

Designating C as the concentration of $\text{Ln}(\text{fod})_3$ added, the expression for K_f is now formulated as

$$K_f = \frac{\Delta \text{PL}}{[(\text{PL}_{\max} - \text{PL}_1) - \Delta \text{PL}]C} \quad (6)$$

Dividing both numerator and denominator of eq 6 by $(\text{PL}_{\max} - \text{PL}_1)$ yields

$$K_f = \frac{\Theta}{(1 - \Theta)C} \quad \Theta = \Delta \text{PL} / (\text{PL}_{\max} - \text{PL}_1) \quad (7)$$

Equation 7 can be rearranged to give

$$\Theta = K_f C / (1 + K_f C) \quad \text{or} \quad 1/\Theta = 1 + 1/(K_f C) \quad (8)$$

The value of K_f is determined from the slope of a double reciprocal plot of $1/\Theta$ versus $1/C$. A typical reciprocal plot of $\text{Pr}(\text{fod})_3$ -induced changes on a type A sol is shown as an inset in Figure 2, and a reciprocal plot of $\text{Pr}(\text{fod})_3$ -induced changes for a type B sol is shown as an inset in Figure 3. The average values of $\log K_f$ for the $\text{Ln}(\text{fod})_3$ solutions studied range from 4.56 to 4.90 and are reported in Table I. The K_f values for a given $\text{Ln}(\text{fod})_3$ complex span a range of $\pm 5\%$, and thus the K_f 's for all of the $\text{Ln}(\text{fod})_3$ complexes investigated are essentially equal. The magnitudes of these binding constants do not reflect the changes in Lewis acidity of the lanthanide ion added, presumably because of the variances in surface morphology from preparation to preparation of the Q-CdS. Such variance is not surprising given that for a 40-Å cluster, for instance, nearly one-third of the total atoms present in the cluster are at the surface.⁹

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At present, the exact mode of coordination of the $\text{Ln}(\text{fod})_3$ complex to the Q-CdS surface is unknown. For single crystal n-CdSe, Ellis has proposed a seven-coordinate binding mode for $\text{Ln}(\text{fod})_3$ complexes to electron-rich sites along the 0001 plane.^{3a} For the Q-CdS studied here, the observed enhancement and dominance of the 530-nm emission by the end of the $\text{Ln}(\text{fod})_3$ titration is consistent with an interaction of these Lewis acids with cadmium vacancies at the surface via a Schon-Klasens mechanism.¹⁰ Gratzel has proposed such a mechanism for the observed enhancement of the 530-nm emission by methylviologen in Q-CdS formed in the presence of polymeric stabilizers.^{5b}

In summary we have detected a unique case of photoluminescence enhancement for quantum-confined CdS upon the addition of $\text{Ln}(\text{fod})_3$ reagents. The observed changes in PL areas clearly fit a Langmuir adsorption isotherm from which adduct formation constants have been determined. Further studies regarding the interactions of these colloidal semiconductor surfaces with other reactive molecular species are in progress.

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Desorption of Aluminum Hydride from Hydrogen Adsorbed Al(111) Surface

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Hydrogen-adsorbed Al(111) single crystal surface was studied by thermal desorption (TD) technique under ultrahigh vacuum. The mass spectra of the desorbing species showed signals corresponding to Al^+ , AlH^+ , AlH_2^+ , AlH_3^+ , AlH_4^+ , and Al_2H_6^+ . Hydrogen atoms adsorbed at 150 K on the surface desorbed at 340 K as aluminum hydride.

Chemisorption of hydrogen on metal surfaces, especially on transition-metal surfaces, has been widely studied and a tremendous volume of results has been accumulated.¹

Although aluminum plays a very important role in catalysis and thin film technology, the surface chemistry of aluminum is not well understood compared with that of transition metals. Moreover, the interaction between hydrogen and aluminum is very important in organometallic chemistry because of the instability of the Al-H bonds. The character of the bond is electron deficient and is related with the diversity of organoaluminum compounds. For example, triethylaluminum² is practically used as Ziegler-Natta catalyst. Due to the high activity of the Al-H bond, LiAlH_4 works as a strong hydrogenation reagent and AlH_3 is a potential rocket propellant.

Hydrogen chemisorption behavior on aluminum single crystals has already been studied by several groups using a variety of

surface science techniques.^{3,4} All these papers reported, however, that the desorption of hydrogen from aluminum single crystal surfaces obeyed zero-order kinetics, i.e., peak top temperatures in thermal desorption (TD) spectra for hydrogen shifted toward higher temperatures with increasing amount of adsorbed hydrogen. This desorption behavior contrasts with the hydrogen desorption from transition-metal surfaces in which the desorption kinetics is second-order, i.e., peak top temperatures in TD spectra for hydrogen shift toward lower temperatures with increasing amount of adsorbed hydrogen.⁵ This second-order desorption suggests

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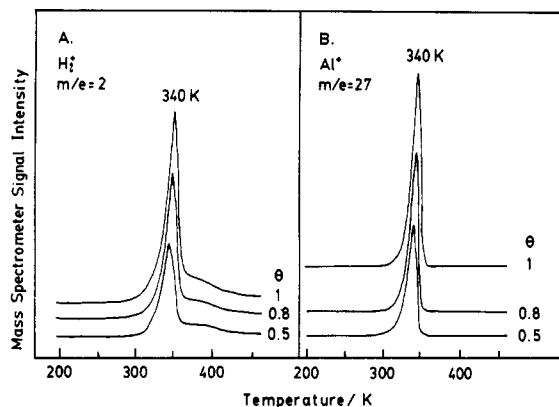


Figure 1. Thermal desorption spectra of $m/e = 2$ (H_2^+) (A) and $m/e = 27$ (Al^+) (B) with various hydrogen coverages.

that the recombination of hydrogen atoms on the surfaces is the rate-determining step. The zero-order desorption of hydrogen from aluminum single crystal surfaces suggests that the mechanism of desorption is different from the intuitively understandable one mentioned above.

Thus we investigated chemisorption and desorption behavior of hydrogen on an Al(111) surface by detailed analysis of TD spectra. In the course of this experiment, we found that aluminum hydride desorbed from the surface. This is the first report on desorption of metal hydride from hydrogen-adsorbed metal surfaces.

The experiments were performed in a stainless-steel ultra-high-vacuum system (base pressure 2×10^{-10} Torr) equipped with a double-pass CMA analyzer, a quadrupole mass spectrometer, four-grid LEED optics, and an ion gun. The Al(111) ($7 \times 7 \times 1$ mm) surface was cleaned by repeated cycles of Ar^+ bombardment at room temperature and annealing at 723 K. Cleanness and ordering of the surface were confirmed by Auger electron spectroscopy and low-energy electron diffraction. Since hydrogen molecules did not adsorb on Al(111), hydrogen was dosed as atoms. Hydrogen atom was generated by thermal dissociation of H_2 (5×10^{-7} Torr) by a heated tungsten filament at ca. 2000 K. The amount of adsorbed hydrogen was controlled by changing the heating time of the filament. The filament was set at a distance of about 5 mm above the surface. The temperature of the sample was kept at 150 K during the exposure to hydrogen atoms. In the thermal desorption experiment, the sample was then heated from 150 to 730 K at a heating rate of 10 K/s. The desorbed species were detected by the quadrupole mass spectrometer in line of sight. The ionization energy of the mass spectrometer was 70 eV.

Figure 1A shows TD spectra of $m/e = 2$ (H_2^+) at various hydrogen coverages. Desorption peaks were observed at ca. 340 K. Coverage of hydrogen on Al(111) surface was estimated by TD experiments of H_2^+ ($m/e = 2$). Areas of TD peaks for H_2^+ were constant above exposure time of 6 min. Since the exact concentration of hydrogen atoms, which were generated by the tungsten filament, was not determined, we used the heating time of the tungsten filament as the measure of the exposure time. Sharp (1×1) LEED spots were observed above exposure time of 6 min. Thus the amount of hydrogen on the surface which was adsorbed by an exposure time of more than 6 min was defined as a full monolayer coverage of hydrogen.

The peak tops shifted toward higher temperatures with the increase of hydrogen coverage. Furthermore, these peaks had common leading edges. This means that TD for $m/e = 2$ obeys zero-order desorption. In Figure 1B, TD spectra for $m/e = 27$ (Al^+) under the same experimental condition are also shown. Peaks of Al^+ were detected at ca. 340 K, where TD peaks of H_2^+ were observed. The intensity of the TD peak of H_2^+ is about a 100 times higher than that of Al^+ for the same coverage of hydrogen. The transmission factor of the mass spectrometer was calibrated by measuring the relative sensitivity for H_2 , He ($m/e = 4$), Ne ($m/e = 20$), and Ar ($m/e = 40$). The ratio of the

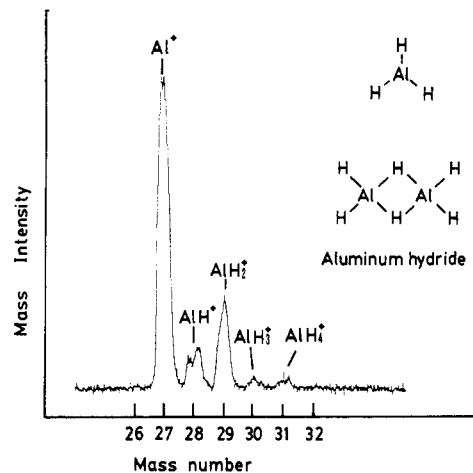


Figure 2. Mass spectrum of the desorbing species at 330 K at hydrogen coverage $\theta = 0.5$. $H/Al(111)$ was heated at the rate of 10 K/s. Scan rate is 125 amu/s.

transmission factors for $m/e = 2$ and $m/e = 27$ was 10/1. Taking into account the difference of the transmission factors, TD peak intensity of Al^+ is not negligible compared with that of H_2^+ . This means that the amount of Al^+ is not a spurious trace.

The coverage dependence of the peak shifts and leading edges of TD peaks for H_2^+ and Al^+ coincide completely. These facts suggest that TD peaks of H_2^+ and Al^+ are due to the fragments of a single desorbed species. On the contrary, a shoulder at around 370 K in TD of H_2^+ does not have a corresponding shoulder in TD spectra of Al^+ at this temperature as shown in Figure 1A. This suggests that the shoulder at ca. 370 K is due to desorption of H_2 .

To get further insight into the desorbed species, a mass spectrum of the desorbing species was measured at 330 K while the sample temperature was raised by the same conditions as the ordinary TD experiment. This snapshot mass spectrum was measured by scanning mass number from $m/e = 25$ to $m/e = 32$ with a mass scan rate of 125 amu/s and stored in a digital oscilloscope. The mass spectrum thus obtained at 330 K is shown in Figure 2 after subtracting a background spectrum. The background spectrum was measured at 150 K, immediately before the start of the temperature rise.

Signals of $m/e = 27, 28, 29, 30$, and 31 were detected at this temperature. The intensity ratio of these signals clearly indicate that these peaks are due to neither hydrocarbons nor CO. The peaks are assigned to Al^+ , AlH^+ , AlH_2^+ , AlH_3^+ , and AlH_4^+ , respectively. The split of the AlH^+ peak ($m/e = 28$) was an artifact caused by the background subtraction of the CO ($m/e = 28$) peak, which had an intensity of about 30% of that of AlH^+ . Furthermore, the signal of $m/e = 60$ ($Al_2H_6^+$), which is not shown in Figure 2, was detected at this temperature. The intensity of the signal for $m/e = 60$ was about half that for $m/e = 30$. AlH_3 (alane) and its dimer, Al_2H_6 , have been reported to exist under vacuum.⁶ These aluminum hydrides are, however, very unstable and easily decompose into Al and H_2 .⁷ Because of their inherent instability, the mass spectroscopic fragmentation patterns of the aluminum hydrides have never been measured. Thus, we cannot determine the exact molecular formulas for the desorbing species from the mass fragment pattern.

From all the results mentioned above, we conclude that at least a large part, perhaps almost all of adsorbed hydrogen, desorbs at around 340 K as aluminum hydrides such as AlH_3 or Al_2H_6 . It is expected that the desorption of aluminum hydrides relates with zero-order desorption kinetics.

The composition and the structure of the desorbed aluminum hydrides and surface reaction between adsorbed hydrogen and aluminum are now under investigation.

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