Phase discrimination in CdSe structures by means of Raman scattering

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Raman spectra of epitaxial layers of CdSe grown by molecular beam epitaxy have been measured for the cubic (zincblende) and hexagonal (wurtzite) phases. The Raman spectra are examined in the light of density functional calculations for these two highly similar structures. Characteristic Raman frequencies and spectral features associated with the different symmetry are discussed and reliable criteria for phase discrimination based on Raman spectroscopy are proposed. Although

LO frequencies are virtually identical in both structures and may be affected by size effects, the observation of a low energy E_2 mode at 33 cm^{-1} unambiguously identifies the wurtzite structure and can be used as a specific fingerprint to distinguish between these two phases in CdSe-based nanostructures. The slightly lower LO frequency measured in the zincblende epitaxial layer is ascribed to residual tensile strain.

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1 Introduction CdSe is a semiconductor material ($E_g \sim 1.7\text{ eV}$) which has a key role in the development of high efficiency solar cell nanostructures. As CdSe displays a high absorption in the solar spectrum range which is complementary to that of ZnO, it is widely used for the sensitization of ZnO nanowires to solar light [1]. Band gap tuning can be achieved by quantum confinement in nanostructures with different sizes and shapes, and since the ZnO/CdSe heterostructure yields a type II band alignment, the absorption profile of ZnO/CdSe core-shell nanowires covers wavelengths longer than those corresponding to the band gap of the CdSe shell and display an increased carrier collection efficiency.

CdSe crystallizes in two lattice structures: the cubic zincblende (ZB) structure and the hexagonal wurtzite (W)

structure. In bulk, ZB is the stable low-temperature phase and transforms to W phase above a critical temperature of 95°C [2], but depending on the growth conditions samples can be obtained at ambient pressure in either ZB or W forms. Although single-crystal bulk CdSe grown by molecular beam epitaxy (MBE) usually adopts the W form, CdSe single-crystal epilayers with ZB structure can be obtained by MBE growth on ZB substrates [3]. By contrast, small CdSe nanocrystals tend to exhibit the ZB phase. Electrodeposited CdSe shells on ZnO nanowires also revealed ZB structure for as-deposited samples and samples annealed at temperatures below 350°C [4]. However, annealing of the ZnO/CdSe core-shell structures at temperatures above 350°C results in the formation of the W phase, which becomes the dominant phase at 400°C [4].

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Crystal structures of polytypes that share a common crystal facet can be used to achieve branching, as in the case of tetrapods consisting of a ZB core and four projecting W nanorods [5]. Seeded growth of CdSe/CdS nanostructures allows the shape of nanocrystal heterostructures to be tailored into nanorods or tetrapods by using CdSe nanocrystals with W and ZB structure, respectively, as seeds. Typical AM1.5 solar power conversions of $\sim 2.1\%$ are obtained in CdSe tetrapod/polymer hybrid solar cells [6]. Recently, CdSe/CdS core-shell tetrapods have been shown to exhibit multicolor emission associated with a higher energy transition that is allowed via spatially indirect recombination [7]. This opens exciting possibilities for controlling carrier localization at the nanoscale in photovoltaic and solar fuel applications.

The characterization of CdSe nanocrystals is primarily done by x-ray diffraction (XRD). Since the ZB and WZ CdSe phases possess very similar XRD patterns, any strain and/or nano-sized effects make their distinction not straightforward, especially when local epitaxy is involved, which requires the use of sophisticated XRD measurements using specific geometries. Optical measurements are also employed to characterize ZB and W phases. The gap between the first and second exciton transitions is wider for ZB than W CdSe nanocrystals, and the peak positions for the exciton transitions with higher energies is also different [8]. However, differences in shape and position of the absorption edge can be influenced by size quantization effects and structural disorder [9].

Recently, Kelley *et al.* [10] made an attempt to differentiate between both CdSe phases by performing a resonant Raman study on spherical nanospheres. However, they could not find any significant difference neither in the frequencies nor in the resonant intensities of the respective LO peaks. In this letter, we have addressed the distinction between the W and ZB phases of CdSe by performing Raman scattering studies on MBE grown CdSe films. This allows us to establish sound criteria to differentiate both phases since it avoids possible effects associated with nanosize crystallites such as surface reconstruction, confinement effects, and/or lattice contraction [11], and the scattering geometry implies a well defined phonon wavevector that rules out possible quasimode effects usually present in nanostructures [12].

2 Experiment The W and ZB CdSe epitaxial layers were grown on GaAs (111)B and ZnTe(100) substrates, respectively, by molecular beam epitaxy (MBE) using a Riber ultra-high vacuum chamber. A GaAs buffer layer was grown at 630 °C under As-rich conditions. Subsequently, the (0001) W CdSe epilayer was deposited at 260 °C under Se-rich conditions. Prior to the growth of the ZB CdSe epilayer, a ZnTe buffer layer was grown at 380 °C under Zn-rich conditions. Subsequently, a 550 nm thick (100) ZB CdSe epilayer was deposited at 280 °C under Se-rich conditions.

Figure 1 Phonon dispersion relations and phonon density of states for wurtzite (top panel) and zincblende (lower panel) CdSe.

The samples were characterized by XRD using a RIGAKU Smartlab diffractometer equipped with a five-circle goniometer. For the W sample, the lattice parameter values $a = 4.299 \text{ Å}$ and $c = 7.0127 \text{ Å}$ were determined, leading to a c/a ratio of 1.631, in close agreement with generally accepted values for bulk W-CdSe [13], indicating that the studied epilayer is mainly relaxed. For the ZB epilayer grown on the ZnTe(100) substrate, an *in-plane* lattice constant $a_{\perp} = 6.102 \text{ Å}$ was determined, whereas the *out-of-plane* lattice constant was found to be $a_{\parallel} = 6.055 \text{ Å}$, suggesting the presence of a residual tensile biaxial strain. The Raman spectra were recorded in unpolarized backscattering configuration using a Jobin-Yvon T64000 spectrometer using the 514.5nm line of an Ar^+ laser as excitation.

3 Results

3.1 DFT calculations To aid in the interpretation of the Raman spectra, density functional theory (DFT) calculations of the phonon dispersion were carried out for both structures. The calculations were performed in the local density approximation (LDA) using the ABINIT code [14]. A $6 \times 6 \times 4$ Monkhorst-Pack grid was used for integration over the Brillouin zone of the W structure, with an energy cutoff of 60 hartree. A full structural relaxation of the W CdSe lattice yields $a = 4.290 \text{ Å}$ and $c/a = 1.632$. These values are in good agreement with the lattice parameters measured by XRD in our sample. For the ZB structure, we used a $(6 \times 6 \times 6)$ $\mathbf{k}$ -point grid with an energy cutoff of 80 hartree. A lattice parameter $a = 6.065 \text{ Å}$ was obtained for

Table 1 Experimental and calculated phonon frequencies in units of cm^{-1} of the Raman active modes of W and ZB CdSe. Calculated values were corrected for the LDA overestimation of the dielectric constant.

ZB CdSe					TO				LO			
					Exp.		Calc.		Exp.		Calc.	
					–		172.3		205.2		211.9	
W CdSe					TO				LO			
E_2					A_1		E_1		E_1		A_1	
low		high										
Exp.	Cal.	Exp.	Calc.		Exp.	Calc.	Exp.	Cal.	Exp.	Calc.	Exp.	Calc.
33.0	31.9	174.0	177.6		–	170.7	–	174.6	–	200.9	207.2	211.3

ZB CdSe, which compares well with the experimental values measured by XRD. For the calculation of phonon frequencies, the dynamical matrix was obtained on a mesh of k points using the perturbation-theory linear-response approach. Figure 1 displays the phonon dispersion along high symmetry lines for W and ZB CdSe. Optical modes, which mainly involve the vibration of Se atoms, span a frequency range between 170 and 206 cm^{-1} , and a phonon gap of 45 cm^{-1} exists between the optical and acoustic bands owing to the atomic mass difference. The phonon density of states (PDOS) shows three distinct bands corresponding to optical, longitudinal acoustic (LA) and transverse acoustic (TA) branches which are very similar in both structures, the main difference being that the longitudinal acoustic PDOS peaks at a higher frequency in the W structure because of the contribution of the optical-like folded-acoustic branches.

It is well known that LDA overestimates the dielectric constant, and this affects the calculated LO–TO splitting [15]. From the DFT calculations, ϵ_∞ values of 7.18 and 8.73 are obtained for the W and ZB phases, respectively. By using the corresponding experimental ϵ_∞ values of 6.1 [16] and 6.56 [17], and taking into account that the squared ion plasma frequency is inversely proportional to the dielectric constant, the DFT LO frequencies can be corrected for the overestimation of ϵ_∞ [15, 18]. A list of the corrected frequency values for the Raman active modes is given in Table 1.

3.2 Raman scattering measurements Figure 2 displays the Raman spectra of the ZB and W epilayers obtained in backscattering configuration from (001) and (0001) faces, respectively. In these configurations, only the LO mode is allowed in the ZB crystal, whereas the E_2 and $A_1(\text{LO})$ modes are allowed in the W crystal. Although the 514.5 nm excitation is far from the $E_0 + \Delta_0$ critical points [19], resonance enhancement effects are observed in the Raman spectra owing to the significant breadth of this optical transition. In the Raman spectra of ZB-CdSe, a significant intensity of the 2LO overtone, which is similar to that of the LO Raman peak, is observed, and a 3LO overtone can also be detected. A residual luminescence background picked up from the ZnTe substrate ($E_g = 2.26 \text{ eV}$) has been subtracted in the spectrum shown in Fig. 2.

The strong absorption through the 550-nm thick ZB-CdSe epilayer completely attenuates any Raman signal from the ZnTe substrate. This has been corroborated by performing Raman measurements with longer wavelength excitation lines that allow the detection of distinct Raman peaks from the ZnTe substrate.

The luminescence background is absent in the spectrum of the W CdSe epilayer. The resonant enhancement of the LO overtones up to third order is also observed in the W sample, although the 2LO/LO intensity ratio is somewhat lower. The most striking difference between the Raman spectra of the W and ZB samples is the sharp, intense E_2^{low} peak at 33 cm^{-1} that dominates the W CdSe spectrum. The extremely long phonon lifetimes of the low-lying E_2 optical modes is a characteristic feature of many W crystals arising from the lack of efficient anharmonic decay channels at such low energies [18, 20]. Indeed, the W CdSe Raman spectrum of Fig. 2 indicates that the intrinsic E_2^{low} line width is well below the spectral bandwidth of the spectrometer. The observation of the E_2^{low} mode, which in the W structure arises from the symmetry lowering and the consequent zone-folding of the TA branch along the Γ –A direction, is a distinctive, unambiguous feature that allows one to identify the W phase of CdSe. As can be seen in

Figure 2 Room temperature Raman spectra of W and ZB CdSe epilayers.

Fig. 2, no Raman signal from the ZB CdSe crystal is detected in this frequency range (the sharp periodic lines observed below 100 cm^{-1} are due to rotational modes of the air molecules). The E_2^{high} mode at 174 cm^{-1} is also characteristic of the W phase, but this feature is less conclusive as its frequency lies close to that of the TO mode of the ZB structure (see Table 1).

Very weak broad bands are observed around 240 and 370 cm^{-1} in both W and ZB CdSe Raman spectra. The location of these bands agrees well with the calculated phonon density of states (see Fig. 1) with the wave number axis scaled by a factor of 2, and therefore they can be assigned to second order overtones of LA and TO modes, respectively. The weak feature observed at 138 cm^{-1} could be due to a TO–TA combination band. The layer thickness of the W sample is low enough to allow the observation of the TO and LO modes of the GaAs substrate at 269 and 292 cm^{-1} , respectively. It is worth noting that the Raman spectra of both samples display narrow LO peaks, with a full width at half maximum (FWHM) of 8.3 and 7.0 cm^{-1} for the W and ZB forms, respectively. These values compare favorably to FWHM values previously reported in nanocrystals (for instance, $\sim 12\text{ cm}^{-1}$ in [10]), which substantiates the high quality of the epitaxial single crystals used in the present study.

3.3 Strain and mode-mixing effects As can be seen in Table 1, except for the E_2^{low} mode the experimental frequencies obtained from the room temperature Raman scattering measurements are $4\text{--}7\text{ cm}^{-1}$ lower than the calculated values. Since DFT calculations model the system implicitly at 0 K , the calculated frequencies do not include thermal renormalization due to anharmonic interactions. These effects tend to decrease the phonon frequencies as temperature increases, and the difference between the CdSe frequencies measured at RT and the DFT calculations are consistent with the typical magnitude of the anharmonic shifts usually observed in binary semiconductors [18]. It should be noted that the E_2^{low} modes of the W structure, related to the TA modes of the ZB structure, exhibit a negative Grüneisen parameter, which may compensate the anharmonic shift [18]. Although the DFT calculations yield LO frequencies which are nearly identical for the W and ZB structures, the LO mode frequency in the Raman spectrum of ZB CdSe is $\sim 2\text{ cm}^{-1}$ lower than in the W CdSe Raman spectrum. As already discussed above, the XRD measurements reveal a residual tensile biaxial strain in the studied ZB–CdSe epilayer. To evaluate the effect of the strain on the LO phonon frequency, we have performed DFT calculations for the tetrahedral distortion ($a_{\parallel}/a_{\perp}$ ratio) obtained from the XRD measurements. We obtain an *in-plane* strain of $\epsilon_{\perp} = 3.1 \times 10^{-3}$ and a corresponding LO phonon shift of $\Delta\omega_{\text{LO}} = -1.7\text{ cm}^{-1}$ relative to the unstrained value reported in Table 1. Therefore, the difference in the LO frequencies observed in the W and ZB CdSe epilayers can be mainly attributed to the residual tensile strain in the ZB sample. In this regard, it is interesting to

note that identical LO Raman frequencies were observed in W and ZB CdSe nanocrystals [10], despite the fact that surface reconstruction and lattice contraction effects were reported to take place in nanocrystalline W CdSe [11]. It should be noted that in nanocrystals the scattering geometry is not as well defined as in the case of oriented epilayers. This may lead to mode mixing in the W phase, giving rise to quasi-LO modes with frequencies between the $A_1(\text{LO})$ and $E_1(\text{LO})$ modes [12]. Then, a lower quasi-LO frequency should be expected in the Raman spectra of nanocrystalline W CdSe that could partly compensate the lattice contraction effects and explain the accord between LO frequencies in W and ZB colloidal nanocrystals.

4 Conclusions We have performed a Raman scattering study of the W and ZB forms of CdSe on high quality, single-crystal epitaxial layers. The W CdSe Raman spectra exhibits a intense, characteristic E_2^{low} peak at 33 cm^{-1} that allows the W and ZB forms of CdSe to be unambiguously identified. By contrast, the differentiation between both phases is more difficult on the basis of the LO Raman peak. Our DFT calculations indicate that the LO frequencies of the W and ZB forms are virtually identical, and the LO frequency shift observed in the ZB epilayer can be attributed to residual tensile strain. In nanocrystalline samples the frequency of this mode can be further affected by subtle strain and mode-mixing effects.

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