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Semiconductor-Olefin Adducts. Photoluminescent Properties of Cadmium
Sulfide and Cadmium Selenide in the Presence of Butenes

by

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Direct evidence for adduct formation between butenes and etched, single-crystal n-CdS and n-CdSe[CdS(e)] surfaces has been obtained from photoluminescence (PL) measurements. Exposure of CdS(e) to butenes causes enhancement of the solids' band edge PL relative to a N_2 ambient. For 30% mixtures of the olefins in N_2, the magnitude of the enhancement follows the order, 1,3-butadiene > cis-2-butene ≃ trans-2-butene > isobutylene ≃ 1-butene, and correlates with the olefin basicities, based on photoionization potentials. Enhancements in PL intensity can be fit to a dead-layer model, allowing the determination of the reduction in depletion width in the semiconductor resulting from olefin exposure; depletion width reductions reach a few hundred Angstroms for adducts of 1,3-butadiene with CdS(e). The PL changes were used in conjunction with the Langmuir adsorption isotherm model to yield equilibrium constants for adduct formation of 1,3-butadiene with CdS(e) of 9 ± 4 atm^{-1} at 293K. Surface interactions that may contribute to the observed PL changes are discussed.

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The ability of irradiated semiconductors to mediate a variety of organic reactions, including the isomerization and oxidation of olefins, has aroused considerable interest.[1] These transformations must be crucially dependent on the binding of the molecule to the semiconductor surface. Although reaction intermediates have been studied,[1] direct evidence for simple olefin adducts with semiconductor surfaces has not, to our knowledge, been reported.

We have recently demonstrated that photoluminescence (PL) from semiconductors is affected by adduct formation with gaseous Lewis acids and bases: relative to a N_2 ambient, band edge PL from etched, single-crystal n-CdS and n-CdSe [CdS(e)] is increased in the presence of Lewis bases like amines and decreased by exposure to Lewis acids like SO_2.[2]

We report herein that this methodology may be extended to a family of unsaturated hydrocarbons, the butenes. Specifically, we demonstrate that exposure of CdS(e) substrates to butenes leads to PL enhancements that can be correlated with the basicities of the butenes; that the PL changes can be fit to a dead-layer model, permitting the semiconductor's depletion width to be tracked between gaseous ambients; and that the PL changes are described by a Langmuir adsorption isotherm model, allowing
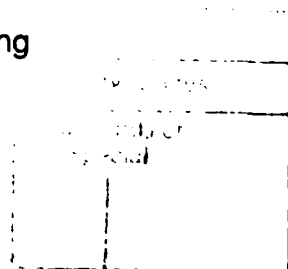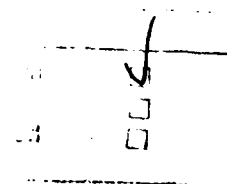
determination of equilibrium constants for adduct formation. The use of

different etchants, 0001 and 000$\overline{1}$ CdS(e) crystal faces, and other

unsaturated hydrocarbons provides some insight into the molecular

interactions underpinning the observed PL effects.

Experimental Section

Materials and Sample Preparation. The following gases were

used as received from Matheson: $\underline{n}$-butane (95.0%); 1,3-butadiene (99.0%);

$\underline{cis}$-2-butene (95.0%); $\underline{trans}$-2-butene (95.0%); 1-butene (99.0%);

isobutylene (99.0%); ethylene (99.5%); allene (93%); acetylene (99.6%); and

propyne (99.0%). Nitrogen (99.5%) was obtained from Badger Welding.

Impurities present in the hydrocarbons, determined by a Kratos MS25

GC/MS system, cause negligible PL changes at the concentrations present.

Methanol, bromine (Fisher; 99.9%), and electronic grade HCl (Columbus

Chemical) were used as received for etching. Single-crystal, vapor-grown

$\underline{c}$-plates (10 x 10 x 1 mm) of n-CdS(e) with resistivity of ~2 Ω-cm were

obtained from Cleveland Crystals, Inc., Cleveland, OH and were prepared

for use by scoring and breaking into ~4 x 4 x 1-mm pieces. One of two

etching procedures was then employed. In one method, samples were

alternately wiped and etched (Br_2/MeOH; 1:30 v/v; 5 s) until the shiny

0001 Cd-rich and matte 0001 S(e)-rich faces were observed, and then ultrasonicated in MeOH. The second etch consisted of exposure to conc HCl for 5 s, followed by a rinse in MeOH. Samples were edge-suspended with DUCO cement from a glass rod and left in air until use.

Gas-Handling Apparatus. The all-glass setup used for exposing the semiconductor to pure N_2 or to mixtures of the hydrocarbons in N_2 under flow conditions has been described.[2a] All such experiments were conducted at a flow rate of 100 mL/min. An apparatus permitting static measurements for adsorption isotherm experiments has also been described.[2a] A search for photoisomerization was conducted using an all-glass cell having a volume of 2 mL. This cell had an opening into which a CdS sample (~0.25 cm^2 surface area; 0001 face exposed to the cell interior), mounted on a glass stopper with DUCO cement, was placed. The glass face opposite the sample was flattened to permit excitation with minimal light scattering. By use of a Schlenk line, a butene gas was introduced into the cell at 1 atm pressure. The CdS sample was then irradiated in the presence of the gas with 10 mW of 457.9-nm light for 10 h. After irradiation, the gas was collected by condensation in an evacuated 5-mL bulb. Aliquots of gas (0.2 to 0.5 mL) were taken for injection into the Kratos MS25 system. The GC was equipped with a Chrompak Model 7815 50-m x 0.32-mm porous layer open tubular (PLOT)

column and a split injector. The splitter was set at 200:1 with a He

pressure of 1 kg/cm^2. Oven temperature was maintained at 80 $^\circ$C for 1

min and then ramped to 200 $^\circ$C at a rate of 20 $^\circ$C/min. The mass

spectrometer detector was used in full-scan mode with a cycle time of 1

scan/s. Under these conditions the butene gases are easily separated. The

photolysis and analysis were repeated for each of the butene gases.

Optical Measurements. The He-Ne and Ar$^+$ lasers used for

excitation and associated PL detection equipment have been described

previously.[2a]

Results and Discussion

Single-crystal, c-plates of n-CdS(e) exhibit band edge PL at 293 K,

when irradiated with ultraband gap light. For CdS, green PL is observed

(λ_{max} ~ 510 nm; E_g ~2.4 eV); for CdSe, the emission is red (λ_{max} ~ 720

nm; E_g ~1.7 eV). Exposure of the solids to a family of butenes causes an

enhancement in PL intensity relative to the intensity in a N$_2$ ambient. In

sections below, we describe the molecular dependence of this effect; its

exploitation in determining semiconductor depletion widths and adduct

formation constants; and the physicochemical interactions that may

contribute to our observations.

Molecular Dependence. The majority of our studies were conducted

with the shiny 0001, Cd-rich face produced by etching CdS(e) with HCl or

Br_2/MeOH. After rinsing with MeOH, the CdS(e) samples were placed in a

gas flow cell and irradiated with ultraband gap light. Switching the

ambient from N_2 to 30% butene gas in N_2 led to the reversible PL

enhancements shown in Figure 1.   Irrespective of the sequence of

exposure, we found for a given semiconductor sample that the degree of

enhancement for 30% mixtures followed the trend, 1,3-butadiene >

cis-2-butene ~ trans-2-butene > isobutylene ~ 1-butene > n-butane (the

alkane's response is barely discernible above baseline); pure butene gases

gave the same trend. A possible complication in this set of experiments is

photoisomerization, which is known to occur when oxide semiconductors

like ZnO and SnO_2 are irradiated in the presence of butenes with

ultraviolet light.[1c] Using a static system and a small volume of each

butene gas, we were unable to see evidence for photoisomerization with

CdS from 457.9-nm excitation; we obtain an upper limit on the

photoisomerization quantum yield of 10^{-3} for our experimental conditions.

With several CdS(e) samples we examined the trend in butene-induced

PL response with both the 0001 and the more weakly emissive, opposing

S(e)-rich, $000\bar{1}$ face. Within experimental error the order of the responses

observed for the two faces was identical. Similarly, the use of aqueous

HCl or Br_2/MeOH as an etchant produced the same trends in butene-induced

PL response.

The direction of the PL change is indicative of a negative shift in the

work function of the semiconductor upon exposure to the alkene,

consistent with the notion that these species are serving as Lewis

bases.[2a,3] The magnitude of the PL enhancements correlates with the

basicities of the butenes, as gauged by the photoionization potentials

(IP's) shown in Figure 1.[4] The correlation depicted in Figure 1 prompted us

to examine several other unsaturated hydrocarbons. Using the 0001,

Cd-rich face of CdS(e) samples, we found no PL response relative to N_2

(<3% change, within our experimental error) with ethylene, which has an IP

(10.5 eV) in excess of those of the butenes. Allene ($CH_2=C=CH_2$) with an IP

of 9.6 eV[4b] shows about a 15% increase in PL intensity (457.9-nm

excitation), close to the butene correlation.

The use of two alkynes, acetylene and propyne, resulted in PL

enhancements of ~10% and 20%, respectively (457.9-nm excitation of

CdS), relative to N_2; the corresponding IP values are 11.4 and 10.4 eV. The

alkyne PL response does increase with a reduction in IP, but the magnitude

of the alkyne response is larger than expected based on extrapolation of

the butene data. These findings underscore the fact that IP is not the sole

factor contributing to PL response and that its use as a predictor of

relative PL intensity is best made for a family of structurally and

electronically related compounds.

Depletion Widths. The PL data for n-CdSe are well fit by a

dead-layer model, which assumes that electron-hole pairs formed within a

distance on the order of the depletion width do not contribute to PL.

Neglecting changes in surface recombination velocity,[2a,5] equation (1)

$$PL_1/PL_2 = \exp(-\alpha'\Delta D) \qquad (1)$$

gives the quantitative form of the model, where PL_1 and PL_2 correspond to

the PL intensities in N_2 and in the olefin ambient, respectively; $\alpha' = (\alpha + \beta)$

is the absorptivity of the solid, corrected for self-absorption effects; and

ΔD is the reduction in dead-layer thickness (equated with the reduction in

depletion width) in passing from the N_2 to olefin ambients. Table I shows

that excellent agreement with the model was found for CdSe using several

interrogating wavelengths whose absorptivities[2a,6] span a factor of ~3:

for one sample that typifies our results, consistent values for ΔD of ~130

Å with 1,3-butadiene and ~90 Å with cis-2-butene were observed. A

smaller range of absorptivities is experimentally accessible for CdS; if

we assume that the dead-layer model applies, excitation at 457.9 nm leads

to a value for ΔD of ~250 Å with 1,3-butadiene.[7]

Adduct Formation Constants. Using a static system,[2a] we

constructed adsorption isotherms at 293 K for the most responsive

adducts, 1,3-butadiene on 0001 CdS(e) surfaces, by plotting the fractional

surface coverage θ (assumed to equal the fractional PL change[2a]) vs.

butene partial pressure P, Figure 2. The expression for the isotherm

contains the adduct equilibrium constant K, equation (2),

$$\theta = KP/(1 + KP); \text{ or } \theta^{-1} = 1 + (KP)^{-1}. \tag{2}$$

Double-reciprocal plots of θ^{-1} vs. P^{-1}, shown in the inset of figure 2, are

linear and permit K to be extracted from the reciprocal of the slope. We

find K to be 9 ± 4 atm^{-1} for 1,3-butadiene on a number of CdS(e)

substrates.

It is noteworthy that the Langmuir model has been successfully

applied to a number of solution-semiconductor interfaces involving

adsorption of halides, amines, and dithiocarbamates.[8] A key assumption

of the Langmuir model, that the adsorbates are noninteracting, appears to

be satisfied for this group of semiconductor-derived interfaces.

Surface Interactions. The aforementioned results raise the issue

of the specific chemical interactions that are responsible for the

butene-induced PL enhancements. As noted above, the direction of the PL

change is consistent with binding a Lewis base to the semiconductor

surface, and the magnitude of the PL enhancement correlates with IP, a

basicity measure for the butenes. For atomically clean CdS(e) samples,

surface Cd^{2+} sites represent possible binding positions of Lewis acidity.

While there is little precedent for Cd^{2+}-olefin complexes, a substantial

body of literature exists describing complexes prepared from olefins and

the isoelectronic Ag^+ ion.[9] However, if the Cd^{2+}-olefin interaction is

dominant, it is surprising that we see little dependence on the choice of

CdS vs. CdSe substrate: our expectation was that surrounding Cd^{2+} with

the more electronegative sulfide would enhance its acidity, yet we see

comparable adduct formation constants. Similarly, the insensitivity to

$000\bar{1}$ and $000\bar{1}$ crystal faces (with either etchant employed), as judged by

the same order of PL response to the butenes, indicates that the type of

site(s) needed for butene coordination is present on both faces.

While the independence of PL response on chalcogen and on crystal

face may just reflect an intrinsic insensitivity to these chemical

environments, it may also signal the presence of other species on these

ambiently-prepared surfaces. The preparative conditions that we have

employed can leave halide, water, and/or methanol on the surface, for

example, and these compounds or species derived therefrom may play

important roles in adduct formation: surface protons, for example, could provide Lewis acidic sites.

It is worth emphasizing that the butene-CdS(e) adducts are weak and easily dissociated at room temperature. We have now seen semiconductor-gas interactions ranging from that of CdS(e) with ethylene, which showed no response, to butenes and other unsaturated hydrocarbons - acetylene, propyne, and allene - that do have sufficient π-electron density to engage in adduct formation. Even stronger PL responses were found with amines, which are yet stronger bases with lower IP's.[4a] As these and related equilibria, including adduct formation at the semiconductor-solution interface,[8] are studied, we should be able to develop a better understanding of the steric and electronic interactions that govern them.

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Table I. Dead-Layer Analysis of CdS(e) PL Properties in Butene Ambients[a]

Solid	Butene[b]	λ_{ex}, nm[c]	α^{-1}, Å [d]	PL ratio[e]	ΔD, Å [f]
CdSe	1,3-diene	457.9	570	1.31	130
		514.5	740	1.22	130
		632.8	1500	1.11	130
CdS		457.9	1100	1.30	250
CdSe	cis-2	457.9	570	1.21	90
		514.5	740	1.15	90
		632.8	1500	1.07	90
CdS		457.9	1100	1.15	130

[a]Analysis of olefin-induced changes in band edge PL intensity of an etched

(Br$_2$/MeOH; 0001 face) CdS and CdSe sample exposed to the indicated

gases (30% mixtures in N$_2$).

[b]Data are shown for the two butenes that gave sufficiently large PL

responses to permit meaningful dead-layer calculations. Data for

trans-2-butene is virtually identical to that shown for the cis isomer.

[c]Excitation wavelength used in PL experiments.

[d]Optical penetration depth of the exciting wavelength in the preceding column, taken as the reciprocal of the absorptivity.[6,7]

[e]Ratio of PL intensity in the indicated ambient (30% olefin in N_2) to that in pure N_2, both at a pressure of 1 atm.

[f]Contraction in dead-layer thickness in passing from N_2 to the indicated gas, calculated with eq. 1; corrections for self-absorption ($\beta = 1.2 \times 10^4$ cm^{-1} for CdSe; 5.5×10^3 cm^{-1} for CdS) were estimated from data in refs. 6 and 7.

Figure Captions

Figure 1. Changes in PL intensity at 510 nm resulting from alternating

exposure of an etched n-CdS sample to N_2 (initial response) and the

indicated gases, each present as a 30% mixture in N_2. Below each gas is

its photoionization potential, taken from ref. 4a. Superimposed on the plot

is the original PL spectrum, obtained in N_2. Flow rates were 100 mL/min

at 1 atm of pressure. The sample was excited with 457.9-nm light.

Figure 2. Fractional surface coverage θ, assumed to equal the fractional

change in PL intensity, as a function of the partial pressure of

1,3-butadiene for etched single crystal n-CdS (diamonds) and n-CdSe

(squares) substrates; data were taken in random order for each

semiconductor. The inset presents these same data in a double-reciprocal

plot; the lines shown are least-squares best fits to the data and lead to

adduct formation constants (eq. 2) of 8.8 ± 0.2 and 8.9 ± 0.2 atm^{-1} for CdS

and CdSe, respectively, at 293 K.

Fig. 1

Axis labels (main plot): Θ (vertical), P (atm) (horizontal)

Inset axis labels: $1/\Theta$ (vertical), 1/P (atm^{-1}) (horizontal)