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Authors

Tobin, JG

Colvin, VL

Alivisatos, AP

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Photoemission investigation of compound semiconductor monodisperse clusters

J. G. Tobin

Lawrence Livermore National Laboratory, Livermore, California 94551

V. L. Colvin and A. P. Alivisatos

University of California, Berkeley, California 94720

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We have used synchrotron radiation photoemission to probe the valence and core level electronic structure of compound-semiconductor monodisperse clusters (nanocrystals). These clusters exhibited a 10% or less variation relative to the mean diameter and were attached to the metal substrates via alkane chains. Direct evidence of gap broadening due to size variation in CdS clusters was observed. The novel utilization of alkane chain attachment is the key to eliminating the otherwise debilitating problem of sample charging, as occurs with powders. The quality of sample preparation was confirmed by other methods such as transmission electron microscopy, Raman scattering, and x-ray diffraction. This work provides a direct link between photoemission studies of epitaxial ultrathin films of compound semiconductors, the photon-spectroscopy measurements of cluster powders and the existing theories of quantum confinement in reduced dimensionality structures.

I. INTRODUCTION

Understanding the relationship between structures and properties on an atomic scale remains a crucial goal in the study of reduced dimensionality systems. One avenue of attack upon these important questions is the study of the size dependence of the electronic structure in compound semiconductor nanocrystals. In these monodisperse (single-size) clusters, the finite size (diameters of 2 to 20 nm, 20 to 200 Å, 10^2 to 10^5 atoms) and crystallinity can combine to create effects such as novel variations of their optical properties and catalytic capabilities. The thrust of the experiments described here is to probe the occupied valence electronic structure with synchrotron radiation photoemission, using a unique wet chemical method for growth and attachment of the nanocrystals to the metallic substrates.

II. CLUSTER SYNTHESIS

One of our goals is to prepare semiconductor clusters in the condensed phase with very narrow size distributions.¹ Clusters of CdS in the 20 to 200 Å size regime with diameter distributions of 3% are routinely synthesized in our laboratory. The chemical preparations rely on the fact that, in the very early stages of crystal growth in solution, small crystallites are formed which all grow in parallel, distributed uniformly in size. By terminating the crystal growth at this stage one is able to capture the crystallites. This is normally done by reaction the crystallites with an organic terminating moiety. This organic group "caps" the cluster surface, preventing the clusters from aggregating or growing further. By appropriately choosing the organic group on the surface one can adjust the solubility of the clusters. Thus the clusters can be dissolved in polar or nonpolar solvents, or they can be dispersed in a polymer film; in addition, all solvent can be removed and one obtains a powder of coalesced clusters (these can subsequently be redissolved); finally, the organic

group can be bifunctional, so that the other end can be used to attach the clusters to a variety of substrates. We have developed a method to attach the clusters to Au and Al surfaces using short chain alkanes as bridges. This is shown schematically in Fig. 1.

III. CLUSTER CHARACTERIZATION

Once the clusters are made they are characterized by the following methods:¹

(i) Transmission electron microscopy is performed at the National Center for Electron Microscopy at Lawrence Berkeley Laboratory. These experiments allow us to determine particle size and shape. From the electron diffraction pattern one can determine the crystallinity of the samples.

(ii) X-ray powder diffraction is used to determine the crystallinity of the samples. The width of the x-ray diffraction lines are consistent with the finite size of the clusters, and indicate that the material is highly crystalline.

(iii) Resonance Raman scattering is used to measure the vibrational spectra.

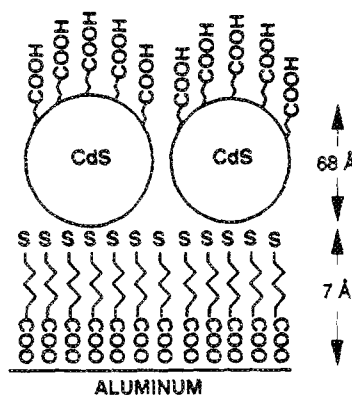


FIG. 1. Schematic representation of the attachment of the CdS clusters to the aluminum substrate via alkane chains.

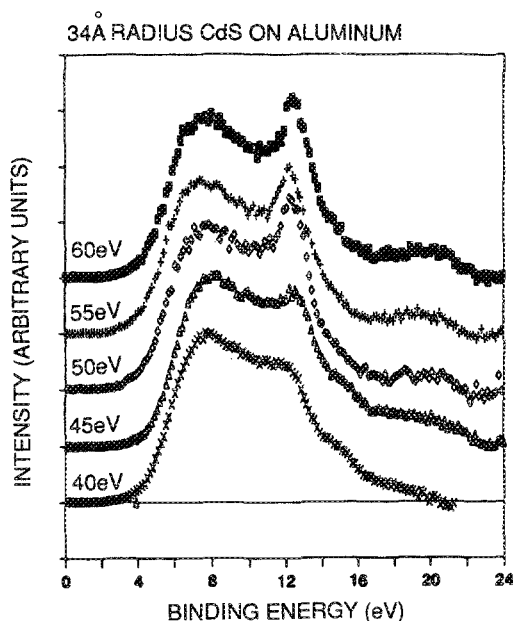


FIG. 2. Photoemission spectra of 34 Å radius CdS clusters on an aluminum substrate. The photon energies are shown on the side. The binding energy is relative to the Fermi energy, established via gold evaporation. Note the Cd 4d core level peak at a binding energy of about 12 eV. The valence-band maximum edge can be seen at a binding energy of about 4 eV. Backgrounds have been subtracted from these spectra.

(iv) Optical absorption is measured to study quantum size effects.

(v) X-ray fluorescence is used for elemental analysis.

(vi) In-house x-ray photoelectron spectroscopy (XPS).

IV. SYNCHROTRON RADIATION PHOTOEMISSION

The occupied electronic structure of the clusters was probed with photoemission,² using synchrotron radiation from the 4-m NIM beamline on the 1-GeV ring, Aladdin, at the University of Wisconsin Synchrotron Radiation Center. An example of our data is shown in Fig. 2. The novel use of the alkane chain attachment of the cluster to the metal sub-

strate is essential for the avoidance of sample charging. As described above, the quality of the sample preparation was confirmed by several other methods and the distribution of cluster diameters is 10% or less of the mean diameter.

One of the most interesting properties of the clusters is the strong dependence of the valence-band maximum on size. The crystallites we make are smaller than the bulk semiconductor exciton diameter, and consequently show quantum size effects. We have observed these effects in photoemission spectra which were obtained for CdS clusters ranging in size from 32 to 70 Å diameter.³ The clearest result to emerge from these experiments is that the valence band collapses in the smaller clusters. That is, the valence-band maximum moves to smaller binding energies as the nanocrystals increase in size. This shift is due to both a quantum confinement in the initial state and size-dependent final state charge solvation, as described in Ref. 3.

In the future, we expect that at sufficiently high resolution we should be able to observe a discrete series of states in the valence bands of the smallest clusters. Additionally, we recently have begun work using GaAs clusters⁴ and have collected preliminary photoemission data of the GaAs clusters at the Stanford Synchrotron Radiation Laboratory.⁵

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