

## Observation of the satellite signal in Co 2*p* photoemission spectra: Evidence of a localized electronic structure in thin films

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A strong thickness dependence of the correlation-induced satellite signal in Co 2*p* photoemission spectra is observed for Co films. It is found that the relative photoemission intensities around the satellite to the main peak increase when the Co film [on Cu(001)] thickness decreases. For example, for a 1-ML deposited film on Cu(001), the satellite is more intense than that for 3- or 5-ML Co on Cu(001). By using the oxygen surfactant effect, we were able to intentionally change the growth mode of 1-ML Co, and the 1-ML Co on O/Cu emerged as the most preferable one to map out the maximum satellite intensity. The results are explained from the viewpoint of dimension-dependent electronic structures of Co films, where the influences of the status of the *d*-band, *d*-*d* interaction, and the Cu 4*s*–Co 3*d* hybridization together with the adatom (Co)-substrate (Cu) intermixing play vital roles in determining the satellite strength.

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### INTRODUCTION

Photoemission spectroscopy is an important tool for investigating the electronic structures of matter. The spectrum can be directly compared with the density of states (DOS) for any weakly interacting system. In the case of strongly interacting systems, however, the photoemission spectral features become complex. In such cases, the picture related to the DOS breaks down. The correlation-induced satellite structure<sup>1,2</sup> observed in the photoemission spectra for some transition metals is a typical example of the effect of electron correlation. Interpreting such a special spectral feature requires a suitable many-body model.

The scenario of electron correlation has stimulated a great deal of interest in strongly correlated systems, their corresponding photoemission features, and so on. According to Kotani and Toyozawa,<sup>3</sup> satellites in the core or valence band are a direct consequence of the formation of a multihole bound state during the photoemission process. A well-known and typical example is the Ni 6-eV satellite, an excited two-hole bound state.<sup>3</sup> According to Ref. 3, a different screening channel during the photoionization is the origin of Ni-satellite. The final state  $c^{-1}3d^{10}4s^1$  ( $c^{-1}$  is the core hole) shows a main peak where an additional charge from the *sp* conduction band can be put into the 3*d* orbital, leading to the formation of the 3*d*<sup>10</sup> configuration. On the other hand, in the final state  $c^{-1}3d^94s^2$ , a two-hole bound state is formed where an additional charge from the *sp* conduction band can screen the two-hole state within the wide 4*s* band. In this case, this final state appears as a satellite peak. A similar mechanism is also valid for valence-band satellites. Much attention has been given to the origin of the Ni 6-eV

satellite,<sup>2,3</sup> its resonant effect,<sup>1–3</sup> spin-polarization, etc.<sup>4,5</sup>

Though Ni is an itinerant ferromagnet, it shows a localized *d*-band nature, and the localization nature is the origin of the satellite. Co, another transition metal next to Ni in the Periodic Table, is situated on the borderline of the itinerant-localized transition region.<sup>6</sup> Unlike Ni, the Co satellite has not yet been studied thoroughly. At the same time, the issue of the Co satellite for both the valence<sup>7,8</sup> and core levels<sup>9–11</sup> is controversial. For the valence band, questions as to (1) whether the valence band satellite is a subthreshold Auger emission or a normal Auger, and (2) whether the observed satellite is just the O 2*p* emission, are subject to controversy.

In the case of core levels, such as Co 2*p*, this controversy is raised because the satellite signal is very weak to observe.<sup>9–11</sup> Although the authors of Ref. 9 observed no indication of a satellite, Raen<sup>10</sup> and Schneider *et al.*<sup>11</sup> reported the existence of a Co 2*p* satellite. However, it was reported in Ref. 10 that the signal was too weak to distinguish. On the other hand, the claim of having observed the satellite by Schneider *et al.*<sup>11</sup> was mainly based on the magnetic dichroism signal, where the satellite signal in photoemission spectra was itself weak.

In general, correlation-induced structures depend not only on the nature of the *d*-*d* electronic interaction but also on additional factors such as the single-particle band structure, the band filling, the weight and center of gravity of the DOS, and the crystal structure. These factors thus introduce some interesting phenomena when any reduced-dimension system, such as a thin film, surface, or cluster, is considered. It is well known that a surface with a smaller number of nearest-neighbor atoms shows an altered electronic configuration featuring a dehybridization of the wave function and a narrowing of the *d* band, features are different from the bulk.

According to the recent calculation by Chen,<sup>12</sup> many-particle effects may be enhanced in a reduced dimension system. Indeed, Chen<sup>13</sup> predicted that a strong satellite could be seen for a two-layer bcc-Co {001} film. However, the interfacial hybridization effect (Cu  $4s$ –Co  $3d$ ) should be minimized by selecting a proper substrate. It is therefore understood that we need to provide special condition by properly choosing both the dimension and substrate in order to observe the satellite. Though a weak satellite was observed previously for a 5-ML film,<sup>11</sup> there has been no thickness-dependence study of such a satellite reported so far.

In this paper, we demonstrate the strong influence of dimension on the electronic structure and hence the modification of the Co  $2p$  satellite signal for Co thin films on Cu(001) and O/Cu(001). There are several reasons we have chosen to observe a Co  $2p$  satellite rather than a valence-band one. First, the Co  $2p$  photoemission spectrum ensures an element-specific emission, whereas the valence-band satellite is overlapped with the tail of the broad Cu  $3d$  emission (substrate emission), especially for thinner films. Second, the large spin-orbit splitting value of Co  $2p$  is advantageous for observing the main peak and the satellite peak clearly. Finally, any kind of chemical shift peak in Co  $2p$  spectra is easily detectable.

The modification of the electronic structure of transition-metal films as a function of thickness has already been established. For example, Srivastava *et al.*<sup>14</sup> reported a variation of  $3d$  hole numbers as a function of Ni thickness on Cu(001). The epitaxy of Co on Cu(001) (Ref. 15) is considered to be a typical example of layer-by-layer growth. Even so, the layer-by-layer growth starts after the deposition of a 2-ML film. In our experiment, along with the conventional growth, we modified the initial growth of Co by using oxygen as a surfactant on Cu. The surfactant-mediated epitaxy gives a different growth mode and a modified electronic configuration, as well. It is therefore expected that the surfactant-mediated epitaxy will significantly modify the intensity of the Co  $2p$  satellite.

## EXPERIMENTS

All Co films were grown on Cu(001) at room temperature. The thickness of the film was checked by a quartz-crystal thickness monitor before and after deposition on the substrate. The pressure of the vacuum chamber was about  $8 \times 10^{-10}$  torr during the deposition. The conventional methods comprising mechanical polishing, chemical etching, Ar-ion sputtering, and annealing were used to clean the substrate. All photoemission spectra were excited by Mg  $K\alpha$  x-ray source ( $h\nu=1253.6$  eV), and were collected by a hemispherical electron analyzer installed in the VG-ESCALAB220-iXL spectromicroscopy system.<sup>16</sup> The photoemission detection area was less than  $1 \times 1$  mm<sup>2</sup>, and the total energy resolution was less than 0.7 eV at  $h\nu=1253.6$  eV.

In order to obtain a surfactant-rich Cu(001) surface, an exposure of 1200 L (1 L =  $10^{-6}$  torr sec) oxygen at room temperature was used on Cu(001). Before the oxygen exposure, we carefully confirmed the cleanness of the substrate

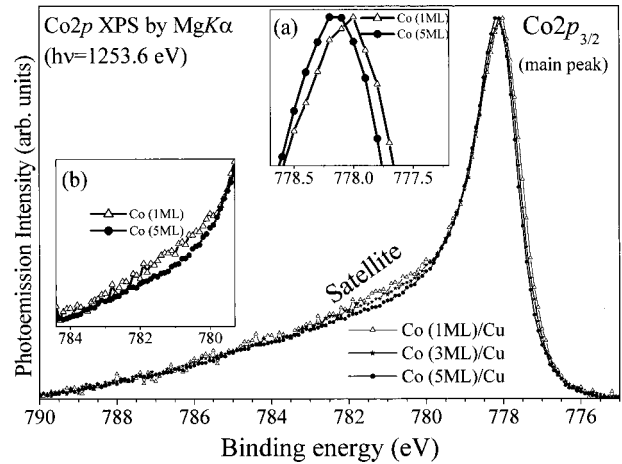


FIG. 1. Co  $2p_{3/2}$  photoemission spectra for several Co films grown on Cu(001) taken at  $h\nu=1253.6$  eV. Insets (a) and (b) are enlarged views of the main peak region and satellite region, respectively for 1- and 5-ML Co films.

surface. The oxygen-rich surface shows a reconstructed ( $\sqrt{2} \times \sqrt{2}$ ) $R45^\circ$ -O phase.<sup>17</sup> Upon deposition of 1- or 5-ML Co on that reconstructed surface, the  $c(2 \times 2)$  pattern was observed. The segregation of oxygen to the Co surface was also detected using O  $1s$  photoemission spectra.

## RESULTS AND DISCUSSION

Figure 1 shows the Co  $2p$  core-level photoemission spectra for Co films (1-, 3-, and 5-ML thick) grown on clean Cu(001). The prominent signal at 778.0 eV is the main Co  $2p_{3/2}$  peak, and identified as  $c^{-1}3d^94s^1$ , where  $c^{-1}$  is the core hole. The intensities of all spectra were normalized with respect to the spectrum for the 5-ML film as it has the maximum intensity for the main peak. Besides the main peak, there is another signal around 781.0–782.0-eV binding energy, but it is clearly visible only for thinner films. According to Raen<sup>10</sup> and Schneider *et al.*<sup>11</sup> the signal, which is about 4.0 eV higher than the main peak, is identified as a satellite. As seen in Fig. 1, the satellite intensity depends on the film thickness.

The insets show enlarged views of the satellite and main peak. In inset (a), it is seen that the main peak for 1-ML Co is shifted toward lower binding energy by 0.15 eV. According to Ref. 18 such a peak shift is likely to occur in a reduced-dimensional system, which has a modified DOS different from the bulk one. The peak shift confirms a different electronic structure for a 1-ML Co film from that of a 5-ML Co. In inset (b), the intensity difference around the satellite region is distinguishable; the signal for 1-ML film is higher than that for a 5-ML film. These results show that low-dimensional systems possess favorable conditions to observe an intense Co  $2p$  satellite.

The results in Fig. 1 give a hint that a Co  $2p$  satellite is likely to be observed even with an intense signal if we modify the electronic structure of the film by changing the growth mode. In practice, the 1-ML deposited film on Cu(001) does not consist of a long-axial atomically flat layer.

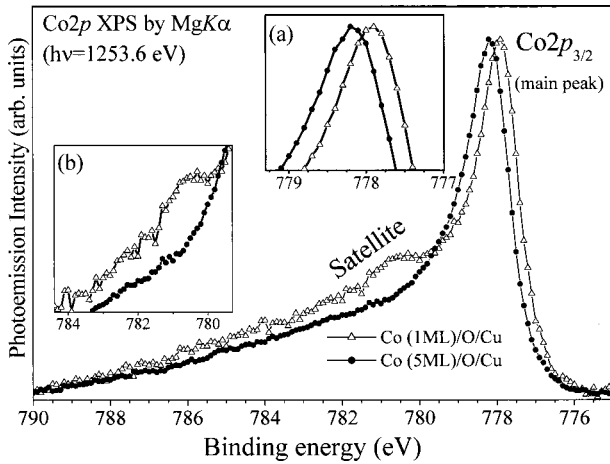


FIG. 2. Co  $2p_{3/2}$  photoemission spectra for two Co films (1 and 5 ML) grown on O (1200 L)/Cu(001) taken at  $h\nu=1253.6$  eV. Insets (a) and (b) are enlarged views of the main peak region and satellite region, respectively, for 1- and 5-ML Co films.

Instead, there are several islands 1– to 2 ML high.<sup>15</sup> As the morphology of a 1-ML film is far from homogeneous, we applied a unique technique, the surfactant-mediated epitaxy, in order to modify the Co growth mode. Oxygen was selected as a surfactant and 1- and 5-ML films were grown on oxygen-rich Cu(001) surfaces.

Figure 2 shows the Co  $2p$  photoemission results for 1- and 5-ML Co grown on O/Cu(001). Similar to Co/Cu in Fig. 1, the spectra also show the main peak and the satellite peak. The peak shift for the main peak [in inset (a)] is 0.30 eV, larger than that for the Co/Cu case. The reason will be discussed later. In inset (a), the relative intensity for the satellite is drastically increased for 1-ML Co on O/Cu. Compared with Fig. 1, one can easily observe a strong enhancement in satellite intensity. However, the satellite peak in Fig. 2 is broader than that in Fig. 1. This is probably due to (1) the higher background signal originating from the presence of the strong satellite, and (2) the possible presence of multiplet structures similar to the multiplets in the Ni valence band<sup>19</sup> and in Ni  $2p$  core-level<sup>20</sup> satellites. For instance, in Ni, several multiplet peaks, such as  $^1S$ ,  $^1G$ ,  $^3P$ ,  $^1D$ , and  $^3F$ , are located around the 4–9.5-eV binding energy region of the Ni 6-eV satellite in the valence band.<sup>19</sup> In the case of the Ni

$2p_{3/2}$  core level, the satellite peak is also broadened due to the multiplets located from 856- to 863-eV binding energy, where the satellite peak position is 858.2 eV.<sup>20</sup>

In Fig. 2, both the main peak shift and the enhanced satellite signal demonstrate that the modified initial growth of Co on O/Cu due to the surfactant is the origin of these spectral variations. This means that the electronic structure for 1-ML Co on O/Cu is also changed as well. We believe that, to date, this is the first observation of such an intense satellite in the Co  $2p$  spectrum. In the following, we will give an explanation of our findings.

The use of oxygen as a surfactant may raise a question as to whether there is any oxide formation or not. The surfactant nature of oxygen for the similar system (Co/O/Cu) was already discussed elsewhere.<sup>17</sup> In Ref. 17, we reported the results for low-energy electron-diffractions (LEED) patterns, O  $1s$  core-level spectra, oxygen segregation pathways, and the magnetic stability of Co films on O/Cu(001), and concluded that the oxygen on Co was chemisorbed, not the oxide one. In order to make the present paper self-contained, we will briefly summarize those results below.

Table I summarizes the results for the LEED patterns, O  $1s$  photoemission spectra, and chemical states of oxygen and magnetic phase of Co, as well. The surface of sample 1, i.e., O(1200 L)/Cu(001) is identified as a missing row phase.<sup>21</sup> The corresponding O  $1s$  binding energy is 530.0 eV. Samples 2 [Co(1 ML)/O/Cu(001)], 3 [Co(5 ML)/O/Cu(001)], and 4 [O(3.2 L)/Co(5 ML)/Cu(001)] show an ordered  $c(2\times 2)$  phase. The corresponding O  $1s$  binding energy is the same, i.e., 530.3 eV. The LEED patterns (not shown here) for samples 2 and 3 indicate that crystalline Co overlayers are achieved on an oxygen-rich surface. According to a previous report,<sup>22</sup> 1–7 L of absorbed oxygen on a Co film represents the chemisorbed state with  $c(2\times 2)$  surface symmetry. The identical O  $1s$  peak and crystalline phase for Co films (1 and 5 ML) on O/Cu support the existence of chemisorbed oxygen, similar to that for O(3.2 L)/Co/Cu (sample 4).

In addition to LEED and O  $1s$  photoemission results, the magnetic properties of Co films are also used to verify the surfactant effect of oxygen.<sup>17</sup> It was already established that Co films on clean Cu(001) show a ferromagnetic phase.<sup>11</sup> In Ref. 11, the magnetic dichroism in angular distribution in a

TABLE I. Summary of the LEED, O  $1s$  photoemission results, and magnetic phases for oxygen-rich Cu(001), chemisorbed Co films, and oxide Co film.

No. of sample	Sample	LEED pattern	O $1s$ peak (in eV)	Chemical state of oxygen	Magnetic state
1	O(1200 L)/Cu	$(\sqrt{2}\times\sqrt{2})R45^\circ$ -O, Missing-row (MR)	530.0	MR phase	-
2	Co(1 ML)/O/Cu	$c(2\times 2)$	530.3	Chemisorbed	-
3	Co(5 ML)/O/Cu	$c(2\times 2)$	530.3	Chemisorbed	Ferromagnetic
4	O(3.2 L)/Co(5 ML)/Cu	$c(2\times 2)$	530.3	Chemisorbed	-
5	Co(5 ML)/Cu	$p(1\times 1)$	-	-	Ferromagnetic
6	CoO/Co(5 ML)/Cu	$p(1\times 1)$	529.75	Oxide	-

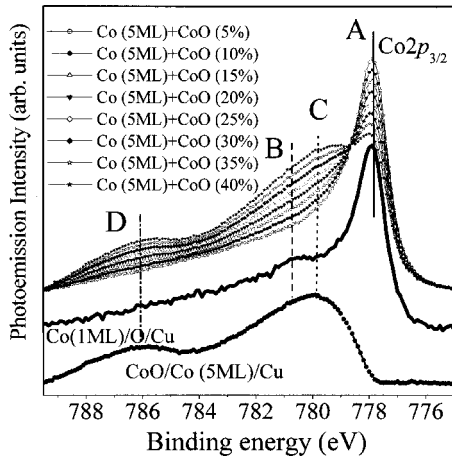


FIG. 3. The convoluted (Co5 ML+CoO) spectra for different CoO percentages together with the spectrum for Co (1 ML)/O/Cu and CoO/Co(5 ML)/Cu. A: the main peak in Co. B: the satellite in Co. C: the chemically shifted main peak in CoO. D: the charge-transfer satellite in CoO.

photoemission study was used to study the magnetic phase of a Co film. We also used the same technique to study the magnetic phase of Co films on O/Cu.<sup>17</sup> Both samples, i.e., 5-ML Co films on Cu(001) and O/Cu(001), as described in Ref. 17, show nearly equal dichroism signals. This means, even in the presence of segregated oxygen on 5-ML Co (sample 3), a ferromagnetic state remains stable. This is unlikely to happen if segregated O chemically reacts with Co, and converts Co into an anti ferromagnetic or paramagnetic CoO layer. The magnetism study is therefore considered to be one of the proofs that oxygen on Cu plays only a surfactant role, does not participate in any chemical reaction with the adatoms, and stays on the Co surface as a chemisorbed phase.<sup>17</sup>

Before going into a detailed discussion, it is necessary to distinguish the satellite from other peaks, such as the chemical shift peak of CoO.<sup>23</sup> In Fig. 3 we show some fitting results for Co  $2p$ , where some convoluted spectra of Co and CoO are shown together with spectra for 1-ML Co on O/Cu, and CoO/Co. The CoO part was taken from the O/(100 L)/Co(5 ML)/Cu(001) system. An exposure of 100-L oxygen on a Co (5 ML) film was used to obtain a thick CoO overlayer. In the case of the Co elemental part, Co (5 ML) on Cu was selected because the satellite is very weak to observe in this spectrum.

The reasons CoO was chosen over other oxides like  $\text{Co}_3\text{O}_4$  are (1) in the reference spectrum for CoO, which was grown as a 5-ML Co film, no  $\text{Co}_3\text{O}_4$  peak was observed; and (2) according to Ref. 24, the binding energy for Co in  $\text{Co}_3\text{O}_4$  (779.6 eV) is lower than that in CoO (780.5 eV). Now, if any  $\text{Co}_3\text{O}_4$  is present at the surface of 1-ML Co on O/Cu, then the Co  $2p_{3/2}$  peak position for that  $\text{Co}_3\text{O}_4$  must stay at the lower binding energy. This means the energy separation between the Co satellite and the  $\text{Co}_3\text{O}_4$  peak would be larger, and any ambiguity from possible overlapping would be even less. Another reason CoO was chosen is that it was already reported that  $\text{Co}_3\text{O}_4$  can be grown on Co films only at lower temperatures (such as 150 K).<sup>22</sup> Exposing Co film to oxygen

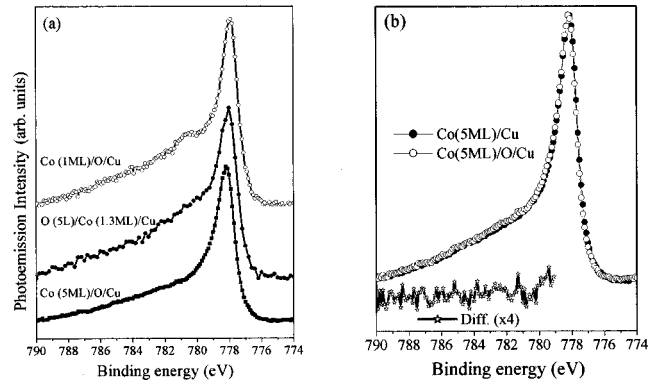


FIG. 4. Comparison of Co  $2p$  spectra for the chemisorbed-oxygen decorated different Co surfaces. (a) From top, spectra represent Co (1 ML)/O/Cu, O(5 L)/Co(1.3 ML)/Cu, and Co(5 ML)/O/Cu, respectively. (b) Direct comparison of two 5-ML Co films deposited on O/Cu and clean Cu. In the lower part, the difference spectrum around the satellite region is shown.

at room temperature gives only the CoO phase.

In Fig. 3, the peaks are  $c^{-1}3d^94s^1$  (the main peak in Co),  $c^{-1}3d^84s^2$  (the satellite in Co),  $c^{-1}3d^8L$  (the chemical shift main peak in CoO), and  $c^{-1}3d^8L + c^{-1}3d^7L^2$  (the charge-transfer satellite in CoO), ( $c^{-1}$  is the core hole, and  $L$  is the ligand state) are labeled A, B, C, and D, respectively. In the lower percentage (5–15 %) spectra, no peak comparable with the Co elemental satellite (B) is observed. Instead, the spectral shape broadens due to the CoO peak (C). Along with the peak C, the charge transfer satellite (D) starts to become visible. In the higher percentage (40%) spectrum, both peaks C and D become prominent. Compared with the spectrum for 1-ML Co on O/Cu, it is understood that the origins of peaks C and B are completely different. The comparison of different spectra in Fig. 3 clearly demonstrates that the Co elemental satellite (B) is totally free of a CoO contribution.

Furthermore, we also checked whether there was any chemisorbed induced peak, but there was no indication of such a peak. This will be shown in the following figure. Figure 4(a) comprises the Co  $2p$  spectral features for Co(1 ML)/O/Cu, O(5 L)/Co(1.3 ML)/Cu, and Co(5 ML)/O/Cu. The surface of each system contains chemisorbed oxygen. Except for O(5 L)/Co(1.3 ML)/Cu, where direct oxygen exposure (5 L) gives chemisorbed oxygen on a 1.3-ML Co, chemisorbed oxygen on the surfaces of the other two systems was formed after segregation of oxygen during Co deposition. We assume that 1-ML Co and 1.3-ML Co films are very comparable according to their low dimension.

In spite of the presence of similar chemisorbed oxygen on the surfaces of these three systems, only the spectrum for Co(1 ML)/O/Cu shows a Co satellite peak. It is argued that, if the chemisorbed oxygen causes any charge transfer and enhances the Co satellite intensity, then all surfaces should behave in a similar way. This means an intense satellite should be observed for every surface. But that has not happened as seen in Fig. 4(a), and only Co(1 ML)/O/Cu shows the satellite signal.

Furthermore, a direct comparison of Co  $2p$  spectra is given in Fig. 4(b) for two 5-ML Co films, where one of them has chemisorbed oxygen on its surface. The difference spec-



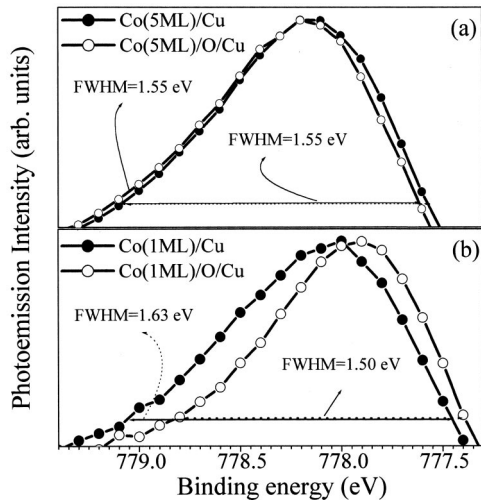


FIG. 5. Comparison of the FWHM of different Co  $2p$  spectra. (a) The values of the FWHM of Co  $2p_{3/2}$  main peak for two 5-ML films, and (b) these for two 1-ML Co films. Among these four spectra, the lowest and highest values are 1.5 eV in Co(1 ML)/O/Cu, and 1.63 eV in Co(1 ML)/Cu.

trum around the satellite region is shown in the lower part. The difference spectrum shows no extra signal for the satellite, and this is obvious. As pointed out above, even chemisorbed oxygen has no effect in observing satellite peaks; the spectra for the two 5-ML Co films are thus identical. Therefore, the satellite in the spectrum for 1-ML Co on O/Cu, where the Co surface contains 1-L oxygen, represents only the elemental Co emission, neither any oxide nor a chemisorbed-induced one.

In Fig. 5, a qualitative comparison considering the values of full width at half maximum (FWHM) is given for each set of thick (5-ML) and thin (1-ML) films on both Cu and O/Cu. In Fig. 5(a), the FWHM values for the main Co  $2p_{3/2}$  peak, which are shown in an enlarged view, are the same (1.55 eV). This indicates that the electronic structures for both 5-ML films on Cu and O/Cu are indeed the same in spite of having chemisorbed oxygen on the surface of Co/O/Cu.

On the other hand, the difference between the two 1-ML Co films on Cu and O/Cu in Fig. 5(b) is apparent. The FWHM for a 1-ML film on O/Cu is 1.50 eV, and that for 1-ML Co on Cu is 1.63 eV. As mentioned earlier, the 1-ML deposited Co on Cu(001) consists of 1- and 2-ML-high islands. The larger value of the FWHM for Co/Cu indicates the presence of more than one component. Among the four spectra, the FWHM for 1-ML Co on O/Cu is the lowest. This clearly demonstrates the existence of a single component in Co(1 ML)/O/Cu. The presence of a single component suggests that the growth mode of 1-ML Co on O/Cu is likely to be homogeneous, consisting of either a long-axial uniform metallic layer or dense 1-ML-high islands. This growth condition is preferentially helpful in observing the intense satellite. Previously, Binns *et al.*<sup>25</sup> also reported a dimension-dependent satellite intensity for vanadium thin film. As reported in Ref. 25, an intense satellite in vanadium  $3s$  core level photoemission was observed when an islanded film was

studied. Surprisingly, the thicker film did not even show any satellite signal.<sup>25</sup>

The lowering of the Co  $2p$  binding energy for the thinner film shown in Fig. 5 is explained in the following way. It has been known that a reduced coordination number of atoms on the surface results in a narrowing of the valence band.<sup>18</sup> This is caused by a redistribution of charges at the Fermi level. This charge redistribution decreases the energy difference between the narrowed  $d$ -band and the Fermi level. As a result, the DOS at the surface is pulled up to the lower binding energy side. The core levels of surface atoms also “feel” these changes, and they are forced to shift to a lower binding energy. This is exactly what we observed in the present study.

Although we did not check the surface morphology by using any microscopy technique, our claim of achieving a homogeneous film in a 1-ML Co on O/Cu is based on the results in Fig. 5(b) and the following discussion of the surfactant-mediated growth. It has been established that, due to the presence of surfactant atoms, the growth mode changes from three to two dimensions. This two-dimensional (2D) growth at the initial stage ultimately favors a layer-by-layer growth for further deposition in general.<sup>26–30</sup> The initial growth of Cu on O/Cu(001),<sup>26</sup> Cu on Pb/Cu(111),<sup>27</sup> Ag on Sb/Ag(111),<sup>28</sup> and Co on O/Cu(110) (Ref. 29) was reported to be 2D growth followed by layer-by-layer growth.<sup>30,31</sup>

For a particular case reported in Ref. 28, higher density 2D islands were observed for the first layer of Ag deposition, when Ag was deposited on a Sb/Ag(111) surface instead of on a bare Ag(111) surface. This growth precedes the layer-by-layer mode, for example, only a few third-layer islands are present in a 1.7-ML Ag film. On the other hand, a detailed structural analysis by scanning tunneling microscopy (STM) for Co on O/Cu(110) showed a different picture.<sup>32</sup> In Ref. 32, it was reported that, due to oxygen, initial growth of Co ( $\sim 1$  ML) gives flat monolayer structures. For thicker film ( $>1$  ML), 3D clusters begin to grow, and finally the layer-by-layer growth resumes at above 5 ML. From these previous results, it is fairly conclusive that a 1-ML metallic film on a surfactant-rich substrate consists of either an overlayer with high-density 2D structures or a flat monolayer with a few second-layer islands. The structure of that 1-ML film is thus completely different from that of 1-ML film on a surfactant-free surface. Therefore, it is reasonable to consider that our 1-ML Co on O/Cu(001) has homogeneous structure.

From the discussion of Figs. 3–5, Table I, and the  $d$ -band narrowing, we confidently state that the intense satellite seen in the Co  $2p$  spectrum for 1-ML Co on O/Cu is nothing but the Co elemental emission, and the satellite originates from the modified electronic structure due to surfactant-mediated growth. We now consider the effects of both the Co  $d$ - $d$  interaction and Cu  $4s$ –Co  $3d$  hybridization, which depend on the film geometrical structure. First we will take into account the effect of Co  $d$ - $d$  interaction. The narrowed  $d$  band, i.e., the localized  $d$  band in the thinner films, leads to a strong  $d$ - $d$  interaction. This strong  $d$ - $d$  interaction therefore poses a situation in which the satellite structure can be observed; because the strong  $d$ - $d$  interaction is considered to be the origin of satellite formation.<sup>3</sup> This is exactly what hap-

pened for a 1-ML film on clean Cu. As the film becomes thicker, the  $d$  localization as well as the  $d$ - $d$  interaction strength decrease. As a result, the satellite signal finally becomes invisible in the thicker films.

As we see in Fig. 5(b), there is a single component in the Co  $2p$  main peak and the lowest binding energy position of the main peak for 1-ML Co on O/Cu; the  $d$ - $d$  interaction is therefore the strongest one for this film. The strongest  $d$ - $d$  interaction, which is the ultimate effect of a homogenous Co overlayer grown on O/Cu due to the surfactant effect, therefore promotes the observation of an intense satellite. Quantitatively, we observed a 34.5% increase (compared with 5-ML film) of a satellite for Co(1 ML)/O/Cu and 14.0% for Co(1 ML)/Cu.

Apart from the Co  $d$ - $d$  interaction, the Cu  $4s$ /Co  $3d$  interfacial hybridization effect ( $s/d$ -IHE) is also considered. Earlier, Chen<sup>12</sup> pointed out theoretically that the  $s/d$ -IHE substantially reduces the satellite signal. However, the discussion of the  $s/d$ -IHE should be correlated with the effect of Cu incorporation within the Co matrix during Co deposition.

It has been reported that a Co film grown on a Cu(001) surface at or above room temperature contains an intermixed interface.<sup>33</sup> As reported in Ref. 33, about 25% of the first layer consists of Cu atoms in a slow deposition rate condition (0.003 ML/s). They also pointed out that the morphology of 0.5-ML films deposited either at a fast rate (0.3 ML/s) or at a slow rate (0.003 ML/s) is identical, though the slow rate is favorable for layer-by-layer growth starting from 1 ML. In the case of the present Co/Cu, the rate is not as slow as 0.0003 ML/s, and the initial growth is of bilayer type. Compared with the previous result,<sup>33</sup> we conclude the present 1-ML Co on Cu is also decorated with diffused Cu atoms. Similarly, Kief and Egelhoff,<sup>34</sup> also reported 45% Cu incorporated in the surface for a 1-ML Co on Cu deposited at 300 K. As seen in Fig. 1, the Co  $d$ - $d$  interaction is strong enough to dominate the Cu incorporation-induced  $s/d$ -IHE, and the satellite becomes visible.

In the case of surfactant-mediated growth, the scenario of the  $s/d$ -IHE is different. Through the following discussion, we draw the conclusion that the surfactant-mediated Co growth reduces the decoration of Cu atoms within the Co matrix, and hence reduce the number of neighboring Cu atoms to Co. The situation is ultimately favorable to reduce the  $s/d$ -IHE more from that of 1-ML Co on Cu, and together with strong Co  $d$ - $d$  interaction, an intense satellite is observed for 1-ML Co on O/Cu.

It is well established that the use of a surfactant reduces the probability of substrate atom segregation or adatom diffusion.<sup>26,32,35–38</sup> For example, O on Cu(001) helps to suppress the surface diffusivity of Cu adatoms,<sup>26</sup> O on Cu(001) blocks the agglomeration and/or segregation of Cu to deposited Cu,<sup>26</sup> and S (Refs. 36 and 37) and Se (Ref. 35) on GaAs(001) largely reduce the segregation of substrate atoms, i.e., mainly As during Co<sup>35,36</sup> and Fe (Ref. 37) deposition. The above action of the surfactant is clearly observed when the film is thicker. However, the situation for the monolayer range is rather complicated. In our study, we used Cu  $2p$  x-ray photoemission spectroscopy (XPS) spectra for deter-

mining the possible differences of the degree of the Cu segregation for 1-ML Co on both the Co and O/Cu surfaces. In the XPS measurements, we did not observe any drastic change for the two systems. According to Table I, the formation of an ordered  $c(2 \times 2)$  is obvious for 1-ML Co on O/Cu, where O segregates on top of the Co surface. Therefore, it is assumed that, as O locates on top of Co, the segregation of O reduces the number of Cu atoms to be within the Co matrix in a 1-ML film. Furthermore, with the slightly smaller electro-negativity of Co than Cu (Co, 1.8; Cu, 1.9),<sup>39</sup> the probability of any charge transfer is very small, and hence the electronic structure of 1-ML Co on O/Cu is unaffected by the Cu intermixing.

In addition to the Cu  $4s$ -Co  $3d$  hybridization, it is reasonable to make some comments on the Cu  $3d$ -Co  $3d$  hybridization, because the nearly occupied Cu  $3d$  band is situated very close ( $\sim 3$  eV, below the Fermi level) to the free-electron-like  $sp$  band. In the thin film system, however, the Cu  $4s$ -Co  $3d$  hybridization is energetically favorable because the narrow Co  $3d$  band is located closer to the Fermi level, in a similar position as the broad Cu- $sp$  band. In a previous experimental and theoretical magnetic linear dichroism in angular distribution (MLDAD) study, Fanelsa<sup>40</sup> showed that there was no prominent MLDAD signal for Cu  $3d$  states for a 1-ML Cu film on ferromagnetic Co. According to Ref. 40, the zero-MLDAD signal for Cu  $3d$  states indicates that no hybridization occurs between Cu  $3d$  and Co  $3d$ . Similarly, an x-ray emission spectroscopy study for a buried Cu layer in Ni showed that the occupied Cu  $3d$  states remained mostly unaltered, and there was no significant hybridization for Cu  $3d$  states.<sup>41</sup> We therefore do not include any possible influence of the Cu  $3d$ -Co  $3d$  hybridization on the Co  $2p$  satellite signal.

Here we suggest to carrying out a further combined STM and photoemission study, and a comparative study with theoretical calculations related to the Co  $d$ - $d$  interaction and the Cu  $4s$ -Co  $3d$  hybridization for Co films on O/Cu(001), which can give more insight into this problem. In addition, we propose to carry out a dynamical mean-field theory (DMFT)<sup>42,43</sup> calculations to find out the atomic volume, ground-state total energy of the atom, the number of  $d$  electrons, and the width of the DOS for a low-dimensional homogenous Co film. Similar to plutonium (Pu),<sup>43</sup> the DMFT calculation might be very useful to find out the itinerant vs localized behavior of Co in a quantitative way.

## CONCLUSION

In conclusion, we have found evidence of a localized electronic structure for Co thin films by observing an intense correlation-induced satellite in Co  $2p$  core-level photoemission spectra. We observed a regular change of the relative satellite intensity as a function of Co film thickness on Cu(001). We also demonstrated an alternative way to extract the maximum satellite intensity in Co  $2p$  photoemission spectra for Co films on O/Cu(001). By using surfactant (O)-mediated epitaxy, we are able to change the growth condition of a 1-ML film. The surfactant-assisted 1-ML film thus represents the most favorable condition for observing the in-

tense satellite due to strong Co *d-d* interactions and/or the possible reduced interfacial hybridization effect. The present results confirm that the satellite can be observed not only for Ni but also for Co.

Our results might be very useful in studies of magnetic quantum dots or nanostructures to examine their electronic structures, i.e., whether they show itinerant or localized band profiles. The observation of satellites in low-dimensional systems, which are very different from bulk ones, can be used as a textbooklike concept. Our findings may be useful

in other transition-metal systems where the satellite issue is still controversial.

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