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Quantum size effects on $CdTe_xS_{1-x}$ semiconductor-doped glass

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We present experimental evidences of quantum confinement in borosilicate glasses with a new microcrystallite $CdTe_xS_{1-x}$ semiconductor. The microcrystallite sizes are controlled by the heat-treatment time and temperature. Transmission electron microscopy measurements show the microcrystallites average diameters near 55 Å for the sample treated for the longest time. We observe a red shift from 570 to 640 nm in the absorption and photoluminescence spectra as the size increases. These shifts agree with the expected quantum-confined energies, varying from 0.80 to 0.60 eV. The absorption spectra also show a second feature which can be assigned to the second quantum-confined transition.

Quantum-confined effects in semiconductor systems of low dimension have attracted considerable attention. Beside the well-known multiple quantum well structures[1] which provide confinement in one dimension, semiconductor microcrystallites with sizes comparable to the exciton Bohr radius exhibit three-dimension quantum confinement. For II-VI semiconductors, the Bohr radii are typically in the range of 20–80 Å. Most of the experimental investigations have been concentrated in materials like $CdSe_xS_{1-x}$ and CuCl in the form of crystallites grown in borosilicate glass hosts or precipitated colloids in solution.[2–5]

The quantum confinement strongly modifies the optical properties like absorption, photoluminescence, and the nonlinear refractive index and opens up interesting problems in the physics of low-dimensional systems. Furthermore, the nonlinear properties of these materials[6–8] may have important applications in optoelectronics, such as picosecond optically bistable switches and fiber or other waveguides of highly nonlinear materials.[9–11]

Theoretical and experimental studies show an enhancement in the nonlinear properties due to confinement effects in the semiconductor microcrystallites.[12–14] The quantum confinement increases with the ratio between the Bohr radius and the crystallite size, and is strongly dependent on the bulk semiconductor properties. $CdTe_xS_{1-x}$ alloys have larger Bohr radii (74 Å) than $CdSe_xS_{1-x}$ (54 Å) alloys. Therefore, it is easier to reach the strong confinement region in the $CdTe_xS_{1-x}$ system which makes it more promising than $CdSe_xS_{1-x}$ for optoelectronics applications, as has been pointed out before.[14]

In this letter we give experimental evidences of quantum confinement in $CdTe_xS_{1-x}$-doped borosilicate glasses. We controlled the microcrystallite sizes with an adequate choice of heat-treatment time and temperature. From the absorption data we estimate the particle's diameters of different heat-treatment time samples. The shortest diameter is 44 Å while the largest is 54 Å. Transmission electron microscopy (TEM) performed on the smallest and the largest crystallite samples give an average particle's diameters of 39 and 55 Å with a typical 18% dispersion. When the particle size increases, we observe a red shift in the photoluminescence and absorption peaks. The absorption spectra also show another feature, assigned to the next subband transition, which together with the red shift are strong evidences of quantum confinement effects.

Experimental glasses were prepared by melting a glass host containing SiO_2, H_3BO_3, Na_2CO_3, and ZnO mixed with CdO, Te, and S in the $CdTe_{0.9}S_{0.1}$ stoichiometry. Other aspects of the growth are described elsewhere.[15] Subsequent heat treatment produces the semiconductor microcrystallites. The four samples used here were annealed at 580 °C for 40, 60, 90, and 110 min. Optical absorption measurements were done with a Cary–Varian 2300 model spectrophotometer and the photoluminescence spectra were obtained with 10 mW of the 488.8 nm line of a Spectra Physics argon laser and a Spex monochromator.

TEM micrographs were obtained in a Zeiss EM 902 microscopy equipped with an electron-energy-loss spectrometer (EELS). We used an agata mortar to fracture the doped glass. The resulting fine particles were dispersed in *n*-propanol and applied over parlodium-carbon-coated copper mesh grids. The observation was done on sharp edges or bubbles, in which there was sufficient contrast. Figure 1 shows a typical micrograph. The electron diffraction rings shown in the inset reveal a typical crystalline structure. Figure 2 shows the size histograms for two samples with 40 min [2(a)] and 110 min [2(b)] annealing time at 580 °C. The average diameters are 39 ± 7 Å and 55 ± 10 Å for the 40 and 110 min samples, respectively. Although the two distributions overlap ($39 + 7 \approx 55 - 10$ Å) their size separation (16 Å) is much larger than the average's dispersion $\approx \sqrt{10} \approx 3$ Å. Therefore there is a clear average size difference for the several annealing times.

Figure 3 shows the absorption spectra measured at room temperature for samples of the same batch with different heat treatment times. The inset shows the room-temperature photoluminescence spectra of the same samples. In the absorption spectrum of the sample with the shortest heat-treatment time, there is a clearly resolved first feature followed by a plateau and a shoulder. The photoluminescence peak is about 100 meV below the first ab-

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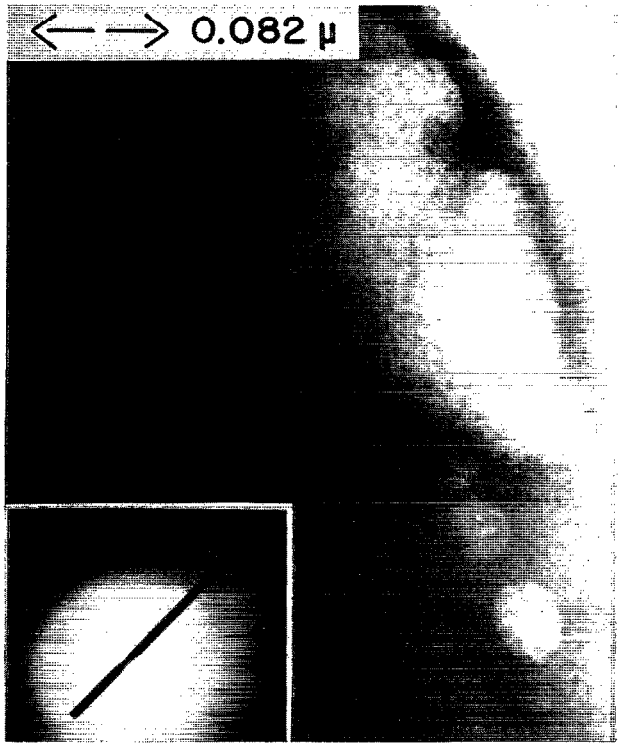

FIG. 1. TEM micrograph and electron diffraction pattern of $CdTe_xS_{1-x}$ doped glass for 110 min annealed sample with an average diameter 55 Å.

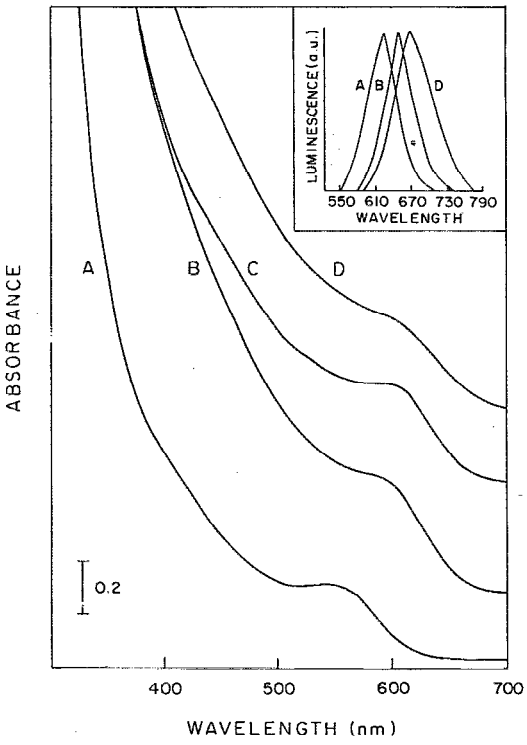

FIG. 3. Room-temperature absorption spectra for the samples annealed at 580 °C for (a) 40, (b) 60, (c) 90, and (d) 110 min.

sorption peak. As the heat-treatment time increases, the whole absorption and photoluminescence spectra shift to longer wavelengths, but with less separation between the shoulder and the first feature. The clear subband structures and the shift in both the absorption and photoluminescence spectra to longer wavelengths with heat-treatment time are consistent with quantum confinement effects due to the microcrystallite size. The first absorption feature is consistent with the $1S$ heavy-hole subband to the $1S$ conduction-subband transition, whereas the shoulder is consistent with the $1P$–$1P$ heavy hole to conduction the quantum-confined transition.[14]

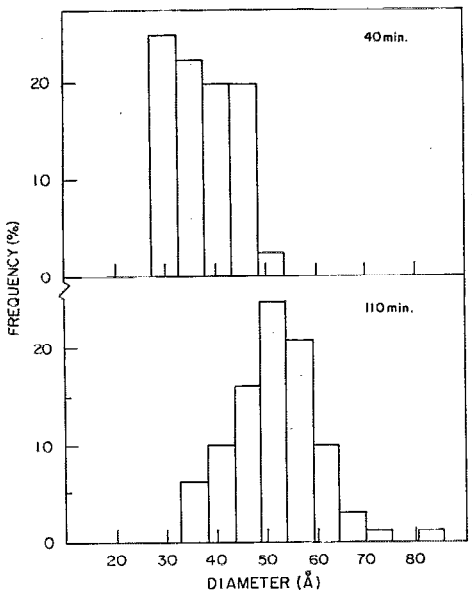

FIG. 2. Histogram of microcrystallite sizes obtained from TEM measurements for the 40 and 110 min annealed samples.

Our data can be explained accordingly to current models[2] which take into account the confinement energies under the effective mass approximation and neglect the Coulombic interaction. The energy E_j of the jth optical transition is given by

$$E_j = E_g + \frac{\hbar^2}{2\mu a^2}\chi_j^2, \tag{1}$$

where a is the particle's radii, μ is the reduced electron-hole mass, E_g is the bulk band gap, and the two values $\chi_s = 3.1416$ and $\chi_p = 4.493$ are the first non-null roots of the zero and first-order spherical Bessel functions.

In this model the separation between the first two transitions ($1S$–$1S$ and $1P$–$1P$) $\Delta E_{sp} = (\chi_p^2 - \chi_s^2)(\hbar^2/2\mu a^2)$ depends only on the reduced mass and the particles radii. Figure 4 shows a plot of E_s vs $E_p - E_s$. We measured both E_s and E_p by taking the average between the maximum and the minimum on the first derivative of the spectrum. The straight line which fits the points has a slope of 0.93, very close to $\chi_s^2/(\chi_p^2 - \chi_s^2) = 0.96$ value obtained with the above model. The constant term is 1.45 eV, which is consistent with the reported values for the CdTe bulk band gap. We estimate the microcrystallite diameter using an effective mass $\mu = 0.1$ and Eq. (1) as 44, 48, 50, 54 Å for the 40, 60, 90, and 110 min of heat treatment at 580 °C,

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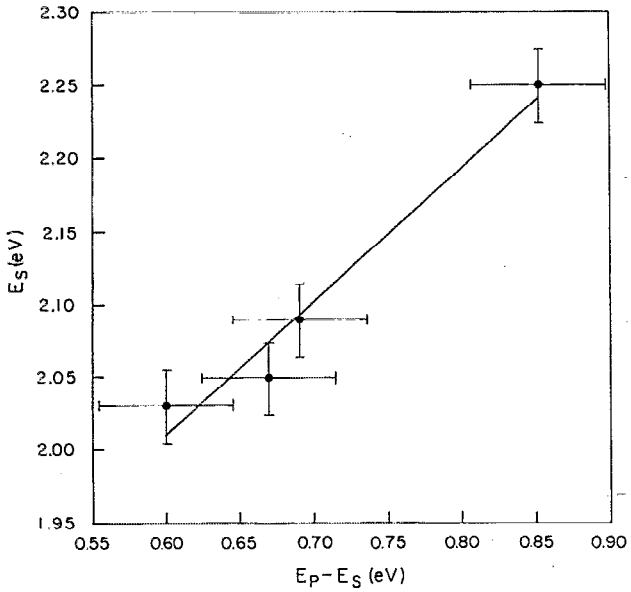

FIG. 4. Plot of the first transition energy E_S vs $E_P - E_S$ obtained from the absorption spectra.

respectively. These estimates are in good agreement with the TEM measurements 39 ± 7 Å and 55 ± 10 Å for the 40 and 110 min treatment time samples, respectively.

In conclusion, we show quantum confinement behavior in the new $CdTe_xS_{1-x}$ semiconductor microcrystallite-doped glass. This semiconductor can be more attractive than the presently used $CdSe_xS_{1-x}$ quantum box due to its smaller Bohr radii. The red shift in the absorption spectra as the size increases agree with a particle in a spherical well model. The estimated sphere's diameters are 44, 48, 50, and 55 Å with the correspondingly confinement energies of 0.80, 0.64, 0.60, and 0.58 eV for the 40, 60, 90, and 110 min annealing time at 580 °C, respectively. TEM measurements on the 40 and 110 min annealing time samples give an average diameter of 39 ± 7 Å and 55 ± 10 Å, respectively.

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