Quantum confinement effects at the L point in CdTe

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We report quantum-size-related shifts in optical transitions originating away from the center of the Brillouin zone of a II-VI semiconductor. CdTe-glass composite thin films, containing isolated semiconductor crystallites with average sizes ranging from 46 to 158 Å, exhibit a size-dependent blue shift of the E_1 and $E_1+\Delta_1$ transitions occurring at the L point of the zinc-blende Brillouin zone. Analysis of the effect, in the context of current zone-center confinement theory, supports the existence of bound electron-hole pairs whose internal motion is restricted to two dimensions. The effective mass governing the energy shift of each transition falls within at least 5% of the corresponding total transverse mass of the electron and hole calculated using $\mathbf{k}\cdot\mathbf{p}$ theory for the bulk material. It thus appears that, within the crystal size regime of the present study, optical absorption into these energy states results in the formation of a fully correlated two-particle state whose behavior is analogous to that of a single quasiparticle confined within the crystallite.

INTRODUCTION

The effect of finite crystal size on observed optical transitions in various II-VI and III-V compound semiconductors has received considerable attention in recent years. Not only do these lower-dimensional systems allow the decomposition of bulk electronic states to be examined as the number of participating atoms in the structure decreases, but carrier population redistribution within the quantum-confined electronic structure under high incident electromagnetic radiation can also result in many significant nonlinear-optical effects.

Three-dimensional confinement of II-VI semiconductors has been studied typically using samples consisting of an ensemble of crystallites embedded in an optically transparent, insulating matrix. Silicate glasses,[1–4] polymers,[5] zeolites,[6] and organic solutions[7] have all served as suspending media. Through reduction in the average size of the semiconductor crystallites, a blue shift in the fundamental absorption edge energy of the composite sample is observed, the result of carrier localization effects on the valence and conduction bands at the center of the Brillouin zone. In extremely small crystallites, a breakup of the energy bands into discrete electron and hole subbands is predicted, as evidenced by optical absorption features above the threshold absorption edge.

This paper reports the first study of quantum-related shifts in optical transitions of a II-VI semiconductor originating from states lying away from the $k=0$ or Γ point of the Brillouin zone. Specifically, we observe and analyze size-dependent blue shifts in the E_1 and $E_1+\Delta_1$ direct transitions known to occur in CdTe near the L point of the zinc-blende Brillouin zone.

EXPERIMENTAL RESULTS

The samples used in the present study were composite thin films consisting of approximately 2–10 vol % CdTe crystallites embedded in a borosilicate glass matrix deposited on a fused silica substrate. Their production, using a sequential rf magnetron sputtering technique, has been discussed elsewhere.[8] The film microstructure was examined using transmission electron microscopy. This allowed the average crystallite size and size distribution to be determined and enabled the examination of crystallite morphology. A post-deposition heat treatment allowed controlled variation in the average crystallite size from 46 to 158 Å through a diffusion-controlled growth process. Crystallite morphology appears circular in the extraction replica TEM samples examined. Recent cross-sectional TEM analyses have shown the crystallites to be spherical, in contrast to our earlier hypothesis that the crystallites may be disklike.[8] The distributions of crystal diameters in the TEM analysis exhibit widths ranging from 20% to 30% about the smallest and largest average sizes, respectively. Selected area electron diffraction together with x-ray diffraction of the films showed the precipitated crystallites to possess a zinc-blende structure. Linear-optical absorption was collected at room temperature with the incident beam normal to the film plane. A representative spectrum of a composite film containing CdTe crystallites of an average size of 106 Å is presented in Fig. 1. With decreasing wavelength, the first increase in absorption at approximately 769 nm corresponds to the fundamental absorption edge. At shorter wavelengths, the absorption rapidly increases to plateaus at 315 and 371 nm, identified in bulk CdTe as the E_1 and $E_1+\Delta_1$ transitions.[9–11] The energetic position of a given absorption feature is taken to be the inflection point of the spectrum found using the first derivative spectrum shown in the inset of Fig. 1. (Also evident in this figure are interference-related oscillations due to the thin-film geometry of the sample.) These uv transitions are typically observed in reflection measurements of the bulk material[9–11] and are only observed here due to the low absorption of the films.

Figure 2 contains the energy of these uv transitions

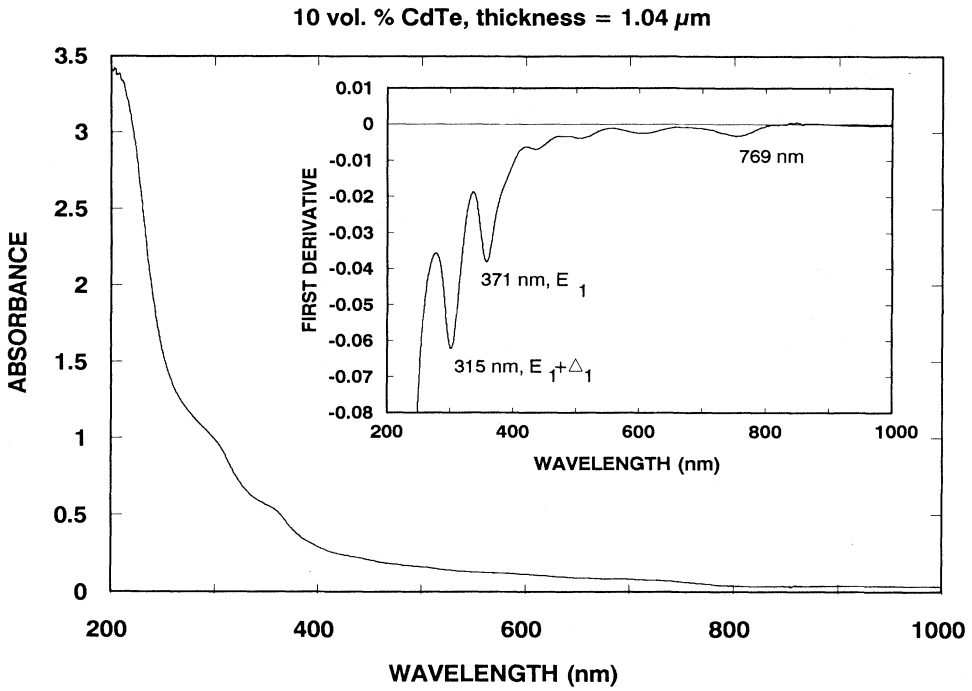

FIG. 1. Room-temperature optical absorption spectrum exhibited by a CdTe-glass composite thin film containing crystallites of average size 106 Å. The inset depicts the first derivative of the absorption spectrum. The film is 10 vol % CdTe with a thickness of 1.04 μm.

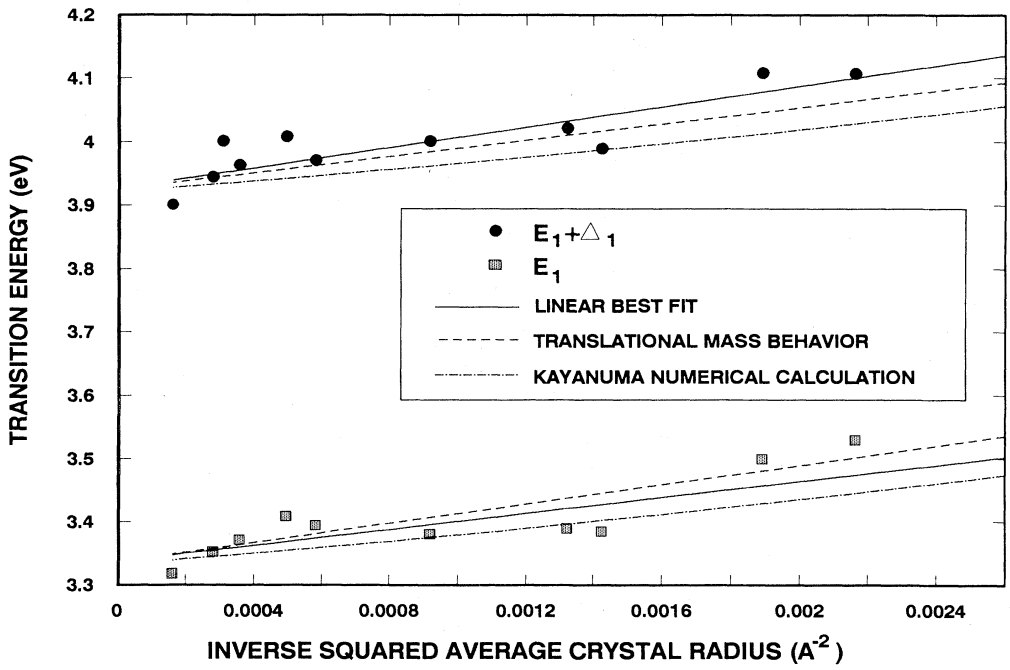

FIG. 2. Plot depicting the E_1 and $E_1+\Delta_1$ transition energies as function of the inverse average crystallite size squared measured from TEM extraction replicas. Also included for comparison are the predicted behaviors in this crystal size regime using the interpretations of Efros and Efros (Ref. 16) and Kayanuma (Ref. 17) originally developed for transitions at the center of the Brillouin zone.

plotted as a function of inverse squared average crystallite size, the parameter of interest in the study of quantum confinement. A small but significant increase in the transition energies is observed as the average size of the crystallites is reduced.

DISCUSSION

Ultraviolet feature interpretation

Myers, Edwards, and Schetzina[12] identify peaks observed in reflectivity spectra of their polycrystalline CdTe thin films, in the same energy region as the absorption plateaus exhibited in the present samples, as transitions occurring at the L point of the zinc-blende Brillouin zone between the spin-orbit split valence bands and the conduction band. Some uncertainty, however, does exist regarding this identification in the literature prior to Myers, Edwards, and Schetzina. While Cardona and Harbeke[13] also identify the L point as the origin of these transitions, Cardona and Greenaway[10] and Chadi *et al.*,[9] for example, subsequently identify the transitions as occurring at the Λ point, in accordance with a pseudopotential band-structure calculation which predicts a significantly smaller oscillator strength for the L-point transition than is observed in reflectivity (e_1 and $e_1+\Delta_1$ are then used as the designations for the L-point transitions).

Cardona and Harbeke[13] originally suggested the mediation of a Coulomb interaction between carriers to form excitons at this point in the Brillouin zone as an alternate explanation for the sharpness of the absorption they observed in CdTe thin films. Since the L point corresponds to an inflection point in the valence–conduction-band separation as a function of k, i.e., represents an M_1 or saddle-type critical point in the band structure, the group velocities of the electron and hole are known to be equal allowing the concept of correlated motion to exist at this point in the Brillouin zone.[13]

Kane[14] theoretically treats the effect of a significant Coulomb interaction between carriers at an M_1 point in the zinc-blende structure on the imaginary portion of the dielectric function. In the adiabatic approximation, using a large, negative longitudinal mass in comparison to the smaller transverse values, it is found that the two-dimensional state eigenenergies developed for the light masses predict effectively the position of features found in spectra obtained by Marple and Ehrenreich[15] for CdTe. Close agreement with the line shape of the experimental spectrum is also permitted when contributions from one-dimensional motion along the heavy mass coordinate within the adiabatic potential created by the orbital motions of the light masses are included. As will be discussed shortly, the existence of a correlated electron-hole pair appears to be substantiated by our data.

Quantum confinement

Elementary theoretical treatments of quantum shifts exhibited by transitions occurring at the Brillouin-zone center in lower-dimensional semiconductor structures generally take the form of a "particle-in-a-box" problem. The Schrödinger wave equation is solved with a Hamiltonian which includes the kinetic-energy operators of both excited carriers and interparticle Coulomb interactions. In the case of three-dimensional confinement, spherical coordinates are generally chosen with infinite potential boundary conditions imposed at a distance corresponding to the radius of the semiconductor crystallite. The general expression describing the shift in the threshold absorption energy has been derived by a number of authors. The treatments of Efros and Efros[16] and of Kayanuma[17] are most appropriate to our studies. In the Efros and Efros analysis, the shift in the absorption-edge energy is found to be $E_{\text{shift}}=\hbar^2\alpha_{n,l}^2/(2m_{\text{eff}}a^2)$, where $\alpha_{n,l}$ is a root of the spherical Bessel function, a is the potential well radius, and m_{eff} is a mass term whose value varies from the translational mass to the reduced mass of a bulk Wannier exciton in the semiconductor, depending upon the relative magnitudes of the Coulomb interaction and the kinetic energy of localization.[16] Thus the mass value gives an indication of the degree of correlated motion exhibited by the electron and hole while in the quantum well.

Translational confinement of the bulk Wannier exciton, in agreement with the Efros and Efros treatment, has been observed and analyzed previously[4] in CdS-doped optical filter glasses. In crystallite sizes larger than the bulk exciton, $2a_0$, i.e., reduced sizes greater than 1 (where reduced size $=a/a_0$), the experimentally determined mass value was found to be within 10% of the total mass of the exciton in CdS.

In contrast, studies of the fundamental absorption edge in the present CdTe-glass films have reported an intermediate behavior.[8] Blue shifts as high as 0.44 eV above the bulk edge energy have been observed with a linear inverse-square size dependence of the shift yielding a mass term intermediate between the reduced and translational masses of the CdTe exciton. This suggests that the interparticle Coulomb interaction is still significant even at crystallite sizes as small as 0.31 times the bulk exciton diameter. The result was not in agreement with a variational approach used by Kayanuma[17] which predicts nearly uncorrelated carriers at reduced crystal sizes less than 1.0.

Returning to the present study and the edge of the Brillouin zone, Fig. 2 contains the linear best-fit lines calculated from the data. Assuming the theories discussed above to be equally appropriate for the L point in the Brillouin zone with the corresponding electron and hole effective masses, it is possible to calculate the m_{eff} values for each of the transitions examined from the slopes of these lines. Using the lowest-order root of the Bessel function ($\alpha_{1,0}=3.14$), the experimental m_{eff} parameters for the light- and heavy-hole transitions are $0.47m_0$ and $0.59m_0$, respectively.

Comparison of the calculated effective-mass values to known, bulk carrier effective masses at this point in the Brillouin zone is possible using expressions for the transverse carrier masses adapted by Cardona and Greenaway[18] to II-VI semiconductors from similar equations developed by Ehrenreich[19] for the III-V's using $k\cdot p$ per-

turbation theory. The transverse masses for the electron (L_1 band) and the heavy (L_4 band) and light (L_6 band) holes can be calculated as follows:

$$m_0/m_e(L_1)=1+E_p/(E_1+\Delta_1/2)\ ,$$

$$m_0/m_{\rm hh}(L_4)=-1+E_p/2E_1\ ,$$

and

$$m_0/m_{\rm lh}(L_6)=-1+E_p/2(E_1+\Delta_1)\ ,$$

where m_0 is the free electron mass, $m_{e({\rm hh,lh})}$ is the effective mass of the electron (heavy hole, light hole), E_1 is the gap energy at the L point, Δ_1 is the spin-orbit splitting of the valence bands, and E_p is proportional to the square of the linear momentum matrix element, taken to be 25 eV for CdTe.[10]

The bulk E_1 and $E_1+\Delta_1$ transition energies are assumed to be equal to the y intercepts of the best-fit lines in Fig. 2, i.e., these values are approached asymptotically as the crystallite size increases. The energies are found to be 3.337 and 3.926 eV, respectively, falling well within the range of energies reported in the literature for the bulk transitions.[11–13] Using these transition energies, the resulting transverse masses of the electron and light and heavy holes at the L point are calculated to be $0.127m_0$, $0.364m_0$, and $0.458m_0$, respectively. The translational (total) masses of the two-dimensional Coulomb bound states originating from each valence band are then $0.491m_0$ and $0.585m_0$ and have been used to generate the Efros and Efros translational mass behavior plotted in Fig. 2. Comparison to the masses calculated using the confinement behavior exhibited in Fig. 2 shows that the experimentally derived values are within 5% and 2% of the expected, bulk translational masses for excitons formed from the light- and heavy-hole valence bands, respectively. Figure 2 also shows the results of Kayanuma's[17] numerical calculations, which underestimate the shifts exhibited by both the experimental data and the Efros and Efros translational mass treatment.

The close agreement between the bulk excitonic translational masses and the values obtained from the size-dependent transition energy data substantiates the existence of correlated electron-hole pair motion at the L point of the Brillouin zone of CdTe. It appears that the transverse mass components are, in fact, coupled through the Coulomb interaction to form a bound state, as discussed by Kane.[14] This two-particle state interacts with the potential step imposed by the crystallite boundaries in an analogous manner to that of a confined quasiparticle whose mass is equal to the total mass of its constituents.

Since Kane finds that the energetic position of the ε_2 peak in CdTe is given by the discrete eigenenergy of the $n=0$ state for the hydrogenic solution to the two-dimensional Coulomb equation, shifts in the position of this energy with size suggest that the electron and hole motion in the plane of their orbits is being restricted by the boundaries. The behavior of transitions originating from both the light- and heavy-hole valence bands appears to be analogous to the case of confinement at the zone center when the crystallite size is larger than the bulk exciton diameter.

Kane calculates the binding energy of the ground state for the two-dimensional (2D) bound state as being four times that originally calculated for the 3D case by Elliot.[20] Consequently, the spatial extent of the 2D wave function should be approximately one-quarter the value normally used for the bulk 3D exciton. Using the static dielectric constant for CdTe (10.4) and the transverse effective masses calculated above, the diameter of the 2D, correlated electron-hole pairs is found to be approximately 29 Å for the light hole and 27 Å when the heavy hole participates. Thus the reduced size of the CdTe crystallites examined ranges from 1.6 to approximately 5.8 for both light and heavy holes, well within the size regime characterized by translational confinement concepts according to Efros and Efros and by the intermediate-size behavior of Kayanuma.

These reduced-size values contrast those found at the Γ point where, because the appropriate carrier effective masses are smaller than those at the L point, the bulk Wannier exciton diameter is 150 Å. This results in a reduced-size range for the same crystallites of 0.31 to 1.1. Consequently, the kinetic energy of localization of the excited particles represents a greater proportion of their total energy than that found in larger confining structures. This causes a decrease in the degree of correlated motion exhibited by the electron-hole pair and the corresponding transition energy displays a much steeper increase with reduction in crystal size than predicted by center-of-mass confinement only (see Ref. 8).

CONCLUSIONS

A quantum-size related shift in transitions occurring at the L point of the zinc-blende Brillouin zone of CdTe has been observed in linear-optical absorption spectra of CdTe-glass thin films. These transitions occur between the two spin-orbit split valence bands and the conduction band. The shifts observed allow an estimate of the effective masses for the confined species to be calculated. It is found that the calculated masses agree, within at least 5%, with the total mass values obtained from the bulk transverse masses for the electron and hole participating in each transition. This suggest that within the crystal size range of this study, the electron and hole moves in an almost fully correlated manner throughout the crystallite.

The evidence substantiates the calculations of Kane[14] who models the experimental ε_2 data of bulk CdTe by assuming a significant Coulombic interaction between the excited particles, thus giving rise to bound states whose correlated motion in the transverse plane is described by a two-dimensional wave function. The ground-state energy of this electron-hole pair is found to accurately predict the position of an ε_2 peak observed experimentally.[15] The observed shift in this energy therefore suggests that confinement of the electron-hole translational motion occurring in the plane of their orbits is the dominant factor contributing to the effect.

The simultaneous observation of quantum confinement effects at both the center[8] and edge of the Brillouin zone

in the same crystallites permits the effect of crystal-lattice truncation and subsequent structural distortion to be examined from the perspective of two different real-space size scales. Theoretical treatments involving zone-center effects have shown that not only must Coulomb-related interparticle forces be included, but also interactions of the excited particles with the crystalline-matrix interface must be considered to provide a closer approximation to observed behavior.[7] While significant crystallite size-related variations are already observed in these longer-range, surface-sensitive optical transitions, occurring near $k=0$ in the present samples,[8] the effects of the potential boundary on local, short-range crystallite structure are only just beginning to emerge, reflected in the behavior of transitions at the edge of the Brillouin zone.

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