PHYSICAL REVIEW B VOLUME 53, NUMBER 23 15 JUNE 1996-I

Measurement of the optical band gap and crystal-field splitting in wurtzite CdTe

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(Received 30 January 1996)

CdTe nanocrystals embedded in a sodium borosilicate matrix, obtained by a sol-gel process, present a wurtzite (hexagonal) structure. Low-temperature photoluminescence and absorption spectra are measured for samples containing bulklike nanocrystals large enough to suppress confinement effects. Thus, the fundamental free-exciton gap and the splitting between the A ($\Gamma_9^v-\Gamma_7^c$) and B ($\Gamma_7^v-\Gamma_7^c$) excitons of bulk wurtzite CdTe are measured. We find $E_g^A=1653\pm1$ meV and $E_g^A-E_g^B=46.5\pm1.0$ meV, which corresponds to a crystal-field splitting $\Delta_{\rm cr}=71.6\pm1.5$ meV. [S0163-1829(96)04523-7]

Intensive studies, during the 1960s and 1970s, allow us to know quite well the band-structure parameters of cubic (sphalerite) CdTe.[1,2] As a matter of fact, the usual structure of bulk single crystals of CdTe is zinc blende, at atmospheric pressure. However, CdTe can also exist in the hexagonal (wurtzite) form,[3–5] like other II-VI semiconductors (CdS, CdSe, etc.), but this phase is metastable: the structure mainly depends upon the growth conditions[2] (substrate orientation, partial pressures, temperature, etc.). For this reason, this phase has been essentially identified by x-ray analyses in thin epitaxial films. Nevertheless, to our knowledge, spectroscopic data, such as the optical interband gap and the crystal-field splitting of valence bands, have not been measured yet. Now, the wurtzite structure has been recently observed by Murray, Norris, and Bawendi[6] by x-ray diffraction on CdTe nanocrystallites. This structure is probably induced by the specific physical and chemical growth mechanisms, i.e., the pyrolysis of organometallic reagents by injection into a hot coordinating solvent. Thus, optical studies of such crystallites may give us the opportunity to measure some near-band-gap optical characteristics of wurtzite CdTe. In practice, for crystals of very small radii—typically smaller than the Bohr radius of excitons in CdTe, i.e., ~7 nm—like those studied in Ref. 6, the optical particularities of the hexagonal structure are wiped out by the interplay of complex valence-band mixings, excitonic effects, and inhomogeneous broadening, due to the statistical distribution of crystal sizes.[6] These points are already well known in the case of small CdS and CdSe nanocrystals.[7–10] On the other hand, for CdS or CdSe crystallites with radii much larger than the Bohr radius and with an adequate crystalline quality, well-resolved, slightly blueshifted, excitonic signatures associated with the three upper valence bands of hexagonal CdS or CdSe have been observed by absorption spectroscopy.[9,11]

This paper presents absorption and photoluminescence (PL) spectra obtained at $T=2$ K on sodium borosilicate glasses containing ''large'' CdTe crystallites, obtained by a sol-gel procedure.[12] These data show two well-resolved, reproducible, contributions that we assign to excitonic transitions related to the $\Gamma_9^v-\Gamma_7^c$ and $\Gamma_7^v-\Gamma_7^c$ optical band gaps of wurtzite CdTe. These allow us to derive the crystal-field splitting $\Delta_{\rm cr}$ of this material.

The samples have been prepared by using a sol-gel technique described elsewhere.[12] Sodium borosilicate glasses are produced by thermal processing of a gel obtained from an aqueous solution of boric acid and sodium metasilicate. The quantities of reactants are such that the final composition of the glass is 1 $\mathrm{Na_2O}$–1 and $\mathrm{SiO_2}$–1 $\mathrm{B_2O_3}$. Precursors of cadmium and tellurium are introduced in the starting solution in the form of cadmium hydroxide and telluric acid.[9,12] The average size of the semiconductor clusters is essentially controlled by the initial concentrations of precursors. One specificity of this process is its efficiency for the fabrication of glasses doped with rather ''large'' nanocrystals with an excellent crystalline quality. In such samples, very small and variable blueshifts (of the order of 10 meV) of the excitonic lines of hexagonal CdS or CdSe have been observed by absorption spectroscopy. They testify to the weak confinement of excitons, typical of crystal radii larger than ~2 exciton Bohr radii of bulk materials.[13]

We demonstrate below that the samples studied here contain such ''very large'' nanocrystals of CdTe. Data obtained on samples 1–3, the characteristics of which are gathered in Table I, are discussed. It is worth noting that these samples have been obtained from three different molar concentrations of cadmium precursor: the average radius of the crystallites is different in each case.

Figure 1 displays the cw absorption and PL spectra of sample 1. Instead of the classical single excitonic peak at

TABLE I. Characteristics of samples 1, 2, and 3. Absorption peaks A and B refer, respectively, to the energies of the maxima of the peaks. They correspond to 1s excitons associated with the $\Gamma_9^v-\Gamma_7^c$ and $\Gamma_7^v-\Gamma_7^c$ interband gaps. FE corresponds to the high-energy shoulder observed in PL spectra: the energy has been determined by using a numerical fitting procedure.

Sample	Initial molar concentration of Cd	Absorption peak A (eV)	Absorption peak B (eV)	PL peak FE (eV)
1	4×10^{-4}	1.6520	1.6988	1.6537
2	2×10^{-4}	1.6518	1.6982	1.6538
3	1×10^{-1}	1.6514	1.6981	1.6528

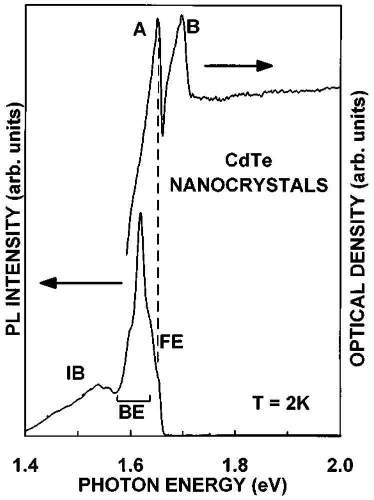

FIG. 1. Photoluminescence and absorption spectra of sample 1.

~1596 meV (Ref. 1), characteristic of cubic CdTe, the absorption spectrum shows two narrow features. Peak *A* lies at 1652.0 meV, while peak *B* lies at 1698.8 meV. Moreover, peak *A* corresponds almost exactly to the high-energy shoulder of the PL spectrum, as shown by a dashed line in Fig. 1. This shoulder is thus readily assigned to the free exciton (FE) line, measured at 1653.7 meV, to be compared to the FE line in cubic CdTe: 1596.1 meV (Ref. 14). In fact, the general shape of this PL spectrum is quite comparable to that usually observed for bulk cubic CdTe of good quality, except for the energies of the various contributions: the FE line, a set of defect-bound excitons[14] (BE), between 1.59 and 1.64 eV, and an impurity-related band[14,15] (IB), between ~1.40 and ~1.56 eV. This ''bulklike'' shape of the PL spectrum and the sharpness of absorption features are very strong indications of quasibulk nanocrystals, i.e., extremely small confinement effects.

Indeed, simple effective-mass calculations, assuming parameters of cubic CdTe, show that the present blueshift of the absorption onset (~56 meV) would be compatible with an average radius of the nanocrystals of ~5 nm, which is smaller than the effective Bohr radius in CdTe. In such cases, it is well known that absorption spectra should be much broader, due to valence-band mixings and to the substantial effect of the statistical distribution of crystal sizes. In addition, for such small crystals, the near-band-gap PL spectrum would be rather made of a single broad peak[16,17] corresponding to the inhomogeneous broadening of the line of the intrinsic, confined, free exciton. Extrinsic lines related to ''classical'' acceptors and donors would disappear, or be replaced by bands, related to states localized at the surface of the crystallites, lying at quite lower energy than the present IB and BE features. Moreover, from our previous studies, we know that the average radius of the crystallites is very sensitive to the initial concentration of cadmium precursor. Now, as shown in Table I, samples 1–3 show almost identical optical features, in spite of their different conditions of preparation. This is again in favor of bulklike crystallites, the spectra of which are almost insensitive to their average size.

The above remarks allow us to conclude quite safely that the observed blueshift of ~56 meV of the optical gap is not due to quantum confinement. By the way, we also exclude strain effects on cubic CdTe: the clear-cut splitting of the *A* and *B* peaks could be assigned to some *axial* strain. However, it is easy to show that, for cubic CdTe, the particular values of deformation potentials (a, b, and d) and of elastic constants (S_{11}, S_{12}, and S_{44}) are such that any kind of axial strain provokes a *redshift* of the optical band gap. This is totally inconsistent with the present blueshift.

Thus, our observations indicate that samples 1–3 contain bulklike CdTe nanocrystals with a wurtzite structure, since their spectra are very similar to those obtained for such large crystallites of wurtzite CdS and CdSe.[9] Then, the excitonic gap of wurtzite CdTe, at $T=2$ K, can be estimated as 1653 ± 1 meV; the splitting E_1 between the Γ_9^v and Γ_7^v valence bands[1,18] is estimated as $E_1=46.5\pm1.0$ meV.

These results are in good agreement with the most recent band-structure calculations of II-VI compounds in both zinc-blende and wurtzite configurations, performed by Zakharov *et al.*[19] by using the local-density approximation method, corrected by the GW approximation. In these calculations, the spin of electrons is not included: they provide directly the so-called crystal-field splitting Δ_{cr} of the Γ_{15} triply degenerate valence band of the zinc-blende phase into the $\Gamma_5(x,y)$ fundamental doublet and the $\Gamma_1(z)$ singlet[1,18] of the wurtzite phase. The calculated Δ_{cr} for CdS, CdSe, and CdTe are 0.06, 0.05, and 0.08 eV, respectively. In practice, due to spin-orbit coupling effects, optical measurements rather provide the above-mentioned E_1 splitting, which is related to Δ_{cr} by[1,18]

$$E_1=(\tfrac{1}{2})(\Delta_{SO}+\Delta_{cr})-(\tfrac{1}{2})[(\Delta_{SO}+\Delta_{cr})^2-8\Delta_{SO}\Delta_{cr}/3]^{1/2}, \tag{1}$$

where Δ_{SO} is the spin-orbit splitting between the Γ_8 ($J=\frac{3}{2}$) fundamental doublet (light- and heavy-hole bands) and the Γ_7 ($J=\frac{1}{2}$) singlet (split-off band), in the zinc-blende material. From the values of this parameter taken from the literature,[20] the above values of Δ_{cr}, and by using Eq. (1), one gets the following E_1 values for CdS, CdSe, and CdTe, respectively: 0.02, 0.03, and 0.05 eV. These theoretical results are to be compared with the experimental splittings of the *A* and *B* excitons: 13 meV in CdS, 25 meV in CdSe (Ref. 20), and the present measurement of 46.5 meV in CdTe. The overall agreement is very good, especially considering the usual accuracy of band-structure calculations and the fact that they do not account for excitonic effects. In addition, Zakharov *et al.*[19] have also found that the fundamental optical gap of hexagonal CdTe is larger than that of the cubic phase by ~0.04 eV (without spin-orbit coupling or excitonic contributions). This agrees qualitatively with the blueshift of ~56 meV, which is measured here. By using Eq. (1), and the well-known value of Δ_{SO} in cubic CdTe [927 meV (Ref. 1)], we can thus propose the following value for the crystal-field splitting in wurtzite CdTe: $\Delta_{cr}=71.6\pm1.5$ meV.

In summary, we have seized the opportunity, offered by the specificities of nanocrystalline growth, to measure low-temperature PL and absorption spectra of good-quality CdTe in its wurtzite form. We find that the fundamental free-exciton gap is 1653 ± 1 meV in this material. We also measure a splitting between the 1s excitons A ($\Gamma_9^v-\Gamma_7^c$) and B ($\Gamma_7^v-\Gamma_7^c$) of 46.5 ± 1.0 meV, which corresponds to a crystal-field splitting $\Delta_{cr}=71.6\pm1.5$ meV.

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