Size dependent 2p$_{3/2}$ binding-energy shift of Ni nanoclusters on SiO$_2$ support: Skin-depth local strain and quantum trapping

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ABSTRACT

An in situ X-ray photoelectron emission investigation revealed that the size trend of the 2p$_{3/2}$ binding-energy shift (BES) of Ni nanoclusters grown on SiO$_2$ substrate follows the prediction of the bond order–length–strength (BOLS) correlation theory [30]. Theoretical reproduction of the measurements turns out that the 2p$_{3/2}$ binding energy of an isolated Ni atom is 850.51 eV and its intrinsic bulk shift is 2.70 eV. Findings confirmed that the skin-depth local strain and potential well quantum trapping induced by the shorter and stronger bonds between under-coordinated surface atoms provide perturbation to the Hamiltonian and hence dominate the size dependent BES.

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1. Introduction

The under-coordinated surface atom experiences a different local bonding environment from that of atoms in the bulk interior. The atomic distance and binding energy (BE) associated with the surface atom will, in general, be different from those in the bulk. In the traditional continuum medium approaches of large trunks of materials, such surface geometry relaxation and BE difference are typically neglected because they are associated with only a few surface atomic layers and the ratio of the volume occupied by such under-coordinated atoms is extremely small compared with the entire body of the material. However, for nano-sized particles, wires and films, the surface-to-volume ratio becomes significant, and so does the effect of surface bonds. Therefore, understanding the energetic behavior of atoms and electrons localized in the surface covering sheet is of great importance, as many chemical and physical processes such as reaction and nucleation and the intrinsic properties of thermal stability and mechanical strength are determined by the atomic interactions and the electronic energetics.

Metal nanoclusters have attracted tremendous interest in recent years owing to their intriguing properties in electronic structure [1,2], mechanical strength [3], chemical and thermal stability [4], magnetism [5], and catalytic performance [6–8] and their potential applications in devices, such as solar cell, at the nanoscale [9]. The degree of the size freedom of metal nanoclusters has been indeed fascinating because the size reduction enables all the otherwise constant quantities such as atom bond length [10,11], melting point [12], and band gap [13,14], to be tunable. The occurrence of surface relaxation and reconstruction causes surface morphology and electronic configuration to be different [15–20].

It has been confirmed that the BE of metal nanoclusters shifts positively from higher (smaller absolute value) to lower energies as the solid size is reduced [21–25]. However, the physical mechanism of the size- and surface-induced core level shift is still under debate. Amongst the available models, the Coulomb effect [22,26] of charged nanoclusters with one hole left after an electron being ejected is suggested to be responsible for the corresponding BE shift. However, the Coulomb effect is unable to explain the fact that the BE values of dissimilar core levels of the same specimen shift differently. Another model is the “initial and final state” effect [21,27], which defines the “initial state” effect as the shift induced by the electron configuration modification and chemical environment variation of nanoclusters before being excited by the incident X-ray. The “final state” effect means the relaxation energy arising from the excitation by the X-ray radiation. Although this model has been widely used, quantitative information regarding which of the “initial state” or the “final state” is dominant cannot be extracted accurately from measurement. The global existence of the aforementioned effects could not over shed the significant size trend [28,29]. It is our opinion that the core level shift is determined intrinsically by the perturbation of the Hamiltonian. The interaction between under-coordinated atoms and the fraction of such atoms in the sample are factors of dominance. Without interatomic bond-
ing, no bulk shift; without coordination reduction, no surface and size effect at all. Therefore, it would be more meaningful to study the size dependent BE shift from the perspective of Hamiltonian perturbation. Other extrinsic effects can be treated as background that can be excluded if the experimental process is properly calibrated. In this manuscript, we reported our findings on the relation between the size dependent BE shift from the perspective of Hamiltonian induced local strain and surface potential well quantum trapping.

2. Principle

According to the BOLS theory [30], bonds in the surface region are shorter and stronger because of the under-coordination effect [10,32,33]. Recent investigations [34] revealed that the effective bond strength gain, the surface crystal potential well goes deeper or shorter and stronger because of the under-coordination effect [30,35,36]. Therefore, the BE shift of a specific core level of nanosolid becomes, $\Delta E_i(V) = \Delta E_i(\infty)(1 + \delta_i)$, or alternatively:

$$E_i(K) - E_i(\infty) = \frac{\Delta E_i(K)}{\frac{\Delta E_i(\infty)}{1 + \delta_i}}$$

Based on the BOLS correlation [30,35] and the high-resolution XPS, accurate value of $E_i(0)$ and the $E_i(\infty) - E_i(0)$ can be obtained following:

$$E_i(0) = (1 + \delta_i)^{\frac{1}{-\theta}} E_i(K) - (1 + \delta_i)^{\frac{1}{-\eta}} E_i(K)$$

which method has enabled us to understand and quantify the BE of an isolated Ni [37], Pt [38,39], Au [40–42], Cu [43], Pd [44], and C [45] atom and their intrinsic bulk shifts from the measurements.

3. Experimental procedures

All in situ XPS were performed using VG ESCALAB 220i-XL instrument. Monochromatic Al Kα (1486.7 eV) is set as the X-ray source. The XPS BE was calibrated using pure gold, silver, and copper standard samples by setting the Au-4f7/2, Ag-3d3/2, Cu-2p3/2 peaks and Ni Fermi edge at BE of 83.98 ± 0.02, 368.26 ± 0.02, 932.67 ± 0.02 and 0.00 ± 0.02 eV, respectively. The pass energy of 20 eV was used for all spectroscopy. SiO2 substrate was obtained by the silicon oxidation, which is dipped into the mixture of HCl, H2O2 and diluted water with volume ratio of 1:2:5 for 30 minutes at 80 °C. Prior to Ni deposition, as-prepared SiO2 substrate was cleaned using ultrasonic treatment in acetone solvent, then, annealed at 773 K in the high vacuum chamber. Ni nanoclusters were deposited by an Omicron EF M3 e-beam evaporator in the ultra high vacuum. After deposition, it was transferred to the analysis chamber directly without any exposure to air. JOEL 2100 TEM was chosen to get the morphology of Ni deposition.

4. Results and discussion

Fig. 2 shows the TEM images of Ni nanoclusters deposited on SiO2 substrate for different deposition times and respective...
Fig. 2. TEM observation of Ni nanoclusters deposited on SiO₂ substrate for deposition time of (a) 2 min and (c) 30 min. (b and d) Corresponding nanoclusters size histogram. The circled boundary of nanocluster in (a) is for viewing convenience.

Histogram of nanoclusters removed. As shown in Fig. 2(a), for 2 min deposition, spherical Ni nanoclusters are observed, whose morphologies are similar to the results reported for Ni growing on TiO₂(100) and (110) [43,44] and teflon substrates [46]. The radius size distribution is calculated as 1.13 ± 0.03 nm as shown in Fig. 2(b). In Fig. 2(c), as the deposition time prolongs to 30 min, the Ni nanoclusters still keep the spherical shape with radius size distribution of 3.54 ± 0.07 nm, as shown in Fig. 2(d). Thus, the growth of Ni nanoclusters on SiO₂ substrate follows the Volmer–Weber (island) mode. In Fig. 2(c), the coalescence between bigger Ni nanoclusters appears, although every isolated nanocluster in coalescence is facile to be differentiated. Some smaller Ni nanoclusters also turn out at this moment, which may be induced by the second nucleation for continuous Ni deposition. From the comparison between Fig. 2(b) and (d), a narrow size distribution for Ni nanoclusters with short deposition time (2 min) compared with that of long deposition time (30 min) confirms a much more uniform nucleation and growth at the initial stage of Ni nanoclusters.

Fig. 3(a) shows the Ni 2p₃/₂ spectra as a function of deposition time. For comparison purpose, the Ni 2p₃/₂ spectra are normalized with respect to their respective maximum. Comparing the 2p₃/₂ spectra of Ni nanoclusters for different deposition time, a positive shift towards the high BE is observed, which is consistent with the previously reported trends [47–49]. In order to obtain the peak position, we decomposed the spectrum using the AVANTAGE software by subtracting the spectral background that is in the Shirley mode. Fig. 3(b) shows the best fit of a typical spectrum that was collected after 5 min deposition. It is derived from the decomposition that the 2p₃/₂ peak shifts from 854.08 to 853.25 eV as the Ni deposition time increases from 20 s to 60 min. Fig. 3(c) shows the Full-Width-at-Half-Maximum (FWHM) of Ni 2p₃/₂ peak for different deposition time. The FWHM of Ni 2p₃/₂ peak decreases rapidly from 2.0 eV for 20 s Ni deposition to 1.0 eV for 60 min. The latter is the same to the bulk Ni value [47]. This FWHM size trend is within the BOLS expectation of quantum trapping and the polarization of the otherwise conducting electrons by the densely trapped binding electrons [50]. The smaller the particle size, the stronger the effect of trapping and polarization, and therefore the wider the spectrum would be. A subtraction of the 5 min spectrum by the 60 min one after normalization each, as shown in Fig. 3(d), the residual spectrum shows that the effect of quantum trapping at lower binding energy is more significant for smaller size. No apparent polarization peak at the high binding energy side is observed because of the size effect dominance in nanostructures.

Increasing evidence supports the expectation that surface modifications become significant as small size [10,28,29]. For example, Mironets et al. [29] demonstrated that the mean lattice constant of Co nano-islands deposited on Cu(0 0 1) substrate contracts by 6% from the bulk value of 0.251 to 0.236 nm when one moves from the center to the edge of the nano-islands. Since lattice strain occurs at surface skin up to a few atomic layers, an additional depression of the potential well takes effect on the BE of the core electrons. For Cu₁₈ and Ni₁₈ atomic clusters, calculations [28] suggested that the BE for both the initial and the final states undergo positive shifts from 0 to 0.7–0.8 eV when the average strain of the clusters is increased from 0% to 6%. An atomic layer-resolved XPS of Ni sur-
Fig. 3. (a) XPS Ni 2p3/2 profiles. (b) Peak fitting of 2p3/2. (c) The FWHM variation with deposition times ranging from 1/3 to 60 min. (d) The residual spectrum shows the effect of under-coordination-induced quantum trapping.

face [37] revealed that the surface core level shifts positively and that the outermost layer shifts most. All the observations confirm the BOLS theory prediction and the current experiment that the enhanced quantum trapping at surface skin is the cause for the size dependent core level shift for nanoclusters.

Fig. 4 compares the BOLS reproduction of the experimental data as a function of Ni cluster size. Based on the measurement of Ni clusters size and the 2p3/2 peak positions obtained by fitting to the individual components of the convoluted spectra, as shown in Fig. 3(b), we can obtain the \( (E_v(\infty) - E_v(0)) \) and \( E_v(0) \) values. Decomposing all the available spectra for different sizes, we determined that the Ni 2p3/2 BE of an isolated atom is 850.51 eV and the bulk BE is 853.21 eV by using Eq. (6). In the calculation, \( m = 1 \) and \( \tau = 3 \) were used for the three-dimensional Ni nanoclusters as observed using TEM. The bulk BE value of Ni 2p3/2 agrees with those reported in the open literature [26,42]. The corresponding bulk shift \( (E_v(\infty) - E_v(0)) \) for Ni 2p3/2 core level is 2.70 eV.

The \( (E_v(\infty) - E_v(0)) \) and \( E_v(0) \) can also be obtained by direct fitting to the experimental data using the established linear dependence of the BE on solid size [51,52]: \( E_v(K) = A + B/K \). \( K \) is the dimensionless form of size. Equating this relation to the BOLS expression given in Eq. (5), we could find the correspondence: \( A = E_v(\infty) \) and \( B = [E_v(\infty) - E_v(0)] \times \tau \times \delta \). Thus, parameter \( A \) represents the bulk BE and the slope \( B \) the integrated effects of intrinsic bulk BE shift such as the growth mode and the perturbation of Hamiltonian in the surface skin. The bulk shift of \( [E_v(\infty) - E_v(0)] \) could be calculated by the values of \( A \) and \( B \) which are gained following the linear fitting of experimental data. From this fitting as shown in the inset of Fig. 4 are determined as 853.26 and 1.71 eV, respectively. The bulk shift is 2.62 eV, close to the value of 2.70 eV obtained in BOLS calculation. Therefore, both spec-
in situ XPS measurement, we have determined the 2p \( \frac{3}{2} \) BE of 850.51 eV for an isolated Ni atom and the bulk shift of 2.70 eV from the measured size dependent spectra. It has been clarified that the size dependent BE shift for Ni nanoclusters originates from the perturbation in the Hamiltonian by the shorter and stronger bonds between under-coordinated atoms. The size dependent FWHM change confirms the BOLS expected quantum trapping states due to atomic under-coordination.

5. Conclusions

Combining the tight-binding theory, BOLS correlation, and the in situ XPS measurement, we have determined the 2p \( \frac{3}{2} \) BE of 850.51 eV for an isolated Ni atom and the bulk shift of 2.70 eV from the measured size dependent spectra. It has been clarified that the size dependent BE shift for Ni nanoclusters originates from the perturbation in the Hamiltonian by the shorter and stronger bonds between under-coordinated atoms. The size dependent FWHM change confirms the BOLS expected quantum trapping states due to atomic under-coordination.

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