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Size Dependence of the 2p-Level Shift of Nanosolid Silicon

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Modeling exercises on the size-induced blue-shift in the photoluminescence (PL) of nanosolid Si (*J. Phys. Chem. B* **2002**, *106*, 11725) have been extended herewith to the size dependence of the Si-2p energy-level-shift measured using X-ray photoelectron spectroscopy (XPS). Results show consistency in both the origin and trend of the core-level shift with that of band-gap expansion upon Si nanosolid formation. Most strikingly, decoding the size dependent XPS peak shift leads to quantitative information about the 2p-level atomic trapping energy of an isolated Si atom (−96.74 eV) and the crystal binding intensity (−2.46 eV) upon bulk solid formation, which is beyond the scope of direct measurement using currently available techniques.

When a solid forms at nanometer size, the gap between the conduction and the valence band expands;[1,2] the energy peak of a core level and the chemical satellites measured using X-ray photoelectron spectroscopy (XPS) will also shift up in magnitude simultaneously.[3] The extent of core-level shift depends on both the original core-level position of the isolated atom and the reduced particle size. There have been a number of reports on the size dependence of the core-level shift of nanosolid materials such as Cu(O)-2p,[4] Cu-2p,[5] Au-4f,[6] Sn-3d, Sn-4d, and Ta-4f.[7] Experimental results show that the size (*D*)-induced shift follows a D^{-1}-dependent fashion. However, the underlying mechanism for the size-induced core-level shift is under debate. For instance, the size-induced core-level shift of the Cu−O nanosolid[4] was attributed to the enhancement of *ionicity* due to the reduction of the particle size. This means that an oxygen atom bonds more strongly to the Cu atoms in a nanosolid than does the oxygen atom to the Cu atoms inside the bulk. The enhanced core-level shift of the O−Sn and O−Ta covered metallic clusters was attributed to the contribution from *interfacial dipoles* of the nanoparticles.[7] The number or the momentum of the dipoles increases with reducing particle size. The thermochemical or

the "initial-final state" model[5,8,9] defines the shift as the difference in energy that is needed to remove a core electron either from a surface atom or from a bulk atom. The final states, or cohesive energy, of atoms at the curved surface of a nanosolid was expected to increase when the particle size is reduced. The surface atom is assumed as a "Z + 1 impurity" on the Z metal substrate. Recently, Ohgi and Fujita[6] found that the trend of Au-4f core-level shift coincides with the change of the inverse capacitance of the Au particles measured using scanning tunneling spectroscopy. However, the mechanism behind the size-induced core-level shift of nanosolid Si is desirable.

Differing from the band gap, $E_G(D)$, of a nanosolid Si that can be measured approximately using the photoluminescence (PL) spectroscopy due to the involvement of electron−phonon coupling, the atomic trapping determined core-level energy, E_v, of an isolated atom, and the bulk crystal binding caused shift of the E_v, $\Delta E_C(\infty) = E_C(\infty) - E_v$, can be hardly detectable with currently available techniques. With the laser cooling technology, one can measure the energy separation between different levels of gaseous atoms trapped by the laser beams.[10] What one can measure using an XPS are the broad peaks of the core-levels resulting from contributions of atomic trapping,

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TABLE 1: Measured PL and E_{2p} and the Derived Information of Particle Size D, Band Gap E_{PL}, Atomic E_{2p}, and Bulk Shift $\Delta E_{2p}(\infty)$ of Nanosolid Si

sample	D (nm)	λ_{PL} (nm)	E_{PL} (eV)	$E_{2p}(D)$ (eV)	$\Delta E_{2p}(\infty)$ (eV)	E_{2p} (eV)
A	1.4	575.31	2.16	102.16		
B	1.6	591.91	2.07	101.98		
C	1.7	611.79	2.03	101.68		
D	1.9	650.40	1.91	101.41		
E	2.1	683.44	1.81	101.27		
bulk	∞		1.12	-99.2	-2.46	-96.74

bulk crystal binding and the effects of surface relaxation or nanosolid formation. Therefore, separating the atomic trapping from the crystal binding in a bulk solid is a big challenge. In the following, we show that this problem for Si can be resolved by decoding the size dependence of the core-level shift of nanosolid Si, which may be extended to cases that are more general.

In the previous work,[1] we applied the bond order−length−strength (BOLS) correlation[11] mechanism to the size-induced PL blue-shift of the nanosized porous Si or nanosolid Si. It is found that the band-gap expansion arises from the coordination-imperfection-induced bond contraction and the associated bond energy rise of atoms at the curved surface of a nanosolid, of which the surface-to-volume ratio changes with the shape and dimension of the solid. At the lower end of the size limit, the band gap approaches the corresponding level separation of an isolated atom and the band-gap expansion is related to the contraction of a single bond at the surface.

Actually, the BOLS correlation contributes to the overall potential in the Hamiltonian of an extended solid, which gives rise to the electron energy potential of a nanosolid with dimension D_j:[1]

$$V(D_j) = V_{atom}(r) + V_{cry}(r + R_C)[1 + \delta_j] \quad (1)$$

The intra-atomic trapping potential, $V_{atom}(r)$, defines the core-level position of an isolated atom, E_ν. The crystal potential of an extended solid, $V_{cry}(r + R_C)$, being the sum of the interatomic bonding to electrons in the particular site r over the entire solid, defines not only the band gap, E_G, but also the shift of the core-level energy away from the original position, $E_\nu(\infty) - E_\nu$. R_C is the lattice constant. δ_j, being independent of the particular form of the interatomic potential, is the contribution from the large portion (surface-to-volume ratio, γ_{ij}) of the lower-coordinated surface atoms to the Hamiltonian. According to the band theory, the size dependence of both E_G expansion and E_ν shift follows the relations

$$\frac{E_G(D_j) - E_G(\infty)}{E_G(\infty)} = \frac{E_\nu(D_j) - E_\nu(\infty)}{E_\nu(\infty) - E_\nu} = \delta_j \quad (2)$$

where[1]

$$\begin{cases} \delta_j = \sum_{i \leq 3} \gamma_{ij}(c_i^{-m} - 1) \\ \gamma_{ij} = \dfrac{D_{out,i}^{\tau} - D_{in,i}^{\tau}}{D_j^{\tau}} \propto \dfrac{\tau c_i}{K_j} \\ c_i = d_i/d = 2/\{1 + \exp[(12 - z_i)/(8z_i)]\} \end{cases} \quad (3)$$

$D_{out,i}$ and $D_{in,i}$ correspond to the outer and inner diameter of the ith atomic layer of d_i thickness ($d_i = D_{out,i} - D_{in,i} = c_i d$)
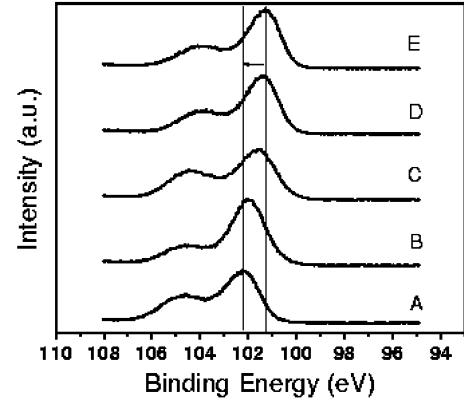

Figure 1. XPS profiles showing the size dependence of the 2p level shift of nanosolid Si. The data of sizes and the corresponding PL blue shift are given in Table 1.

with which the γ_{ij} would be more precisely described than using the γ_i in ref 1 for particles near the lower end of the size limit. z_i is the effective coordination number (CN) of an atom in the ith atomic layer and $d = 0.2632$ nm is the diameter of a Si atom. $\tau = 1-3$ correspond to the dimensionality of a thin plate, a rod, and a spherical dot. It is important to note that the $\sum_{i \leq 3} \gamma_{ij}$-drops in a D_j^{-1} fashion from unity to infinitely small when the solid dimension grows from atomic level to macroscopic scale.

In eq 1, the band gap for bulk Si, $E_G(\infty)$, is known but the bulk core-level shift $E_\nu(\infty) - E_\nu$ is unknown. With the known bulk value of $E_G(\infty) = 1.12$ eV, $m = 4$ has been obtained in matching the predicted curve with the measured size dependence of the PL shift without considering the electron−phonon coupling effect.[3] According to refs 12 and 13, z_1 varies with the diameter D (=$2Kd$) of a spherical dot as $z_1 = 4(1 - 0.75/K)$. $z_2 = 6$ and $z_3 = 8$ are assumed independent of the surface curvature. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_3 = 12$ improve the match between the predicted and the measured PL profile (by ∼1% only). Therefore, contribution from the third layer is negligibly small because of γ_3 (<15%) and c_3^{-1} (=−3%). Recent refinement[14] shows that the energy shifts of both the PL and photoabsorption (PA) depends not only on the crystal binding energy but also on electron−phonon interaction (W), which follows the relation

$$\left.\begin{array}{r} \dfrac{\Delta E_{PL}(D)}{E_{PL}(\infty)} \\[2mm] \dfrac{\Delta E_{PA}(D)}{E_{PA}(\infty)} \end{array}\right\} = \frac{\Delta E_G(D) \mp \Delta W(D)}{E_G(\infty) \mp W(\infty)} \cong$$

$$\sum_{i \leq 3} \gamma_i[(c_i^{-4.88} - 1) \mp 0.91(c_i^{-2} - 1)] \quad (4)$$

Matching the predictions with both the experimental data on PA[14] and PL of nanosolid Si as reported in ref 1 gives $m = 4.88$ and the coefficient $B = 0.91$, which refines the original value $m = 4$, of which the electron−phonon interaction, i.e., $E_G = E_{PL}$, was out of concern. Nevertheless, the theoretical PL curve of $m = 4$ and $B = 0$ is identical to the PL curve of $m = 4.88$ and $B = 0.91$. The precise band-gap expansion due to crystal binding is hence the first term of $m = 4.88$.

Methods of fabrication of the nanosolid Si are the same as described in ref 1. The particle size can be obtained by matching the measured PL shift with the predicted PL profile that has matched numerous sets of PL data of porous Si reported in the literature. This method ensures the precision of size as listed in Table 1. Figure 1 shows the XPS Si-2p profiles of the fresh
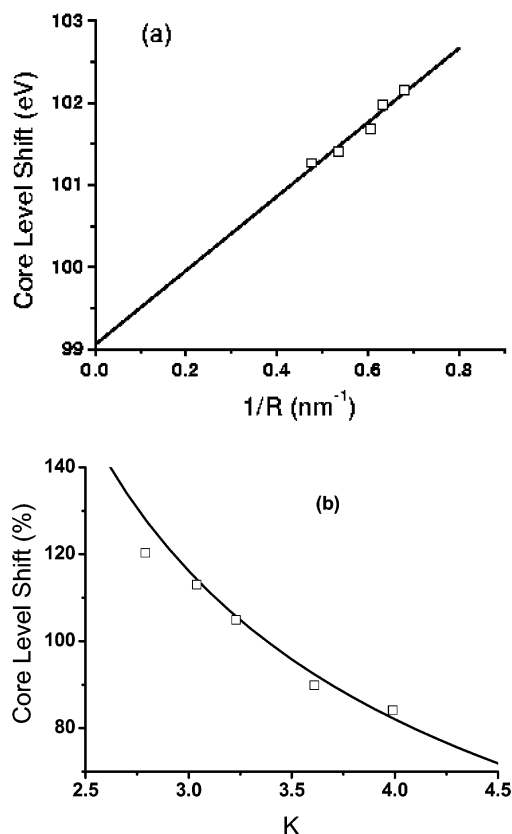
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Figure 2. (a) Least-root-mean-square linearization of the energy shift gives $E_{2p}(D) = 99.06 + 4.52/D \pm 0.04$. The slope is used to derive the atomic trapping and crystal binding of the bulk solid; the intercept is used to calibrate the equipment due to the surface electrostatic charge effect. Panel b shows the agreement between prediction (solid line) and the measured size dependence of the Si-2p core level shift, where $K = R/d$.

nanosolids (avoid chemical and aging effect) measured using a Kratos AXIS spectrometer with monochromatic Al K_α ($h\upsilon = 1486.71$ eV) radiation at ambient temperature. The size-dependent peak energy was then linearized with the least-root-mean-square optimization method to find the slope and intercept at the vertical axis ($1/D \rightarrow 0$ in Figure 2a). Thus, the following line can represent the experimental results ($\upsilon = 2p$):

$$E_{2p}(D) = E_{2p}(\infty) + b/D = 99.06 + 4.52/D \qquad (5)$$

This D^{-1} trend agrees with those reported by others[4-7] obtained from other materials despite the slope that changes from situation to situation. The intercept $E_{2p}(\infty)$ corresponds to the bulk $E_{2p}(\infty)$ position -99.2 eV and therefore a 0.16 eV ($=99.2 - 99.06$) shift is necessary for E_{2p} and $E_{2p}(\infty)$. The slight shift is

due to the surface electrostatic charge effect during the measurement. However, the shift has no effect on the crystal binding intensity, $\Delta E_{2p}(\infty) = E_{2p}(\infty) - E_{2p}$.

Matching the prediction in eq 1 with the experimental results represented by eq 3, one can find that the crystal binding intensity

$$E_{2p}(\infty) - E_{2p} = \frac{4.52}{D_j \delta_j} \qquad (6)$$

is readily available now because $\delta_j \propto D_j^{-1}$ and $D_j \delta_j$ is a constant provided with the known $m = 4.88$ for the effect of crystal binding on the band gap, which was obtained from the Both PA and PL matching.[3,14] As listed in Table 1, the atomic trapping energy of the 2p electron of an isolated Si atom E_{2p} is found to be -96.74 eV and the bulk crystal binding intensity $\Delta E_{2p}(\infty)$ to be -2.46 eV. Consistency between the predicted and the measured core-level shift is given in Figure 2b. Agreement of the predicted with both the observed E_{PL} shift and E_{2p} shift ensures the reliability of the data obtained and evidence that the BOLS correlation describes adequately the true situation. Accuracy of the determination is subject strictly to the precision of XPS measurement.

Thus, the BOLS correlation has enabled the E_{2p} shift and the E_G expansion upon nanosolid Si formation to be consistently decoded and understood in terms of surface CN imperfection and its contribution to the Hamiltonian. Decoding the E_{2p} shift leads to quantitative information about the atomic trapping energy of the 2p electrons (-96.74 eV) of an isolated Si atom and the binding intensity (-2.46 eV) of bulk Si crystal to the 2p electrons.

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