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CHARACTERIZATION OF SEMICONDUCTOR ELECTROLYTE INTERFACE BY MODULATED PHOTOLUMINESCENCE

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Abstract - We will show that photoluminescence, modulated by small periodic changes of electrode potential serves as a powerful tool for monitoring the potential distribution at the semiconductor electrolyte interface. Results will be presented for thin film and single crystal CdSe in electrochemical photovoltaic cells.

Previous studies (1) have shown that as CdSe electrode is aged under illumination in polysulfide electrolyte, an exchange reaction occurs in which Se is replaced by S at the surface of the electrode. We have shown (2,3) that photoluminescence and Raman scattering can be used for in situ determination of the slow chemical changes that occur on the surface of such an electrode. Since the electric field in these systems is localized at the interface we have decided to increase the sensitivity of these techniques by modulating the electrode potential and monitoring through phase sensitive detection the component of the photoluminescence which is in phase with the modulated electrode potential. We will summarize here the main results on the new electrodes of both single crystal and polycrystalline CdSe in Na2S/S/NaOH 1/1/1M. Details concerning the electrode preparation, the construction of the cells, the photovoltaic performance of these devices and their electrochemical, spectroscopic and photoelectrochemical characterization were previously published (2,3,4). The photoluminescence setup was also previously described (2,3) and this setup was modified to enable us to modulate the DC bias with an AC signal (f = 44 Hz, p.p. amplitude 0.2 V) and to use phase sensitive detection to monitor the luminescence. The modulated photoluminescence spectrum is similar to the unmodulated one, which was described earlier (3) and consists of unresolved contributions of free excitons, bound excitons and donor acceptor pairs which can be fully resolved only at 4.2°K. The variation of the peak intensity with the modulation amplitude, was found to be linear over an extended modulation range.

Fig. 1 - Variation of the modulated photoluminescence peak intensity with electrode potential, for single crystal CdSe in S_2/NaOH solution.
Figure 1 shows the variation of the modulated photoluminescence with electrode potential for the single crystal electrode. Identical results were observed with the polycrystalline electrode. In both cases the signal is strong in two potential regions: region $-A-$ close to the flatband potential and region $-B-$ around the rest potential, which in this case coincides with the potential under short circuit conditions.

The signal in region $-A-$ fits well with the dead layer theory\(^{(5)}\) which predicts that dissociation of the excitons in the space charge layer will compete effectively with the radiative relaxation. Accordingly, within the Mott-Schottky approximation, the amplitude will vary with the potential in the following way:

\[
\Delta I_f = \frac{-0.5\alpha \phi I_a \left( \frac{2\epsilon_o K}{eN_p} \right)^{1/2} \exp \left(-\frac{W}{W}\right)}{(U - U_{fb} - kT/e)^{1/2}} \Delta U
\]

where $\phi$ is the quantum efficiency at the flatband potential ($W = 0$), $W$ - the thickness of the space charge layer given by:

\[
W = \frac{2\epsilon_o K}{eN_p} (U - U_{fb} - kT/e)^{1/2}
\]

$\alpha$ is the absorption coefficient, $I_a$ - the excitation light intensity, $\epsilon_o$ - the permittivity of free space, $K$ is the relative dielectric constant, $N_p$ the effective doping concentration, $U$ - the electrode potential and $U_{fb}$ the flatband potential.

The signal in region $-B-$ varies linearly with the excitation light intensity as required by Eq. 1. In addition Fig. 2 compares the doping level obtained from Mott-Schottky capacitance plot and the one obtained from the modulated photoluminescence, using Equation 1. They agree within factor of two - $3.6 \times 10^{17}$ cm$^{-3}$ from the capacitance data and 7.2 $\times 10^{17}$ cm$^{-3}$ from the photoluminescence. The signal in region $-B-$ does not follow the dead layer theory. It varies linearly with the square of $I_a$ and is being reduced to zero in the absence of polysulfide. This is true for both the single crystal and the polycrystalline electrodes.

We conclude that the signal in region $B$ appears when the Fermi level of the semiconductor coincides with the potential of the surface states which are created by the adsorption of the sulfide ion. At this potential, the electric field at the surface is being screened by the ions, preventing the dissociation of the excitons and promoting radiative recombination. Full account of these results will be presented in the full manuscript that will follow.
References


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