Nanocrystal Spectroscopy and Photophysics: Direct Gap CdSe and Indirect Gap Silicon

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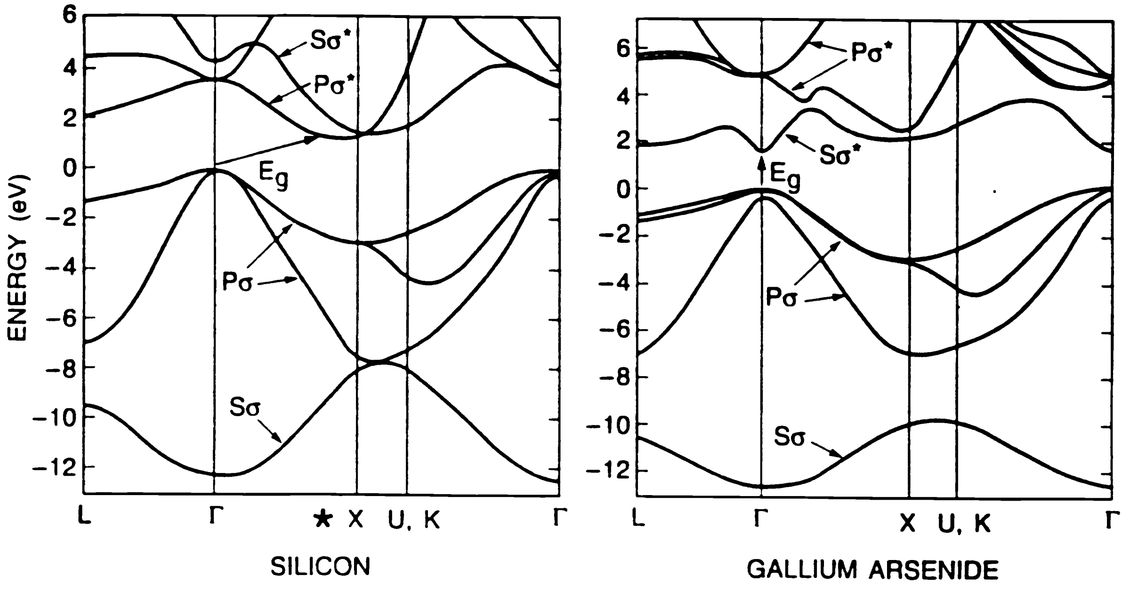
1. Introduction

Semiconductor nanocrystals containing 10^2-10^3 atoms show significant electronic quantum size effects at energies near the band gap. In solid state terms, this happens because of the large delocalization lengths (ie, small effective masses) that naturally occur for electrons and holes at band extrema in bulk crystals. This size dependence also has a clear, physically equivalent explanation in the language of molecular orbitals. Close analogies exist with the spectroscopy of large aromatic hydrocarbons. In this short manuscript, I compare two nanocrystal systems that have become prototypes for direct and indirect gap behavior: CdSe and Si. Despite the fact that both materials are tetrahedrally hybridized semiconductors of similar band gaps, the effects of quantum confinement are quite different.

2. Band Structure and Spectral Quantum Confinement

Figure 1 compares the band structures of GaAs and Si. The conduction and valence bands of zinc-blende CdSe are quite similar to GaAs. The valence bands of all three semiconductors are very similar: there is strong delocalization of the bonding electrons, and the resulting occupied molecular orbitals are determined principally by tetrahedral symmetry.



SILICON

GALLIUM ARSENIDE

Fig. 1 Band structures of Si and GaAs.

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In Si the degenerate, $P\sigma^*$ silicon antibonding saddle point type conduction band is lowest at Γ. However, electronegativity differences in the two compound semiconductors have the effect of pulling the nondegenerate, $S\sigma^*$ (charge transfer in nature) conduction band down to be lowest at Γ. In all three semiconductors, increasing S-P hybridization occurs as K increases away from the Γ point. In Si the absolute minimum occurs at * near the Zone boundary; silicon has an indirect, 1.1 eV band gap. In the two compound semiconductors, the absolute minimum is direct at Γ; there are higher, secondary minima near the Zone boundary. CdSe has a direct, 1.7 eV band gap.

Figure 2 from Murray, Norris, and Bawendi shows optical absorption of CdSe nanocrystals as a function of size. There is a wealth of size dependent structure; the continuous optical absorption of the bulk crystal becomes discrete, and the band gap increases as size decreases. In the CdSe system, photophysical hole burning and selective luminescence excitation methods have been developed as methods to separate the homogenous and inhomogeneous(sample distribution dependent) spectral widths of discrete transitions(2-4). In the hole burning spectra, structure is more apparent(1b,3). These discrete transitions above the blue shifted nanocrystal band gap can be explained by quantum confinement of the internal bands, without participation by surface states(1b,5).

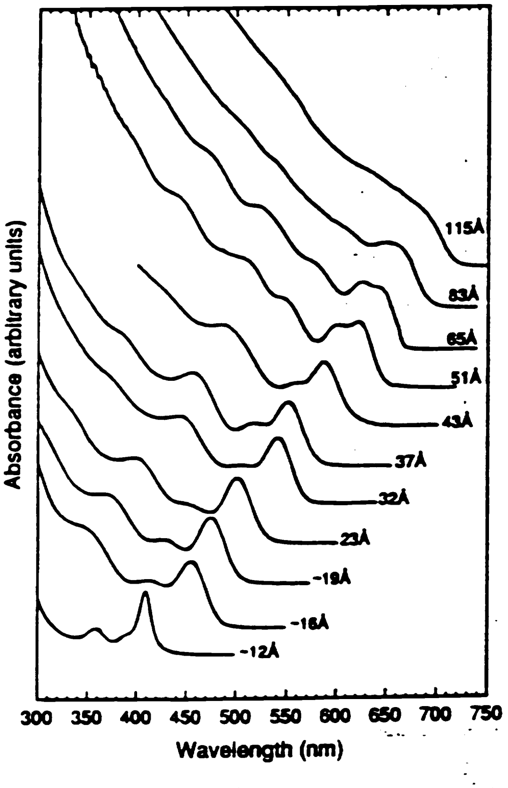

Fig. 2 CdSe Optical absorption spectra at 293 K from ref. 1.

Figure 3 shows the luminescence excitation spectra of surface oxidized, < 2nm Si nanocrystals emitting at 600 nm, 0.9 eV above the bulk band gap(6,7). No discrete structure is observed, either in the visible indirect gap region, or the ultraviolet direct Pσ^* gap region. There is less structure than in bulk silicon small particles, whose computed spectrum is shown as the Mie curve in the figure. In the visible region, the nanocrystal spectrum shows an indirect-gap-like, square root extrapolation to the 600 nm emission wave length.

In both CdSe and Si, quantum confinement in the P type valence bands creates similar, moderately dense manifolds of discrete molecular orbitals at a given size. Optical structure appears in the CdSe spectrum because of the sparse manifold of quantum confined states in the S type conduction band, deriving from the fact that the electron effective mass is small (0.12) and isotropic, for a limited region near Γ. Eight of the nine discrete transitions identified for CdSe actually represent electron excitations from different valence band levels to the same, lowest 1S conduction band state(1b). The observed complexity in the spectrum is complexity in the P type valence band.

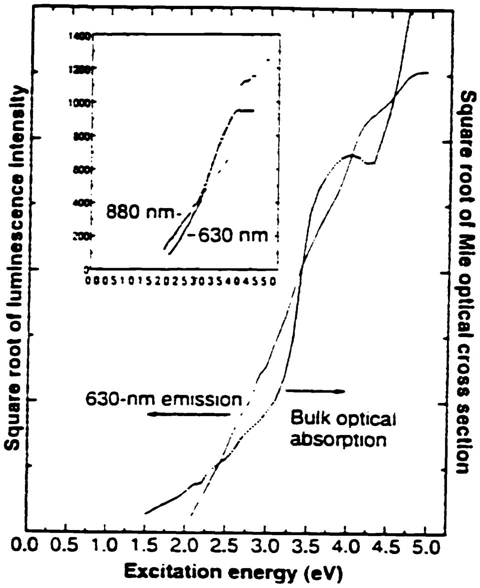

Fig. 3 Si luminescence excitation spectra, and bulk Si Mie absorption spectra, from ref. 7.

In the silicon ultraviolet direct gap at 3.4 eV, both valence and conduction bands are P type. Moreover, the conduction band splits and diverges as K increases, with one branch increasing and one branch decreasing in energy. The spectrum should be quite complex, with the main effect at low resolution being a broadening. This is apparently observed. In the indirect gap region, the conduction band has a strongly anisotropic effective mass, with values of 0.9 and 0.19. The electron confinement state manifold will be more dense than that of CdSe for the same size. Structure is not observed with present samples; with perfectly monodisperse samples structure might someday be observed if the homogenous widths prove to be not too large. Moreover, there is relatively little transfer of oscillator strength from the ultraviolet to the visible as a result of confinement, with the result that the spectrum experimentally remains indirect-gap-like in the dependence of absorption coefficient upon increasing energy.

3. Photophysics and Quantum Confinement

In oxidized silicon nanocrystals, the principal effect of confinement is kinetic rather than spectroscopic. The 2-3 nm nanocrystals show an approximately 5% room temperature quantum yield for visible and near IR luminescence. This occurs due to a change in the competition between radiative and nonradiative recombination(7). In bulk silicon, a bound electron-hole pair undergoes vibronically inducted emission with a lifetime of about 100 microseconds. However, electron-hole pairs quickly thermally dissociate at 293 K. The mobile free carriers can recombine nonradiatively in a three carrier Auger process, or by finding a rare bulk defect center. Luminescence is negligible.

In nanocrystal silicon, confinement in individual crystallites keeps the electron-hole pairs superimposed, and isolated from each other, at 293 K. The bulk Auger and point defect nonradiative processes are suppressed, allowing slow, millisecond radiative recombination to compete favorably. The quantum yield increases, while the lifetimes are quite long. Theory predicts that the radiative recombination rate increases from milliseconds to microseconds as size decreases, due to confinement of the wavefunction. However, experimentally the dominant effect seems to be the suppression of nonradiative recombination. It is remarkable that surface oxide passivation on nanocrystals introduces so few additional nonradiative recombination defects. A similar process involving suppression of recombination at rare impurities is known in indirect gap AgBr nanocrystals(8). In a sense the kinetics become <u>compartmentalized</u>, as would occur in a ensemble of noninteracting molecules.

In CdSe nanocrystals, luminescence from the lowest exciton is dipole allowed and strong for all sizes. However, there is presently no surface passivation method that is as electrically efficient, as SiO_2 on Si. Detailed studies on nanocrystals with surfaces capped with organic phosphine and phosphine oxide groups show evidence for quantum mechanical <u>resonance</u> between the lowest 1S-1S exciton state and surface states(4). It is thought that a surface state corresponds to the electron in a 1S internal orbital, with the hole localized in a Se lone pair orbital on the surface. This resonance creates an asymmetric broadening of the exciton homogeneous lineshape, and a complex kinetic decay scheme involving anomalously long lifetimes.

4. Conclusion

The consequences of electronic quantum confinement propagate to relatively large nanocrystal sizes in both Si and CdSe nanocrystals. In a heuristic sense, the consequences in Si are principally kinetic, while the consequences in CdSe are principally spectroscopic.

5. References

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