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Evidence for Adduct Formation at the Semiconductor-Gas Interface. Photoluminescent Properties of Cadmium Selenide in the Presence of Amines

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Abstract: Exposure of etched samples of single-crystal *n*-CdSe to gaseous amines causes enhancement of the red band edge photoluminescence (PL) of the semiconductor relative to a N_2 ambient. The magnitude of the enhancement (for 10% mixtures of the amines in N_2) follows the order $NF_3 < NH_3, ND_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$ and typically ranges from 20% for NF_3 to 600% for $(CH_3)_2NH$. This trend can be correlated with the basicities of the amines, providing evidence for adduct formation between the gaseous amine and the semiconductor surface atoms. Only for the four least basic amines are the PL changes readily reversible by returning to N_2. For all of the amines, the enhancement in PL intensity can be quantitatively fit to a dead-layer model, permitting determination of the reduction in depletion width in the semiconductor that results from amine exposure; typical depletion width reductions found in passing from N_2 to 10% amine/N_2 ambients range from 200 Å (NF_3) to 1000 Å ($(CH_3)_2NH$). Samples of *n*-CdSe that have been cleaved along the *c* axis but not etched yield the same trend in PL enhancements with exposure to the aforementioned amines. However, PL changes of the cleaved samples cannot be fit to a dead-layer model, indicating that they arise, at least in part, from changes in surface recombination velocity. The PL changes observed for etched *n*-CdSe substrates with NH_3 and CH_3NH_2 were used to construct Langmuir adsorption isotherms; good fits were obtained for several samples, yielding equilibrium constants for adduct formation ranging from 15 to 30 atm^{-1} for NH_3 and from 30 to 70 atm^{-1} for CH_3NH_2 at 293 K. The increase in PL response with amine partial pressure, from $\sim 10^{-3}$ to 10^{-1} atm for NH_3 and CH_3NH_2, permits use of these interfaces for optically coupled chemical sensing over this pressure range. Mechanistic aspects of the PL response have been examined through the use of a diverse set of volatile compounds.

The physicochemical properties of semiconductor-derived interfaces have both fundamental and technological significance. We have found that photoluminescence (PL) is a versatile in situ technique that can be used to characterize interfaces of semiconductors with electrolytes, metals, and covalently bonded, redox-active species.[1-3] A feature that unifies these interfaces is that their PL properties conform to a dead-layer model that permits mapping of the electric field in the semiconductor: Electron-hole pairs formed within a distance on the order of the depletion width do not contribute to PL.[1,4]

Because PL measurements are nondestructive and contactless, they embrace interfaces to which an external potential is not applied (semiconductor with molecular species) as well as those to which one is applied (semiconductor with metal, semiconductor, and electrolyte). An interface that is particularly amenable to characterization by PL is that of a semiconductor with its gaseous ambient. To date, such studies have largely focused on interactions with N_2 and O_2.[5] It occurred to us, however, that a semiconductor surface may have sufficiently well-defined acid-base character to permit adduct formation between the surface and an appropriate gas. In previous studies, we saw that a Lewis acid and base, gaseous SO_2 and NH_3, caused diminution and enhancement of PL, respectively, relative to a N_2 ambient.[6] In a recent study of aqueous CdS colloidal dispersions, the semiconductor's PL was enhanced by adding amines to the solution.[7]

In this paper we demonstrate that bulk PL from etched or cleaved *n*-CdSe single crystals is strongly affected by exposing the crystals to a family of gaseous amines. Moreover, the magnitude of the interaction can be correlated with the intrinsic basicity of the amines, thereby evidencing adduct formation with the surface. For etched samples, the PL data are in good agreement with the dead-layer model; cleaved samples exhibit PL properties that do not fit the dead-layer model, indicating that the PL changes arise, at least in part, from changes in surface recombination velocity. We also show that PL changes can be used to construct Langmuir adsorption isotherms.[8,9] The good fits obtained provide additional evidence for adduct formation and permit extraction of the equilibrium constants for two of the amines studied. This ability of PL to reveal surface interactions can be exploited in the design of optically coupled chemical sensors. Finally, we show that exposure of etched *n*-CdSe substrates to other volatile classes of compounds can be used to probe the nature of the interactions that perturb the PL response.

Experimental Section

Materials and Sample Preparation. The following gases were used as received: ammonia (Matheson; 99.99%); methylamine (Aldrich; 98+%); dimethylamine (Aldrich; 99+%); trimethylamine (Aldrich; 99+%); trifluoroamine (Air Products; 99.4+%); perdeuterated ammonia (Cambridge Isotope Laboratories; 99.5%); oxygen, nitrogen, helium, and argon (Badger Welding; 99.95%); nitrous oxide (Matheson; 99.0%); carbon monoxide (Matheson; 99.9%); and carbon dioxide (Matheson; 99.99%). Impurities in the amines were determined by mass spectroscopy using a Kratos MS80RFA mass spectrometer. Methanol, bromine (Fisher; 99.9%), and glacial acetic acid (Columbus Chemical; 99.7%) were used as received for etching. Cyclohexane (Aldrich; 99+%), cyclohexene (Aldrich; 99%), pyridine (Aldrich; 99+%), 1-chlorobutane (Aldrich; 99+%), ethyl acetate (Fisher; 99.9%), and benzene (Aldrich; 99+%) were dried over $CaCl_2$, and acetonitrile (Aldrich; 99+%) was dried over activated alumina. *n*-Butylamine (Aldrich; 99%) and 2-butanone (Fisher; 99%) dried over CaH_2 (Alfa; 95%), methanol (Fisher; 99.9%) dried over Mg (Aldrich; 98%), and dipropyl ether (Aldrich; 99%) dried over $LiAlH_4$ (Alfa; 95%) were distilled before use. Single-crystal, vapor-grown, *c*-plates (10 × 10 × 1 mm) of *n*-CdSe with resistivity of ~2 Ω cm were

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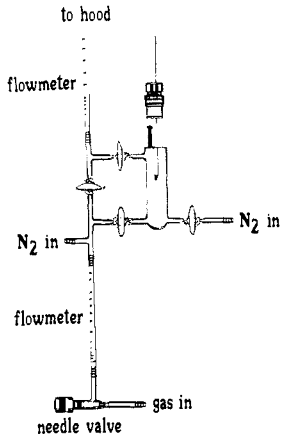

Figure 1. Apparatus used for measuring PL changes as a function of gaseous ambient. A more detailed description is given in the Experimental Section.

obtained from Cleveland Crystals, Inc., Cleveland, OH, and were prepared for use by either etching or cleaving. In the etching procedure, samples were scored and broken to ~4 × 4 × 1 mm dimensions, alternately wiped and etched (Br_2/MeOH, 1:30 (v/v); 5 s) until the shiny, Cd-rich, 0001 face was observed, ultrasonicated in MeOH for 15 min, and edge-suspended with DUCO cement from a glass rod. The samples were left in air until use. In some experiments, samples were twice rinsed for 3 s in 1% CH_3COOH/MeOH and dried in air between runs. For the cleaving procedure, the CdSe crystals were simply cleaved parallel to the *c* axis with a razor blade, mounted on a glass rod with the cement, and left in air until use. The 1-mm edge produced by cleaving was irradiated in PL measurements. Samples cleaved and mounted in a solvent-free, N_2-filled glovebox gave similar results.

Gas-Handling Apparatus. An all-glass setup for exposing *n*-CdSe to various gases under flow conditions is shown in Figure 1. The mounted crystal was placed in an adapter that served as a stopper for a 20-mm-diameter tube that surrounded the sample. Two diametrically opposed stopcocks, placed near the bottom of the tube and below the semiconductor, served as gas inlets, and a stopcock near the top of the tube and above the semiconductor served as the gas outlet and was connected to a Gilmont Model 11 glass flowmeter that was vented into a hood. One inlet was used for pure N_2; the other was used for gas mixtures and was connected to a Gilmont Model 10 flowmeter (or a Gilmont ruby-ball microflowmeter) and a cell bypass. Experiments were conducted at atmospheric pressure and flow rates of 100 mL/min. Except for concentration studies, the gas of interest was mixed with N_2 so as to be present as a 10% component (flowmeter values were corrected for gas density). In most experiments, new gases were introduced without changing the sample geometry. In experiments requiring the sample to be rinsed with 1% CH_3COOH/MeOH between runs (vide supra), an alternate sample holder, consisting of a glass rod fused to a glass stopper, was used. This sample holder was sufficiently rigid that the sample could be removed and repositioned in the same geometry.

A similar 30-mL cell was used for exposing *n*-CdSe to vapor from various liquids for static measurements. An additional ground-glass side arm provided connection to a 300-mL glass bulb containing the liquid of interest, previously degassed by several freeze–pump–thaw cycles on a vacuum line. One stopcock was connected to a vacuum pump, allowing the cell to be evacuated to approximately 0.5 Torr. Briefly opening the glass bulb to the cell introduced gas at its vapor pressure. Cell evacuation and subsequent reintroduction of vapor from the bulb permitted multiple trials without changing the sample geometry. Use of a vacuum line allowed the bulb to be filled with a known pressure of gas for adsorption isotherm measurements; gas pressures were corrected for expansion into the cell volume.

Cells were cleaned between experiments in a saturated KOH/*i*-PrOH bath, rinsed with distilled water, and oven-dried at 200 °C.

Optical Measurements. Irradiation sources included a Coherent Radiation Model CR-12 Ar^+ laser (457.9 and 514.5 nm) and a Melles Griot Model 80 He–Ne laser (632.8 nm). Laser plasma lines were eliminated by passing the beam through Oriel interference filters (fwhm of 10 nm, centered at the laser line). The beams from both lasers were passed through a 10× beam expander and masked to illuminate only the semiconductor surface. Laser intensity was measured with a Coherent Model 212 power meter and corrected for spectral sensitivity. Uncorrected, low-resolution (~3-nm) PL spectra were obtained with a McPherson Model 270, 0.35-m monochromator, equipped with a grating blazed at 500 nm, a R928 PMT, and an EG&G rate meter; laser excitation was filtered by placing a Corning 2-58 filter at the entrance slit to the emission monochromator. The PL signal was brought to the spectrometer by a 3-mm-diameter optical fiber. Spectra were displayed on a Houston Model 2000 X-Y recorder. Typically, PL intensity was monitored by sitting at the band maximum (~720 nm), with the recorder operated in time–base mode as the gaseous ambient was varied. The detection optics were positioned between the incident and reflected excitation beams.

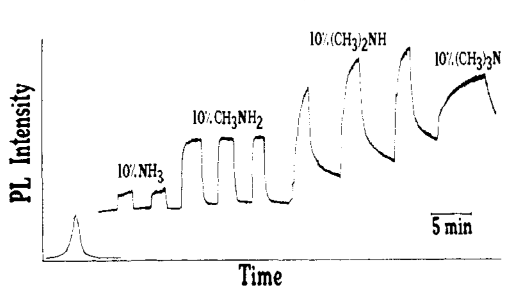

Figure 2. Changes in PL intensity at 720 nm resulting from alternating exposure of an etched *n*-CdSe sample to N_2 (initial response) and the indicated amine. Superimposed on the plot is the original PL spectrum obtained in N_2. Flow rates for all gases were 100 mL/min at 1 atm of pressure. The sample was excited with 457.9-nm light.

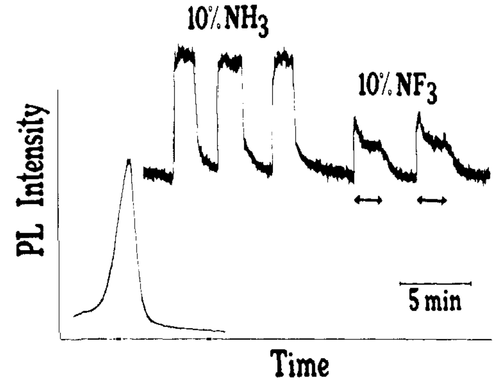

Figure 3. Changes in PL intensity at 720 nm resulting from alternating exposure of an etched *n*-CdSe sample to N_2 (initial response) and the indicated amine. Superimposed on the plot is the original PL spectrum obtained in N_2. Other experimental conditions are as described in Figure 2. Arrows in the figure indicate the duration of the exposure to NF_3.

Results and Discussion

Single-crystal, *c*-plates of *n*-CdSe emit in the red with a band maximum at 720 nm. Exposure to gaseous NF_3, NH_3, ND_3, CH_3NH_2, $(CH_3)_2NH$, or $(CH_3)_3N$ causes a substantial enhancement in PL intensity relative to the intensity in a N_2 ambient. In most cases, the increase is readily seen by the dark-adapted eye. In sections below, we describe qualitative and quantitative aspects of this phenomenon for etched and cleaved samples, the construction of Langmuir adsorption isotherms from the PL response, and mechanistic features underlying the PL response.

Etched Samples. Use of Br_2/MeOH as an etchant yields a shiny, Cd-rich, 0001 face for CdSe that was used for the majority of our studies. At low resolution, the PL spectral distribution was unaffected by exposure to the amines, permitting PL changes to be monitored by sitting at the band maximum. Several qualitative features of the CdSe–amine interaction are highlighted in Figures 2 and 3, wherein an etched sample was alternately exposed to N_2 and 10% mixtures of various amines in N_2.

The magnitude of the PL increase follows the order $NF_3 < NH_3, ND_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$, with enhancements typically ranging from 20% for NF_3 to 600% for $(CH_3)_2NH$; we write the inequality preceding $(CH_3)_3N$ as shown to indicate that we see some variation in its position along the series but that it always yields a weaker PL change than does $(CH_3)_2NH$. To more firmly establish this ordering of amines, we exposed individual samples to pairs of amines, obtaining the same trend in each case; this result was independent of the order of exposure within each pair of amines.

Table I. Dead-Layer Analysis of *n*-CdSe PL Properties[a]

				etched		cleaved	
gas	PA[b]	λ_{ex},[c] nm	$1/\alpha$,[d] Å	PL ratio[e]	ΔD,[f] Å	PL ratio[e]	ΔD,[f] Å
NF_3[g]	556	457.9	570	1.5	220	1.5	220
		514.5	740	1.4	230	1.3	180
		632.8	1500	1.2	230	1.3	330
NH_3	858	457.9	570	3.2	620	3.6	680
		514.5	740	2.5	620	3.5	850
		632.8	1500	1.6	600	2.6	1200
CH_3NH_2	896	457.9	570	5.7	930	4.5	800
		514.5	740	4.2	980	4.0	940
		632.8	1500	2.1	940	3.4	1600
$(CH_3)_2NH$	923	457.9	570	7.0	1000	4.9	850
		514.5	740	6.1	1200	4.3	990
		632.8	1500	2.6	1200	3.5	1600
$(CH_3)_3N$	938	457.9	570	1.9	340	3.8	710
		514.5	740	1.7	360	3.7	890
		632.8	1500	1.3	330	2.8	1300

[a] Analysis of amine-induced changes in band edge PL intensity of one *n*-CdSe sample that has been etched in Br_2/MeOH and one *n*-CdSe sample that has been cleaved along the *c* axis, as described in the Experimental Section. [b] Proton affinity, in kilojoules per mole, from ref 10 and 11. [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. Absorptivities are those for which the electric vector of the incident light oscillates perpendicular to the *c* axis ($E \perp c$); absorptivities for light with $E \parallel c$ give ΔD values that are within 10% of those presented in the table. Absorptivities for *n*-CdSe were taken from ref 15. [e] Ratio of PL intensity in the indicated gas (10% amine/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; an absorptivity of 1.2×10^4 cm^{-1} (β) was used to correct for self-absorption. [g] For this experiment, a different cleaved sample was employed.

With the exception of the reversal at $(CH_3)_3N$, the PL trend parallels the intrinsic basicities of these gases; proton affinities of the amines are summarized in Table I.[10] The correlation with intrinsic basicity supports the notion that acid–base interactions involving the semiconductor surface atoms underlie the PL changes. When such a conclusion is drawn, it is worth emphasizing that we are working with ambient surfaces. With such atoms as Cd, Se, O, and H likely present thereon, there are ample opportunities for adduct formation. Moreover, we have found that gases with weaker or less well-defined acid–base characteristics—He, Ar, CO, CO_2, and N_2O—give PL signals within 5% of that of N_2 under the same experimental conditions.

The reversal in the basicity trend with $(CH_3)_3N$ parallels the aqueous basicities of this family of amines.[11] A trend in hydrogen-bonding ability that runs counter to the trend in basicity is generally offered as the explanation for the aqueous basicity maximum at $(CH_3)_2NH$. Hydrogen bonding could be contributing to our results in like fashion. However, experiments using ND_3 showed the same PL response within experimental error as observed with NH_3. The lack of a measurable deuterium isotope effect suggests that the interaction between NH_3 and the surface is not dominated by hydrogen bonding. Alternatively, we could be seeing the result of steric effects. This possibility is supported by the increase in PL response time with degree of methyl substitution: Figures 2 and 3 reveal that $(CH_3)_2NH$ and $(CH_3)_3N$ require the most time to produce their maximum PL enhancements and to return to the N_2 level.

Seeking ways to more quickly return to a PL reference level after exposure to the amines, we found that rinsing the CdSe sample in 1% CH_3COOH/MeOH provided a reproducible reference level after the sample is returned to the same geometry in a N_2 ambient. Although this reference level differs from that of an unrinsed sample under N_2, the amines exhibited the same PL enhancement order.

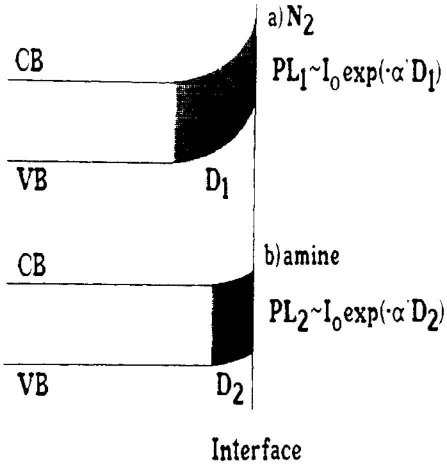

Figure 4. The dead-layer model for analyzing changes in PL intensity for two states, a and b. As indicated in the figure, state a corresponds to the PL intensity in a N_2 ambient and state b corresponds to the PL intensity in the presence of a gaseous amine. The symbols CB and VB represent the solid's conduction and valence band edges, respectively. For each state, the PL intensity is proportional to the amount of incident light (intensity I_0; absorptivity α') absorbed beyond the nonemissive layer whose thickness is D. The ratio of the two PL intensities leads to eq 1.

Analyzing our data, we were concerned about potential contributions from thermal effects and gaseous impurities. We think thermal effects are minimal for several reasons. First, heating the samples causes the PL intensity to decline not to increase. Second, at the low incident powers employed (~1 mW/cm^2) and with the convective cooling supplied by a substantial gas flow rate (100 mL/min), the sample should remain near ambient temperature. In fact, even when incident intensities were boosted to ~40 mW/cm^2, the PL enhancements were unchanged from their values at 1 mW/cm^2. Finally, there appears to be no correlation between PL response and thermal conductivity: the thermal conductivities of NH_3, CO, and N_2 are similar, while those of CO_2 and SO_2 (which caused PL intensity to decline[6]) are smaller and that of He is 1 order of magnitude larger.[12] We emphasize, too, that in most of our experiments we are only changing the gas composition by 10%.

The effects of gaseous impurities are, we believe, also minimal. We examined the methyl-substituted amines by mass spectroscopy and found that they contain traces of other methyl-substituted amines. There may be an effect on PL from these other alkylated amines, but the PL signatures are so different (Figure 2) as to imply that they are dominated by the principal gas present. For NF_3, we found no evidence of impurities by mass spectroscopy. Besides these gases, we assessed the effects of O_2 and H_2O. Oxygen decreases PL intensity relative to N_2, but the effect is only a few percent. On the other hand, when the cell is "spiked" with a few drops of water, evaporation results in a slow, steady increase in PL. At this point, the exposure to NH_3 gives only small PL changes. Once the sample has been dried in a stream of N_2, however, the original PL response to NH_3 returns.

If the qualitative PL effects induced by the amines are driven by changes in the depletion width, they should be fit by the dead-layer model. The quantitative form of the model is given in eq 1, and its derivation is illustrated in Figure 4. In this

$$PL_1/PL_2 = \exp(-\alpha'\Delta D) \tag{1}$$

equation, PL_1 and PL_2 are the PL intensities before and after exposure to the amine, ΔD is the corresponding change in dead-layer thickness (equated with the change in depletion width, W), and $\alpha' = \alpha + \beta$, where α and β are the absorptivities for the exciting and emitted light; this treatment assumes that the surface

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recombination velocity is either very large or insensitive to the introduction of the amine.[1] The operational test of the model is the calculation of a constant value for ΔD, independent of interrogating wavelength.

We find that once the PL intensity is reproducibly cycling between its values in pure N_2 and 10% amine/N_2 ambients, excellent agreement with the dead-layer model is obtained for etched *n*-CdSe samples. Table I reveals that for absorptivities spanning roughly a factor of 3 ΔD values vary by no more than 20% for any of the amines studied and are more generally constant to better than 10%. The magnitude of ΔD is itself noteworthy: the strongest interaction, obtained with $(CH_3)_2NH$, caused a decrease in depletion width of ~1000 Å, while NF_3, the weakest base, still produced a decrease of ~200 Å.

Carrying out these measurements, we noted that in some cases reproducible cycling of PL intensity between N_2 and amine ambients does not occur immediately. Rather, the PL intensity in N_2 often shifts after the first exposure of CdSe to the amine, and it is at this shifted level that cycling occurs. We are uncertain as to why this "conditioning" period occurs in some cases; it may reflect some form of surface reconstruction.

We attempted to conduct PL experiments with the Se-rich, $000\bar{1}$ face of CdSe, but the matte surface was far less emissive. For the few samples where both $000\bar{1}$ and 0001 faces could be examined, we saw no significant difference in PL response to the amines.

Cleaved Samples. Cleavage of *n*-CdSe *c*-plates along the *c* axis provides an alternative surface preparation for analyzing the effects of amines on PL. In a N_2 ambient, the cleaved samples generally emit more efficiently by at least 1 order of magnitude than their etched counterparts. Yet, the response to amines qualitatively matches that obtained with etching: Individual cleaved samples exhibit substantial PL enhancements upon exposure to 10% amine/N_2 ambients in the order $NF_3 < NH_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)_3N$. Additionally, five separate samples, cleaved in parallel from a single block of CdSe and each exposed to a single, different amine, showed the same order of PL enhancement.

Quantitatively, the PL changes observed for the cleaved samples are poorly fit by the dead-layer model. Table I gives representative data showing that, far from being constant, ΔD typically increases by a factor of 2 in passing from short to long interrogating wavelengths. This discrepancy with the model indicates that changes in surface recombination velocity S contribute to the PL properties of the cleaved samples. If the PL changes were solely due to S, our data would indicate that S declines with amine exposure. However, both W and S can be changing, precluding a simple interpretation of the PL changes found for cleaved samples. It is worth noting that cleaved samples that have been etched exhibit PL changes that are in better agreement with the dead-layer model.

Langmuir Adsorption Isotherms. The notion that adduct formation depends on concentration and the prospect that such a dependence could serve as the basis for an optically coupled chemical sensor prompted us to investigate the sensitivity of PL changes for etched *n*-CdSe samples. Because NF_3 yields only a weak response and $(CH_3)_2NH$ and $(CH_3)_3N$ produce slow responses, we confined these studies to NH_3 and CH_3NH_2.

The assumptions in Langmuir's model for adsorption[9] are the following: (1) the solid contains a fixed number of adsorption sites, and, at any temperature and gas pressure, a fraction θ of these are occupied at equilibrium; (2) each site holds one adsorbed molecule; (3) the heat of adsorption is the same for all sites and is independent of θ; and (4) there are no intermolecular interactions between adsorbed molecules.

The formation of an adsorbed monolayer can then be represented by eq 2, where A is the amine, σ is an active site on the surface, and Aσ represents an adsorbed amine molecule. The

$$\mathrm{A} + \sigma \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}\sigma \tag{2}$$

rate of desorption is given by $k_{-1}\theta$; the rate of adsorption is $k_1(1 - \theta)P_A$, where P_A is the partial pressure of the adsorbing gas. Equating these rates at equilibrium results in eq 3. Defining the

$$\theta = k_1P_A/(k_{-1} + k_1P_A) \tag{3}$$

$$\theta = KP_A/(1 + KP_A) \tag{4}$$

$$1/\theta = 1 + 1/(KP_A) \tag{5}$$

equilibrium constant for adsorption, $K = k_1/k_{-1}$, leads to eq 4, which can be rewritten as eq 5. Thus, a double-reciprocal plot of θ^{-1} vs P_A^{-1} should be linear with an intercept of unity and a slope of K^{-1}.

Using a static system, we constructed adsorption isotherms at 293 K by plotting the fractional increase in PL intensity (the fractional change between the intensity in N_2 and the maximum intensity observed at high amine pressure) as a function of amine partial pressure. In doing this, we are assuming that the fractional increase in PL intensity is proportional to the fraction of the surface covered by the amine. Figure 5 presents the raw data for the two amines and indicates that there is a limiting pressure of gas beyond which all surface sites are covered and no further PL change is observed, as predicted by eq 4. The inset of Figure 5 shows that our data yield an excellent fit to eq 5. Data like that in the figure, obtained from several samples, lead to adduct formation constants that range from 15 to 30 and 30 to 70 atm^{-1}, respectively, for NH_3 and CH_3NH_2.

The dependence of PL intensity on gas pressure can be used for constructing chemical sensors. Figure 6 demonstrates that the substrate responds within seconds to changes in NH_3 partial pressure under flow conditions. Figure 7 presents working plots for NH_3 and CH_3NH_2. The two curves shown indicate that a

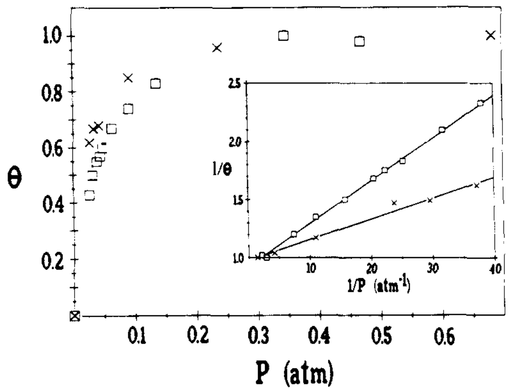

Figure 5. Fractional surface coverage θ, equated to the fractional change in PL intensity, as a function of the partial pressure of NH_3 (□) and CH_3NH_2 (×) for an etched single-crystal *n*-CdSe substrate excited with 514.5-nm light; data were taken in random order for each gas. The inset presents these same data as a double-reciprocal plot; the lines shown are least-squares best fits to the data and lead to adduct formation constants of 27 ± 1 atm^{-1} for NH_3 and 59 ± 3 atm^{-1} for CH_3NH_2, using eq 5 in the text.

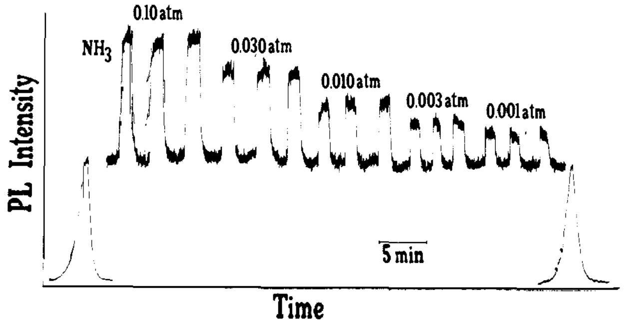

Figure 6. Changes in PL intensity at 720 nm resulting from alternating exposure of an etched *n*-CdSe sample to N_2 (initial response) and the indicated partial pressures of NH_3 in a N_2/NH_3 mixed flow. Superimposed on the plot are the original and final PL spectra obtained in N_2. Flow rates were 100 mL/min at 1 atm of total pressure. The sample was excited with 457.9-nm light.

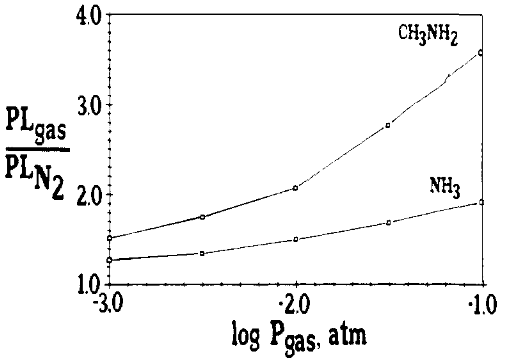

Figure 7. PL response of an etched *n*-CdSe sample to NH_3 and CH_3NH_2 relative to N_2 as a function of the partial pressure of the gas in a NH_3/N_2 or CH_3NH_2/N_2 mixture. Flow rates of 100 mL/min were used in all experiments. The sample was excited with 457.9-nm light.

PL enhancement is readily seen at amine partial pressures of 10^{-3} atm and that the enhancement increases monotonically to 10^{-1} atm. At 1 atm of pressure we often see a large initial response that decays to a substantially lower value.

Mechanistic Features. The correlation of PL enhancement with amine basicity for *n*-CdSe samples and the fit to the Langmuir adsorption isotherm provide compelling evidence for adduct formation between the gaseous amines and atoms on the semiconductor surface. Moreover, the fit to a dead-layer model for etched samples indicates that these surface interactions, whatever their origin, can dramatically alter the depletion width of the underlying substrate. Such effects prompt the question of how a process like adduct formation, involving gaseous molecules and semiconductor surface atoms, might so profoundly affect semiconductor properties at a substantial depth from the surface. To further explore this question, we investigated the PL response of etched *n*-CdSe samples to other gaseous species.

Table II presents PL data obtained under static conditions for a variety of volatile organic compounds. With the exception of pyridine, the vapor pressures of these compounds at 293 K are all within 30% of the amine partial pressures employed in the flow experiments. The table reveals that good bases such as a representative alcohol and amine (methanol and *n*-butylamine) show substantial PL enhancements. So does pyridine, even with its lower vapor pressure. But benzene and representative alkanes, alkyl halides, alkenes, esters, ketones, ethers, and nitriles showed little PL change relative to N_2. In some cases, as with dipropyl ether, this insensitivity may reflect steric hindrance, since sites of Lewis basicity are present in the molecule. We should qualify comparisons based on Table II data by noting that the entries represent determinations at a single pressure for which we do not know the corresponding fractional coverage.

Table II. Response of *n*-CdSe PL to Organic Vapors[a]

compd	vapor pressure[b]	PL ratio[c]
methanol	97	2.0
cyclohexane	95	1.0
n-butylamine	82	2.7
1-chlorobutane	80	1.1
2-butanone	79	1.0
ethyl acetate	76	1.0
benzene	75	1.0
acetonitrile	73	1.1
cyclohexene	67	1.1
dipropyl ether	55	1.1
pyridine[d]	18	1.3

[a] Effect on PL intensity of an etched *n*-CdSe substrate upon exposure to the vapor of the indicated compound. Additional details are given in the Experimental Section. [b] Pressure in millimeters of mercury at 20 °C. Data taken from ref 16. [c] Ratio of PL intensity in the presence of the indicated vapor to that in 1 atm of N_2. Data were obtained with 514.5-nm excitation. [d] PL response not directly comparable due to difference in vapor pressure.

Collectively, our data indicate that interactions of *n*-CdSe with a variety of gaseous bases enhance PL intensity. The reduction in depletion width inferred from these spectral changes corresponds to a shift in the work function of the semiconductor surface, moving the work function closer to the vacuum level. Such shifts have previously been reported for the interaction of metal and metal oxide surfaces with gaseous bases and have been interpreted in terms of adduct formation.[13] For the system at hand, we can envision the nonbonding lone pair of electrons from an amine being donated to a vacant orbital at surface Cd or H sites, for example, to provide the bonding interaction needed for adduct formation.[14] Such an interaction can modify the energetics and population of surface states so as to provide additional electron density to the semiconductor, yielding a reduction in work function, as illustrated by the reduced band bending in Figure 4. Adduct formation can also affect recombination dynamics through the perturbation of the semiconductor's surface electronic structure, as inferred from our data on cleaved samples.

In summary, we have shown that PL provides a sensitive in situ technique for exploring molecular surface interactions. Studies of related gas–semiconductor systems should enable us to better map the steric and electronic landscape at these interfaces and are under way in our laboratories.

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(14) We attempted to identify adduct formation using surface spectroscopic techniques. Unfortunately, we were unable to detect a fluorine signal by Auger and ESCA for the NF_3 adduct, and attempts to see the other amines were unsuccessful due to the coincidence of the N 1s and Cd 3d energy levels. Carbon was detected on both freshly etched and amine-exposed surfaces.

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