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Valence-Band Photoemission from a Quantum-Dot System

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We report the first application of valence-band photoemission to a quantum-dot system. Photoemission spectra of cadmium sulfide quantum dots, ranging in size from 12 to 35 Å radius, were obtained using photon energies of 20 to 70 eV. The spectra are qualitatively similar to those obtained for bulk cadmium sulfide, but show a shift in the valence-band maximum with size.

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The electronic structure of semiconductor quantum dots is strongly size dependent when the dot diameter is comparable to or smaller than the bulk exciton diameter.[1] Theoretical studies of such systems have predicted many interesting effects in semiconductor cluster electronic structure including discrete, well-defined states near the edges of the band.[2-4] Optical studies have confirmed these models of quantum confinement.[5-7] Further investigation into quantum-dot electronic structure away from the band edge has been limited by the inability to prepare adequate samples for nonoptical spectroscopies.

In Fig. 1 we present first nonoptical observations of the electronic structure of semiconductor quantum dots. A synthetic advance in dot preparation allowed the clusters to be bound to a metal surface, thereby decreasing the problem of charging, and allowing for the use of photoemission. Such spectra give very different information from existing optical studies. Figure 1(a) shows the photoemission spectrum in the 0–20-eV binding-energy regime of 38-Å-diam CdS quantum dots. This spectrum provides information about both the shape and absolute energy of the valence band, in contrast to ultraviolet-visible spectra, which specify energies of the bands relative to each other, and give useful information only at the band edge. Figure 1(b) shows the top of the valence bands of two sizes of quantum dots. There is a small, but measurable, blueshift in the valence-band edge in the smaller dots. The magnitude of the blueshift depends on quantum confinement, as well as the ability of the dots to stabilize the positive hole left behind by photoemission. The solvation of charge in confined systems, although well studied in gas-phase alkali-metal clusters, has not previously been measured in condensed-phase semiconductor dots. Unlike optical spectra, the photoemission data in Fig. 1 represent contributions from *all* electronic states of the system and yield information about both the interior of the dot and its surface.

The experimental application of valence-band photoemission to quantum dots was made possible by chemi-

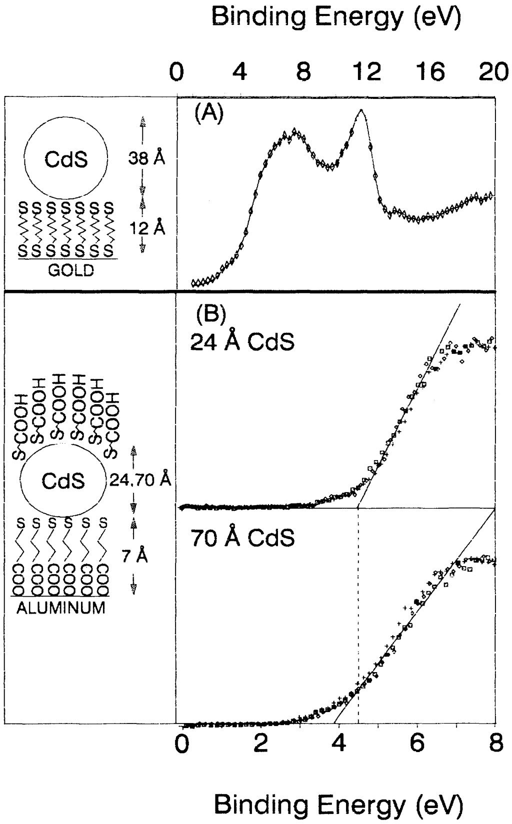

FIG. 1. Photoemission spectra from CdS quantum dots bound to metal surfaces, and schematic illustration of the samples. (a) The spectrum in the 0–20-eV binding-energy regime of 38-Å-diam CdS bound to gold using hexane dithiol. (b) Expanded view of the photoemission valence edge from 24- and 70-Å-diam clusters bound to aluminum surfaces. These raw data have been scaled so that the two spectra give approximately 3000 counts from 7 to 8 eV (typical count values were 3000 counts/sec), and include points obtained from 50, 55, and 60 eV energies. Extrapolation of the rising edge gives the valence-band maximum, which is observed to shift to the blue by 0.63 eV in the smaller clusters.

cally binding the dots to a metal surface with a short bridging alkane chain. Quantum dots of the prototypical II-VI semiconductor CdS with narrow size distribution (±3% in diameter) were prepared in colloidal solution and then bound to a metal surface.[8,9] Three different sizes of CdS quantum dots were prepared by established techniques.[10] Characterization of these samples included x-ray diffraction, ultraviolet-visible spectroscopy, transmission electron microscopy (TEM), and resonance Raman scattering. All data were consistent with monodisperse, highly crystalline clusters of 12, 19 and 35 Å radii.[8,9] Bifunctional organic groups were used to covalently bind the clusters on one side and the metal surfaces on the other. In one case, the 19-Å-radius CdS clusters were bound to a gold surface via hexane dithiol [see Fig. 1(a)] using the strong gold-sulfur bond as an anchor.[11] In a second method, the 12- and 35-Å-radii CdS were coated with carboxylate groups which then formed bridging bonds to an aluminum surface[12] [see Fig. 1(b)]. Tight-binding calculations[13] of the band gap in small particles were used to extract the sizes of the clusters from their solution-phase ultraviolet-visible spectra. These sizes were in agreement with those obtained from TEM images. The cluster-coated metal surfaces were characterized by contact angle, x-ray photoemission spectroscopy, resonance Raman scattering, Rutherford backscattering (RBS), and TEM measurements. The size-dependent resonance Raman spectra and resonance Raman excitation spectra of the metal/cluster samples both provide a measure of the size of the quantum dots bound to the metal surface.[14] The size measured this way is in agreement with measurements of the quantum-confined optical spectra of the dots in solution. From this we conclude that the dots are deposited intact and without aggregation on the metal surface. From Raman cross-section measurements and RBS, we estimate the coverage to be 0.4 monolayer,[8,9] where 1 monolayer is a close-packed array of CdS clusters.

Photoemission studies of the clusters were performed on the 4-m normal-incidence monochromator at the University of Wisconsin Synchrotron Radiation Center's 1-GeV ring, Aladdin. Photons in the 20–70-eV range were selected with 50-meV resolution. The metal-bound semiconductor cluster samples were mounted on a copper block attached to a liquid-nitrogen-cooled manipulator in a UHV chamber with a base operating pressure of 3×10^{-9} torr. Tantalum masks exposed only the center of each film, and allowed the film to make electrical contact with the rest of the spectrometer. Several samples composed of cluster powders pressed into aluminum foil were also loaded on the sample holder. (These samples yielded broad, low signal levels due to sample charging.) The capabilities of the photoelectron spectrometer used in these experiments have been demonstrated elsewhere.[15] Although the spectrometer is angle resolved, the spectra in this experiment are inherently angle averaged since the clusters have a random orientation with respect to the metal. Typical pass energies were 20 eV or less, resulting in an upper limit of 140 meV for the resolution. All binding energies in this paper are reported with respect to the Fermi energy of freshly evaporated gold.

Photoemission spectra of CdS clusters bound to metal surfaces are shown in Fig. 1. The photoemission spectra of the CdS clusters are qualitatively similar to bulk CdS data. We assign the peak at 11.66–12.52 eV to the shallow 4*d* cadmium core; photoemission on bulk CdS indicates this core level to occur at 11.35±0.55 eV.[16] This peak increases in size relative to the rest of the spectrum as the ionizing photon energy is increased, consistent with theoretical calculations of the 4*d* cadmium cross section, which indicate a resonance near 60 eV.[17]

The second broad feature at 6 eV is due to the valence band of the clusters. These bonding electrons belong to both the interior and the surface of the cluster, given that the escape depth of the photoelectrons in this range is 10–30 Å.[18] The shape of the spectrum resembles that of the angle-integrated CdS single-crystal data, with some additional broadening.[19] The absolute position of the valence-band edge depends on cluster size, as shown in Fig. 2. By definition the valence-band maximum E_{vb} is the intercept of the linear extrapolation of the leading edge with the energy axis.[15] From Fig. 1 it is evident that as the cluster becomes smaller the valence edge shifts to higher binding energy. (The data shown in Fig. 1 are raw data, obtained from 50, 55, and 60 eV photon energies. The *x* axis, binding energy, was determined by subtracting the kinetic energy of the electrons plus the

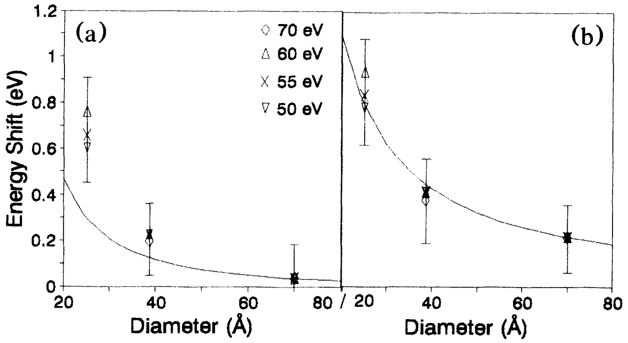

FIG. 2. Energy shift of the valence-band maximum vs cluster size. The points are experimental, and unlike the data in Fig. 1, have been reported for each photon energy separately and include 70-eV data for 38- and 70-Å-diam dots. (a) Since the shifts are independent of absolute position, the largest size shift was fixed to be 0.038 at a radius of 35 Å in agreement with Eq. (1). The other two data sizes are then in poor agreement with the predicted size dependence which includes only quantum confinement. (b) As in (a) the 35-Å shift was fixed to be 0.217 in agreement with Eq. (3). The additional two data points are then in good agreement with theory, which includes a dielectric polarization term as well as quantum confinement.

work function from the photon energy.) The magnitude of this shift is 0.63 ± 0.15 eV between the largest and smallest quantum dots studied here. This effect is not a translation of the entire spectrum as would be the case with band bending; rather it manifests itself as a change in the slope of the photoemission threshold. This effect is due to changes in the electronic structure of the quantum dots.

The valence-band edge shifts to larger binding energy in smaller clusters. This observed shift corresponds to a narrowing of the valence band and correlates well with optical measurements of band-gap broadening. The simplest model of quantum confinement, within the effective-mass approximation, predicts a shift of the valence edge with size according to[1]

$$\Delta E = \hbar^2\pi^2/2m_h R^2 , \tag{1}$$

where m_h is the hole effective mass and R is the cluster radius. We expect an additional shift, from the loss of dielectric solvation energy in smaller particles. Since the final state in photoemission is ionic, its energy is stabilized by the polarization of the surrounding atomic cores. Brus has considered the magnitude of this stabilization for a finite dielectric surrounded by vacuum.[1] Inside a dielectric sphere of radius R the potential from a point charge is

$$U(r) = \frac{e^2}{2R}\sum_{n=1}^{\infty}\frac{(\epsilon-1)(n+1)}{\epsilon(\epsilon n+n+1)}\left(\frac{r}{R}\right)^{2n} , \tag{2}$$

where r is the position of the charge and ϵ is the high-frequency dielectric constant of cadmium sulfide. Equation (2) reduces to the bulk result for large R. The shift due to the ionization potential can then be found by calculating a weighted average of Eq. (2) over the hole wave function. This term, in addition to the kinetic-energy term, describes the shift of the valence band with size:

$$\Delta E = \hbar^2\pi^2/2m_h R^2 + (e^2/2R)\bar{U} , \tag{3}$$

where $\bar{U}$ is the average of Eq. (2) over the $1S$ wave function of the hole in the crystallite. The two terms, one due to the kinetic energy and one due to the polarization, have the same sign.

Figure 2(b) shows a plot of the energy of the maximum of the valence band versus cluster size as predicted by Eq. (3) versus the data from our experiment. We have also included the predictions of just the quantum-confinement model from Eq. (1) for comparison [Fig. 2(a)]. In these graphs, the energy shift of the largest dot relative to bulk CdS was adjusted to agree with theory, with the two remaining points plotted relative to it. It is impossible to use literature values of the bulk $E_{\rm vb}$ to set this point since literature values of $E_{\rm vb}$ for CdS single crystals vary over 1 eV.[15,18,20] Such variation is not surprising given that the exact difference between the experimental E_F and the $E_{\rm vb}$ is sensitive to many experimental conditions, such as surface cleanliness, Ohmic contact between the sample and detector, artificial doping, and intrinsic sample impurities.[15] Thus, it is only possible to compare values of $E_{\rm vb}$ obtained within the same experiment. Figure 2 illustrates that in the size regime in which we are working the contributions to the shift from quantum confinement and from solvation are comparable in size, and both must be included to achieve satisfactory agreement with experiment. While we are assuming the $1/R$ and $1/R^2$ dependences to be from hole destabilization and quantum confinement, future experiments in which the dot to metal distance, the nature of the spacer, and the identity of the metal are systematically changed will further test this model.

One feature of the data presented in Fig. 1 is that unlike bulk CdS valence bands obtained from angle-resolved photoemission,[16] the valence bands of these samples have no structure. Since the crystalline clusters are randomly oriented, their valence bands are smeared by the inherent angle averaging of this experiment. Also, the total density of electronic states in the clusters, as reflected in the photoemission spectra, has a contribution, particularly in the 6–9-eV range, from the organic molecules on the surface.[21] This contribution can be elucidated by studies in which dot diameter is kept constant, and the nature of the surface species is systematically varied.

Another feature of the data presented in Fig. 1 is that the clusters, whether bound to gold or aluminum, give qualitatively similar spectra. This insensitivity to the metal surface is not surprising given that the escape depth of the photoelectrons at these energies, 30–70 eV, is 10–30 Å.[16] With a uniform coverage of clusters 24 to 70 Å in diameter, the spectra only reflect the density of states of the cluster. In contrast to these ultraviolet photoemission spectroscopy spectra, x-ray photoemission data on these same samples show significant features from the metal surfaces, reflecting the increased escape depth of the higher-kinetic-energy electrons.

Photoemission spectra have been obtained for clusters of CdS ranging in size from 12 to 35 Å radius. The preparation of a film of clusters bound to a metal was crucial since spectra from powders gave broad, small signals. Features in the spectra could be assigned to the cadmium $4d$ core and the CdS valence band. The surface of the cluster did not contribute a noticeable feature to the data. The data show a small, but measurable shift of the valence-band maximum to higher energy in smaller clusters. We attribute this shift to a combination of quantum confinement and loss of dielectric solvation energy in smaller particles. This study establishes the feasibility of using photoemission to study quantum dots. Using the method we have developed for attaching the quantum dots to the metal surface, it is possible to change the metal, the chemical nature of the organic linker, and the distance from the quantum dot to the metal. Thus we will be able to further test the origin of the observed changes in the photoemission spectra with dot size.

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