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\(^8\) 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, \(E_C\), of an isolated atom, and the bulk crystal binding caused shift of the \(E_C(\infty) = E_C(\infty) - E_C\), 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.
The intra-atomic trapping potential, by decoding the size dependence of the core-level shift of Si, we show that this problem for Si can be resolved with the bonding strength (BOLS) correlation mechanism to the size-in-

According to the band theory, the size dependence of the band gap approaches the corresponding bulk value of $E_G(\infty)$ as the diameter of a Si atom. According to refs 12 and 13, $z_1$ varies with the diameter $d = 0.2632$ nm. At the lower end of the size limit, the band gap expansion is related to the contraction of a single bond at the surface. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_1 = 12$ improve the match between the predicted and measured PL profile (by ~1% only). Therefore, contribution from the third layer is negligibly small because of $\gamma_1 = 0.91$, which refines the original value $m = 4$. 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. According to refs 12 and 13, $z_1$ varies with the diameter $d = 0.2632$ nm. At the lower end of the size limit, the band gap expansion is related to the contraction of a single bond at the surface. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_1 = 12$ improve the match between the predicted and measured PL profile (by ~1% only). Therefore, contribution from the third layer is negligibly small because of $\gamma_1 = 0.91$, which refines the original value $m = 4$. 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. According to refs 12 and 13, $z_1$ varies with the diameter $d = 0.2632$ nm. At the lower end of the size limit, the band gap expansion is related to the contraction of a single bond at the surface. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_1 = 12$ improve the match between the predicted and measured PL profile (by ~1% only). Therefore, contribution from the third layer is negligibly small because of $\gamma_1 = 0.91$, which refines the original value $m = 4$. 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. According to refs 12 and 13, $z_1$ varies with the diameter $d = 0.2632$ nm. At the lower end of the size limit, the band gap expansion is related to the contraction of a single bond at the surface. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_1 = 12$ improve the match between the predicted and measured PL profile (by ~1% only). Therefore, contribution from the third layer is negligibly small because of $\gamma_1 = 0.91$, which refines the original value $m = 4$. 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. According to refs 12 and 13, $z_1$ varies with the diameter $d = 0.2632$ nm. At the lower end of the size limit, the band gap expansion is related to the contraction of a single bond at the surface. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_1 = 12$ improve the match between the predicted and measured PL profile (by ~1% only). Therefore, contribution from the third layer is negligibly small because of $\gamma_1 = 0.91$, which refines the original value $m = 4$. 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. According to refs 12 and 13, $z_1$ varies with the diameter $d = 0.2632$ nm. At the lower end of the size limit, the band gap expansion is related to the contraction of a single bond at the surface. Further fine-tuning herewith shows that $z_1 = 4(1 - 0.7836/K)$ and $z_1 = 12$ improve the match between the predicted and measured PL profile (by ~1% only). Therefore, contribution from the third layer is negligibly small because of $\gamma_1 = 0.91$, which refines the original value $m = 4$. 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.
nanosolids (avoid chemical and aging effect) measured using a Kratos AXIS spectrometer with monochromatic Al Kα ($h\nu = 1486.71$ 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 ($\nu = 2p$):

$$E_{2p}(D) = E_{2p}(\infty) + b/D = 99.06 + 4.52/D$$  \hspace{1cm} (5)

This $D^{-1}$ trend agrees with those reported by others\textsuperscript{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

$$E_{2p}(\infty) - E_{2p} = \frac{4.52}{D}$$  \hspace{1cm} (6)

is readily available now because $\delta_j \propto D_j^{-\lambda}$ 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.\textsuperscript{5,14} 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 $E_{2p}$ 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 $E_0$ 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.

References and Notes