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Anomalous behavior of satellite features at the surface and interface in the Ni *L*-edge x-ray absorption spectra

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The behavior of satellite features appearing in the Ni *L*-edge x-ray absorption spectrum has been investigated for Cu-capped Ni films on Cu(100) by extracting the interface component of the absorption spectrum. By comparing the results with the surface component, it was revealed that the satellite feature at ~6 eV above the L_{III} peak is suppressed only at the surface. This behavior was well reproduced by a one-electron multiple-scattering calculation. On the other hand, an enhancement in the 3-eV satellite was observed at the surface, associated with an increase in the *d*-hole number. This is interpreted as an increase in the $3d^8$ configuration in the ground state.

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The Ni *L*-edge x-ray absorption spectrum has been extensively investigated, especially concerning a strange behavior of satellite features appearing at several eV above the main peak.[1–7] It was reported that the absorption spectrum from bulk Ni exhibits a satellite feature at ~6 eV above the L_{III} main peak (6-eV satellite), while the x-ray magnetic circular dichroism (XMCD) difference spectrum shows a 3-eV satellite.[1] The origin of the satellite features has been discussed for a long time.[2–5] Jo and Sawatzky[2] attributed these satellites both to the configuration mixing between $2p^5 3d^9$ and $2p^5 3d^{10}$ in the final state and to the presence of a $3d^8$ character in the ground state. However, the disappearance of the 6-eV satellite in the XMCD difference spectrum could not be completely explained. Smith *et al.* treated this problem in a one-electron relativistic tight-binding band-structure approach.[3] Their satisfactory calculation reproduced the behavior of the 6-eV satellite, but no 3-eV satellite appeared in the XMCD difference spectrum. Tjeng *et al.*[4] attributed the 6-eV satellite to the critical point in the band structure by means of the 2*p* resonant photoemission measurement with circularly polarized x rays. They assigned the 3-eV satellite to the many-body $2p^5 3d^9$ and $2p^5 3d^{10}$ configurations. Nesvizhskii *et al.*[5] also claimed that the 3-eV satellite is attributed to a multiplet effect, while the 6-eV one is reproduced by a one-electron real-space multiple-scattering calculation.

Another striking fact was reported for ultrathin Ni films. Srivastava *et al.* measured the x-ray absorption spectrum from ultrathin Ni films as a function of film thickness, and revealed that the 6-eV satellite decreases with decreasing thickness.[6] Nietubyć *et al.* also reported similar results for ultrathin (⩽2 ML) Ni films, but they claimed that the satellite intensity is almost constant between 1 and 2 ML.[7] Although it seems reasonable to attribute the disappearance of the satellite to the surface or interface effect, it was impossible to separate the surface and interface components from each other due to the lack of depth resolution in the conventional measurements. Recently, we have developed a depth-resolved XMCD technique.[8–10] We revealed that the 6-eV satellite disappears at the surface,[10] but could not get any information on the interface spectrum.

In the present study, we have succeeded in extracting the interface component of the x-ray absorption spectra of Ni films by capping Ni/Cu(100) films with Cu layers. We also extracted high-quality XMCD difference spectra by adopting a magnetically saturated Ni film in order to investigate the behavior of the 3-eV satellite. By comparing the sequentially obtained data from bare and Cu-capped film, it is unambiguously shown that the 6-eV satellite disappears only at the surface. This behavior is well reproduced by a one-electron multiple-scattering calculation, and the scattering paths which contribute to the satellite are identified. Moreover, the 3-eV satellite is suggested to be enhanced at the surface, which can be interpreted as the change in the electron configuration, associated with the increase in the *d*-hole number.

All the experiments were performed in an ultrahigh-vacuum chamber at the soft x-ray stations, BL-7A and BL-11A, in the Photon Factory, High-energy Accelerator Research Organization.[11,12] Circularly polarized x rays (circular polarization factor, $P_c = \sim 0.85$) were obtained by collecting light emitted up or down the electron orbit plane of the storage ring. The experimental layout of the depth-resolved XMCD measurement is described elsewhere.[9,10] In short, electrons emitted after x-ray absorption were separately collected at different detection angles which correspond to different mean probing depths (electron escape depths), λ_e. A partial electron yield mode with a retarding voltage of 500 V was adopted. λ_e ranged from 0.6 to 1.7 nm, which was experimentally determined from the thickness dependence of the Ni edge jump.[8] A Cu(100) single crystal was cleaned by repeated cycles of Ar^+ bombardment (1.5 kV) and annealing to ~900 K. Ni and Cu were deposited at room temperature by an electron bombardment heating. The film thickness was controlled by an *in situ* reflection high-energy electron diffraction observation. The sample was magnetized with a yoke coil (~1500 Oe) and the remanent magnetization was examined. The spectra were recorded at normal and grazing x-ray incidences (0° and 60° from normal) for the samples with perpendicular and in-plane magnetizations, respectively. All the measurements were performed at room temperature.

Figure 1 gives the probing depth (λ_e) dependence of averaged *L*-edge absorption spectrum, $(\mu_+ + \mu_-)/2$, from a 9 ML Ni film before and after Cu capping. Note here that the

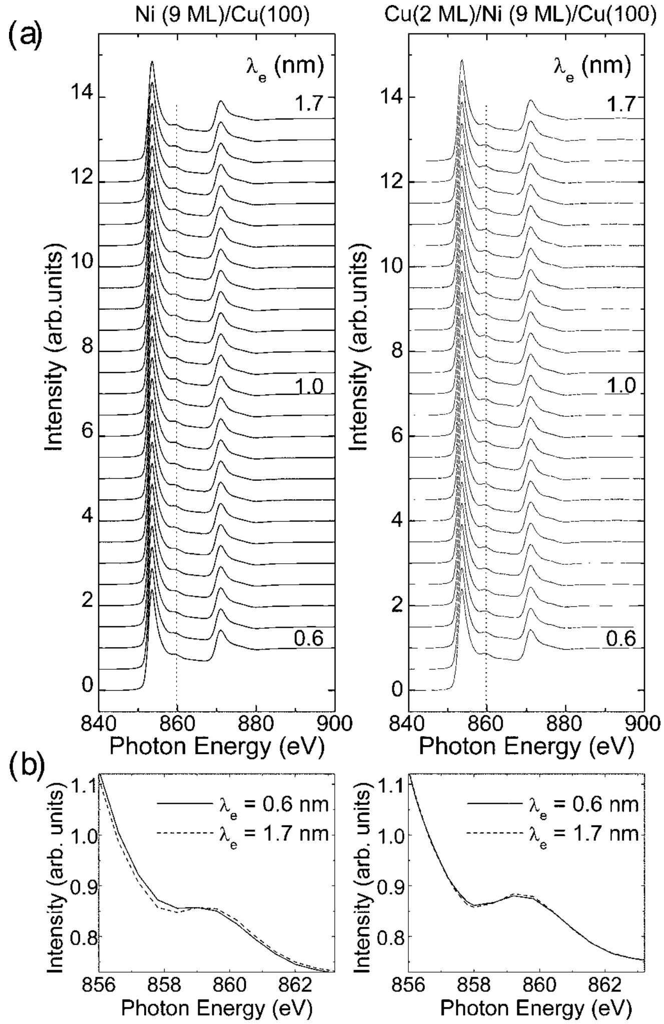

FIG. 1. Ni L-edge x-ray absorption spectra from bare (left) and Cu capped (right) a 9 ML Ni film with different probing depths, λ_e, taken at room temperature (a), together with the enlarged spectrum around the $L_{\rm III}$ satellite features with λ_e of 0.6 and 1.7 nm (b).

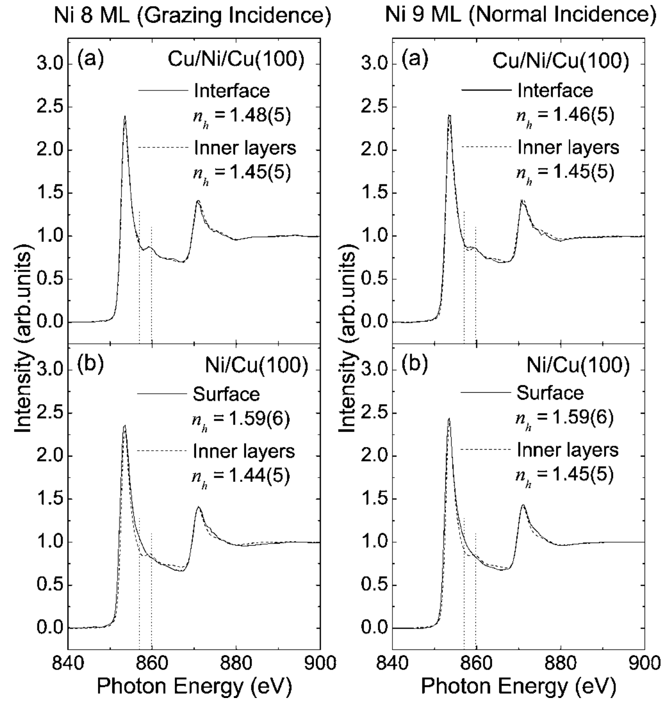

FIG. 2. Surface, interface (solid line), and inner layer (dashed line) components of the averaged x-ray absorption spectrum extracted from the data from (a) Cu/Ni/Cu(100) and (b) Ni/Cu(100) with Ni thickness of 8 and 9 ML. The d-hole number, n_h, estimated from the white line intensity, is also indicated.

spectrum becomes more surface sensitive at smaller λ_e for the bare film, while the Ni-Cu interface component increases with decreasing λ_e in the case of the Cu-capped film. All the spectra seem basically identical, irrespective of λ_e, but by a close observation around the satellite features, some λ_e dependence is recognized for the bare film; at smaller λ_e, the 6-eV satellite is less prominent while absorption around the 3-eV satellite is stronger. In contrast, no such difference can be seen in the spectra from the Cu-capped film.

Then we extracted the surface, interface, and inner layer components from a series of the spectra with different λ_e.[8–10] The total number of the detected electrons, $Y(E)$, normalized by the original x-ray intensity, $I_0(E)$, is given by

$$Y(E) = C\sum_{n=1}^{N} \mu_n(E)\exp\left[-d\left\{\frac{n-1}{\lambda} + \frac{1}{\cos\theta}\sum_{k=1}^{n-1}\mu_k(E)\right\}\right] + aB(E), \tag{1}$$

where C is the detection efficiency, $\mu_n(E)$ the absorption coefficient for the nth layer from the surface, N the layer number, E the photon energy, θ the x-ray incidence angle from surface normal, $B(E)$ the signal from a bare Cu substrate, and a the attenuation factor for $B(E)$. The constants C and a can be determined at each λ_e by using the known absorption coefficients at the pre- and postedge energies.

We at first analyzed the data from the Cu-capped film by dividing the Ni film into three regions; the top and bottom interface layers, and the rest, inner ones. Here, we assumed that the top and bottom interface layers give the same spectrum, i.e.,

$$\mu_n(E) = \mu_{\rm interface}(E)(n = 1 \text{ and } N), \tag{2}$$

$$\mu_n(E) = \mu_{\rm bulk}(E)(2 \leq n \leq N-1). \tag{3}$$

We then optimized $\mu_{\rm interface}(E)$ and $\mu_{\rm bulk}(E)$ independently at each photon energy, so as to minimize the difference between the observed spectrum and the calculated one obtained from Eq. (1).

The extracted spectra are depicted in Fig. 2. As expected from Fig. 1, the interface spectrum is similar to the inner layer one. Moreover, no significant difference can be seen between the spectra from 8 and 9 ML films, which were recorded in grazing and normal x-ray incidences, respectively, because the films exhibited in-plane and perpendicular magnetizations. We also estimated the d-hole number, n_h, from the white line intensity of the absorption spectrum after step function subtraction, assuming that the integrated white line intensity is proportional to n_h, and that n_h for bulk Ni is

1.50. Again, no significant difference can be found either between interface and inner layers or between 8 and 9 ML films.

Next, we extracted the surface component from the bare film data. Although we have already reported the results,[10] it is important to analyze the data taken just before Cu capping in order to exclude a sample-dependent artifact. Moreover, we can safely assume that the bottom (interface) Ni layer exhibits the identical spectrum to that of the inner layers because the interface spectrum is similar to the inner layer one. As shown in Fig. 2, the 6-eV satellite disappears at surface and the absorption intensity around the 3-eV satellite is stronger compared to the inner layers. The reduction in the 6-eV satellite is thus unambiguously attributed to the surface effect. This seems to contradict the previous study,[7] which reported that the 6-eV satellite intensity is almost constant between 1 and 2 ML. However, such an ultrathin region is not suitable to be discussed in the simple model consisting of surface, interface, and inner layers.

To interpret this anomalous behavior of the satellite features at the surface and interface, the origin of the satellites should be discussed. The early work by Jo and Sawatzky[2] attributed both the 3-eV and 6-eV satellites to the configuration-interaction effects, but the recent studies[4,5] pointed out that the 6-eV one should be explained in the one-electron picture such as the band structure or multiple scattering. For the 3-eV satellite, however, most of the previous works unanimously attributed it to the many-body configuration effects. The 3-eV satellite is related to the $3d^8$ character in the ground state, whose population was estimated to be 15–20%.[2]

Based on these results, the enhancement of the 3-eV satellite at surface can be related to the increase in the d-hole number, n_h, as indicated in Fig. 2. The increase in n_h can be associated with the increase in the $3d^8$ configuration in the ground state, which results in the enhancement of the 3-eV satellite. Note that no significant increase in n_h can be seen at interface, which is consistent with the fact that no enhancement of 3-eV satellite is found at interface. Here, we should point out that the behavior of n_h seems to contradict the previous studies.[6,7] Although the origin of the contradiction is not clear, we should emphasize the following points. First, we did not perform the thickness dependent experiment, so that the thickness dependence of n_h of the whole film is not excluded. Second, the previous data were recorded in the total electron yield mode, in which the background from the Cu substrate is relatively large. Such a large background might cause some artifact in the Ni spectrum, as the Ni thickness decreases.

For the 6-eV satellite, it was reported that the satellite feature is well reproduced by a multiple-scattering calculation with a Ni cluster consisting of 50 atoms, while no satellite can be found in the case of a smaller cluster (13 atoms).[5] This strongly suggests that the suppression of the 6-eV satellite at the surface is attributed to reduction in the number of surrounding Ni atoms. To confirm this idea, we performed a spectral simulation with the multiple-scattering code, FEFF8.2,[13] by using a model structure consisting of a 5 ML Ni film and a 2 ML Cu(100) substrate. Here, the Ni-Ni and Cu-Cu interlayer distances were fixed at those for the bulk structures, while the in-plane distance was assumed to be the same as that for bulk Cu. The simulated spectra are given in Fig. 3, which completely reproduce the different behavior of the 6-eV satellite between the surface and interface.

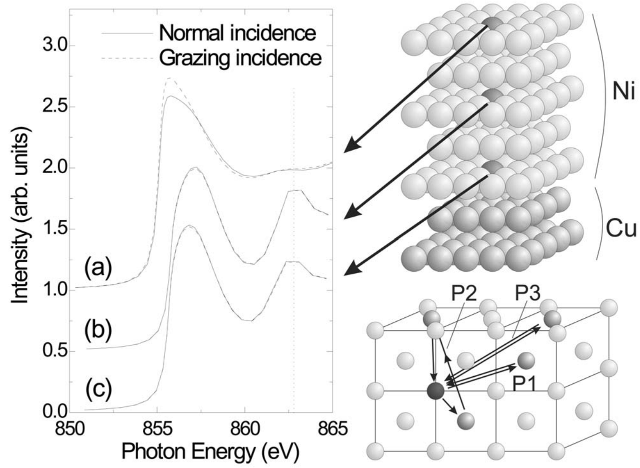

FIG. 3. Multiple-scattering simulation of the x-ray absorption spectrum at surface (a), inner layer (b), and interface (c) atoms, together with the cluster model used for the calculation. Some dominant scattering paths which exhibit positive (P1 and P2) and negative (P3) contributions to the 6-eV satellite are also indicated.

In order to clarify which scattering paths are responsible for the satellite, we examined the contribution of each scattering path by using the path expansion mode in FEFF8.2. Some of the dominant paths are indicated in Fig. 3. It is noticeable that half of the paths equivalent to P1 are lost at the surface due to the lack of atoms above the absorber. Moreover, in the case of P2, all the equivalent paths are lost at the surface because every path requires two atoms both above and below the absorber. There are quasiequivalent

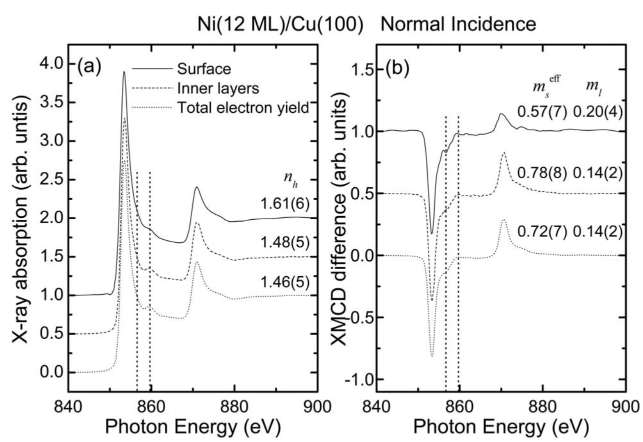

FIG. 4. Extracted surface (solid line) and inner layer (dashed line) component of the x-ray absorption (a) and XMCD difference (b) spectrum obtained from a 12 ML Ni/Cu(100) film, together with the total electron yield spectrum (dotted line). Estimated d-hole number, n_h, and effective spin and orbital moments, $m_s^{\rm eff}=m_s+7m_T$ and m_l, are also given. Here, m_s and m_T represent the spin magnetic and magnetic dipole moments, respectively.[15]

paths, however, where the z coordinate (surface normal direction) is exchanged with the x or y coordinate. Some such paths remain even at the surface. Although the reduction of the 6-eV satellite is thus interpreted as the reduction in the scattering paths, one may think that a small satellite should appear in the surface spectrum because some paths remain. However, there are other paths which exhibit negative contribution to the satellite as shown in Fig. 3. The behavior of the 6-eV satellite is determined by a balance of the scattering paths with positive and negative contributions.

Finally, let us turn our attention onto the XMCD difference spectrum. In order to obtain a high-quality spectrum, we chose a 12 ML film to achieve magnetic saturation at room temperature. Another reason to adopt such a relatively thick film is to check the reliability of the present technique. The total electron yield (TEY) spectrum should be dominated by the inner layer component, since the probing depth is 2−3 nm. Therefore, by comparing the TEY spectrum with the extracted inner layer one, we can check the reliability of the present technique. The obtained x-ray absorption and XMCD difference spectra are shown in Fig. 4. The extracted inner layer spectra are similar to the TEY ones. Moreover, the magnetic moments estimated by applying the sum rules[14,15] are also almost the same. The slight reduction of surface magnetization is probably due to some CO contamination, since CO adsorption drastically reduces the surface magnetization.[10]

As for the satellite features, the reduction of the 6-eV satellite at the surface is again clearly seen in the absorption spectra. In the XMCD difference spectra, in contrast, the 3-eV satellite seems enhanced at the surface, which is again consistent with the increase in the *d*-hole number as disscussed above. The contrastive behavior of the 3- and 6-eV satellite features is thus confirmed.

In summary, we have extracted the surface, interface, and inner layer x-ray absorption spectra from bare and Cu-capped Ni/Cu(100) films. It was unambiguously revealed that the 6-eV satellite disappears at the surface, while no reduction is found at the interface. This anomalous behavior was well reproduced by multiple-scattering calculations, and the scattering paths which dominantly cotribute to the satellite are identified. In contrast, the 3-eV satellite was suggested to be enhanced at the surface. The enhancement is interpreted as the increase in the d^8 configuration in the ground state, which is consistent with the increase in the *d*-hole number.

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