

## **IN SITU CHARACTERIZATION OF SEMICONDUCTOR-LIQUID JUNCTIONS: SURFACE OPTIMIZATION OF n-CuInSe<sub>2</sub>\***

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### **Summary**

Electrolyte electroreflectance and frequency dispersion of the impedance are used to characterize the dielectric properties of the interface between single-crystal n-CuInSe<sub>2</sub> and aqueous electrolytes, which was optimized to yield high solar conversion efficiency by chemical etching and thermal oxidation. The changes in the flat-band potential, the doping density and the density and distribution of the surface states were monitored as a function of the surface treatment. We shall demonstrate that the oxidized layer forms a non-insulating porous structure in which the electrolyte serves as the conductive medium.

The oxidation provides a mechanism for an order of magnitude reduction in the doping level of n-CuInSe<sub>2</sub> at the interface, which fully accounts for the increase in conversion efficiency.

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### **1. Introduction**

Recently, the attempts to use photoelectrochemical systems for direct conversion of solar energy to electrical and chemical forms have expanded beyond the classical search for an ideal compound in an ideal electrolyte that will meet the stringent requirements of optimized band gap, energetics and catalytic activity, together with long-term stability and low cost.

Following the increased activity in the chemical modification of electrodes to increase their selectivity to charge transfer reactions at the interface, an increasing amount of effort is being aimed at the chemical modification of the semiconductor-electrolyte interface (for a recent conference proceedings see for example ref. 1). For modified interfaces that amount to less than a monolayer it is clear that the electric field which serves as the driving force for the light-induced charge separation processes is located at the solid-electrolyte interface and that, as a result, the system

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\*Paper presented at the Fifth International Conference on Photochemical Conversion and Storage of Solar Energy, Osaka, Japan, August 26 - 31, 1984.

retains its photoelectrochemical character. In contrast, if the modified interface constitutes a separate phase with a thickness which is considerably larger than a monolayer, the location of the space charge layer is less obvious and as a result an uncertainty persists as to whether the space charge layer is at the solid–electrolyte interface or, alternatively, between two solid phases, in which case the system will be best described as a solid state photovoltaic device which is connected to an electrochemical cell. This is a central issue in photoelectrochemistry that was hotly debated at the previous meeting [2].

During the last few years, our laboratory has concentrated on the development of analytical tools for *in situ* characterization of the potential distribution at the solid–liquid interface (for a recent review see ref. 3). We have concentrated on three methods: frequency dispersion of the impedance, electrolyte electroreflectance and modulated photoluminescence. These methods are based on spectroscopic phase-sensitive detection of the system's response to modulation of the electrode potential.

The rest of this article will be aimed at the application of two of these methods, namely frequency dispersion of the impedance and electrolyte electroreflectance, which were used to investigate the nature of the interface between n-CuInSe<sub>2</sub> and an aqueous electrolyte in which the interface was optimized to produce a considerably improved photoelectrochemical photovoltaic cell.

## 2. n-CuInSe<sub>2</sub>

The work on this system was motivated by the reports that the efficiency of n-CuInSe<sub>2</sub> as a photoanode in a photoelectrochemical cell with polyiodide as the electrolyte can be considerably improved by chemical (etching) and thermal (oxidation) surface treatment [4]. Efficiencies as high as 11% under tungsten–halogen illumination were reported. The stability of the system was evaluated at short circuit and under maximum power conditions; more than 15 kC cm<sup>-2</sup> of photocharge was passed without change in the output characteristics. Since the surface treatment improves the performance characteristics in polysulfide and polyiodide, the experiments were carried out in both electrolytes.

The polysulfide had the standard composition 1 M S<sup>2-</sup>, 1 M S and 1 M NaOH and the polyiodide was the optimized electrolyte developed by Cahen *et al.* [4] for optimum stability and performance characteristics. The composition of this electrolyte is 6 M KI, 0.1 M Cu<sup>2+</sup> and 0.1 M In<sup>3+</sup> at approximately pH 6. The single crystals of n-CuInSe<sub>2</sub> were grown by Bachmann *et al.* [5] and were obtained through the Solar Energy Research Institute.

## 3. Electrolyte electroreflectance

Figure 1 shows the variations with the electrode potentials [6] of the electrolyte electroreflectance spectrum of n-CuInSe<sub>2</sub> in polysulfide solution.

Three transitions can be observed, marked as A, B and C in Fig. 1, located approximately at 1.02 eV, 1.175 eV and 1.26 eV respectively. Peaks A and C correspond to the low temperature spectrum that was reported by Shay *et al.* [7] and assigned to the direct gap transition and its spin orbit splitting. The position of peak B is at a higher energy than that observed for the crystal field splitting and, as a result, we are at this time uncertain as to the origin of this transition. Away from the flat band, the amplitude of the spectrum varies linearly with the modulation amplitude and the low field regime [8] was assumed to hold. In this regime the electrolyte electroreflectance signal is given by

$$\frac{\Delta R}{R} = - \frac{2eN_D V_{sc}}{\epsilon_s} L(h\nu) \quad (1)$$

where  $V_{sc}$  is the modulated amplitude,  $N_D$  is the density of the ionized donors,  $\epsilon_s$  is the static permittivity,  $e$  is the electronic charge and  $L(h\nu)$  is a spectral line shape function given by

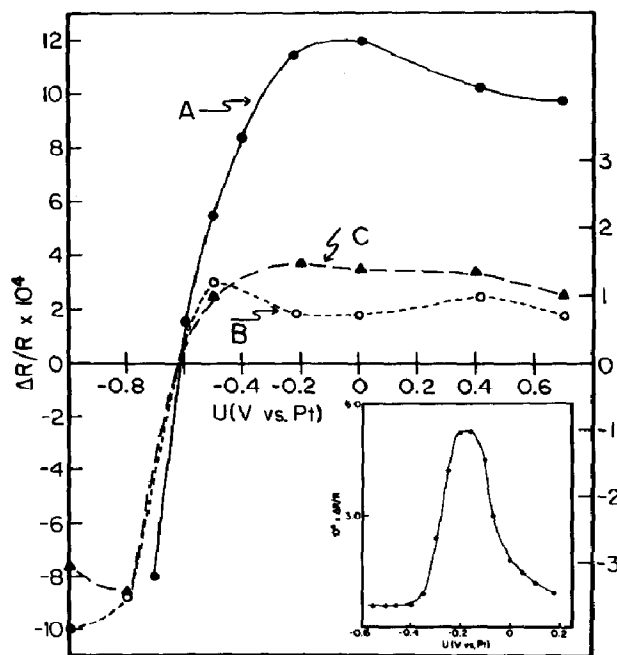
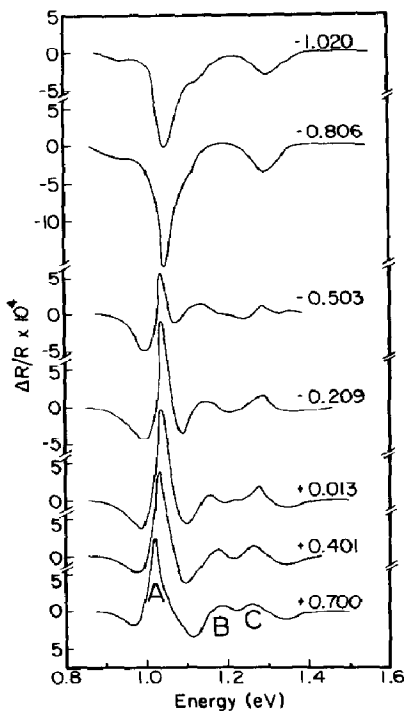


Fig. 1. Electrolyte electroreflectance spectra for single-crystal  $n\text{-CuInSe}_2$  in an aqueous polysulfide solution of composition 1 M  $\text{S}^{2-}$ , 1 M S and 1 M NaOH, as a function of the electrode potential measured with respect to a platinum electrode (resistivity,  $0.1 \Omega \text{ cm}$ ; mobility,  $700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).

Fig. 2. Variation in the amplitude of the three peaks in Fig. 1 with electrode potential after etching with 2% bromine-methanol for 10 s followed by washing in 10% KCN. The inset shows the variation in the electrolyte electroreflectance amplitude of peak A with the electrode potential before etching.

$$L(h\nu) = \text{Re}\{\exp(i\theta)(E - E_g + i\Gamma)^{-n}\} \quad (2)$$

where  $\theta$  is a phase factor,  $n$  determines the nature of the critical point,  $E_g$  is the energy gap and  $\Gamma$  is a broadening parameter related to the lifetime. The line shape of peak A was analyzed according to eqn. (2) with the following results [6]:  $E_g = 1.01$  eV,  $\Gamma = 0.04$  eV,  $\theta = -85^\circ$  and the transition corresponds to a three-dimensional critical point. The theory predicts that the amplitude of the electrolyte electroreflectance signal should be independent of the electrode potential. Figure 2 shows the dependence of the amplitude of the three peaks on electrode potential after etching in bromine-methanol solution. Figure 2, inset, shows the variation with potential of the amplitude of peak A before etching. After etching, the behavior is fully compatible with theory: the three peaks change sign at  $-0.62$  V measured with respect to a platinum electrode, which corresponds to the flat-band potential of the system, and at potentials positive to  $-0.3$  V (platinum electrode) the amplitude is independent of the potential of the electrode. The behavior before etching, as shown in Fig. 2, inset, is different. Most noticeable here is the sharp decline in the amplitude as we go to reverse bias. This phenomenon was observed earlier [9] and interpreted in terms of unpinning of the band edges (or pinning of the Fermi level). According to this argument the change  $dU$  in the electrode potential due to the modulation will be divided between the modulation of the potential drop  $V_{sc}$  in the space charge layer and the modulation of the potential drop in the Helmholtz layer. When this is taken into account, eqn. (1) will be modified to yield

$$\frac{\Delta R}{R} = -\frac{2eN_D}{\epsilon_s} \left(1 - \frac{e}{C_H} \frac{dN_{ss}^+}{dU}\right) L(h\nu) dU \quad (3)$$

where  $C_H$  is the capacitance of the Helmholtz layer and  $N_{ss}^+$  is the area concentration of the ionized surface states. The data in Fig. 2 were analyzed using eqn. (2) to yield approximately a monolayer of states with gaussian energy distribution centered around 0 V (platinum electrode) with a width of distribution of 0.1 eV. Within the accuracy of the electrolyte electroreflectance measurements, etching almost completely removes these states and eliminates the unpinning of the band edges.

When the surface of  $\text{CuInSe}_2$  is oxidized, three drastic changes take place in the electrolyte electroreflectance spectra: considerable broadening of peaks B and C, a decrease in the amplitude of the spectra and changes in the line shape with the electrode potential. We could not account for these changes on the basis of our present degree of understanding of electrolyte electroreflectance. New techniques are required that might shed some additional light on oxidized  $\text{CuInSe}_2$ .

#### 4. Impedance [10, 11]

The impedance spectrum of the unetched crystal in aqueous electrolytes did not give any comprehensible results. The impedance spectrum of the

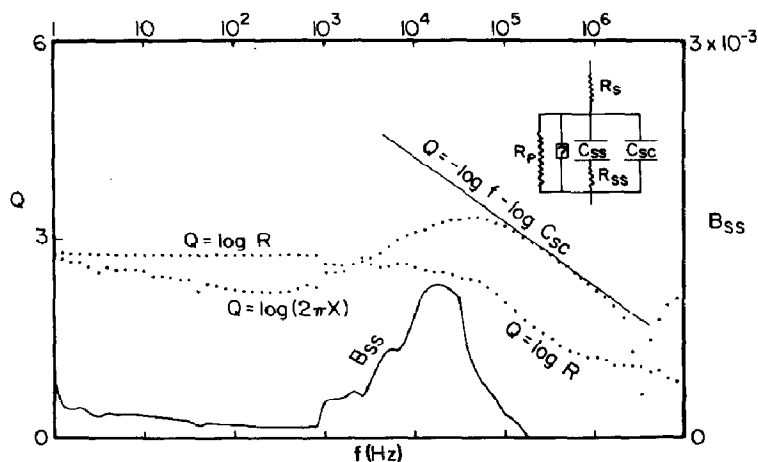


Fig. 3. Impedance response curves for  $n\text{-CuInSe}_2$  in a solution of composition 6 M KI, 0.1 M  $\text{CuI}_2$  and 0.1 M  $\text{InI}_3$  (area,  $0.045 \text{ cm}^2$ ; potential, 0 V (platinum electrode)).

etched crystal in polyiodide solution is shown in Fig. 3. This spectrum resembles closely the spectrum for an abrupt junction interface which we have observed in many other photoelectrochemical systems (see for example ref. 12). Accordingly, it was analyzed using the technique of relaxation spectrum analysis for parallel RC elements. The equivalent circuit is shown in Fig. 3, inset. Only the two fastest elements were evaluated. The box with the question mark symbolizes additional information in the low frequency range, which was not analyzed. The potential dependence of the passive elements was analyzed. The fastest-relaxing capacitive element  $C_{sc}$  obeys the Mott-Schottky relation over a limited potential range, from which a doping level of  $8 \times 10^{16} \text{ cm}^{-3}$  was evaluated. The Mott-Schottky relation shows pinning of the Fermi level near zero bias and near the flat band. The potential dependence of  $C_{ss}$  shows gaussian dependence, characteristic of surface states where two kinds of states are present: one state centered at  $-0.24 \text{ V}$  (platinum electrode) with a width of  $0.14 \text{ eV}$  and a density of  $4.6 \times 10^{12} \text{ cm}^{-2}$  and the other state centered at  $-0.6 \text{ V}$  (platinum electrode) with a width of  $0.053 \text{ eV}$  and a density of  $1.6 \times 10^{13} \text{ cm}^{-2}$ .

As the electrode is oxidized, the impedance, particularly its imaginary part, changes drastically. This can be seen in Fig. 4. Two peaks, marked I and II, can be seen in the imaginary part of the impedance. This behavior was seen before and is predicted to take place where two or more different dielectric materials are placed in series [13]. Such an equivalent circuit with two elements is shown in Fig. 4, inset. If all the elements are frequency independent and no additional charge accumulation modes are present, each peak is predicted to have a lorentzian line shape. This is true with respect to the high frequency peak but not for the low frequency peak. The high frequency capacitive element  $C_1$  was evaluated and its potential dependence indicates that it obeys the Mott-Schottky relation from which a doping level of  $7.5 \times 10^{15} \text{ cm}^{-3}$  and a flat-band potential of  $-0.7 \text{ V}$  (platinum electrode)

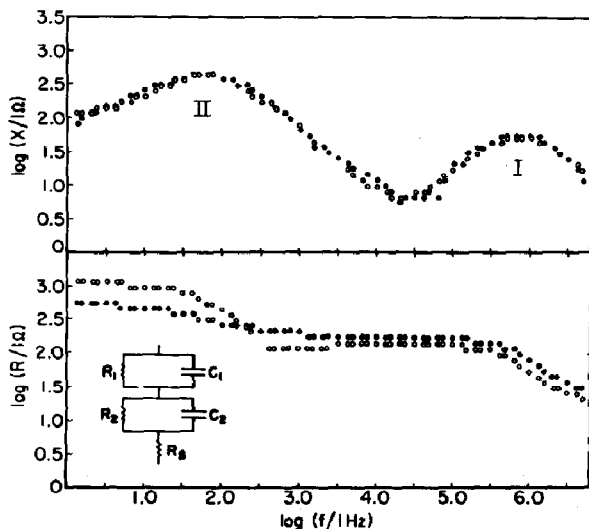


Fig. 4. Frequency dispersion of the real and imaginary parts of the impedance of the system which was described in Fig. 3 (the theoretical fit is according to eqn. 4; the parameters were adjusted to fit the imaginary part):  $\circ$ , theory;  $\bullet$ , experiment.

were derived. The doping level is about one order of magnitude lower than that for the same unoxidized crystal.

As mentioned before, the low frequency peak is not lorentzian. However, the high frequency part of this peak can be interpreted as originating from a single capacitive element. When the potential dependence of this capacitive element was evaluated, we again found it to obey the Mott-Schottky relation but for a p-type material with a flat-band potential of +0.2 V (platinum electrode) and a doping density of  $10^{23} \text{ cm}^{-3}$ . Such a high doping density would indicate a highly degenerate semiconductor; electron spectroscopy for chemical analysis and Auger analysis [14] have indicated that copper is absent in the oxide and that the oxidized layer is some form of indium oxide which is unknown in p-type form. If these results are to be taken literally, then it might be expected that the space charge layer would be located between the semiconductor and the conductive oxide with no direct contact with the electrolyte and that the device would operate as a solid state photovoltaic cell in series with the electrochemical cell. In that case, the photovoltaic activity and the impedance should be preserved in the absence of the electrolyte. Such an experiment was carried out and no photovoltaic activity was observed. The low frequency peak of the impedance disappeared and electrical measurements have indicated that the oxide is non-conductive. A solution to this apparent contradiction is to assume that the oxide is porous and that the conductivity is an ionic conductivity of the electrolyte within the pore structure. A general theory for closed-form calculation of the dielectric function of a composite media is known as the effective medium theory. For reasons that will be mentioned elsewhere, we

chose the differential form of the effective medium approximation [15]. According to this theory the complete dielectric function is given by

$$P = \frac{\epsilon - \epsilon_2}{\epsilon_1 - \epsilon_2} \left( \frac{\epsilon_1}{\epsilon} \right)^d \quad (4)$$

where  $P$  is the porosity,  $\epsilon$ ,  $\epsilon_1$  and  $\epsilon_2$  are the complex dielectric constants of the composite, the conductive medium and the insulating medium respectively, and  $d$  is a parameter smaller than unity which characterizes the geometry of the inclusion. The theoretical curves in Fig. 4 are based on this equation. Despite the fact that the fit is not perfect, when the number of parameters involved and the fact that the work on detailed understanding of this system is still in progress are taken into consideration, the combination of the solid state measurements and the fit of the impedance data to the theory provides strong support for the basic features of the model.

A theory for electroreflectance at an interface of a composite medium and a semiconductor is not yet available. Whether the unexplained features that we have observed in the electroreflectance of oxidized CuInSe<sub>2</sub> are due to the composite nature of the ambient is still to be demonstrated. An effort to fill this gap and to extend the theory of electroreflectance to include some form of effective medium approximation is now in progress.

## 5. Conclusions

I have discussed in some detail the applications of two analytical techniques, electrolyte electroreflectance and impedance spectroscopy, in the investigation of the dielectric properties of the interface between n-CuInSe<sub>2</sub> and two aqueous electrolytes and the changes that take place at the interface as a result of chemical modifications which were designed to optimize the performance of the photoelectrochemical device. As far as performance characteristics are concerned, the two most important results from the oxidation of the surface are the reduction in the doping level by one order of magnitude and the resulting increased width of the space charge layer on the semiconductor side of the interface and cleaning of the surface from fast recombination centers. The full simulation of the current-voltage characteristics as a function of the surface treatment, using the information from the spectroscopic measurement, will be published elsewhere [10]. More interesting for the general applications of chemically modified electrodes is our ability to obtain information on the resulting composite structures and to distinguish between electronic and ionic conduction mechanisms prevailing at the modified interfaces.

## Acknowledgment

This work was supported by the Solar Energy Research Institute.

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