PHYSICAL REVIEW B **72**, 153313 (2005)

Calculation of electronic density of states induced by impurities in TiO_2 quantum dots

J. L. Movilla, G. Garcia-Belmonte,* J. Bisquert, and J. Planelles
Departament de Ciències Experimentals, Universitat Jaume I, Box 224, E-12080 Castelló, Spain

(Received 20 July 2005; published 26 October 2005)

We have theoretically calculated and analyzed the electronic density of states (DOS) in crystalline TiO_2 nanoparticles in air (or vacuum) affected by the presence of impurities near the particle surface. The effect of temperature has been incorporated by changing the permittivity value of the quantum dot, in accordance with reported dependences. Our model is described by a truly three-dimensional effective mass Hamiltonian with a realistic finite steplike confining potential and the Coulomb terms, including dielectric mismatch effects. The presence of impurities in nanometer systems naturally induces band tailing with details depending on the dielectric response of involved media. Our calculations predict a dependence of the DOS on temperature. Moreover, a high degree of electronic density delocalization within the quantum dots is found, which has important implications on developing transport models.

DOI: 10.1103/PhysRevB.72.153313 PACS number(s): 73.20.At, 73.22.Dj

Assemblies of semiconductor particles of nanometer scale (often referred to as quantum dots, QD) are being studied as potentially useful in the fields of electronics, optics, catalysis, photovoltage conversion, and energy storage. In all these systems, the one-particle density of states (DOS) becomes a key factor for the description of relevant physical properties.[1,2] Moreover, an accurate knowledge of DOS would be a fundamental piece in device engineering. Well-controlled sizes of nanocrystals in the 1–10 nm range show discrete atomiclike energy levels due to the size confinement, although experimental observation of quantum effects on charge transport needs a fine control over particle size and shape to preclude electronic disorder.[3,4] In materials with less-demanding technical requirements the simple, atomic-like picture cannot be straightforwardly seen due to the inherent structural disorder and the presence of impurities.

One of the most studied nanostructures is based on assemblies of titanium dioxide particles that form porous layers into which a liquid or solid electrolyte can penetrate. For this type of structure there are indications for storage of electrons in band gap states.[5,6] Since one-particle DOS determine to a high degree the device performance, it is interesting to study, from a fundamental point of view, the role of size dispersion and impurities to gain insight into the origin and effect of such band gap levels.

Electronic states within the gap is believed to be distributed following approximately an exponential form as[7]

$$g(E) = \frac{N}{E_0}\exp\left(\frac{E}{E_0}\right), \tag{1}$$

where E is the energy which is taken equal to zero at the bottom of the conduction band and decreases downwards in the band gap, N corresponds to the total density of band gap states, and E_0 stands for the width of the distribution. It has been found that the distribution width lies within the range of 30–100 meV (Refs. 7–9) and N results of the order of $10^{19}\ \mathrm{cm}^{-3}$. In addition, surface states related to the uncoordinated Ti^{+4} appear at energies of $\sim$350 meV below the conduction band edge.[10] There exists a variety of methods for measuring DOS in such nanostructures. One of them consists of determining directly the variation of the electronic density caused by a variation of the Fermi energy.[2,7,11] The amount of available states is then monitored by means of a change of the applied potential in conditions close to the thermodynamic equilibrium. Accurate measurements of nanoporous TiO_2 films permeated with aqueous solution indicated a distribution of states within the gap which presents an exponential tail far below the conduction band edge, and tends to saturate near this energy limit.[7]

Other methods determine the DOS indirectly by measuring the open-circuit photovoltage decay after switching it off.[12] V_{oc} evolution depends on the Fermi level position on time that changes the electron recombination rate and can be used to estimate state distributions. In this study, distribution width resulted in 53 ± 11 meV.[12] In addition, exponential tails have also been invoked to account for the electron diffusivity dependence on illumination in nanoporous TiO_2-based solar cells.[13] There is an experimentally observed power-law dependence of the diffusion coefficient with the charge density generated by illumination,[14] usually explained by means of multiple trapping electron transport models.[6,15,16] It has been also reported that the distribution width varies as a function of the amount of Li^+ ions intercalated into the TiO_2 structure.[17]

Optical absorption techniques (porous TiO_2 in low partial oxygen pressure conditions) show the occurrence of absorption tails with E_0 of the order of 0.1 eV which increases with increasing temperature.[18] This entails that DOS may be affected by variations of underlying parameters, such as the dielectric constants of TiO_2 and the surrounding media, induced by the change of temperature. The extremely strong temperature dependence of the TiO_2 permittivity is otherwise well documented.[19]

Summarizing experimental evidence it can be said that the width of the exponential tail depends not only on the particular TiO_2 preparing route, but also on changes in the type of surrounding medium and temperature.

The issue of band tailing in bulk semiconductors has received much attention for decades.[20] Impurities can induce tails in the density of states by perturbing the band edge as a consequence of local Coulombic interactions and dislocations of the lattice.[21] The aim of this work is to ascertain the influence that the nanometer size confinement could have by itself on the experimentally observed tails in the DOS. To this end, we have theoretically calculated and analyzed the electronic DOS in crystalline TiO_2 nanoparticles in air (or vacuum) affected by the presence of impurities near the particle surface. In our theoretical method the electric response of materials is assumed to follow the electrodynamics of continuous media, so that a parameter, the dielectric constant, characterizes the material response.[22] The validity of such a macroscopic model has been well established for semiconductor QDs.[23] The effect of temperature has been incorporated by changing the permittivity value of the quantum dot, in accordance with reported dependences.[19]

Within the framework of the envelope function approach and effective mass approximation, the electronic Hamiltonian for a QD in the presence of a hydrogenic donor impurity reads, in atomic units,

$$H = -\frac{1}{2}\nabla\left(\frac{1}{m^*(\mathbf{r})}\nabla\right) + V(\mathbf{r}) + \phi_c + \phi_s. \tag{2}$$

The first term in Eq. (2) is the generalized kinetic energy operator, $V(\mathbf{r})$ corresponds to a realistic three-dimensional (3D) steplike spatial confinement potential, and ϕ_c stands for the Coulombic potential generated by the impurity, including the effects of the polarization charges induced at the QD border as a consequence of the dielectric constant mismatch between the QD and the surrounding medium. The electron itself also induces polarization charges at the dot boundaries, whose effects are described by the self-polarization potential term ϕ_s. When an $\epsilon(\mathbf{r}) = \epsilon(r)$ steplike dielectric function is assumed, ϕ_c and ϕ_s admit analytical expressions. We carry out an exact (numerical) integration of Eq. (2) by means of a discretization scheme based on the finite differences method. The explicit expressions of ϕ_c and ϕ_s together with a detailed description of the integration method employed can be found in Refs. 24 and 25. As we will show next, the presence of impurities in nanometer systems naturally induces band tailing, with details depending on the dielectric constant (particularly on the relative weight of bare Coulomb vs polarization).

Figure 1 shows the bottom of the electronic energy spectrum (specifically, the states which energy is located in the gap region) of a 10 nm radius spherical TiO_2 nanocrystallite embedded in air or vacuum in the presence of a hydrogenic donor impurity vs the QD dielectric constant ϵ_{QD}. The impurity has been located close to the QD surface (at a distance of 9 nm from the QD center) since it is expected that the doping of nanostructured TiO_2 films mostly occurs close to the QD's border. In our calculation the origin of energies has been set at the bottom of the conduction band, and the QD dielectric constant ranges from 6 (TiO_2 dynamic dielectric constant) to 60 (corresponding to a static dielectric constant).[19,26] The surrounding air (or vacuum) dielectric constant is $\epsilon_0 = 1$ and the employed electron effective masses are $m^* = 1$ for both, vacuum and TiO_2.[27] The spatial confinement step potential height is assumed to equal the TiO_2 electroaffinity,[28] $EA = 3.9$ eV.

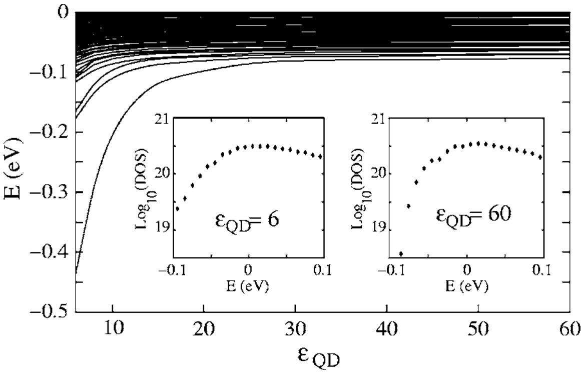

FIG. 1. One-electron energy levels of a 10 nm radius spherical TiO_2 nanocrystal with a hydrogenic donor impurity located at 9 nm from the QD center, as a function of the QD dielectric constant. Insets show the common logarithmic representation of the density of states in the vicinity of the conduction band edge of a statistical distribution of doped TiO_2 QDs (with an average 10 nm radius and a dispersion of 10%), for two different values of the QD dielectric constant. In all cases, the outer medium is air or vacuum.

As mentioned previously, a high dependence of the TiO_2 dielectric constant on temperature is well documented.[19] ϵ_{QD} decreases as the temperature is raised up. Then, an enhanced Coulomb potential yields a larger penetration of electronic states into the gap, as it can be seen in Fig. 1. The representation of the corresponding electron wave functions shows that, in general, the electronic charge density associated to these gap states spreads over the whole QD volume (nanoscopic confinement). Only in the case of the low-lying states (and only for QD dielectric constants smaller than about 15) the charge density is localized in a few lattice cells around the impurity site, so that we can actually refer to these last states as trapping states. The previous observation may have important implications when the problem of electronic transport in nanostructured layers is faced. Electronic density delocalization within each QD suggest that long-range electron motion may be mainly determined by the energetic mismatch between neighboring particles rather than effects associated with inner displacement.

Figure 1 also shows that in the region of dielectric constant ϵ_{QD} higher than 25 no appreciable changes can be seen, and that for dielectric constant values as high as 60, many states still come into the energy gap. Since the dielectric response of media may be formally described by the electric field produced by an effective charge distribution in vacuum, we can understand the effect of an increase of the QD dielectric constant as an effective charge transfer from the impurity position to the dielectrically mismatched surface. The effective charge located at the impurity position (which is responsible for the bare Coulomb term) is proportional to $1/\epsilon_{QD}$, while the induced charge at the QD boundaries (connected with polarization terms) scales as $1-1/\epsilon_{QD}$. Hence, as ϵ_{QD} increases, the electron trapping capability of the impurity site and the associated states stabilization diminishes. In contrast, the enhancement of polarization charge can still stabilize the states pushing them into the energy gap. It is worth noting out that as the polarization charge is distributed over the whole QD surface, the polarization-induced gap states are spread over the whole QD volume and not trapped in the surroundings of the impurity site.

The different penetration of the electronic states into the gap is also reflected in the DOS profile. Insets in Fig. 1 show the calculated DOS for $\epsilon_{QD}=6$ (that would correspond to high temperature, left panel) and for $\epsilon_{QD}=60$ (low temperature, right panel).[29] We have assumed in these calculations a statistical distribution of QDs (with an average 10 nm radius and a 10% dispersion, usual values for technological materials). Insets in Fig. 1 show that the calculated DOS profiles do not fit an exponential law [Eq. (1)]. However, it resembles the experimentally observed DOS near the conduction band lower edge.[7]

The exponential model, Eq. (1), allows characterizing the DOS profile by means of a constant parameter E_0, inversely proportional to the slope of the logarithmic representation of the DOS. However, in our calculations it is not a constant but depends on energy. We can observe, though, that the inverse of the mentioned slope increases with temperature at any energy value in the gap (see insets in Fig. 1). This agrees qualitatively with the increment of E_0 with temperature found in literature in case of QDs in air or vacuum.[18] The number of states in the gap, as it can be inferred from data in insets of Fig. 1, is of the same order as the experimentally determined.[7]

Both insets show a maximum in the DOS, approximately located in the bottom of the conduction band. It is the result of the interplay of two different sources of confinement, namely, the QD spatial confinement potential and the Coulombic potentials. The deepest states in the gap are the most influenced by the Coulomb terms, providing a DOS which increases with energy. However, for highly excited states where the spatial confinement is most relevant, the situation is reversed: DOS decreases with energy. The energy domain characterized by the DOS maximum could be referred to as a transition region between these two regimes.

Summing up, Coulomb terms (bare Coulomb and surface polarization) may explain the presence of states in the energy gap, as derived from impurity doping in semiconductor nanostructures. They also predict a dependence of the DOS on temperature. We have proven that in addition to well-known explanations for band tailing in bulk semiconductors (local Coulombic interactions and lattice dislocation) the nanometer size confinements are able to induce similar effects. Moreover, our approach predicts a high degree of electronic density delocalization within the QD, which has important implications on developing transport models.

Financial support from MEC-DGI Project No. CTQ2004-02315/BQU and UJI-Bancaixa Project No. P1-B2002-01 is gratefully acknowledged. A MECD of Spain FPU grant is also acknowledged (JLM).

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*Electronic address: garciag@uji.es

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[29] Both panels show the DOS in the range of energies from −0.1 to 0.1 eV. We must point out that although Fig. 1 shows that deeper states are present for $\epsilon_{QD}=6$, the extremely discrete character of this region of the energy spectrum does not allow us to properly talk about DOS for energies below −0.1 eV.