

**A charge-induced absorption-edge shift  
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formation of H<sub>2</sub>O in the reaction of H<sub>2</sub> and O<sub>2</sub> on Ni(100) surface is a hexagonal OH compound,<sup>15,16</sup> and that for the NH<sub>3</sub> formation reaction is also a c(2×2) ordered surface compound. These facts might suggest that the two-dimensional gaslike model assumed in the traditional mechanism such as the Langmuir-Hinshelwood mechanism may not be applicable in these cases, and the reaction of such ordered intermediates may proceed some times along the domain boundaries of the ordered intermediates. For this reason,

the formation mechanism of such key compounds will be an important object to be solved.<sup>17</sup>

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## A Charge-Induced Absorption-Edge Shift in CdS Semiconductor Films

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By application of either a negative or positive potential of sufficient magnitude across the interface between an evaporated CdS film and MeCN solution, a charge-induced absorption-edge shift toward the blue was observed. The blue shift is explained in terms of a Burstein shift, i.e., an increase in the optical band gap because of population of the conduction band.

We report, for the first time, the observation of a charge-induced absorption-edge shift of CdS semiconductor thin films using a spectroelectrochemical technique. This electrochemically induced shift provides evidence to support our recent model,<sup>1,2</sup> which predicts that, in excess electron induced degenerate semiconductors, the Fermi level in the conduction band rises as the electron concentration,  $n$ , increases. The optical absorption edge involves vertical transitions from the filled band to the lowest unfilled level in the conduction band because of momentum conservation. Thus,  $E_{g,opt}$ , the optical energy gap, is a function of  $n$  in degenerate n-type samples. A similar argument holds for excess hole induced degenerate semiconductors. In either case,  $E_{g,opt}$  will be larger than the minimum separation between the bands ( $E_g$ , the width of the forbidden energy gap), as shown in Figure 1. This can lead to an absorption-edge shift toward the blue.

CdS semiconductor thin films (ca. 200 Å thick) used as working electrodes were made by evaporating highly purified CdS powder (99.999%, Aldrich Chemical Co., Milwaukee, WI) onto indium (tin) oxide coated glass slides in a vacuum chamber (ca.  $2 \times 10^{-6}$  Torr). The films were not intentionally doped or annealed. The surfaces of these films were quite smooth, as observed under a scanning electron microscope (×30 000), but were still rough on the atomic scale, as revealed by scanning tunneling microscopy. Since the substrates were also rough, we could not determine the size of the CdS particles in the film. The electrochemical cell, which was fitted with two flat windows so that the analysis beam could pass perpendicularly and uniformly through the electrode, was placed in the cell chamber of an HP Model 8451A (Hewlett-Packard, Palo Alto, CA) diode array spectrophotometer. During the measurements under different applied potentials, the cell chamber remained closed and data were stored in the computer. A platinum flag was used as the counter electrode with a silver quasi-reference electrode; the potential of the CdS film was controlled with a Princeton Applied Research (PAR) Model 173 potentiostat (Princeton, NJ). All experiments were carried out in acetonitrile ("photrex" reagent, J. T. Baker, Inc., Phil-

lipsburg, NJ) containing 0.1 M tetra-*n*-butylammonium fluorophosphate (electrometric grade, Southwestern Analytical Chemicals, Inc., Austin, TX).

Figure 2 shows the charge-induced absorption-edge shifts. Note that potential only remained at the applied value for a few seconds for each measurement; the labels a, b, c, and d in this figure indicate the experimental sequence. The usual, open-circuit absorbance of CdS film appeared at 0 V. The absorbances at wavelengths longer than those of the band gap of bulk CdS (2.4 eV or 520 nm) are probably attributable to defect or surface states at energies near the band edges that are especially important in these thin films composed of small particles. However, when a potential of +2 V was applied, a blue shift of about 12 nm was produced, as shown in Figure 2b. We attribute this shift to positive charging of the semiconductor, making it degenerate and leading to an  $E_{g,opt} > E_g$  (Figure 1b). Since the Franz-Keldysh effect can only induce an absorption-edge shift toward longer wavelengths,<sup>3,4</sup> the observation here has to be attributed to an excess charge effect or Burstein shift.<sup>5</sup> Depopulation of the band gap states, for example, near the valence band edge, under these conditions would lead to an absorbance decrease in the long-wavelength region, as shown. The absorption edge returned to that of  $E_g$  when the potential was stepped back to 0 V (Figure 2c). Note that an almost complete recovery could also be obtained when a negative potential of about ca. 0.4 V was applied. At -1 V, a blue shift of about 9 nm was observed (Figure 2d) with a decrease in the absorbance at the foot of the curve. In this case, the excess negative charge raised the Fermi level into the CdS conduction band (Figure 1a) causing filling of the band gap states, if present, near the conduction band edge, again causing a decrease in the absorbance at longer wavelengths. According to our model,<sup>1</sup> this shift corresponds to about four excess electrons on a CdS particle with diameter of 70 Å. If the potential was then changed from -1 to 0 V, the spectrum again returned to the original one.

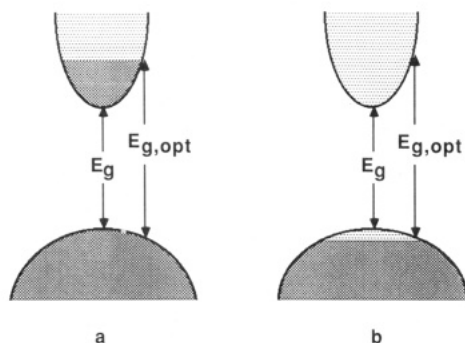
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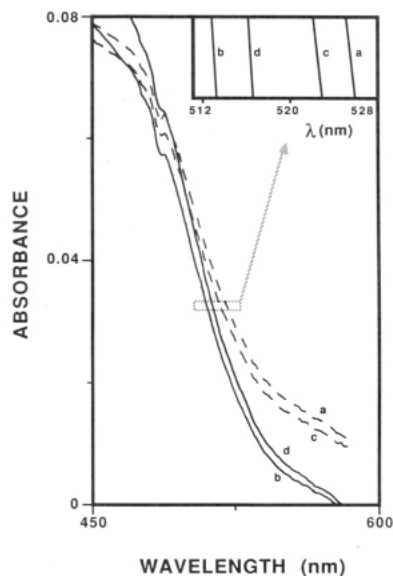
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**Figure 1.** Absorption-edge shift in the energy-momentum diagram of excess electron (a) and excess hole (b) induced degenerate semiconductors.



**Figure 2.** Absorption spectra of CdS semiconductor film under different potentials: (a) 0 V, (b) +2 V, (c) 0 V, (d) -1 V vs Ag in MeCN solution.

This reversible absorption-edge shift could be observed for at least five cycles of potential. Usually, an inversion surface layer can be created at certain potentials, even for heavily doped bulk semiconductors. For example, the surface of silicon with an electron concentration of  $6 \times 10^{19} \text{ cm}^{-3}$  could be changed to p-type when a potential of 3 V was applied at the semiconductor/electrolyte interface.<sup>6</sup> We cannot be more quantitative about the distribution of charge within the CdS particles that constitute the 200-Å-thick film. It seems likely that the charges are at the surface of the particles. If a degenerate layer only 10 Å thick formed on a CdS particle of 80-Å diameter (representing more than 50% of the CdS particle volume), this layer would show decreased absorbance at the longer wavelengths in the band edge region and higher absorbances at shorter wavelengths compared to the case of the original particles. This would produce the observed blue shift. Even if the film is considered an undoped (intrinsic) uniform layer of CdS 200 Å thick, with the total applied voltage drop across the film, a degenerate surface layer  $\sim 40 \text{ Å}$

thick (i.e.,  $\sim 20\%$  of the total film thickness) would develop. Interestingly, a detectable blue shift was only obtained when the applied potential was positive of +1.85 V or negative of -0.85 V. The sum of these two values is greater than  $E_g = 2.4 \text{ eV}$ , suggesting that no effective charge could be obtained when the Fermi level was located within the energy gap, consistent with our model.

Similar measurements with indium (tin) oxide coated glass without a CdS film indicated that no contributions to the blue shifts came from the substrate. Moreover, we found no evidence of CdS decomposition in our experiments. As confirmed by cyclic voltammetric studies, the dark current was only a few microamperes over the entire potential region used. This agrees with a recent study of CdS corrosion,<sup>7</sup> where cathodic decomposition of CdS started negative of about -1.4 V (SCE), and only very low dark currents ( $< 5 \mu\text{A}/\text{cm}^2$ ) were seen, even at positive potentials as high as +10 V (SCE) in an oxygen-saturated 0.1 M KCl solution.<sup>7</sup>

Though CdS usually appears as a n-type semiconductor, p-type CdS and CdS p-n junctions have been reported.<sup>8-12</sup> A positive charge induced p-type CdS surface that does not decompose might be attributed to partial compensation of the charge by anions at the surface and in the double layer.

Heavy doping is frequently employed to make bulk degenerate semiconductors, but observation of blue shift has been restricted to only a few semiconductors, such as InSb,<sup>13-15</sup> which have very small energy gaps. We show here that spectroelectrochemical techniques can be used to study this shift on thin films or small particles of large-gap semiconductors. The application of potential across the semiconductor/liquid interface can produce either excess electrons or excess holes and induce blue shifts in the absorption edge. These studies support the excess-charge model of photoeffects on colloidal semiconductor particles.<sup>16-26</sup>

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