The long range goal of our investigations is to understand the dynamics of heterogeneous electron transfer reactions. The primary method we use to monitor the carrier dynamics is the fluorescence of the bandgap emission. This all optical approach circumvents the RC limitations of photopotential and photocurrent methods. Before such studies on a reactive system can be informative, it is necessary to understand the dynamics of the photogenerated carriers under nonreactive conditions. Presently we are concentrating on carrier dynamics in the materials, cadmium selenide (CdSe) and cadmium sulfide (CdS). Under these conditions the carriers recombine either directly or through intragap electronic states.

Modeling Carrier Capture

As discussed in last year's progress report to the DOE and in our two recent papers [1,2], the diffusion model for carrier capture used by previous workers has significant limitations in describing the carrier recombination in semiconductor electrodes. In this past year we have identified three ways in which the properties of the electrode need to be better modeled so that the carrier dynamics can be adequately treated.

First the radiative recombination of the electron/hole pairs needs to be treated properly in order to describe the fluorescence decay characteristics. Although the material we are studying is n-type with a dopant density on the order of $10^{16}$ to $10^{17}$ cm$^{-3}$, the radiative decay is not well described as being first order. A unimolecular decay rate is a common assumption and used in the diffusion model discussed previously. Even with the relatively weak pulses of a synchronously pumped dye laser system ($10^{13}$ photons per pulse) the material is under high injection at early times. Under these conditions the radiative decay of the carriers should be described as second order, i.e. the collision of a hole and an electron. We have performed two intensity studies in order to show that the materials under study (both CdS and CdSe) undergo a transition from bimolecular recombination ($I^2$ dependence) at early time to unimolecular (I dependence) at long times. The first study is the steady state fluorescence intensity as a function of incident laser power. This study leads to a dependence of the fluorescence counts on the laser intensity to the 1.3 power, i.e. $I^{1.3}$. The second study probes the fluorescence decay curve at different laser intensities. Presently these curves are being analyzed. If the discussion above is accurate we will find the early time part of the fluorescence to be quadratic in intensity.
and the long time part of the fluorescence to be linear in intensity.

A second area in which the model fails is the manner in which the surface recombination is treated. In this model the minority carriers (in our case holes) simply disappear at the interface with some constant probability. We now think that the recombination most likely occurs through interfacial states that have a finite population (or occupation) time. Such a scheme leads to a recombination probability at the interface which is a function of time. We have two pieces of evidence for this phenomenon. The weaker piece of evidence is the computer modelling studies (see enclosed reprint) performed by us which indicates that a trap population lifetime on the order of 15 to 20 ps could explain the trends we observe in the decay curves. The stronger piece of evidence is a subbandgap illumination experiment. We find that subbandgap light incident on the electrode at the same time as the fluorescence decay experiment is performed leads to faster fluorescence decay curves. This observation is consistent with the subbandgap light depopulating the filled traps and hence increasing the recombination probability at the interface.

Lastly the model assumes, for simplicity, that the semiconductor bands are flat under illumination. In fact we find that the illumination is weak enough that the bands appear to be bent, at least at long times. This conclusion implies that a drift term should be included in the diffusion equation which models the decay curve. We believe the bands are bent because the fluorescence decay curve shows a dependence on the bias voltage applied to the electrode. The diffusion equation has been solved under these conditions in the steady state and this solution can be extended to the time dependent case.

Modifying the Interface

In order to clearly demonstrate the sensitivity of the fluorescence decay to surface recombination and to begin to control the recombination of carriers at the interface, we have pursued the chemical derivatization of the interface. In particular we have derivatized the CdSe electrodes with different silane groups \( \text{Si}(\text{Me})_2\text{R} \) where \( \text{R} \) is methyl, phenyl or methoxy, and we have derivatized CdS with thiocarbonate (\( \text{CS}_3^- \)).

We have studied the silane derivatives most extensively and they are discussed here. The derivatization is verified by secondary ion mass spectrometry (SIMS) which clearly shows the presence of these groups. The fluorescence decays (see Figure 1) also show a clear dependence on the derivatization and apparently on the nature of the derivative. At present these are the only two observations which show strong variations. The electrochemical
properties of surface photovoltage and flatband potential are unchanged by this treatment. We do find that the electrodes more readily equilibrate with the solution when these layers are formed but at present this is a qualitative assessment. The change in the fluorescence decay appears to be correlated with the electron withdrawing character of the R group. At present we do not understand the origin of this correlation. We are studying the steady-state photocapacitance spectra of these derivatized layers in order to ascertain if this correlation has its origin in the energy spectrum of the surface states.

![Figure 1: The fluorescence decay curves for the chemically derivatized interfaces are shown (1 is phenyl, 2 is methoxy, and 3 is trimethyl). The unlabeled curve is the clean surface.](image)


During the coming year we will pursue the avenues opened in the first two years of this work and begin the development of time-resolved photocapacitance spectroscopy.

1) The major focus of the work this year will concern the chemical modification of the interface. We plan to further study the silane modified electrodes and to develop different and hopefully better defined interfaces. The studies of the silanized interfaces will focus primarily on determining if they stabilize the interface and how they modify the fluorescence decay (e.g. a surface state energy shift, a difference in surface coverage for the different derivatives, or some other process). The second aspect of this work is to pursue the formation of other derivatives, namely sulfur and selenium based compounds whose size is well suited to the
lattice spacing of the crystal lattice. These avenues will be pursued by two of the graduate students (Shumaker and Dollard).

2) The equipment for the time-resolved photocapacitance spectroscopy has been ordered and should arrive by early fall. The third year graduate student (K. Liao) will begin construction the apparatus this fall and develop this technique during this fiscal year.

3) A third focus will be to develop theoretical models for the carrier dynamics and simulations of carrier diffusion. In particular, the influence of a space charge field and of trap filling will be quantitated.

STUDENTS

Presently three graduate students are active on this project (M. Shumaker, W. Dollard and K. Liao). Two students (M. Shumaker and W. Dollard) are focussing on the CdSe material in order to complete the progress described above. The other student (K. Liao) is working on the similar material CdS so that we can begin to generalize our observations and our chemistry. Liao is also developing the time-resolved photocapacitance spectroscopy.

PUBLICATIONS


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