

BANDGAP EXPANSION OF A NANOMETRIC SEMICONDUCTOR

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Abstract. With the miniaturization of a solid, the band gap expands and the energy levels of the core bands shift towards higher binding energy, and subsequently, properties such as dielectrics change. These intriguing phenomena have been found new applications in microelectronics and photonics for devices. However, the underlying mechanism for these phenomena is still under debate. Here we present a new approach showing that the bond contraction at the surface and the rise in the surface-to-volume ratio of the nanosolid are responsible for these phenomena as the spontaneous bond contraction enhances the interatomic binding energy, which results in the corresponding derivatives.

1. INTRODUCTION

The size-induced physical property change of a nanosolid has attracted tremendous interest because the conventionally detectable quantities are no longer constant but they are tunable by simply controlling the shape-and-size of the solid. However, from a fundamental point of view, the origins for the property change are yet unclear. There are often conflicting models developed for a particular phenomenon. Here we describe a new approach showing that the spontaneous bond contraction at the surface and the rise in the surface-to-volume ratio of a nanosolid are responsible for the bandgap expansion of a nanometric semiconductor.

For the particular concern of electronic and optical properties, a nanosolid exhibits the following properties:

- (i) The band gaps expand, which cause the blue-shift in photoluminescence [1-5];
- (ii) The energy levels of core bands and the adsorbater-induced satellite shift simultaneously towards higher binding energy [6-9];
- (iii) The dielectric constant is suppressed and causes a blue shift in photo absorption [10-12].

Among the various models [1-6] for the size-induced band gap expansion the “quantum confine-

ment” theory [13-15] was recognized as the most successful model. The “quantum confinement” theory adopted the intra-atomic potential to the nanosolid which was treated as a potential box, or “quantum dot”, in the first instance, and then added the terms of electron-hole Coulomb interaction and bulk correlation to the Hamiltonian of the carriers moving freely inside the box. According to the quantum confinement theory, electrons in the conduction band and holes in the valence band are confined spatially by the potential barrier of the surface. Because of the confinement of both the electrons and the holes, the lowest energy optical transition from the valence to the conduction band increases in energy, effectively increasing the band gap. The energy of the freely moving carriers is responsible for the band gap expansion and the width of the confined band gap grows as the characteristic dimensions of the crystallite decrease.

There are also conflicting opinions regarding the size-induced core-level shift of nanosolids. For example, the core level shift of CuO particles was attributed to the enhancement of *ionicity* with reducing particle size [7] while the core level shifts of O-Sn and O-Ta were ascribed as the *dipole contribution* of the oxide-covered nanoclusters [8]. The core level shifts of pure Ru(0001) and pure Rh(001) sur-

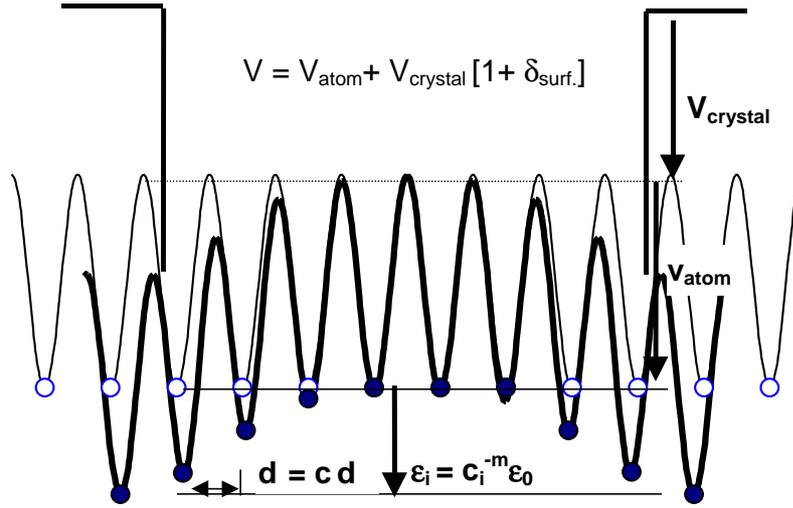


Fig. 1. Schematic illustration of the “surface bond contraction” model. The spontaneous bond contraction at surface lowers the wells of potential energy near the surface while the periodic trapping muffin-tin potential wells remain inside the solid.

faces were explained as the surface relaxation effect [9,10].

Therefore, a consistent understanding of the size effect on the bandgap and core level shift of a nanosolid is desirable. Here we show a new approach that has been able to unify these observations.

2. THEORY

We may suggest a Hamiltonian for electrons moving inside a nanosolid by adding the effect of surface relaxation to the convention for an extended solid (see Fig. 1) [16]:

$$\begin{aligned} \hat{H}(D) &= \hat{H}_0(\infty) + \hat{H}'(D) = \\ &= -\frac{\hbar^2 \nabla^2}{2m} + v_{atom}(r) + V_{crystal}(r)[1 + \delta_{surf}] \\ &= \hat{H}(\infty) + V_{crystal}(r) \delta_{surf}, \end{aligned} \quad (1)$$

where $v_{atom}(r)$ is the intra-atomic trapping potential of an isolated atom, which confines electrons moving around the ion core in the form of standing waves with discrete energy levels. The periodic function $\hat{H}' = V(r) = V(r + R_i)$ is the crystal field that sums the inter-atomic binding potential over the solid. R_i is the lattice constant. δ_{surf} represents the perturbation of surface relaxation.

According to the nearly free electron approximation [17], the bandgap (E_g) between the conduction and the valence band of an extended solid depends on the integration of the crystal field:

$$\begin{aligned} E_g(\infty) &= 2|V_1(k)|, \text{ and} \\ E_n(k) &= \langle \phi(k, r) | V_{crystal}(r) | \phi(k, r) \rangle, \end{aligned} \quad (2)$$

where $\phi(k, r)$ is the Bloch wave for the nearly free conduction electrons. Eq. (2) indicates that $E_g(\infty)$ is simply the first Fourier coefficient of the crystal field. The tight binding approximation [18] indicates that the energy dispersion of electrons in a core band follows the relation:

$$E(k) = E_v - \beta - 2\gamma + 4\gamma \times \psi(k, R_1), \quad (3)$$

where,

- (i) $E_v = \langle \phi_v(r) | \hat{H}_0 | \phi_v(r) \rangle$ is the energy of the core electron of an isolated atom;
- (ii) $\beta = -\langle \phi_v(r) | V_{crystal}(r) | \phi_v(r) \rangle$ is the crystal field effect on the core electrons of the specified coordinate r ;
- (iii) $\beta = -\langle \phi_v(r - R_i) | V_{crystal}(r - R_i) | \phi_v(r - R_i) \rangle$ is the crystal field effect on the coordinate neighboring electrons;
- (iv) $\psi(k, R_1)$ is a structure related function that sums over all the contributions of coordinates of a particular atom in the solid.

Eqs. (2 and 3) indicate that the E_g , the core level shift ($\Delta E_c = \beta + 2\gamma$) and the bandwidth ($4\gamma \times \psi(k, R)$) of an extended solid depend simply on the integration of the crystal field in conjunction with the Bloch waves of the nearly free or the core electrons. The number of atoms (or the size) of the solid determines the number of sublevels in a particular energy band. What differs a nanosolid from an extended

solid is that for the former the number of atoms of the solid may be counted while for the latter the number is too large.

One can easily derive that any change of the crystal field will lead to the variation of the bandgap and the core level shift of the solid based on the modified Hamiltonian (Eq. 1):

$$\frac{\Delta E_g(D)}{E_g(\infty)} = \frac{\Delta E_c(D)}{E_c(\infty)} = \frac{\Delta\gamma}{\gamma} = \frac{\Delta\beta}{\beta} = \delta_{surf} = \frac{\Delta V_{crystal}(r)}{V_{crystal}(r)}. \quad (4)$$

The size-induced crystal field change can be expressed as [18]:

$$\delta_{surf} = \sum_{i \leq 3} \gamma_i \frac{\Delta v(d_i)}{v(d)} + \Delta = \sum_{i \leq 3} \gamma_i (c_i^{-m} - 1) + \Delta, \quad (5)$$

and

$$\Delta = \frac{nV(D)}{N^2 v(d)}.$$

The $v(d_i)$ is the energy density in the relaxed region, which is proportional to the interatomic binding energy, ϵ_i , at equilibrium atomic separation d_i . N is the number of atoms within each particle of a nanosolid and the n is the number of particles of the bulk solid. γ_i is the surface-to-volume ratio of the i th atomic layer. The i is counted from the outmost layer to the center of the particle up to 3 as no CN reduction occurs when $i > 3$. Δ describes the contribution of cluster interaction $V(D)$, which becomes insignificant with increasing particle dimension. The c_i is the coefficient of bond relaxation and $d_i = c_i d$. Here d_i and d are the bond length at i th atomic layer and inside the bulk, respectively. As the relaxation is a spontaneous process, the interatomic binding energy will change as $\epsilon_i = c_i^{-m} \epsilon$. Here m is a parameter introduced to describe the change of binding energy with the reduced bond length.

For example, for a spherical dot, the volume of the i -th atomic shell is $V_i = 4\pi R_i^2 d_i$, and $R_i = (k - (i - 0.5)d)$; the volume of the entire sphere is $V = 4\pi(kd)^3/3$, and k represents the particle size and $k = D/2d$. Then the volume ratio of the i -th atomic shell to that of the bulk sphere is,

$$\gamma_i = \frac{V_i}{V} = \frac{4\pi[(k - (i - 0.5)d)]^2 d_i}{\frac{4}{3}\pi(kd)^3} = \frac{3}{k} \left(1 - \frac{i - 0.5}{k}\right)^2 c_i. \quad (6)$$

Eqs. (4 - 6) indicate that the band structure of a nanometric system results from the surface-bond contraction (c_i) and the rise in the surface-to-volume ratio of the solid, which depends on the shape and size (k) of the nanosolid as well as the type of inter-atomic binding energy (m).

The current approach differs entirely from the "quantum confinement" assumption for the physical origin of the bandgap expansion. Here we add the term of surface relaxation to the Hamiltonian of an extended solid. It is understandable that the intra-atomic interaction defines the discrete energy levels and the inter-atomic binding interaction defines the band structures. Therefore, neither of the intra- or the inter-atomic potential can be replaced, or removed from the Hamiltonian.

3. RESULTS AND DISCUSSION

It is worth emphasizing that the termination of the lattice periodicity in the surface normal leads to two effects. One is the reduction of the coordination numbers (CNs) of surface atoms and the other is the creation of a surface potential barrier or work function [19]. Pauling [20] and Goldschmidt [21] found that the atomic radius shrinks with the reduction of its coordination number. We have extended these premises to the curved surface of a nanosolid. This premise holds irrespective of the nature of the specific chemical bond [22] or the dimension of the solid [23]. Such surface bond contraction has been found with LEED to form one of the four essential stages of O-Cu(001) bond forming kinetics [24,25] and was further confirmed by measuring the enhanced surface stress and Young's modulus of surfaces [26]. The potential barrier [27] confines the nearly free conduction electrons that moving inside the solid.

Fig. 2 shows that the bond contraction model predictions agree with observations of the size-dependent photoluminescence of SiO_x nanoparticles [28]. Bond contraction of 12% and 4% was applied, respectively, to the first two atomic layers of a spherical dot. It can be seen that the curve of $m = 4$ fits well the trend of observation. The prediction also agrees with the trends of core level shift for the O-

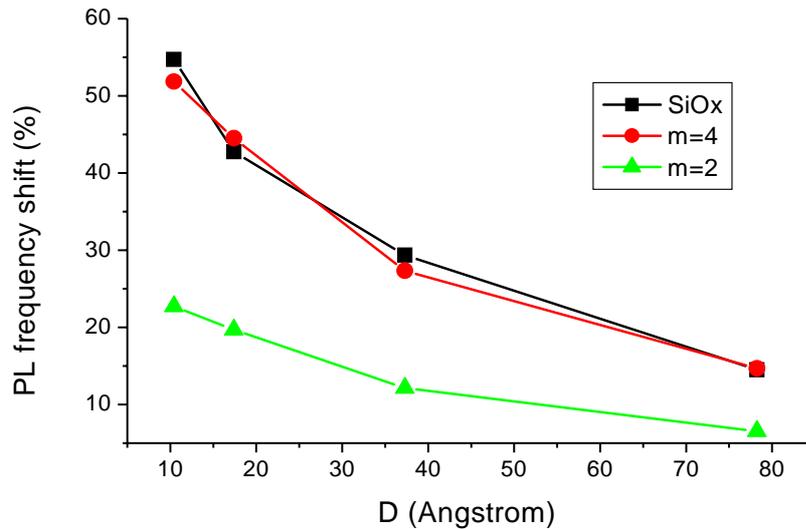


Fig. 2. Agreement between prediction ($m = 4$, see Eq. 5) and observations [29] of the PL blue shift of nano-sized Si oxide.

Cu, O-Sn and O-Ta nanoclusters and Ru(0001) and Rh(001) surface with and without oxygen adsorption [17].

The concept of surface-bond contraction has been incorporated into a number of observations. For instance, the mean lattice contraction of Sn and Bi nanosolids [29], has been simulated [24]. The band-gap expansion of nanometric semiconductors leads to the suppression of dielectric constant and hence the blue shift of the photoabsorption edges of a nanometric semiconductor [13]. The surface stress enhancement has an influence on the Gibbs free energy that determines the ferroelectric [30] and pyroelectric [31] transition properties of nanometric PZT oxides. The sum of the binding energy of a single bond over the CN of an atom at surface determines the thermal energy required for melting the surface atom. This enables the melting behavior of nanosolids [32,33] to be consistently formulated. Further exploitation towards a simple model to generalize the behavior of nanosolid is in progress.

4. CONCLUSIONS

In summary, we have shown that the band-gap expansion and the core-level shift of a nanosolid can be unified with the concept of surface bond contraction without any assumption. It is concluded that:

(i) The conventional band theories are valid for nanometric solid. The difference between a bulk and a nanometric solid is the ability to count the number of atoms of the solid, and subsequently, the number of energy levels in the band. This

may lay the foundation of single-electronic tunneling and oscillating conductance of nanometric conductors with resolvable separation of sublevels of energy.

- (ii) The reduced particle size enlarges the deviation, other than the average, of the momentum of conducting electrons. The reduced dimension has no effect on the *localized* bonding electrons or electrons in the deeper band. Therefore, the small particle size does not contribute to the energy rise of electrons inside the solid.
- (iii) However, *chemical bonds do contract* spontaneously at surface or sites where the atomic CN reduces. As a consequence, the bond contraction enhances the binding energy, the crystal field and all the derivatives.
- (iv) Therefore, the contraction of surface bonds, in conjunction with the rise in the surface to volume ratio of reduced particle size expands the band gap and shifts the energy-level of core bands of the solid, in addition to other detectable properties.

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