Raman spectroscopy of electrochemically self-assembled CdS quantum dots

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We report a Raman spectroscopy investigation of electrochemically self-assembled quasiperiodic arrays of CdS quantum dots with characteristic feature size of 10 nm. The dots were synthesized using electrochemical deposition of CdS into a porous anodized alumina film. Polarization-dependent Raman scattering study over an extended frequency range reveals the quantization of electronic states in the conduction band and intersubband transitions. Raman peaks observed at 2919 and 3050 cm^{-1} are attributed to transitions between the lowest two subbands. The results suggest that quantum dot arrays, produced by inexpensive robust electrochemical means, may be suitable for infrared detector applications. © *2000 American Institute of Physics.*
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Quantum dots represent the ultimate test bed for size quantization of both electrons and phonons. Strong spatial confinement of these entities create an exciting opportunity for reengineering of the optical, electronic, and thermal properties of many technologically important semiconductors through modification of their electronic states and phonon dispersion.[1,2] Intersubband optical transitions in quantum dots are of particular interest because of their potential use in infrared detectors.[3,4] Relative to two-dimensional quantum well structures, quantum dots have many advantages in optical applications due to their delta function-like sharp density of electronic states, and relaxed optical selection rules which allow for detection of normally incident light.[5,6]

To date, optical investigation of quantum dot arrays has been almost exclusively restricted to systems self-assembled in the Stranski–Krastanow (SK) mode of molecular beam epitaxy (MBE) growth.[1,4,7] The study of SK quantum dots has significantly added to the core knowledge of the physical processes in quasi-zero-dimensional (0D) structures. Alternate candidate, which can potentially lead to low cost manufacturing, is electrochemical self-assembly.[8–10] This technique is capable of fabricating dense (density $\rho \sim 10^{12}\,\mathrm{cm}^{-2}$) highly ordered quasiperiodic two-dimensional (2D) arrays of semiconductor quantum dots embedded in an insulating porous alumina matrix. It is a simple and inexpensive approach to self-assembling quantum dots and has an extremely fast throughput because it is a parallel process whereby several arrays can be self-assembled simultaneously.

In this letter we report the Raman scattering polarization study of arrays of cadmium sulfide (CdS) quantum dots self-assembled by the electrochemical technique. CdS is a direct-band gap, II–VI compound semiconductor that can be used for the fabrication of optoelectronic devices such as solar cells, laser diodes, and photoconductors.[11] Raman spectros-copy has been chosen as an experimental tool since it allows for probing of active optical phonon modes, as well as confined electronic structure of quantum dots.[12] The latter is particularly important since the sample structure of self-assembled quantum dot arrays does not allow for Fourier transform infrared (FTIR) spectroscopy in the regular waveguide geometry. Owing to the small amount of CdS deposited inside the nanopores and the large band gap of bulk CdS ($E_G \sim 2.5\,\mathrm{eV}$), it is also difficult to study confined electron levels in this system using photoluminescence excitation (PLE).

The samples for this study have been prepared by following a number of steps. First, a thin foil of aluminum is anodized for a few hours in 15% H_2SO_4 at a dc current density of 40 mA/cm^2 to produce a thick nanoporous alumina film on the surface of the foil. This film is stripped off and the anodization is repeated for a few minutes. The porous alumina film that forms in the second iteration contains an ordered hexagonal array of pores with an average diameter of 10 nm and a pore density of $4 \times 10^{10}\,\mathrm{cm}^{-2}$. The pores are then ''rounded'' by soaking in phosphoric acid for a few seconds and the porous film is subsequently washed in distilled water to remove debris. Finally, the pores are filled up with CdS using ac electrodeposition. This is accomplished by ac electrolyzing the film in H_2SO_4 for a few seconds followed by immersion in a boiling aqueous solution of $CdSO_4$. The Cd^{++} ion in the solution reacts with the S^{--} ion left behind in the walls of the pores from the ac electrolysis step to form CdS.

The amount of CdS that goes into the pores increases superlinearly with the duration of immersion in $CdSO_4$. During the fabrication process, we have carefully avoided overfilling the pores by adjusting the immersion time. For this study, we have chosen CdS since it requires very simple deposition steps, and has a linear expansion coefficient ($\kappa = 5.0 \times 10^{-6}\,\mathrm{K}^{-1}$) matched to that of the alumina substrate

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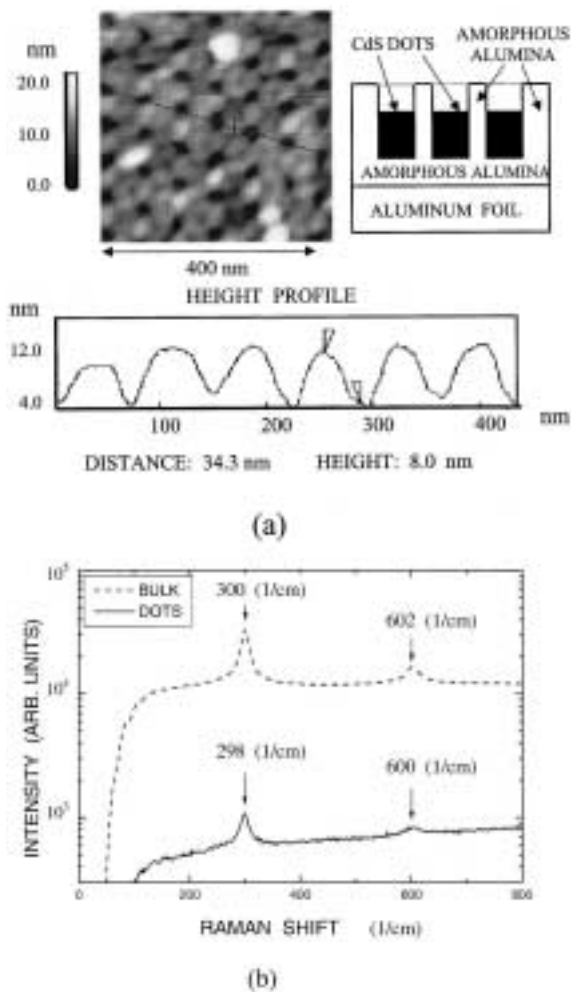
FIG. 1. (a) Atomic force image of the nanoporous alumina (Al_2O_3) template used for electrochemical fabrication of the quantum dot arrays. The interdot separation for this sample is about 30 nm. Inset shows a schematic drawing of the CdS dot array; (b) Raman spectra of the electrochemically self-assembled CdS quantum dots and corresponding bulk material. The intensity of the signal from the dot array is much weaker. The longitudinal optical (LO) phonon peaks of CdS are seen at about 300 and 600 cm^{-1} (second order). A small redshift of the peaks with respect to the bulk position may be due to spatial confinement of phonon modes.

($\kappa = 5.8 \times 10^{-6}$ K^{-1}). An atomic force micrograph (AFM) of the regimented nanoporous alumina template, which was subsequently filled with CdS, is shown in Fig. 1(a). An inset shows a schematic drawing of a cross section of a typical electrochemically self-assembled quantum dots array after the deposition step.

Raman spectra were measured using a Renishaw Raman Imaging 2000 microscope at room temperature. All spectra were excited by the 514 nm line of an Ar ion laser in the backscattering configuration and recorded by a Si charge-coupled device (CCD) camera. The spectral resolution of the instrument was about 0.1 cm^{-1}. The polarization dependent Raman spectra were taken over an extended frequency range from 250 to 4200 cm^{-1}.

The low-frequency part of the spectra for CdS dots and bulk material is shown in Fig. 1(b). One can clearly see two characteristic CdS longitudinal optical (LO) phonon peaks at about 300 cm^{-1} (1LO) and 600 cm^{-1} (2LO). The intensity of peaks from the quantum dot array is much weaker than that from bulk CdS. This is expected owing to the small amount

of material electrodeposited inside the nanopores. We observed a systematic downshift of the 1LO peak of the quantum dot arrays by one to two wave numbers from its bulk position. This result is consistent with the data reported in Ref. 11 for CdS nanoclusters fabricated by the solution growth technique (SGT) on slide glass substrates, and for CdS dots ($D \sim 4 - 10$ nm) embedded in silicon dioxide glass films.[12] The fact that the redshift of the phonon peaks due to spatial confinement of phonon modes[13] is not all that pronounced may be explained by its compensation due to strain-induced blueshift. This situation is similar to the one recently reported by some of us for MBE grown Ge quantum dots on the Si substrate.[3]

All spectra in our study have been excited by the 514 nm line of an Ar ion laser corresponding to the energy $E \sim 2.4$ eV, which is lower than the band-gap energy for CdS. In the past, absorption and photoluminescence studies indicated that the effective band gap (blueshifted due to quantum confinement and strain) is about 3 eV.[8] Under the conditions of extreme resonance, when the laser frequency is close to the effective band gap, the background due to the hot luminescence dominates the spectra.[14] In the extended polarized spectrum $[x(z,z)\mathbf{x}]$ of all examined samples, we observed a pronounced broad peak around 3000 cm^{-1}. It occurred at 2919 cm^{-1} ($E = 361$ meV) in sample A and at 3050 cm^{-1} ($E = 377$ meV) in sample B. We attribute it to intersubband transition within the conduction band of CdS dots (see Fig. 2). The large linewidths of these peaks accrue mostly from inhomogeneous broadening of the intersubband levels due to variations in the dot size across the irradiated portion of the array (the laser spot will typically excite about 10 000 dots simultaneously). The dots are actually somewhat cylindrical in shape (like the pores into which they are "cast"). Although the diameters of these cylinders exhibit less than 5% variation, the heights of these cylinders vary by much more and this variation could easily account for the large linewidth. Other than size nonuniformity, asymmetry of the confining potential and interfacial strain could also contribute to the linewidth broadening. Finally, it is even possible that the high frequency shoulders in Fig. 2 are due to overlap of additional unresolved peaks from other intersubband transitions. Due to this reason, it is not possible to accurately determine the full width at half maximum.

We have excluded free-electron absorption in the aluminum foil as an origin of the peaks in Fig. 2 by measuring the Raman spectra of the bare alumina film without the CdS in the pores. The bare film shows no peak. The peak structure observed when the alumina pores are filled with CdS, and the line shape, are analogous to those associated with previously reported intersubband transitions in Ge quantum dots observed both by Raman spectroscopy[3] and by Fourier transform infrared (FTIR) spectroscopy.[4]

It is reasonable to assume that the peaks are related to the transitions between the two lowest confined electron states ($E1 \leftrightarrow E2$). If we proceed from this assumption, then, using the simple infinite barrier model for these dots and neglecting exciton effects, we can estimate the dot diameter to be $D = 3.9$ nm for sample A and $D = 3.8$ nm for sample B (dots are assumed to have a cylindrical shape with the height equal to the diameter). In this calculation, we assumed that
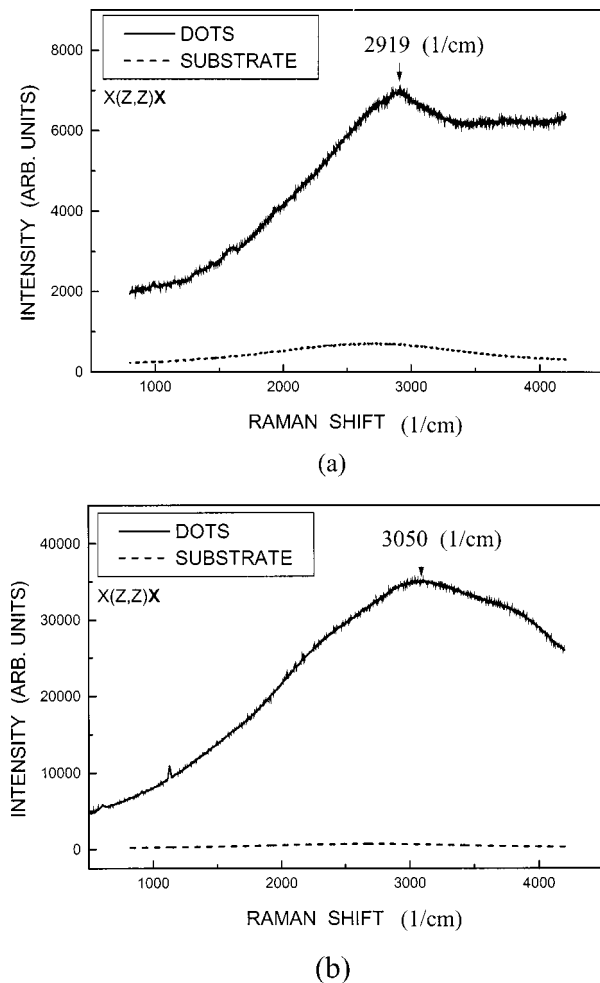
FIG. 2. High frequency polarized Raman spectrum of CdS dots (solid lines) of the sample A (a) and sample B (b) and the aluminum substrates with the layer of alumina (dashed lines) used for their fabrication. The effective optical size of the dots of sample B is smaller than that of sample A. The latter is expected from different anodizing processes applied for fabricating these two samples.

the electron effective mass retains its bulk value of m_e^* $= 0.21 m_0$. The calculated dot sizes are less than what we find in bright field TEM images which show $D \sim 10$ nm. However, this discrepancy can be explained by invoking the side depletion caused by the Fermi level pinning at the CdS-alumina interface, which makes the effective dot diameter smaller. What is important is that Ref. 8 reported an effective dot diameter of 3.5 nm in such samples from an *independent* measurement (blueshift of the band gap measured from interband absorption). The close agreement between these two independent estimates lends credence to our claim of having observed intersubband transition. The high frequency shoulders in Fig. 2 may be attributed to additional unresolved peaks from other intersubband transitions with different peak positions due to quantum dot size variation and possible asymmetricity. The small features in the interval 1000–1500 cm^{-1}, which have been seen in some of the spectra, may have several different origins. A peak around 1200 cm^{-1} can be attributed to the higher-order optical phonon or water bands.

In conclusion, we have reported a Raman scattering study of electrochemically self-assembled CdS quantum dots

and provided the first evidence of the discretization of the conduction band states in these dots. The discretization is evidenced by intersubband transition within the conduction band. It is natural to ask why we do not observe intersubband transitions within the valence band. We believe that this is because the four times heavier effective mass of heavy holes decreases the hole subband spacing commensurately and makes the transitions unresolvable at room temperature. Previous experiments established only the existence of the lowest electron and highest heavy hole subband through a blueshift of the photoluminescence peak[8] thus providing evidence of quantum confinement, but no direct evidence of the discretization of conduction- or valence-band states. Those experiments involved interband transitions whereas the present involves intraband transitions. We have also observed a slight but systematic redshift of LO phonon peaks characteristic of spatially confined phonon modes. Finally, in the context of engineering applications, the observation of intersubband transitions in electrochemically self-assembled quantum dots holds out the hope of developing midinfrared detectors capable of detecting normally incident light. The fabrication technique that was used is robust, inexpensive, and has the high-throughput required for commercial applications.

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