Effect of Quantum Confinement on the Dielectric Function of PbSe

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Monolayers of lead selenide nanocrystals of a few nanometers in height have been made by electrodeposition on a Au(111) substrate. These layers show a thickness-dependent dielectric function, which was determined using spectroscopic ellipsometry. The experimental results are compared with electronic structure calculations of the imaginary part of the dielectric function of PbSe nanocrystals. We demonstrate that the size-dependent variation of the dielectric function is affected by quantum confinement at well-identifiable points in the Brillouin zone, different from the position of the band-gap transition.

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Semiconductor nanocrystals with dimensions below 10 nm possess optical properties that depend strongly on the size and shape of the nanocrystals. This is due to confinement of the exciton wave function in the limited space of the nanocrystal [1]. In many cases, the size-dependent optical properties can be understood by considering the effects of quantum confinement on the band-gap transition, i.e., the electronic transition with lowest energy, and a few other closely related transitions [2]. However, quantum confinement will affect all electronic transitions throughout the entire Brillouin zone and, thus, decide the dielectric function of a semiconductor nanocrystal in a broad energy range. Despite the scientific and technological importance, only a few studies have been published in which the dielectric function of semiconductors nanocrystals is considered [3,4].

Here, we present a study on the effects of quantum confinement on the dielectric function of PbSe nanocrystals in the energy range 1.5–4 eV. Bulk PbSe is a low band-gap semiconductor, with a band-gap transition of 0.26 eV at room temperature (at the L point of the Brillouin zone) and several other critical points (Van Hove singularities) at higher energy (at the L point and along the Δ and Σ directions). PbSe nanocrystals form an ideal case for this study: They can be electrodeposited on a gold substrate with good control over their size and shape [5], and the effects of quantum confinement are expected to be strong due to the low effective masses of the electrons and holes [6]. We studied the dielectric function $\epsilon(\omega)$ of PbSe nanocrystals deposited on gold by spectroscopic ellipsometry. The dielectric function of the PbSe nanocrystals can be described by a sum of two Lorentz oscillators, as reported before for bulk PbSe [7]. This shape of the dielectric function is determined by an increase of the oscillator strength and the joint density of

states near the Van Hove singularities along the directions Δ and Σ in the Brillouin zone [8]. We found that the resonance energies of these oscillators increase strongly relative to the bulk values when the nanocrystal height is less than 5 nm. This blueshift is accompanied by a change of the oscillator width and the oscillator strength. These results are compared with a tight-binding calculation of the dielectric function of an infinite PbSe sheet with varying height. We demonstrate that this profound change of $\epsilon(\omega)$ can be understood only by considering the effects of quantum confinement on the energy bands throughout the entire Brillouin zone. In this way, the present study reveals that quantum confinement can have an important influence on the dielectric function of semiconductor nanostructures.

We deposited PbSe nanocrystal layers from an aqueous solution of lead acetate (2.5 mM) and selenous acid (1.25 mM) [9] on evaporated gold substrates at a potential of −0.5 V vs saturated calomel. The growth of crystalline PbSe was confirmed by x-ray diffraction analysis at layers from 3 to 100 nm in thickness and by transmission electron microscopy at the very thin layers (2 to 5 nm). The topography of the nanocrystals was studied with room-temperature scanning tunneling microscopy. The layers are composed of densely packed nanocrystals with edges ranging from 15 to 25 nm, as shown by Fig. 1(a). These edges did not vary considerably with the nanocrystal height for heights exceeding 2–3 nm. Therefore, the charge consumed in the electrodeposition is a good estimate of the height of the PbSe nanocrystals. For deposits with a height below 2–3 nm, nanocrystals with edges varying from 2.5 to 25 nm can be found [5]. Resonant tunneling spectroscopy of the energy level structure of the nanocrystals shows that nanocrystals with edges of 15–25 nm and a height of a few nm have
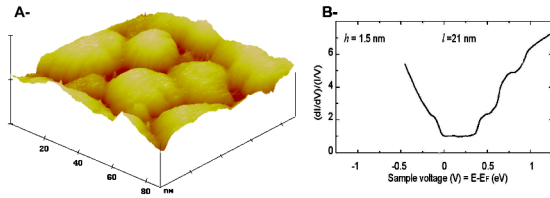
FIG. 1 (color online).   (a) STM image of PbSe nanocrystals on a flame-annealed gold surface. Nanocrystal height estimated from charge deposited: 4 nm. (b) Tunneling spectrum obtained at a PbSe nanocrystal with a height of 1.5 nm and edges of 21 nm. For more details, see Ref. [5].

a density of states (DOS) close to that of a 2D semiconductor [see Fig. 1(b)] [5]. When the edges are reduced, the DOS of the nanocrystals gradually changes to that of a 0D semiconductor. We conclude that our deposition procedure yields a monolayer of 2D nanocrystals with tunable height, keeping in mind that deposits below 2−3 nm in height contain more confined nanocrystals as well.

The color of a monolayer of PbSe nanocrystals varies strongly with the height of the nanocrystals (Fig. 2). Since the energy gap, as determined by scanning tunneling spectroscopy, is below 0.5–1 eV (near IR) for all nanocrystals [5] on the film, this color variation is not due to confinement effects on the PbSe band-gap transition. We investigated this change of the optical properties by spectroscopic ellipsometry at PbSe nanocrystals of varying height (2–15 nm). With this technique, one measures the ratio between the (complex) reflection coefficients for light polarized parallel (r_p) and perpendicular (r_s) to the substrate surface. This ratio is typically written in the form $r_p/r_s = \tan(\Psi)e^{i\Delta}$. For a multilayer system, an approximation of an unknown $\epsilon(\omega)$ can be obtained by fitting a model function with adjustable parameters to the ellipsometric data $\tan(\Psi)$ and $\cos(\Delta)$, if the respective dielectric functions of the other layers are known.

Figure 2 represents ellipsometric spectra, obtained at bare gold and at the PbSe|Au system for three different PbSe nanocrystal heights. As the height of the nanocrystals increases, a systematic change in the spectra occurs. We analyzed the ellipsometric spectra using an air|PbSe|gold three-layer model in the energy range 1.5–3.5 eV. The dielectric function of gold was obtained from measurements on a bare gold substrate. The dielectric function of the layer of PbSe nanocrystals is modeled as a sum of two Lorentz oscillators:

$$\epsilon(E) = \epsilon_{\inf} + \frac{f_1}{E_{01}^2 - E^2 - iE\Gamma_1} + \frac{f_2}{E_{02}^2 - E^2 - iE\Gamma_2}.$$

(1)

In this expression, E_{01} and E_{02} are the resonance energies of the oscillators, f_1 and f_2 are the oscillator strengths, and Γ_1 and Γ_2 are the oscillator widths. This model was chosen since the description of the dielectric function of
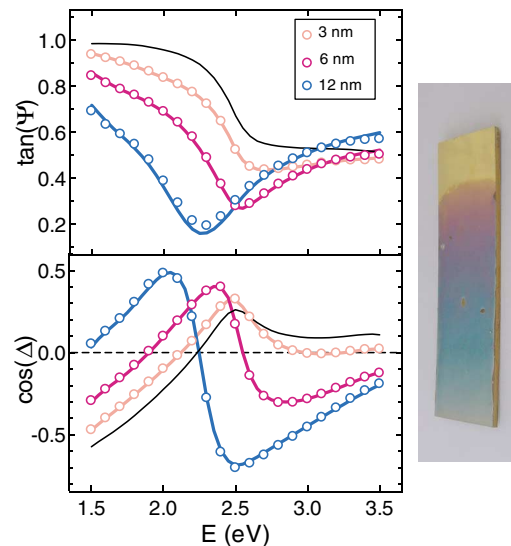

FIG. 2 (color).   (left panel) Ellipsometric spectra obtained on bare gold (full line) and on gold samples with a monolayer of PbSe nanocrystals with thicknesses of 3, 6, and 12 nm, respectively. For clarity, only one in two data points is shown. The full lines represent the results of a fit using a planar three-layer system where the dielectric function of PbSe is described as a sum of two Lorentz oscillators. (right panel) Image of a flame-annealed gold surface on which a layer of PbSe nanocrystals was electrodeposited. During electrodeposition, the sample was retracted from the plating solution, leading to an increase of the nanocrystal height from 2 nm (top) to 20 nm (bottom). As the thickness increases, the color of the layer changes from pink over purple and blue to gray.

PbSe in the visible as a sum of two Lorentz oscillators has been reported before for bulk PbSe [7]. As demonstrated by Fig. 2, this model function fits the measured ellipsometric spectra very well.

The layer thickness as obtained from the data fits is proportional to the charge deposited and corresponds to a deposition efficiency of 75%–85%. The proportionality between layer thickness and charge deposited confirms the idea of one dimensional growth of the nanocrystals. Rather than the layer thickness obtained from each individual fit, we used this conversion efficiency — it being an average over various samples — to estimate the nanocrystals height from the charge deposited.

Figure 3 shows the imaginary part ϵ_{im} of the dielectric function of the PbSe layer, as obtained by fitting the ellipsometric data between 1.5 and 3.5 eV for nanocrystals with a height of 1.6 and 8.8 nm, respectively. The contribution of both Lorentz oscillators is indicated and the resonance energies E_{01} and E_{02} are drawn. Since the width of the oscillator is considerable, the resonance energies are slightly shifted relative to the maximum of ϵ_{im}. The spectrum of ϵ_{im} obtained at the 8.8 nm nanocrystals resembles that of bulk PbSe [7]. Figure 4 represents the resonance energy of the oscillators as a function of the nanocrystal height. Both figures show a profound change
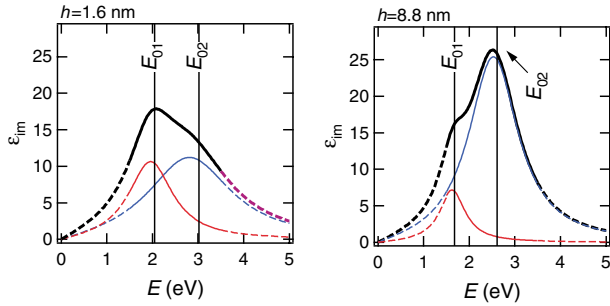
FIG. 3 (color online). Imaginary part of the dielectric function of a layer of PbSe nanocrystals with a height of 1.6 (left) and 8.8 nm (right). The individual contributions of both Lorentz oscillators are drawn and the resonance energies E_{01} and E_{02} are indicated. In the energy range where the ellipsometric spectra have been fitted, the data are drawn in full.

of the dielectric function on reducing the nanocrystal height. First, the relative contribution of both oscillators to the overall dielectric function strongly changes. Whereas oscillator 2 dominates ϵ_{im} for bulk PbSe, both oscillators contribute about equally to ϵ_{im} when the nanocrystal height is reduced to 1.6 nm (Fig. 3). Second, above 5 nm, the resonance energies decrease slowly and tend to the values reported for bulk PbSe ($E_1 = 1.60$ eV and $E_2 = 2.73$ eV, respectively). However, there is a strong increase of the two resonance energies with decreasing height below 5 nm, amounting to a shift of 0.4–0.5 eV at a height of 1.6 nm (Fig. 4).

To interpret the observed evolution of the dielectric function with varying nanocrystal height, we have calculated the imaginary part ϵ_{im} of the dielectric function of PbSe "sheets" with infinite edges and variable height along the (001) direction. The bulk electronic structure is obtained from a tight-binding approach using an $sp^3d^5s^*$ basis and taking into account a screening surface potential [10]. Our calculations show that the Lorentz
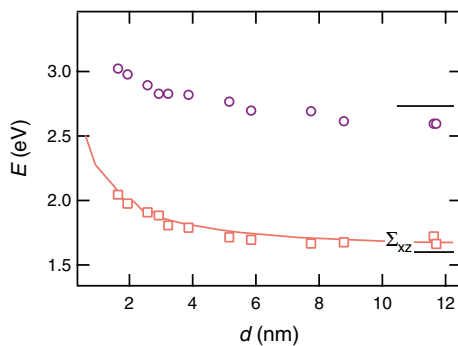
oscillators in the dielectric function are not physically real in the sense that they describe a single electronic transition. Rather, they emerge from an increase of the joint density of states and the oscillator strength of valence-to-conduction band transitions near the energy gap minima (Van Hove singularities) along the Σ direction (oscillator 1 at 1.6 eV) and the Δ direction (oscillator 2 at 2.7–3 eV). This means that ϵ_x is determined by states along the directions Δ_x, Σ_{xy}, and Σ_{xz} [14] and the same holds, *mutatis mutandum* for ϵ_y and ϵ_z. In a good approximation, the upper valence-band and the lower conduction-band eigenstates along Δ_x (Δ_y, Δ_z) are linear chains of p_x (p_y, p_z) states, whereas the eigenstates along Σ_{xy} (Σ_{xz}, Σ_{yz}) are linear combinations of p_x and p_y (p_x and p_z, p_y and p_z) states [15]. Consequently, there is no confinement effect to first order on the states along Δ_x, Δ_y, and Σ_{xy} when the height (z direction) is reduced. This means that height reduction leads to an anisotropic dielectric function. The dielectric function ϵ_z is affected by confinement effects along Δ_z, Σ_{xz}, and Σ_{yz}. Hence, both the shoulder and the peak of ϵ_z will shift. On the other hand, ϵ_x and ϵ_y are affected only by confinement via states along Σ_{xz} and Σ_{yz}, respectively. Hence, only the shoulder at 1.6 eV will vary in this case. This first-order picture is confirmed by the dielectric function as obtained from tight-binding calculations using the full $sp^3d^5s^*$ basis. Figure 5 shows two examples, calculated at sheets with heights of 1.24 and 6.20 nm, respectively. In the latter case, ϵ_{im} resembles closely the dielectric function for bulk PbSe [8]. One sees that $\epsilon_{z,im}$ shows a strong blueshift when the height is reduced. This blueshift is much stronger along Δ_z than along the Σ directions. For $\epsilon_{xy,im}$, a blueshift of the shoulder at 1.6 eV is seen, whereas the main peak only shows a slight redshift.

Figure 6 presents an experimental ellipsometric spectrum obtained at a 1.6 nm deposit and two (almost coincident) theoretical spectra calculated from the theoretical dielectric function of a 1.55 nm thick PbSe sheet. One is obtained taking the anisotropy of ϵ into account, whereas the second assumes a layer with an isotropic dielectric function equal to ϵ_{xy}. First, since the isotropic
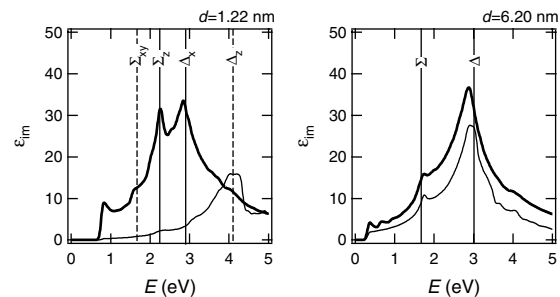

FIG. 4 (color online). Resonance energy of the Lorentz oscillators as a function of the PbSe layer thickness, the squares representing E_{01}, the circles E_{02}. The full line represents the energy gap at the Van Hove singularity along Σ_{xz}. The short horizontal lines represent the resonance energies for bulk PbSe as reported in Ref. [7].

FIG. 5. Calculated spectrum of ϵ_{im} for a PbSe sheet with infinite edges and a height of 1.24 and 6.2 nm, respectively, showing ϵ_{xy} (bold) and ϵ_z (normal). The energy gap minima along the directions Δ_x, Δ_z, Σ_{xy}, and Σ_{xz} are indicated.
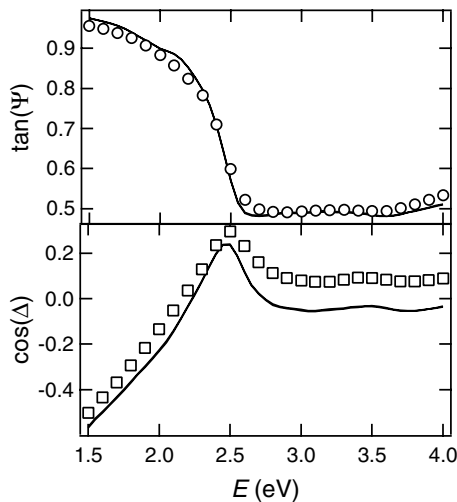
FIG. 6. Comparison of spectroscopic ellipsometry data as measured at a monolayer of PbSe nanocrystals on gold (estimated height: 1.6 nm) and as calculated for a PbSe "sheet" with a height of 1.55 nm. The spectra obtained for an isotropic and an anisotropic dielectric function almost coincide.

and anisotropic spectra coincide, Fig. 6 demonstrates that our experimental setup is sensitive to ϵ_{xy} only. Second, the figure shows that there is a good correspondence between the experimental data and the theoretical calculations. This is confirmed by a comparison of Figs. 3 and 5, which shows that the "experimental" ϵ_{im} resembles closely the theoretical dielectric function ϵ_{xy}. Both the imaginary part of the experimental dielectric function (Fig. 3) and the calculated dielectric function (Fig. 5) evolve from a single peak with a low energy shoulder for thick layers ($d > 5$ nm) to a function with two peaks of equal importance at very thin layers. The fact that the experimental system is a layer of separate nanocrystals rather than an infinite sheet of PbSe may account for the lower magnitude of the experimental ϵ_{im}. As demonstrated in Fig. 4, the resonance energy of the first Lorentz oscillator (E_{01}) follows closely the minimum energy gap along the Σ_{xz} and Σ_{yz} directions. This is in full accordance with our theoretical results. On the other hand, theory predicts an almost invariant value for E_{02}, while our experiments show a blueshift also in this case. However, especially for the deposits below 3 nm in height, confinement in the x and y direction will complicate the measurements since nanocrystals with edges below 5 nm will be present. This may explain the observed blueshift of E_{02}. The inhomogeneous size distribution of the nanocrystals may account for the broadening of the Lorentz oscillators in the experimental dielectric function (inhomogeneous broadening) as well.

We conclude that this work demonstrates that the dielectric function of low-dimensional semiconductors can be strongly influenced by the effects of quantum confinement. The effects depend in a complex way on the band structure throughout the entire Brillouin zone. In the case of PbSe crystals confined in one direction of space, a strongly anisotropic dielectric function is predicted. Experimentally, the lateral dielectric function ϵ_{xy} could be determined. These experiments demonstrate that confinement in PbSe nanocrystals leads to a change of the energy and the relative strength of the electronic transitions that determine the dielectric function.

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