Effect of Quantum Confinement on Higher Transitions in HgTe Nanocrystals

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Spectroscopic ellipsometry measurements on 1-10 bilayers of HgTe nanocrystals and polymer were performed in the spectral range from 0.5 – 5 eV. The experiments show that the band model respectively band energy shifts due to quantization can be applied onto nanocrystals with as few as 5 unit cells in diameter. These nanocrystals exhibit strong transitions at higher critical points. The critical point energies shift up to 0.4 eV. It turns out that transitions between bands which are closer to the Fermi energy and have a smaller carrier mass are more strongly affected by quantum confinement.

Introduction

Recently, a number of devices based on HgTe nanocrystals (NCs) have emerged which use photoluminescence or electroluminescence to create light in the near infrared [1], [2]. Due to quantum confinement, the energy levels in the NCs are changed, and HgTe is transformed from a semiconductor with a negative bandgap of E_g = -0.15 eV to a semiconductor with a bandgap of up to 1 eV, covering the important telecommunication wavelength range at 1.5 µm. All these devices are based on the creation of the bandgap, which takes place when the radius of the NC is reduced below the Bohr exciton radius, which is r = 40 nm in bulk HgTe. The influence of the size, the preparation and deposition method on the bandgap and the emission properties of the NCs have been extensively studied [3], [4]. However, there have been no studies up to now on the effects of the quantum confinement on higher critical point energies for HgTe NCs. For other NCs like CdTe and PbSe, ellipsometric studies have been used before to determine optical properties and the effects of quantum confinement [5], [6]. In this work, we use spectroscopic ellipsometry (SE) to study quantization effects on HgTe NCs, especially the relation between the size of the NCs and the energy shift of higher transitions. These measurements clearly show the existence of critical points in the dielectric function of the NCs and their shift to higher energies compared to the bulk value caused by size quantization. Previous authors adapt concepts coming from bulk semiconductor optics like critical points (CPs) and apply these concepts to NCs, using the same lineshape models for these CPs [6], [7]. In our case, the agreement between model calculations and measurements justifies the use of these models as well.

Experimental

Sample Preparation

We use HgTe NCs prepared from colloidal solution, using an aqueous thiol-capping method [3], [8] with thioglycerol (TG) as stabilizer. The size of the NCs was controlled by post-synthetic heat treatment. We have fabricated 5 different sizes of NCs by using growth times of 0, 90, 150, 300 and 600 minutes, which corresponds [3] to approximate NC diameters of 3.5 nm, which we name “smallest”, 4.1 nm, 5.3 nm, 6.9 nm, and

10.7 nm, which we name “largest”. With these NCs, thin mono- and multilayer films were self-assembled using a layer-by-layer deposition technique driven by electrostatic interaction [1], [9]. Alternative adsorption of poly(diallyldimethylammonium chloride) (PDDA) and TG-stabilized HgTe NCs from their aqueous solution resulted in the formation of a sequence of PDDA/HgTe NCs bilayers. We use samples with 10 bilayers on a glass substrate to determine the properties of these layers by SE. For the purpose of determining the CPs of the HgTe NCs we use samples with only one layer of NCs on one layer of PDDA on a glass substrate, which minimizes the influence of layer thickness and roughness originating from deposition.

Measurements

We performed SE on these samples to determine the dependence of the CP energies on the size of the NCs. Figure 1 shows the measured pseudodielectric function of a sample with 10 bilayers with the smallest NCs on a glass substrate, as well as the fit. We determined independently the dispersion relation of PDDA and used this information to model the compound layers with effective medium approximation [10]. The surface roughness of the sample was taken into account with an additional effective medium modeled layer of polymer, HgTe and air. Due to the shift of the CPs of NCs we cannot use the bulk reference material and therefore model the dispersion of HgTe with three Lorentz oscillators for the three transitions found in the measurement range (E_0, E_1, $E_1+\Delta_1$). This model describes the measured dielectric function remarkably well, and the blueshift of the CPs of the NCs with respect to the values of HgTe bulk material found in literature can be observed. Especially the E_0 HgTe transition can only be observed in NC samples, where a bandgap exists due to quantum confinement, in contrast to bulk HgTe, which has a negative bandgap and does not exhibit this transition. The photoluminescence (PL) energy of this sample is shifted approximately by 190 meV from the E_0 CP.

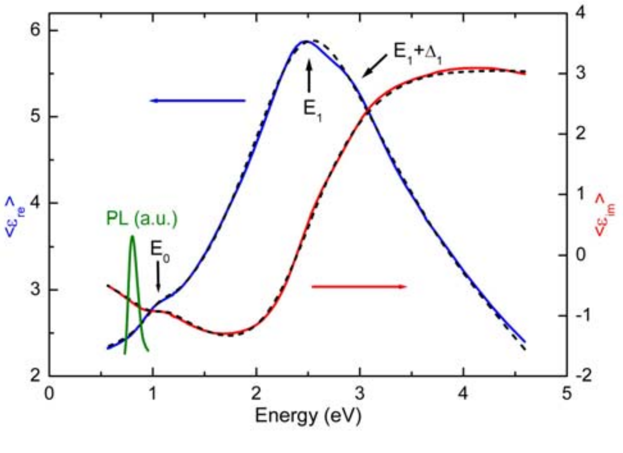

Fig. 1: SE measurement (straight line) and fit (dashed line) as well as PL measurement of a sample with 10 bilayers of HgTe NCs with a diameter of 3.5 nm on glass; inset: TEM picture of a NC with a diameter of ~9 nm

For determining the energy of the CPs, however, we follow the literature and use the second derivative of the pseudodielectric function [11], which facilitates the determination of the CP energy. With simulations we checked for our (with the exception of HgTe) almost dispersion less system (glass / 1 nm polymer / 1 layer of NCs) that the singularities which show up in the second derivative of the measured pseudodielectric function directly correspond to the CPs of the HgTe NCs. We found that the influence of layer thickness and NC content can be neglected, which makes the thin-film approximation applicable. Figure 2 shows the second derivative of the imaginary part of ε for bulk material [12], and the second derivative of the measured pseudodielectric function for the biggest and the smallest NCs. As can be seen, the positions of the E_1, $E_1+\Delta_1$ CPs shift to higher energies with decreasing size, whereas there is almost no change in the position of the E_2 transition. One can also observe the increase of the oscillator width, which is due to the size distribution of the NCs. The oscillator strength of these transitions is much smaller for the NCs than for the bulk material. For bulk material the strength of the E_2 transition is smaller than for the other transitions, whereas in the NCs the relative strength of the CPs is comparable. The change in the type of the singularity is attributed to a different phase caused by a thin film effect, rather than another type of transition caused by a change in the band structure.

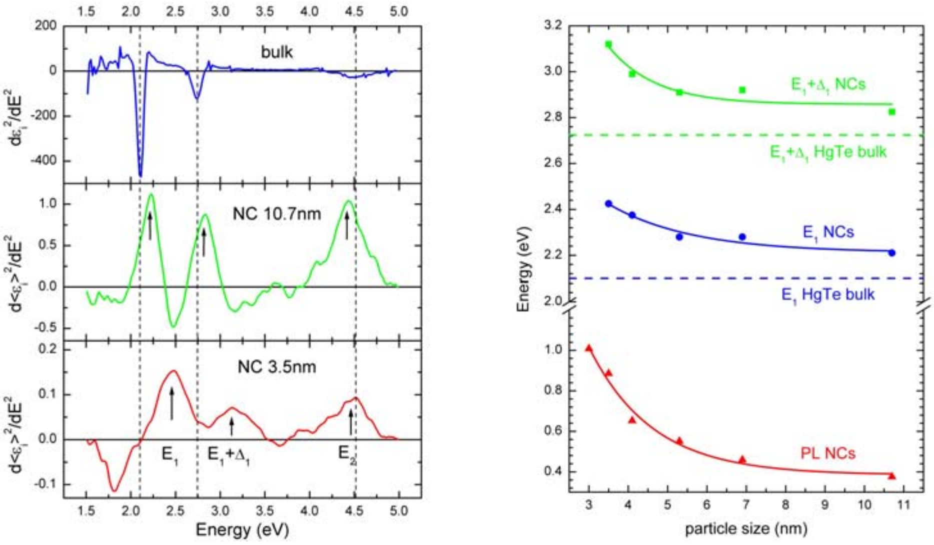

Fig. 2: (a) Second derivative of the imaginary part of the dielectric function of bulk HgTe (top) and the measured pseudodielectric function of HgTe NCs of 10.7 nm diameter (middle) and 3.5 nm diameter (bottom) (b) size dependence of PL wavelength and higher transition energies

The measured transitions were fitted with the same lineshape models used in bulk semiconductor physics. The line-shape of the CPs can be described as [10]:

$$\langle\varepsilon\rangle'' = f\cdot e^{i\Phi}\left(E-E_i+i\Gamma\right)^{-n} \qquad (1)$$

with the dielectric function ε, the oscillator strength f, the oscillator energy E_i, oscillator width Γ and phase Φ. In the absence of theoretical models, the exponent n is set to 3, which is used to describe excitonic effects and the phase Φ is set to 0 [13]. In contrast to the NCs the reference data of HgTe bulk material [11] was fitted with $n = 2$ and $\Phi = 90°$, which corresponds to the line-shape of a 2D Van Hove singularity with a saddle point in the energy band as it is the case for the E_1, $E_1+\Delta_1$ and E_2 transition in HgTe. As mentioned before, the change of the phase for the NC sample is caused by the small thickness of the film. However, the fit of the measured data leads to similar results of the CP energies and oscillator strength irrespective of the used values for n and Φ. The fit of the bulk material gives values of 2.10, 2.73 and 4.52 eV for E_1, $E_1+\Delta_1$ and E_2, respectively, which is in good agreement with values in literature [14]. As can be seen in Figure 2 the shift of the E_2 CP in the NCs is much smaller than the linewidth, and is thus hard to determine. It is also possible that it overlaps with the E_0' transition, which is located at 4.14 eV [14], and has in bulk another phase angle due to the different dimensionality of the CP.

It is well known that the bandgap and consequently the PL energies of NCs increase with decreasing size due to the quantum confinement. In particular, the PL wavelength of the NCs used in this study ranges from 1.4 µm for the smallest NCs to 3.3 µm for the biggest NCs as determined in a previous study [3]. From the SE measurements we can determine that the higher order transitions E_1 and E_1+Δ_1 exhibit the same behavior, even though to a lesser extent. As expected, the energy of these transitions increases with decreasing growth time, i.e. decreasing size (see Fig. 3). For the smallest NCs, the blueshift of the E_1 transition (heavy hole) is about 0.3 eV and the shift of the E_1+Δ_1 (light hole) transition about 0.4 eV to higher energies compared to the bulk HgTe values. It is clear that transitions between bands which are closer to the Fermi energy (E_0) are more strongly affected by quantum confinement. The effect of the quantum confinement depends on the value of the Bohr exciton radius and therefore on the effective mass, which are different at the Γ point and at the band edge, where the higher transitions occur.

The oscillator strength of the E_1 and E_1+Δ_1 transitions increases with increasing NC size, but it is still by far smaller than the values obtained from the fit for bulk HgTe (2.63 and 1.72 for the E_1 and E_1+Δ_1 transitions respectively). The transition strength is given by the product of the dipole matrix element and the joint density of states (JDOS). The JDOS is lower for NCs because due to the finite periodicity in real space less k states (i.e. less unit cells) can contribute to transitions.

Conclusion

In conclusion, we have determined the effect of quantum confinement on the optical properties of HgTe by spectroscopic ellipsometry. A blueshift of the higher energy transitions E_1 and E_1+Δ_1 for the nanocrystals with respect to the bulk material is observed. The blueshift decreases with increasing size and the transition energies approach the bulk value for large sizes of the NCs. There is a broadening of the CPs due to the size inhomogenity of the NCs, and the transition strength is much lower for the NCs than in bulk material and increases with increasing size of the NCs.

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