

Optical determination of Fermi-level pinning using electroreflectance

R. P. Silberstein, Fred H. Pollak, Joseph K. Lyden, and Micha Tomkiewicz

Department of Physics, Brooklyn College of the City University of New York, Brooklyn, New York 11210

(Received 6 May 1981)

We have investigated the low-field electrolyte electroreflectance (EER) spectra of matte, polycrystalline, electrodeposited n -CdSe in the vicinity of the $E_0(A,B)$ transitions (direct gap at $\vec{k}=0$). As the applied bias voltage V_{dc} is varied from near flatband to depletion, the EER amplitude for electrodeposited CdSe decreases by a factor of ~ 40 . We interpret this decrease in EER signal as evidence of Fermi-level pinning, which we attribute to the presence of surface states.

The semiconductor-metal and semiconductor-electrolyte interfaces are of considerable importance from both a practical and fundamental point of view.¹ It is well documented that the barrier height in many semiconductor-metal interfaces is not determined by the difference in work function of the two materials but rather by the high concentration of semiconductor surface states at the interface²; the Fermi level is said to be "pinned" at an energy determined by the surface state distribution. The model for the semiconductor-liquid junction resembles, in many respects, the semiconductor-metal junction.^{3,4} The difficulty in studying metal and liquid junctions involves correlating the behavior of different systems which exhibit highly surface-sensitive phenomena: different metals in the first case and different electrolytes in the second. Few probes exist which are directly sensitive to the behavior of the space charge region (SCR), and which could be used to study Fermi level pinning effects *in situ*.

In this paper, we show for the first time how electrolyte electroreflectance (EER) can be used for simultaneous determination of not only the flat-band potential,⁵ but *the status of the Fermi level in situ*. We demonstrate that for a prototype system, consisting of polycrystalline CdSe in a S^{2-} -S-NaOH 1:1:1 M electrolyte, the nature of the semiconducting material is of prime importance in determining whether the Fermi level is pinned or not. While in single-crystal CdSe the Fermi level is unpinned up to potentials which are $\frac{2}{3}$ of the gap below the conduction band,⁶ the Fermi level in highly polycrystalline CdSe in the same solution is pinned. Using EER, we show that in this particu-

lar case the pinning process is a dynamic phenomenon, strongly dependent on the applied dc bias voltage.

Details concerning experimental techniques⁷ and the preparation, characterization, and EER spectra of single-crystal CdSe in polysulfide solutions have been published elsewhere.⁶ Samples of polycrystalline CdSe were prepared by cathodic electrodeposition of CdSe on a Ti substrate, resulting in matte, highly polycrystalline films 5 to 10 μm in thickness having a cauliflowerlike structure with grain size $\lesssim 3 \mu\text{m}$. When immersed in a solution of S^{2-} -S-NaOH 1:1:1 M with a Ni counterelectrode⁸ they form efficient and relatively stable photovoltaic photoelectrochemical (PEC) cells.^{7,9}

Due to the sensitivity of EER to the fields in the SCR, measurement of the EER spectra is useful in understanding the behavior of E_F . Figure 1 shows the EER spectra for CdSe at $T=300$ K for various values of the dc bias voltage V_{dc} , where representative spectra for the single-crystal material are shown in (a) and those for the electrodeposited films are shown in (b). For the single crystal, the EER line shape has a prominent peak near the fundamental energy gap (1.74 eV), corresponding to the $E_0(A,B)$ transitions¹⁰ [additional peaks are observed at ~ 2.16 eV, corresponding to the $E_0(C)$ transition, but are not shown in the figure]. For the electrodeposited film, however, only a single broad peak is observed, centered at 1.68 eV (7380 Å) with a full width at half maximum of ~ 0.05 eV independent of V_{dc} .

In order to gain further understanding of the relationship between the EER spectra and the applied ac modulation voltage V_{ac} , the equivalent cir-

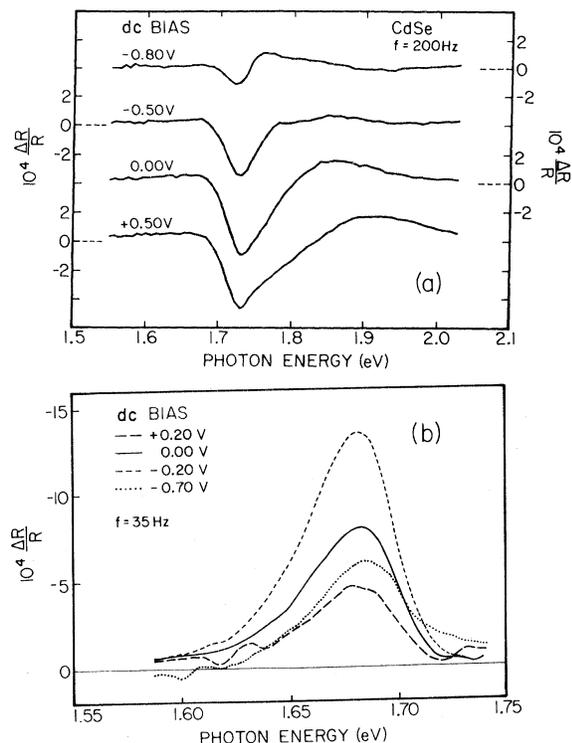


FIG. 1. EER spectra for CdSe for various values of applied dc bias voltage versus Ni counterelectrode (see Ref. 8): (a) single-crystal CdSe, using square-wave modulation 200 mV peak-to-peak at $f = 200$ Hz; (b) electrodeposited CdSe, using sinusoidal modulation 100 mV peak-to-peak at $f = 35$ Hz.

cuits for the PEC cells were determined from measurements of the complex impedance $Z(f)$ as a function of frequency f using a network analyzer.¹¹ For the single crystal, the equivalent circuit consists of passive elements whose values depend only on V_{dc} and are independent of f .⁶ On the other hand, the behavior of $Z(f)$ for electrodeposited CdSe could not be modeled by a small set of resolvable passive elements. For this reason it is particularly difficult to analyze the behavior of the SCR from the measurement of $Z(f)$ alone. The equivalent circuit assumed for this case consists of a frequency-dependent complex impedance $Z_1(f, V_{dc})$ in series with a constant resistance R_s . Although it is not obvious how the capacitance of the SCR is related to Z_1 , the EER measurements are directly sensitive to the electric fields in the SCR and hence can aid in understanding this relationship.

Aspnes has shown¹² for a fully depleted SCR that in the "low-field" regime the electroreflectance signal $\Delta R/R$ as measured by phase-sensitive detec-

tion is given by:

$$\Delta R/R = -(2eN_D V_{sc}/\epsilon_s)L(\hbar\omega). \quad (1)$$

In Eq. (1) V_{sc} is the fundamental harmonic component of the applied voltage across the SCR, N_D is the donor concentration (replaced by $-N_A$ for p -type materials), and ϵ_s is the static dielectric constant. The quantity $L(\hbar\omega)$ is a spectral line-shape function determined by the electric field direction and properties of the material. In the low-field regime, Eq. (1) is independent of bias voltage, modulation waveform, and field inhomogeneity over the penetration depth of the incident light.¹² To verify the low-field regime, we have measured the EER amplitude at $V_{dc} = 0$ for electrodeposited CdSe as a function of V_{ac} in the range 2–200 mV peak-to-peak (sinusoidal modulation) and have found a linear dependence. This implies that for a fixed modulation frequency and V_{dc} , the component of V_{ac} which appears across the SCR, i.e., V_{sc} , is directly proportional to that which appears across Z_1 . The EER signal can thus be used to probe the dynamic behavior of the SCR even though the SCR capacitance itself (C_{sc}) is difficult to measure by electrical means alone.

The significance of the EER measurement becomes apparent when the bias dependence of the EER amplitude for the single crystal is compared with that for the electrodeposited film, as in Fig. 2. Here we show the EER vector amplitude as a function of V_{dc} for the two forms of the material in the low-field regime using $f = 200$ Hz and sinusoidal $V_{ac} = 100$ mV peak-to-peak.⁸ Results for electrodeposited CdSe were obtained for $5 \text{ Hz} \leq f \leq 10 \text{ kHz}$ and were similar to those shown in Fig. 1(b). As shown in Fig. 2, the EER amplitude near the center of the main peak, at $\lambda = 7150 \text{ \AA}$ (1.73 eV) for the single crystal, goes through zero for $V_{dc} = -0.77$ V, close to the flatband voltage,^{5,6} while Fig. 1(a) shows that near this value ($V_{dc} = -0.8$ V), the overall line shape amplitude goes through a minimum.^{5,6} As V_{dc} is increased and the SCR is biased further into depletion, the EER signal for single-crystal CdSe in Fig. 2 increases until it becomes independent of V_{dc} for $V_{dc} \geq 0.2$ V. Further measurements reveal that no significant changes in the line shapes occur for V_{dc} as high as 1.0 V.

In contrast to the results for the single crystal, Fig. 2 also shows that the corrected¹³ amplitude of the EER at the peak of the polycrystalline line shape, $\lambda = 7380 \text{ \AA}$ (1.68 eV), decreases by nearly a factor of 40 as V_{dc} increased from -0.5 to 0.5 V.

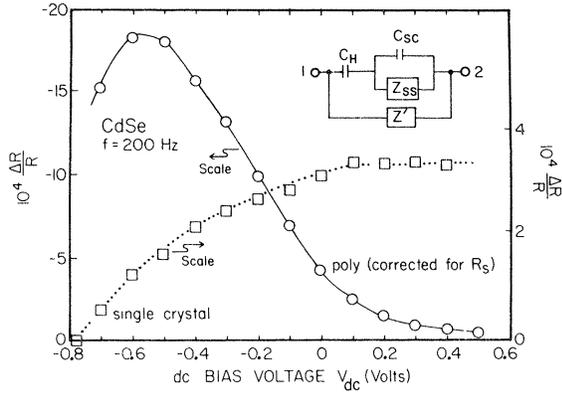


FIG. 2. EER signal amplitude versus dc bias voltage for PEC cells consisting of polycrystalline electrodeposited CdSe (solid curve) and single-crystal CdSe (dotted curve; see Ref. 6). The results for electrodeposited CdSe are shown after correcting for the ac voltage drop across R_s , and normalizing to the original signal at $V_{dc} = -0.4$ V. For both cells the modulation was a 100 mV peak-to-peak sinusoidal waveform with $f = 200$ Hz. The inset shows a schematic equivalent circuit for the interface impedance Z_1 , where C_H is the Helmholtz capacitance, Z_{ss} is the impedance of surface states at the given modulation frequency, and Z' is associated with possible disorder in the system (see Refs. 7 and 9).

This rapid decrease is a significant result which cannot be explained on the basis of the circuit elements we have introduced so far.⁴ As shown in Fig. 1(b), the linewidth is independent of V_{dc} and the peak position is invariant, except for a small shift which occurs for V_{dc} very close to the flat-band value. It is therefore unlikely that the EER decrease in Fig. 2 for $V_{dc} \gtrsim -0.5$ V is associated with field inhomogeneity.

We propose that the quenching of the EER amplitude as V_{dc} is increased toward depletion in Fig. 2 is optical evidence for Fermi level pinning in the electrodeposited material which might result from exchange of charge between surface states and the semiconductor bulk. As V_{dc} increases, the fraction of the modulation voltage across the SCR decreases as indicated by Fig. 2. As will be shown, this occurs when the density of surface states is very high and the relaxation of these states are faster than $1/f$. This relaxation might be bias dependent due to the nonideal dielectric properties of the polycrystalline material, thus considerably enhancing the effect of the surface states. In the inset of Fig. 2, we present a schematic equivalent circuit for Z_1 . Here the Helmholtz capacitance C_H , nor-

mally neglected in the absence of surface states, has been separated from Z_1 of the previous discussions, and C_{sc} is shown explicitly. The impedance Z_{ss} now contains all the elements associated with surface states, while Z' accounts for possible disorder^{7,9} in the system.

If the density N_{ss} of surface states is high enough, then at equilibrium ($V_{dc} = 0$) the Fermi level in the semiconductor will be determined by the distribution $N_{ss}(E)$ where E is electron energy.³ For a fixed dc bias we assume that a small change, ΔV (e.g., the modulation voltage), is applied directly across terminals 1 and 2. This change in voltage will be divided between the Helmholtz layer and the SCR (Refs. 3 and 14): $\Delta V = \Delta V_H + \Delta V_{sc}$ (see inset of Fig. 2). The quantity ΔV_{sc} , responsible for the EER signal, corresponds to the shift in the Fermi level of the semiconductor: $\Delta V_{sc} = \Delta E_F/e$. The shift in E_F results in a charge transfer ΔQ_{ss} to or from the surface states: $\Delta Q_{ss} = C_H \Delta V_H - C_{sc} \Delta V_{sc}$. We can also express ΔQ_{ss} approximately as $\Delta Q_{ss} = e N_{ss}(E_F, f) \Delta E_F$, where $N_{ss}(E_F, f)$ is the density of surface states per unit energy at the Fermi level, with relaxation times faster than $1/f$ (ΔQ_{ss} and N_{ss} are considered per unit area). Thus for $C_H \gg C_{sc}$,

$$\Delta V_{sc} = \frac{\Delta V}{1 + e^2 N_{ss}(E_F, f) / C_H}. \quad (2)$$

If the surface state density is small [i.e., $e^2 N_{ss}(E_F, f) \ll C_H$], or the relaxation times very slow, as is the case for the single crystal, all the modulation voltage ΔV appears across the SCR. However, for a large concentration of fast surface states [$e^2 N_{ss}(E_F, f) > C_H$] only a fraction of ΔV appears across the SCR, and this appears to be the case for electrodeposited CdSe. In addition, since $\Delta V_{sc} = \Delta E_F/e$, the Fermi level energy can be said to be partially pinned because ΔE_F is a function of N_{ss} in this case. Equation (2) can also be derived from the impedances in the circuit of Fig. 2, if ΔV is considered to be across terminals 1 and 2 and the impedance Z_{ss} is dominated by the surface state capacitance $C_{ss} \approx e^2 N_{ss}(E_F, f) \gg C_{sc}$ (see Ref. 7).

As V_{dc} is varied, E_F , and hence $N_{ss}(E_F, f)$, will also change. Since the EER amplitude shown in Fig. 2 (corrected for the effects of R_s) is proportional to V_{sc} in Eq. (1), $\Delta R/R$ in Fig. 2 is also proportional to the quantity $[1 + e^2 N_{ss}(E_F, f) / C_H]^{-1}$ in Eq. (2), where E_F is a function of V_{dc} .

We have shown that EER is a powerful probe

which can be used to study the semiconductor SCR, the flatband potential, and in particular the surface state distribution. In addition, we have demonstrated that electroreflectance measurements can be carried out on small-grain polycrystalline materials with matte surfaces. This technique therefore has a wide applicability to a variety of other semiconductor-electrolyte systems or semiconductor interfaces utilizing a transparent electrode.

ACKNOWLEDGMENTS

The authors would like to thank I. Ling and W. S. Parsons for preparing the CdSe films, and Professor M. Shaw of Wayne State University for useful discussions. Funding was provided by ONR Contract No. N00014-78-C-0718 and DOE Contract No. XS-9-832-1 through the Solar Energy Research Institute.

-
- ¹*Photoeffects at Semiconductor-Electrolyte Interfaces*, American Chemical Society Symposium Series, edited by A. J. Nozik (American Chemical Society, Washington, D. C., 1981), Vol. 146.
- ²A. J. Bard, A. B. Bocarsly, F. -R. F. Fan, E. G. Walton, and M. S. Wrighton, *J. Am. Chem. Soc.* **102**, 3670 (1980); F. -R. F. Fan and A. J. Bard, *ibid.* **102**, 3677 (1980).
- ³S. Roy Morrison, *Electrochemistry at Semiconductor and Oxidized Metal Electrodes* (Plenum, New York, 1980), Chaps. 4 and 5.
- ⁴S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969).
- ⁵F. Holtz, *Phys. Status Solidi A* **21**, 469 (1974); S. F. Pond, *Surf. Sci.* **37**, 596 (1973).
- ⁶M. Tomkiewicz, J. K. Lyden, R. P. Silberstein, and F. H. Pollak, in Ref. 1, p. 267.
- ⁷R. P. Silberstein, J. K. Lyden, M. Tomkiewicz, and F. H. Pollak, *J. Vac. Sci. Technol.* **19**, 406 (1981).
- ⁸The potential of the Ni counterelectrode was measured separately and found to be at -0.75 V versus saturated calomel electrode, and constant under the operating conditions discussed in this work (i.e., weak illumination and low dc current). An electrocatalytic coating of NiS is formed on the Ni electrode, at which the reduction of polysulfide species S_x^{2-} to S_{x-1}^{2-} provides the exchange current; see G. Hodes, J. Manassen, and D. Cahan, *J. Appl. Electrochem.* **7**, 181 (1977); and A. B. Ellis, S. W. Kaiser, and M. S. Wrighton, *J. Am. Chem. Soc.* **98**, 6855 (1976). The linearity of the EER signal as a function of V_{ac} (for the range $5 < f < 2000$ Hz) indicates that the Ni electrode is well behaved at 200 Hz.
- ⁹J. K. Lyden, M. Tomkiewicz, and M. H. Cohen, *Bull. Am. Phys. Soc.* **26**, 282 (1981); J. K. Lyden, M. H. Cohen, and M. Tomkiewicz, *Phys. Rev. Lett.* (in press).
- ¹⁰M. Cardona, K. L. Shaklee, and F. H. Pollak, *Phys. Rev.* **154**, 696 (1967).
- ¹¹M. Tomkiewicz, *J. Electrochem. Soc.* **126**, 1505 (1979); **126**, 2220 (1979). The techniques described here are applicable to the semiconductor-electrolyte interface *in general* and to single-crystal CdSe in particular as shown in Ref. 1, p. 267; a similar type of analysis should be valid for polycrystalline CdSe, provided surface states and surface morphology are taken into account.
- ¹²D. E. Aspnes, *Phys. Rev. Lett.* **28**, 913 (1972); *Surf. Sci.* **37**, 418 (1973).
- ¹³The data have been corrected for the effects of the series resistance R_s by taking into account the change in modulation voltage across Z_1 due only to the changing ratio $Z_1/(R_s + Z_1)$ determined electronically on a very similar PEC cell. The correction for R_s makes the decrease in EER signal, from near flatband to depletion, even more pronounced. For the single-crystal CdSe, correction for R_s was not necessary, due to the larger relative magnitude of Z_1 . We note, however, that the equivalent circuit in Fig. 2 is illustrative and highly simplified; a quantitative fit to the data is not presented here, since $N_{ss}(E, f)$ is not known. See especially Ref. 7.
- ¹⁴Because of the small hysteresis and the absence of anomalies in the I - V curves (under illumination and in the dark), we tend to rule out the formation of an *insulating* layer on the electrodeposited film.