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Title: Nucleation and growth of semiconductor nanocrystals by solid-phase reaction

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The principal goal of this program has been to study and learn to control the nucleation and growth of Cd-chalcogenide semiconductor clusters and nanocrystals in borosilicate glasses. A major goal of the second period of funding for this program was to understand mechanisms by which nanoparticles can be patterned into arrays for photonic applications, enabling systematic research on the generation of such ensembles by creating a reliable microscopic model for nanocrystal nucleation and growth. To this end, we have conducted a detailed study of the evolving atomic-scale structure around reactant atoms in the glass and the connection of that structure to particle properties. In the following, we review some specific achievements of this program.

Pursuant to the goals of this project, we applied for and were granted substantial synchrotron beam time of approximately 2400 hours on the most competitive beam lines (4-2 and 10-2) at the Stanford Synchrotron Radiation Laboratory.

First, we have developed a methodology for the coordinated analysis of optical absorption, Raman scattering, and x-ray absorption for understanding the formation and structure of nanoparticle semiconductors in a wide-band gap matrix. This methodology has been applied to address several issues in nanoparticle growth and properties. Analysis of XAFS is relatively independent of the details of crystallite structure and size. As a result, the analysis of concentration, coordination species and number, and nearest-neighbor bond distances for atoms for which there is a distinct and measurable x-ray absorption edge is straightforward. XAFS does not tell us directly however, whether the detected atoms are in large or small particles or are spread throughout the glass. Composition variation, strain, and size affect both the optical and vibrational properties of II-VI nanoparticles. Optical measurements alone cannot be used to determine size distribution. By simultaneously analyzing XAFS neighbor distances and second neighbor structure, Raman shift of the first TO mode, and HOMO-LUMO optical gap we have been able to separately determine strain and composition. Resonant Raman scattering allows us to identify a vibrational mode with a specific optical absorption energy. The vibrational mode energy, combined with XAFS measurements, allows us to place limits on the composition and strain of the particles. Once the composition and strain of particles are determined, the optical absorption spectrum along with the known size dependence of the HOMO-LUMO optical gap allows us to determine the particle size distribution.

Using the combined optical and x-ray approach we have shown, for larger CdS particles in glass, that properly scaled optical absorption measurements yield semiconductor volume fractions that are consistent with XAS and XAFS measurements. One can then deduce the fraction of Cd that is involved in large particles. (In the case of CdSe and CdTe, we can also determine the fraction of chalcogen in large particles.) We have found that at the earliest stages of heat treatment and particle formation, where there is no clear optical absorption signature for the presence of particles, XAFS shows that a considerable fraction of the Cd is coordinated with the chalcogen (S, Se, or Te) at the corresponding bulk bond length. Therefore, in the early nucleation stages most Cd-chalcogen bonds are in small clusters that are large enough to have bulk-like local structure, but small enough that the HOMO-LUMO transition is near the glass absorption edge (e.g. < 1 nm diameter for CdSe).

We have also been able to use the combination of x-ray and optical spectroscopies to study the evolution of the composition of $Cd_{1-x}Zn_xS$ nanoparticles and to extend tests of thermodynamic ripening models. We have found that the incorporation of Zn into CdS particles in borosilicate glass is controlled by a quasi-equilibrium ratio of Zn to Cd dissolved in the glass and forming the particles. As nucleation and ripening proceeds, Cd is incorporated into CdS particles and the concentration of available Cd in the glass decreases. When the Cd concentration in the glass decreases, the ratio of Zn to Cd dissolved in the glass matrix increases, driving more Zn into the particles. We have developed a model that predicts that the concentration of Zn in particles, x, is proportional to $\exp(-A/R_c)$, where A is a temperature dependent constant and R_c is the time-dependent critical radius for stability of particles. This knowledge gives us new control over the composition of nanoparticles grown in glass. For example, one can decrease Zn incorporation by decreasing the Zn supply, increasing the Cd supply, or by stopping particle formation before the system substantially depletes the Cd.

There has been considerable discussion in the literature of a very substantial surface energy in “bare” CdSe nanoparticles, which leads to strain and electronic defects. Our earlier analysis of the homogeneous nucleation of CdS particles in glass using optical probes suggested that the surface energy of these particles is much lower than bare particles. The energy per unit surface area, or interfacial tension, Γ can be deduced from a measurement of the degree of lattice compression as a function of crystallite size. A simple model for the relationship yields $\Delta a/a = (2/3)\Gamma\kappa/R$, where a is the lattice constant, κ is the volume compressibility, and R is the radius of the particle. We used XAFS to measuring the bond length changes as a function of particle radius deduced from the optical absorption edge. We found that the first and second neighbor distances in CdS particles in glass are insensitive to particle size for particle diameters from 2 to 10 nm. This implies that the surface energy density is much lower than that of bare particles. This result has important implications for the formation and nature of interface defects.

We have also studied the degree of crystalline order in CdS nanoparticles in glass by analyzing the amplitude of the second neighbor peak in XAFS at the Cd K edge. We found that even relatively large CdS nanocrystals grown in glass at temperatures below ~650°C are not well ordered. This surprising result calls into question the theoretical approach that is used to model the optical properties of these materials. We have also found that the degree of order for CdS nanoparticles can be improved dramatically by increasing growth temperature to ~750°C.

We have studied the growth and properties of PbS nanoparticles in glass with quantum-shifted optical absorption edge wavelengths from 800-2400 nm. The nucleation stage is not as well defined as in CdS; we believe that growth occurs on well defined heterogeneous nuclei. We have extensively studied the nonlinear optical behavior of a group of samples with first excited peak around 1550 nm. The nonlinear response at the lowest energy transition displays several interesting characteristics. It is dominated by bleaching. First the rise time of the bleaching effect is of order 200 ns, implying that excited carriers are delayed as they decay to the lowest excited state. The origin of this delay is not as yet understood. We have proposed the presence of a resonant defect either above the LUMO or below the HOMO state. Second, the lifetime of the bleaching is of the order of microseconds. Direct recombination should be much faster. We attribute the slow decay to defect states within the gap. Photoluminescence suggests that these states are near the HOMO or LUMO states and shift along with them as the particle size is changed. It is clear that the presence and nature of both resonances and traps can profoundly limit optical siwtching applications.

Refereed journal manuscripts and conference presentations

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PRESENTATIONS:

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"Optical absorption indicator for homogeneous and heterogeneous nucleation of semiconductor nanoparticles in glass," P D Persans and T M Hayes, American Physical Society Meeting, Los Angeles, March 1998

"Growth and dissolution of CdS particles in glass," T M Hayes, L B Lurio, and P D Persans, X-ray Absorption Fine Structure X, Chicago, August 1998

"Optical probes of nucleation of semiconductor nanoparticles in glass," P D Persans and T M Hayes, MRS Fall Meeting Symposium F, Boston, December 1998

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"Surface energy of CdS nanocrystals in glass," T M Hayes, L B Lurio, J Pant, P D Persans, American Physical Society Meeting, Atlanta, March 1999

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"Cd and Se atomic environment during the growth of CdSe nanoparticles in glass", T M Hayes, P D Persans, A Filin, and C Peng , 14th International Glass Conference, Troy, NY, August 2003.

"Size-Dependent Composition of Semiconductor Nanoparticles in Glass", P D Persans and T M Hayes, 14th International Glass Conference, Troy, NY, August 2003.

<u>Theses and projects completed under this program:</u>

Pratima Rao (Ph.D. thesis 2001), “Growth and Characterization of CdS and PbS Quantum Dots in Glass”.

Feiran Huang (Ph.D. thesis 2003), "Nonlinear Optical Studies of PbS Nanoparticles in Glass".

Weixiao Huang (M.S. project 2002) - "Detection of optically induced heating of CdSe quantum dots in glass".

C Peng (M.S. project 2003) - "XAFS analysis of the Se environment in CdSe doped glasses".

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