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CHARACTERIZATION OF SURFACE STATES AT A SEMICONDUCTOR ELECTROLYTE INTERFACE BY ELECTROLYTE ELECTROREFLECTANCE SPECTROSCOPY

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Abstract - Supra bandgap and subband gap Electrolyte Electroreflectance is being used to characterize surface states at semiconductor liquid interfaces. The surface states can manifest themselves either through direct optical transitions as in the case of n - TiO₂ - aqueous electrolyte interface or through their effect on the response of the Fermi level to small changes in the electrode potential as in the case of single crystal CdIn₂Se₄ in polysulfide solutions.

We will present here, two modes in which Electrolyte Electroreflectance (EER) is being used to detect and characterize surface states at the semiconductor electrolyte interface. In the first mode, which is being demonstrated on single crystal TiO₂, direct optical transitions between the surface states and the conduction band, are being observed. In the second mode, demonstrated here on single crystal CdIn₂Se₄ in polysulfide solution, the surface states are responsible for Fermi level pinning which quenches the EER signal.

Sub-Bandgap EER - TiO₂: The potential distribution at the TiO₂ aqueous electrolyte interface with particular emphasis on the surface states and their dependence on various electrolytes was investigated in detail in our laboratory, using a variety of techniques. These techniques include impedance spectroscopy (1-4), supra and sub-bandgap photoreponse spectroscopies (2), photoelectrochemistry with single and double beam excitation (3) and EER (4). Three main groups of surface states were identified: One state that tails from the conduction band edge and is primarily responsible for the recombination of light generated minority carriers (3), second state which resides 0.8 eV below the conduction band and is being controlled by hydrogen adsorption (2) and a third state 1.3 eV below the conduction band which can be observed only when an adsorbing anion penetrates into the inner Helmholtz layer (4) and is responsible for catalysis of water oxidation. This last state is the subject of the work that will be presented in this section. Whenever comparisons can be made, satisfactory agreement exist between UPS measurements under UHV (5) and the in situ measurements. Details about the electrode, cell and the experimental techniques were previously published (1-4). The doping level of the TiO₂ is 5 x 10¹⁹/cm². Fig. 1 shows the EER spectra of TiO₂ in various electrolytes in the sub-bandgap region. All spectra were taken at a potential which shows a maximum response. The broad peak is centered around 1.3 eV and the peak position does not change with the electrolyte but the intensity of the peak does. Within the halogen series it follows the same trend as the expected strength of adsorption if the latter is dominated by substitution of the hydration shell of the ions (6). In all cases, the potential of the maximum response is 0.1 - 0.3 V more negative than the corresponding flatband potential. We interpret these results by concluding that the sub-bandgap EER originates from optical transitions between filled...
surface states, located 1.3 eV below the conduction band, and the conduction band. The EER signal can be detected only under conditions in which significant portion of the potential drop can modulate these transitions. The position of the EER peak is independent of the nature of the adsorbed species, but the intensity is strongly dependent on the electrolyte. In this sense the states must be intrinsic to the semiconductor and independent on the nature of the adsorbates. When the surface is fully solvated and the Helmholtz is free of adsorbed species, the surface states will interact with the solvent to shift their energies toward the band edges. With the adsorbed species substituting for the solvent, the states will resume their intrinsic energy, provided that the adsorption is purely electrostatic with negligible orbital interactions between the surface states and the adsorbate. Quantitative comparison between the density of these states and \( (N_D)^{2/3} \) give support to the UPS work\(^{(5)}\) that identify these states as defect states.

**FERMI Level Pinning - CdIn\(_2\)Se\(_4\):** In the low field regime the electroreflectance signal is given by:

\[
\frac{\Delta R}{R} = - \left( \frac{2eN_D V_{sc}}{\varepsilon_b} \right) L(\hbar\omega)
\]

where \( L(\hbar\omega) \) is a spectral lineshape function, \( V_{sc} \) - the modulated voltage across the space charge layer, \( N_D \) - the density of the ionized donors, \( \varepsilon_b \) - the static permittivity and \( e \) the electronic charge. The potential drop across the space charge layer can be expressed as:

\[
\Delta \phi_s = U - U_{fb}
\]

where \( U \) is the electrode potential and \( U_{fb} \) the flatband potential. Modulation of the electrode potential will be divided between the space charge layer and the Helmholtz layer according to (6):

\[
\delta U = \delta \phi_s + \delta \phi_o = V_{sc} + \delta \phi_o
\]

where \( \delta \phi_o \) is the potential drop across the Helmholtz layer. The change in the potential drop across the Helmholtz layer due to a change in the number of ionized surface states is given by (9):

\[
\delta \phi_o = n_s \delta \phi_s
\]

where \( C_H \) is the capacitance of the Helmholtz layer and \( n_s^+ \) - the density of the ionized surface states. Combining (1), (2), (3) and (4) will result in:

\[
\frac{\Delta R}{R} = K \left( 1 + \frac{e}{C_H} \frac{dN_{ss}^+}{dU} \right) dU
\]

where

\[
K = - \left( \frac{2eN_D}{\varepsilon_b} \right) L(\hbar\omega) + \frac{e}{C_H} \frac{dN_{ss}^+}{dU} = 0
\]

will represent the condition when the Fermi level is unpinned and any change in the electrode potential will result in corresponding change in the potential drop across the space charge layer, while \( \frac{e}{C_H} \frac{dN_{ss}^+}{dU} = 1 \) represent the condition in which the Fermi level is completely pinned and the EER signal will be reduced to zero. With \( K \) known, \( \frac{e}{C_H} \frac{dN_{ss}^+}{dU} \) can be directly determined from the potential dependence of the EER signal. Since changes in the flatband potential...
originates from the changes in the potential drop across the Helmholtz layer i.e., \( \delta \phi = \delta U_{fb} \) it follows from Eq. (4) and (5) that the changes in \( U_{fb} \) with the applied potential can be directly evaluated from EER without assuming any energy distribution of the surface states. Figure 2 gives the variation with potential of the EER signal of single crystal CdIn₂Se₄ in polysulfide solution with native surface and with photoetched surface. Full experimental details about this system and detailed analysis of the EER spectra will be published elsewhere.(10) Figure 3 shows the variations of \( U_{fb} \) with the applied potential that were calculated from the data in Fig. 2 by the method that was outlined here. Considerable degree of Fermi level pinning is evident under reverse bias conditions. We have evaluated \( K \) here, by assuming that at the potential where the signal is maximum there is no pinning. Detailed analysis of these curves, assuming Gaussian distribution of the surface states, strongly suggest that the pinning is due to a complete monolayer of adsorbed sulfur ions. (10)

**Figures:**

![Figure 1](image1.png)

**Figure 1** - Sub-band-gap EER spectra for \( n - \text{TiO}_2 \) in different electrolytes. Modulating voltage is 200 mV peak to peak.

![Figure 2](image2.png)

**Figure 2** - Variation of the EER signal with the potential for CdIn₂Se₄ in aqueous polysulfide. (a) - Before Photoetching (photon energy = 1.8 eV) (b) - After Photoetching (photon energy = 2.0 eV). Modulating voltage = 0.2 V peak to peak.

![Figure 3](image3.png)

**Figure 3** - Shift in the flatband potential with the potential for CdIn₂Se₄ in aqueous polysulfide, before (a) and after (b) photoetching.
References -

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