

# Effect of ZnS shell on the Raman spectra from CdSe nanorods

Holger Lange<sup>\*,1</sup>, María Machón<sup>1</sup>, Mikhail Artemyev<sup>2</sup>, Ulrike Woggon<sup>3</sup>, and Christian Thomsen<sup>1</sup>

<sup>1</sup> Institut für Festkörperphysik, Technische Universität Berlin, Germany

<sup>2</sup> Institute for Physico-Chemical Problems of Belorussian State University, Minsk

<sup>3</sup> Fachbereich Physik, Universität Dortmund, Germany

Received 15 July 2007, revised 28 August 2007, accepted 17 September 2007

Published online 20 September 2007

PACS 63.22.+m, 78.30.Fs, 81.05.Dz

\* Corresponding author: e-mail [holger.lange@physik.tu-berlin.de](mailto:holger.lange@physik.tu-berlin.de)

We investigated the influence of an epitaxially grown ZnS shell on the phonon spectra of CdSe nanorods of different sizes. The CdSe related Raman peaks shift with addition of a

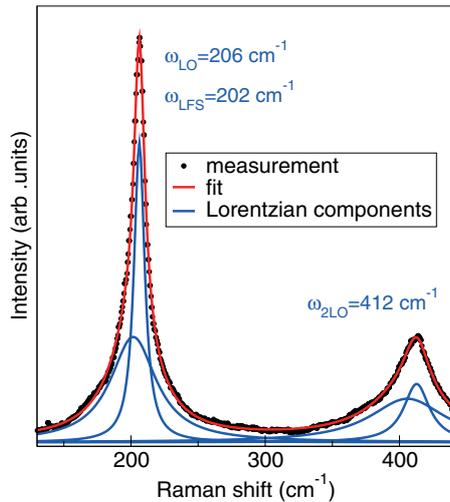
ZnS shell. The longitudinal optical phonon shifts slightly due to strain and the low-energy shoulder shifts stronger, which can be explained within a model for surface optical phonons.

© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** CdSe nanorods (NR) have interesting optical properties with possible applications in low threshold lasers and photovoltaic devices. The synthesis of colloidal CdSe nanocrystals allows the growth of NR with defined aspect ratios and sizes [1]. The growth of a CdS/ZnS graded shell on the CdSe rods increases the luminescence efficiency and decreases the laser threshold [2, 3]. The specific chemical composition of the surrounding shell becomes more and more important, since the shell properties control most of the mechanisms of functionalization of both biological and photonic materials by light-emitting nanocrystals [4]. However, details about the shell and its influence on the CdSe core are difficult to obtain due to the lack of TEM resolution and the small X-ray structure factor of ZnS compared to CdSe. In the work presented here we exploit pure optical techniques for a structural analysis of the core-shell composition. Analyzing the phonon spectra in Raman measurements of CdSe NR with and without ZnS shell we demonstrate that the growth of a crystalline, thin (2–3 monolayer) ZnS shell is evidenced by the appearance of a ZnS related Raman signal at  $271\text{ cm}^{-1}$ . Comparing the Raman spectra from CdSe NR with and without the ZnS shell we find a shift of the CdSe related Raman peak due to strain induced by the shell. The spectral shape of the Raman lines can be explained with a combination of a longitudinal optical phonon and a surface optical phonon.

**2 Experimental details** CdSe core NR were grown by a standard technique based on the high temperature ( $300\text{ °C}$ ) reaction between organometallic precursors of Cd (dimethylcadmium) and Se (trioctylphosphine selenide) in trioctylphosphine oxide in the presence of hexadecylphosphonic acid as a surface growth modifier [5]. An epitaxial ZnS shell, ca. 2–3 monolayers in thickness, was grown atop the CdSe core NR in the second step in hexadecylamine/trioctylphosphine oxide reaction mixture at  $180\text{ °C}$ , diethylzinc and thiourea as Zn and S precursors, respectively [3]. Four samples were investigated. NR with 6 nm diameter and 35 nm length and NR of 8 nm diameter and 80 nm length, each geometry both as uncapped NR and capped with a ZnS shell. For the Raman measurements the nanorod samples were deposited on a Si wafer. The 514 nm line of an  $\text{Ar}^+$ -laser was used as excitation source; the laser power was kept below 10 mW to avoid laser heating. A Dilor-XY triple monochromator system in backscattering geometry was used with a nitrogen-cooled CCD to acquire the spectra. Each spectrum was frequency calibrated with respect to a neon lamp. All measurements were performed at room temperature.

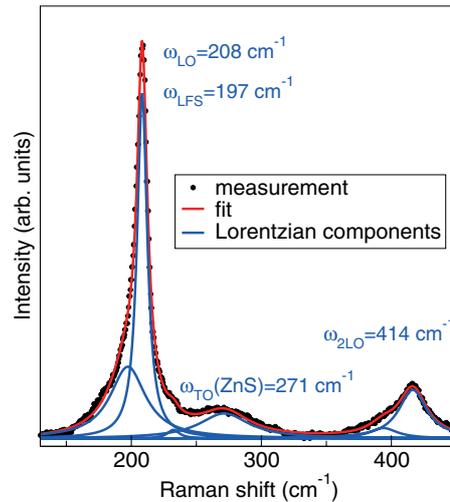
**3 Results** Figure 1 displays the Raman spectrum of CdSe NR with 6 nm diameter and 35 nm length, “small” NR. The CdSe Raman bands of first and second order can



**Figure 1** (online colour at: www.pss-rapid.com) Raman spectrum of 6 nm × 35 nm CdSe NR.

be clearly identified at 206 cm<sup>-1</sup> and 412 cm<sup>-1</sup>, respectively. The bands have an asymmetric lineshape which is often observed in low-dimensional CdSe structures and fitted well with two Lorentzians [6, 7]. The more pronounced peak can be attributed to the longitudinal optical phonon (LO) of CdSe. The origin of the low-frequency shoulder (LFS) of the LO bands is not conclusively clarified. It is often related to surface optical phonon (SO) modes [8]. Other explanations include a shape dependent shift due to anisotropic polarization, broadening due to the contribution of different vibrational states [9] or anharmonic phonon decay [10]. Deviations of the measured LO position from literature values for bulk material,  $\omega_{LO}(\text{CdSe}) = 208 \text{ cm}^{-1}$  [11], result from phonon confinement [12] and lattice contraction [13]. According to the fits the position of the longitudinal optical phonon is 206.2 cm<sup>-1</sup> for the first-order and 411.8 cm<sup>-1</sup> for the second-order peak. The first-order LFS peak is at 201.6 cm<sup>-1</sup> and second-order LFS is located at 376.8 cm<sup>-1</sup>. The full width at half maximum (FWHM) of the first-order LO is 10 cm<sup>-1</sup>, while the FWHM of the first-order LFS is 30 cm<sup>-1</sup>.

Figure 2 displays the spectrum of NR of the same size with an additional 2–3 monolayer ZnS shell. The Raman signal intensity and accumulation conditions were similar for both measurements. The FWHM of the first-order LO is the same as that of uncapped rods: 10 cm<sup>-1</sup>, the FWHM of the first-order LFS is equally unchanged. The components of the CdSe-related Raman bands are slightly shifted and new bands appear. 208.5 cm<sup>-1</sup> and 414.4 cm<sup>-1</sup> are the new positions of the first and second order LO. 198 cm<sup>-1</sup> and 395 cm<sup>-1</sup> are the new LFS peak positions. Additionally, a band with a position close to the ZnS transverse optical (TO) phonon,  $\omega_{TO}(\text{ZnS}) = 272 \text{ cm}^{-1}$  [11], appears between the first and second order CdSe bands. It can be fitted with a Lorentzian centered at 271.4 cm<sup>-1</sup>. The peak is broad so that no statements can be made about its shape. A small high frequency shoulder (HFS) of the CdSe bands appears, which can be fitted with a Lorentzian centered at 232 cm<sup>-1</sup>.



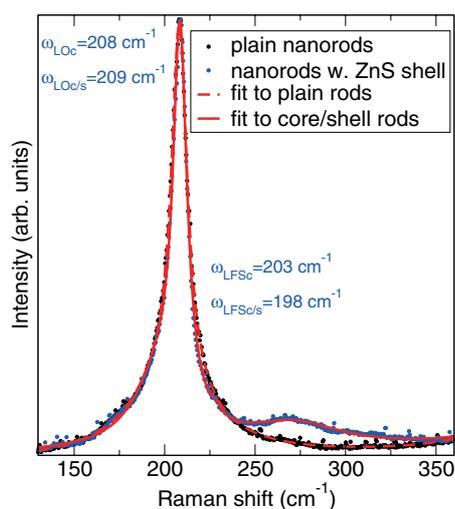
**Figure 2** (online colour at: www.pss-rapid.com) Raman spectrum of 6 nm × 35 nm CdSe NR with 2–3 monolayer ZnS shell.

Spectra for NR of 8 nm diameter and 80 nm length, “large” NR, with and without a 2–3 monolayer ZnS shell are displayed in Fig. 3. The positions of the CdSe related bands in uncapped rods differ slightly from the smaller NR due to the decreased influence of the phonon confinement. Adding a ZnS shell influences the spectrum in the same way as for the smaller NR in Fig. 1. The signal quality is equally unaffected. The FWHM of the first-order LO changes from 10 cm<sup>-1</sup> to 9 cm<sup>-1</sup>. The first-order LO shifts from 208.1 cm<sup>-1</sup> to 208.6 cm<sup>-1</sup> and the first-order LFS from 202.6 cm<sup>-1</sup> to 198.0 cm<sup>-1</sup>. In the core/shell spectrum additional peaks appear at the ZnS TO position at 271.4 cm<sup>-1</sup> along with a high-frequency shoulder of the CdSe bands at 229 cm<sup>-1</sup>. The positions of all peaks are summarized in Table 1.

The measured shift of the LO frequencies between uncapped NR and NR with ZnS shell can be explained by strain in the NR. The strain for a NR is not fully hydrostatic as it is for a quantum dot, it consists of a hydrostatic,

**Table 1** Position of the Raman peaks in cm<sup>-1</sup>.

peak type	sample type	
	small, uncoated	small, coated
CdSe LO	206.2 ± 0.4	208.5 ± 0.4
2CdSe LO	411.8 ± 0.9	414.4 ± 0.9
LFS	201.6 ± 0.6	198 ± 1
2LFS	376.8 ± 0.9	395 ± 1
ZnS TO		271.4 ± 0.8
HFS		232 ± 1
	large, uncoated	large, coated
CdSe LO	208.1 ± 0.4	208.6 ± 0.4
LFS	202.6 ± 0.8	198.0 ± 0.9
ZnS TO		271.4 ± 0.9
HFS		229 ± 1



**Figure 3** (online colour at: www.pss-rapid.com) Raman spectra of 8 nm × 80 nm NR with and without ZnS shell.

compressive component and shear strain. A detailed analysis requires the elastic properties of CdSe with a high accuracy, which are not available at the moment, and additional measurements and calculations which are beyond the scope of this letter and will be published elsewhere. However, the small shift of the LO for the large NR suggests that the lattice contraction induced in the core by the presence of the ZnS shell is smaller, while it is expected to be significantly higher for the small NR.

The large shift of the low-frequency shoulder of the LO compared to the LO itself suggests a strong dependence of the peak position on the surface properties, as expected for surface optical phonons. SO phonon frequencies in NR,  $\omega_{lm}$ , can be calculated by evaluating

$$\frac{\omega_{lm}^2}{\omega_T^2} = \frac{\varepsilon_0 - \varepsilon_D f_{lm}^P(\xi_0)}{\varepsilon_\infty - \varepsilon_D f_{lm}^P(\xi_0)},$$

where  $\omega_T$  is the transversal optical phonon frequency and  $\varepsilon_0$  and  $\varepsilon_\infty$  the static and high-frequency dielectric constants of the rod material,  $f_{lm}^P$  a universal geometry dependent parameter, and  $\varepsilon_D$  the dielectric constant of the host medium [16]. The quantum numbers  $(l,m) = (2,2)$  yield good results. Using the results published in Ref. [16], and  $\omega_{TO}(\text{CdSe}) = 165 \text{ cm}^{-1}$  for the TO phonon frequency at room temperature [11], yields  $\omega_{SO} = 204 \text{ cm}^{-1}$  for the uncapped large NR and  $\omega_{SO} = 201 \text{ cm}^{-1}$  for the uncapped small NR, only  $1 \text{ cm}^{-1}$  away from the observed positions. Using the dielectric constant of ZnS,  $\varepsilon_D = 9.6$ , for the host material results in a shift to  $\omega_{SO} = 192 \text{ cm}^{-1}$  for the larger NR and  $\omega_{SO} = 191 \text{ cm}^{-1}$  for the smaller NR. These shifts differ by a factor of 2–3 from the experimentally observed ones. The calculation involves the dielectric constant of the surrounding medium (ZnS), a macroscopic parameter, which may be not suitable for 2–3 monolayers of ZnS. If we use the dielectric constant of the host material as fit parameter to the LFS position of the capped large NR we ob-

tain  $\varepsilon_D = 2.9$  as effective dielectric constant and a good agreement with the observed positions for both geometries. The asymmetric shape of the CdSe bands for uncapped and core/shell NR can then be explained by the combination of LO and SO modes. The peak around  $270 \text{ cm}^{-1}$  in the core/shell spectra is most probably the ZnS TO. The LO from the ZnS shell was not observed in the capped samples. The reason for the lack of the LO signal is unclear and under investigation. The origin of the high-energy shoulder that appears with addition of the ZnS shell around  $230 \text{ cm}^{-1}$  is not fully understood. Density functional theory calculations suggest Raman-inactive phonon modes in the spectrum of CdSe NR stemming from the core surface. When interacting with the ZnS shell they could become Raman-active due to symmetry lowering [17]. Both peaks that appear with addition of the ZnS shell could also be related to interface optical phonons of the ZnS shell. In Ref. [18] corresponding predictions for spherical structures are made. Using our rod and shell diameter as parameters results in two phonon branches. One close to the shell TO and one at lower frequencies which follows our observations.

Comparing the Raman spectra from CdSe NR with and without the ZnS shell we find a shift of the CdSe-related Raman peak and a change in lineshape. The shape can be explained with a combination of a longitudinal optical phonon and a surface optical phonon. The shift of the LO is attributed to strain. The position of the surface optical phonon shifts strongly with addition of a ZnS shell. This trend can be explained within the surface optical phonon model when using a reduced effective dielectric constant for the ZnS shell.

**Acknowledgement** We acknowledge DFG for financial support within the SPP 1165.

## References

- [1] X. G. Peng et al., *Nature* **404**, 59 (2000).
- [2] M. Kazes et al., *Adv. Mater.* **14**, 317 (2002).
- [3] L. Manna et al., *J. Am. Chem. Soc.* **124**, 7136 (2002).
- [4] U. Woggon, *J. Appl. Phys.* **101**, 081727 (2007).
- [5] L. Manna et al., *J. Am. Chem. Soc.* **122**, 12700 (2000).
- [6] A. V. Baranov et al., *Phys. Rev. B* **68**, 165306 (2003).
- [7] F. Comas et al., *Phys. Rev. B* **65**, 073303 (2002).
- [8] Y. N. Hwang et al., *Phys. Rev. B* **59**, 7258 (1999).
- [9] C. Trallero-Giner et al., *Phys. Rev. B* **57**, 4664 (1998).
- [10] R. Cusco et al., *Phys. Rev. B* **75**, 165202 (2007).
- [11] Landolt Börnstein, Group III Condensed Matter, Vol. 41 Semiconductors, II–VI and I–VII Compounds; Semimagnetic Compounds (Springer, Berlin, 1999).
- [12] H. I. H. Campbell et al., *Solid State Commun.* **58**, 739 (1986).
- [13] Y. N. Hwang et al., *Phys. Rev. B* **54**, 15120 (1996).
- [14] A. P. Alivisatos et al., *J. Chem. Phys.* **89**, 5979 (1988).
- [15] G. Scamarcio et al., *Phys. Rev. B* **45**, 13792 (1992).
- [16] F. Comas et al., *Solid State Commun.* **130**, 477 (2004).
- [17] M. Mohr et al., to be published.
- [18] F. Comas et al., *Phys. Rev. B* **67**, 115301 (2003).