Synthesis and characterization of PbSe quantum dots in phosphate glass

A. Lipovskii, E. Kolobkova, and V. Petrikov
\textit{St. Petersburg State Technical University, Department of Solid-State Physics, St. Petersburg 195251, Russia}

\textit{Department of Applied Physics, Cornell University, Ithaca, New York 14853}

Q. Shen and S. Kycia
\textit{Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York 14853}

(Received 26 August 1997; accepted for publication 7 October 1997)

The controlled synthesis of PbSe nanocrystal quantum dots with narrow size distributions was achieved through a process known as colloidal growth techniques. This method involves the synthesis of PbSe quantum dots in a phosphate glass host. Structural characterization by electron microscopy and X-ray diffraction shows that the dots have mean diameters between 2 and 15 nm. The exciton Bohr radius \( a_B = 46 \) nm in PbSe, so these quantum dots provide unique access to the regime of strong quantum confinement. The optical absorption spectra are compared to predictions of a theoretical treatment of the electronic structure. The theory agrees well with experiment for dots larger than \( \sim 7 \) nm, but for smaller dots there is some deviation from the theoretical predictions. © 1997 American Institute of Physics. [S0003-6951(97)01749-X]

The electronic and optical properties of semiconductor quantum dots (QDs) have recently attracted much attention due to their interesting physical nature and potential utility applications. Extensive work has been done on II–VI semiconductors, and more recently colloidal growth techniques have been extended to the synthesis of some III–V materials such as InP and InAs. In all of these materials it is possible to fabricate structures of radius \( R \) smaller than the exciton Bohr radius \( a_B \). Although the exciton can be strongly confined, there is a significant asymmetry between the individual charge carriers owing to the large difference in their effective masses. The Bohr radius of the hole in most II–VI and III–V materials is \( \sim 1 \) nm, so it is effectively impossible to achieve strong confinement of the hole. This leads to a net charge inhomogeneity in small QDs, which has important implications for the exciton-phonon coupling and thus the single-particle lineshape in these materials.

QDs of IV–VI materials such as PbS and PbSe offer unique access to the regime of strong quantum confinement in the sense that the electron, hole, and exciton all have relatively large Bohr radii. The electron and hole masses are almost identical in the bulk, so the electron and hole wavefunctions will be similar, approximating an ideal quantum dot in the strong-confinement limit. In PbSe the electron, hole, and exciton Bohr radii are 23, 23, and 46 nm, respectively. These large radii allow strong confinement to be achieved in relatively large structures. Thus, sparse electronic spectra can be obtained in quantum dots that do not have a large fraction of surface atoms. These QDs will also be advantageous for some optical applications since the lowest-energy exciton transition occurs at technologically important wavelengths in the 1–2 \( \mu \)m range.

Initial attempts to fabricate IV–VI QDs produced samples with absorption spectra blueshifted from the bulk material, but discrete exciton peaks were not observed. More recently, PbS QDs with narrow size distributions have been fabricated in polymers and in silicate glasses. Less work has been done on PbSe. Borrelli and Smith attempted to synthesize PbSe QDs similar to their high-quality PbS QDs but found that the PbSe phase was quite dilute due to poor Se retention during melting. Quantum size effects were recently observed in solution-deposited thin films of nanocrystalline PbSe, but the size distribution is broad in these samples.

Here we describe the synthesis and structural characterization of PbSe quantum dots in a phosphate glass host. Sizes ranging from 2 to 15 nm in diameter are produced with narrow size distributions. The ratio of quantum dot to exciton radii \( R/a_B \) is taken as a measure of the degree of confinement, and is very small: \( R/a_B \) ranges from 0.04 to 0.16 for these quantum dots. These samples provide previously unavailable access to the strong-confinement limit. For comparison, \( R/a_B \sim 0.16 \) is the minimum possible value for CdSe. The optical absorption spectra agree with theoretical predictions for QDs between 7 and 15 nm in diameter, but for smaller dots the observed energies deviate from the calculated values.

A ubiquitous problem in the preparation of semiconductor-doped glasses is the difficulty of obtaining a high concentration of the semiconductor in the final product. This is due to the low solubility of semiconductors in melts of glasses that are conventionally used as well as the volatility of the chalcogenides (the glass formation temperature is usually \( \sim 1600 \) °C). To allow for increased concentration of the semiconductor a novel phosphate-based glass system with increased solubility of chalcogenides has been designed. The composition of the glass is \( \text{P}_2\text{O}_5-\text{Ga}_2\text{O}_3-\text{ZnO}-\text{AlF}_3-\text{Na}_2\text{O} \), and CdS QDs have been fabricated successfully in this host. The solubility of PbSe in melted batches of the glass exceeds 1.5% by weight, which is roughly an order of magnitude larger than the solubility of II–VI semiconductors in commercial silicate glasses used as color filters. To reduce the loss of PbSe through evaporation, the composition of the glass was chosen to have a batch melting and preparation temperature of \( \sim 1150 \) °C, which is \( \sim 400 \) °C less than that of silicate glasses. The glass

\textsuperscript{a}Electronic mail: ago2@cornell.edu
transition temperature is in the range 415–440 °C depending on the sodium and gallium concentrations. A closed crucible was used for the glass preparation. In addition to preventing the loss of PbSe during the hour-long preparation, this allowed us to maintain a reducing atmosphere during processing of the glass batch and thus to eliminate oxidation of the semiconductor. After preparation the glass was quenched, and the final glass samples were transparent or slightly yellowish to the eye in spite of the 0.8% weight concentration of PbSe in the final glass.

Annealing of the glasses produced brownish to black coloring of the samples, indicating the development of a new phase. Initial electron microscope images and x-ray diffraction measurements confirmed the presence of a nanocrystalline PbSe phase. The annealing conditions were then varied empirically to produce a series of samples with different QD sizes in the range 2–15 nm. In general the particle size increases with longer annealing and/or higher temperature, as expected. Annealing temperatures were in the range of 395–430 °C, and, as a rule, were below the glass transition temperature. The duration of the anneal varied from several minutes to 1–2 h depending on the temperature and glass composition. The duration and temperature of the anneal are both less than those used in the synthesis of semiconductor-doped silicate glasses, for which the duration can be as long as tens of hours, and the temperature usually exceeds 600 °C.

Standard techniques were used to characterize the structure of the PbSe QDs. The sizes, crystalline structure, and composition of the QD-doped samples were determined using scanning transmission electron microscopy (STEM), x-ray fluorescence, and x-ray diffraction. The samples were prepared for transmission electron microscopy by grinding in an agate mortar and pestle under methanol. A holey carbon film was then swept through the methanol, picking up numerous microscopic pieces. A Vacuum Generators HB501 scanning transmission electron microscope operating at 100 keV and equipped with a high-resolution pole piece was used to acquire the images. Bright-field and annular dark-field images were simultaneously acquired using software developed at Cornell. The annular dark-field signal provides an image that is sensitive to the atomic number of elements in the specimen, and clearly shows the presence and size of the PbSe clusters. The x-ray diffraction measurements were performed at the A2 station of the Cornell High Energy Synchrotron Source (CHESS). Most measurements were done in transmission mode and x rays with energies of 17–35 keV were used.

The STEM image of a typical field of PbSe QDs is shown in Fig. 1. The particles are approximately spherical, with an average diameter of 8.5 nm. Lattice fringes are observed in some portions of the precipitate, and the measured lattice constant is 0.65 nm, in agreement with that of bulk PbSe. The images also indicate the presence of some nano-clusters of PbSe of size smaller than ~1.5 nm remaining from PbSe dissolved in the glass. The secondary x-ray emission spectrum of the PbSe-doped glass sample confirms the presence of lead and selenium as well as the glass-forming elements.

X-ray measurements of the QD samples exhibit clear diffraction peaks superimposed on the diffuse background from the glass host. Typical examples are shown in Fig. 2. The peak positions agree well with the bulk PbSe reflections, which confirms that the QDs have the sodium-chloride lattice structure. The particle size can be inferred from the width of the diffraction peaks. However, the background scattering from the host reduces the dynamic range of the measurements, and we find that only particle sizes larger than ~5 nm can be determined reliably from the analysis of the line shape. For particles larger than 5 nm the sizes inferred from x-ray diffraction and electron microscopy agree.

Optical spectra clearly exhibit the effects of quantum confinement. The optical absorption edge varies from ~4 eV in the doped but unannealed glass to nearly 0.4 eV with increasing anneal time. The absorption band around 0.4 eV is a feature of the undoped glass host. Figure 3 shows the room-temperature absorption spectra of quantum dots ranging in size from 2 to 10 nm. The onset of absorption is shifted substantially to the blue of the bulk band gap of 0.28 eV, with the 1.8-nm particles (bottom curve) showing a shift of 0.7 eV. An excitonic feature is visible in all but the smallest QDs, and in most cases one or more higher transitions are observed. We measured the absorption spectra at 10 K and found that the width of the lowest exciton peak decreases by at most 15%. Thus the linewidth is due primarily to inhomoge-
gnerous broadening, and we infer the width of the distribution $\Delta R/R = \pm 7\%$. The narrow size distribution indicates that oversaturation of the solid solution has not decreased to its minimal value, where coalescence begins, and independent growth of semiconductor crystallites is occurring even for the largest particles synthesized (since theory predicts about 50% size distribution for coalescent growth). This is possible due to the initial high values of oversaturation that were achieved with the phosphate glass matrix.

The electronic structure and optical properties of PbS and PbSe QDs were modeled by Kang using the envelope-function formalism. The calculation is based on a bulk $k \cdot p$ Hamiltonian with all parameters determined by experiment, assumes infinitely deep potential wells, and accounts for the correct symmetry of the band-edge Bloch functions. The predictions of this calculation agree very well with the measured optical transitions of PbS QDs with diameter between 3 and 15 nm. The lowest exciton energy predicted by the envelope-function calculation for PbSe is shown as a solid line in Fig. 4 for dot sizes up to 20 nm. The Coulomb correlation between the electron and hole is included in the calculation as a perturbation. The effect of Coulomb interaction (10–50 meV) is negligible compared to the confinement energy. The measured energies agree with the theoretical values for dots larger than 7 nm, but deviate from the calculations as the dot size is decreased below 7 nm. The envelope-function theory is not expected to be valid for the smallest (1.6 nm) QDs. However, the discrepancy between theory and experiment between 3.5 and 7 nm is systematic and significant. This discrepancy is worthy of attention since it occurs under the conditions of strongest confinement. One possible explanation is that the observed trend is simply a manifestation of the finite depth of the electron and hole potential wells. On the basis of preliminary modeling we conclude that this is unable to account quantitatively for the experimental data, and thus more work is needed to address this point. When the envelope-function calculation agrees with the observed lowest-exciton energy (i.e., for sizes >7 nm), it also accurately predicts higher transitions (Fig. 4 inset).

In conclusion, we have demonstrated the synthesis of PbSe quantum dots with controllable size in the range 2–15 nm and narrow size distributions. These samples will be extremely useful for probing the properties of electrons and phonons in the limit of strong confinement. The synthetic approach demonstrated here should also be applicable to the growth of PbS QDs. Since most existing models only describe the coalescent growth of nuclei under conditions of low oversaturation, modeling of the regime of relatively high oversaturation will also be desirable.

This work was supported by the National Science Foundation under Grant No. DMR-9321259, and made use of Materials Science Center facilities supported by Grant No. DMR-9632275. The STEM Laboratory is also supported by the Materials Science Center and was acquired through National Science Foundation Grant No. DMR-8314255. CHESS is supported by Grant No. DMR-9311772.