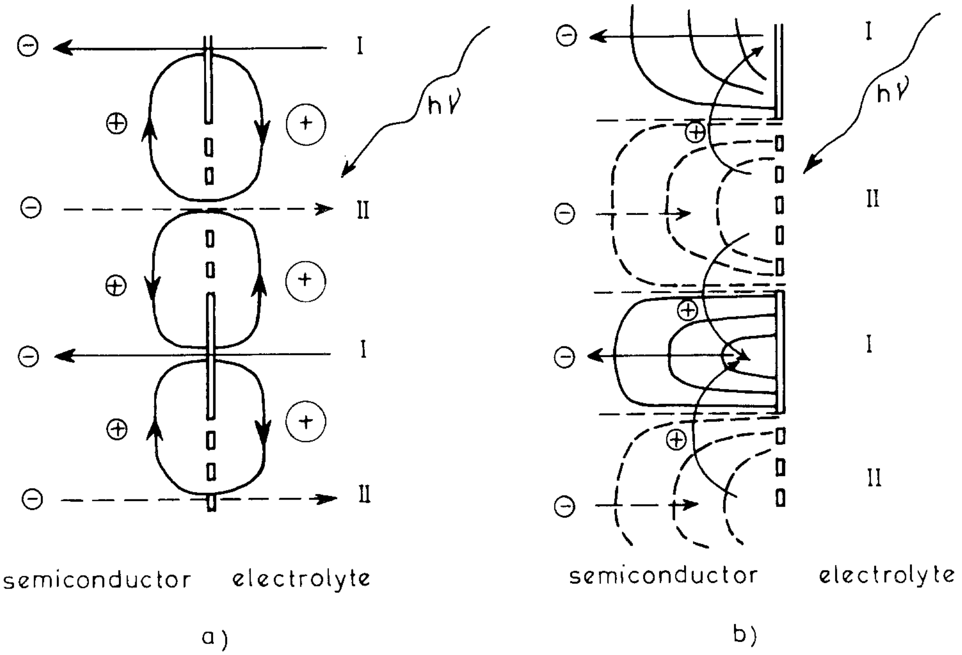

Fig. 9. Simplified presentation of the electrodes/electrolyte interface showing a circular current flow between patches of different coexisting semiconductor surfaces (a) during illumination with open-circuit conditions, (b) during solar energy conversion (the different polarity of adjacent space-charge regions and their effect on the drifting of charge carriers is shown).

conductor I already generates positive charges which displace the energy band position towards positive voltages (Fig. 8a). During illumination the Fermi level rises, thereby withdrawing these positive charges. A negative shift of the energy bands is the consequence. Since the Fermi level starts intersecting the conduction band of semiconductor II, negative charges accumulate at the interface thus shifting the energy bands still further to the negative (Fig. 8b). The combined action of the photoeffects generated in a heterogeneous interface consisting of an n-type and a compensated semiconductor together with a potential drop caused by a recharging of the interface can consequently explain the extraordinarily high photoeffect observed.

Some energetic aspects of the photosystem studied remain to be discussed. The most important question is to explain at what expense the energy is provided for a photoeffect exceeding the band gap of the semiconducting materials. In Fig. 9 we have schematically drawn the interface of our electrode consisting of patches of semiconductor I (full lines) and semiconductor II (broken lines). Since the photocurrents across these two semiconductor types have the opposite sign we have indicated the current flow with arrows. Even if the total photocurrent is zero, anodic and cathodic photocurrents will cross the interface (Fig. 7). In this case, however, the current flow will be circular (Fig. 9a). The surface will consist of microscopic local photoelements which can be compared to local elements of corrosive interfaces. These microscopic solar cells dissipate energy and it is at the expense of this energy that the photopotential of the macroscopic electrode can exceed the value of the forbidden gap. Fig. 9b shows the situation in the space-charge region of the heterogeneous semiconductor during solar energy conversion. In this case there will be a net anodic photocurrent crossing the semiconductor–electrolyte interface. However, part of the photocurrent generated will be lost to a circular current flow between the different semiconductor patches. The manner in which the flow of electrons is affected by the presence of a neighbouring semiconductor material of different conduction properties is seen in Fig. 9b, which depicts the adjacent space-charge layers of different signs. Photogenerated carriers will in part be deflected in the electric field between neighbouring semiconductor regions and reverse their direction of drift. They will be lost for the photocurrent generation but by polarizing the interface they are able to sustain a photovoltage which can be higher than the energy of absorbed photons.

Due to the dissipation of a part of the solar energy in a circular current flow, the photocurrent efficiency of the material investigated will certainly be lower than the photocurrent efficiency of homogeneous WSe_2/electrolyte junctions. However, some of the loss is compensated for by the higher photovoltage. The efficiencies which we have estimated above (between 1.5 and 5%) lead us to believe that satisfactorily high outputs may be obtained. There are still many experimental details to be clarified. We do not, for example, presently understand the reason for there being a maximum photovoltage between a few per cent and 12% solar intensity and not at full illumination. This phenomenon, as well as the unusual power output characteristics observed with electrodes 4 and 5 (Fig. 1), will only be completely understood when the photoelectrochemistry of each of the two semiconductors coupled in the electrode surface can be analysed separately. For the time being we cannot even provide information on the chemical or structural differences between the interfaces of semiconductors I and II. We believe that capacity measurements would be helpful for understanding the behaviour of these uncommon interfaces; at the present time we are making such measurements.

Although many details of the phenomenon investigated have not yet been clarified, the conclusions may be of importance. It became evident that heterogenous electrodes consisting of two different semiconductor materials interacting with each other in a favourable way can produce photovoltages exceeding the band gap of each compound. Such electrodes can be intentionally prepared in the form of polycrystalline samples. We do not need to emphasize the high voltage photoelectrodes may be valuable for a number of difficult research subjects such as, for example, the photodecomposition of water into oxygen and hydrogen.

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References

[1] J. H. Gobrecht, H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.* **82** (1978) 1331.

[2] H. Tributsch, H. Gerischer, C. Clemen and E. Bucher, *ibid* **83** (1979) 655.

[3] H. J. Lewerenz, A. Heller and F. J. Di Salvo, *J. Amer. Chem. Soc.* **102** (1980) 1877.

[4] Fu-Ren F. Fan, H. S. White, B. Wheeler and A. J. Bard, *J. Electrochem. Soc.* **127** (1980) 519.

[5] A. J. Bard, Fu-Ren F. Fan, A. S. Gioda, G. Nagasubramanian and H. S. White, 'Faraday Discussion 70: Photoelectrochemistry', Royal Society of Chemistry, London (1980).

[6] B. A. Parkinson, T. E. Furtak, D. Cranfield, K. Kam and G. Kline, 'Faraday Discussion 70: Photoelectrochemistry', Royal Society of Chemistry, London (1980).

[7] B. A. Parkinson, Contribution to *Faraday Discussion 70: Photoelectrochemistry, Oxford* (September 1980).

[8] W. Kautek, H. Gerisher and H. Tributsch, *J. Electrochem. Soc.* **127** (1980) 2471.

[9] C. Clemen, X. I. Saldaña, P. Munz and E. Bucher, *Phys. Stat. Solidi (a)* **49** (1978) 437.

[10] J. I. Pankove, 'Optical Processes in Semiconductors', Dover Publications, New York (1971) p. 323.

[11] H. Kallmann, G. Marmore Spruch and S. Trester, *J. Appl. Phys.* **43** (1972) 479.

[12] W. Kautek, H. Gerischer and H. Tributsch, *Ber. Bunsenges. Phys. Chem.* **83** (1979) 1000.

[13] H. Tributsch, H. Gerischer, C. Clemen and E. Bucher, *ibid* **83** (1979) 655.

[14] A. J. Bard, A. B. Bocarsly, F. R. Fan, E. G. Walton and M. S. Wrighton, *J. Amer. Chem. Soc.* **102** (1980) 3671.

[15] H. Tributsch, *Solar Enegy Mater.* **1** (1979) 257.

[16] S. Menezes, F. J. Di Salvo and B. Miller, *J. Electrochem. Soc.* **127** (1980) 1751.

[17] S. Menezes, F. J. Di Salvo and B. Miller, *J. Electrochem. Soc.* **127** (1980) 1751.