

Effect of reduced hybridization at the surface: Ni-3*d* photoemission line shape in Ni/Cu(111)

T. Susaki and Maki Kawai

RIKEN (The Institute of Physical and Chemical Research), Wako 351-0198, Japan

(Received 16 January 2003; revised manuscript received 21 May 2003; published 29 September 2003)

We have studied electronic states of the Ni impurities deposited on a Cu(111) surface by ultraviolet photoemission spectroscopy and have resolved the 3*d* line shape of an individual transition-metal adatom. The Ni-3*d* peak has shifted away from the Fermi level when the Ni atoms have been embedded into the top surface layer, reflecting an increase in the impurity-host hybridization strength in going from adatom systems to surface alloys.

DOI: 10.1103/PhysRevB.68.113411

PACS number(s): 79.60.Dp, 71.27.+a, 73.20.Hb

Recently, 3*d* transition-metal adatoms deposited on noble-metal surfaces have been attracting much attention as possible surface Anderson impurities which are accessible by various spectroscopic methods.¹ A very narrow dip which is asymmetric with respect to the Fermi level (E_F) has been found in the scanning tunneling spectroscopy (STS) spectra for some 3*d* transition-metal adatoms on noble-metal surfaces and has actually been reproduced with the Anderson impurity model (AIM) calculation. On the other hand, photoemission spectroscopy (PES) is another powerful technique to probe the electronic states near E_F . While STS is sensitive to the *sp* electronic states of the substrate in such systems, PES can probe the 3*d* electronic states of the adatoms according to the photoionization cross sections.² Based on AIM it has been pointed out that a sharp “Kondo peak” may appear just at E_F in the 3*d* spectral function of Co/Au(111).^{3,4} In a previous work, we observed a narrow Fe 3*d* peak near E_F in Fe/Cu(111) and pointed out that the 3*d* electron of a surface adatom resembles the 4*f* electron in bulk Ce or Yb compounds.⁵ However, the spectral line shape of an individual Fe adatom has not been fully resolved in that work due to the Fermi cutoff and the effect of the interaction between the adatoms which is finite even at 0.03 monolayers (ML's).

To answer the question above we have studied a Ni/Cu(111) system by ultraviolet PES and have observed a clear single-impurity adatom 3*d* spectrum, where the effect of the Fermi cutoff and the deposition-amount dependence have been found to be very small. Since Ni 3*d* electrons in bulk CuNi alloys are in a 3*d*⁹-3*d*¹⁰ (3*d*¹-3*d*⁰ in the hole picture) mixed-valent configuration,^{6,7} one could study almost whole the adatom 3*d* spectral line shape in the Ni/Cu(111) system by PES, which probes occupied states only.⁸ Another advantage of the Ni/Cu(111) system is a surface-alloy formation at room temperature, which enables one to observe the effect of a change in the impurity-host hybridization strength (Δ).

A single crystalline Cu(111) substrate was cleaned by Ar-ion sputtering and annealing until the threefold low-energy electron diffraction (LEED) patterns appeared and the Shockley surface state was observed at ~ 0.4 eV in the normal photoemission spectrum. We have deposited a small amount of Ni atoms onto the surface by electron bombardment heating. The substrate was ~ 95 K or room temperature when Ni was deposited. According to the electron-energy-loss spectroscopy (EELS) study¹¹ submonolayer Ni adatoms

on Cu(111) essentially remain isolated with each other at 95 K while they form a CuNi two-dimensional (2D) alloy in the top surface layer at room temperature. However, in the case of 95-K deposition, we show only the data collected within 10 min of deposition since the Ni-3*d* spectrum varies slightly on the time scale larger than that.¹² Before each deposition we removed the surface layers of the previous sample completely by Ar-ion sputtering. Regardless of the deposition temperature we measured photoemission spectra at ~ 95 K. The excitation photon is He I resonance line ($h\nu = 21.2$ eV) and Mg $K\alpha$ line ($h\nu = 1253.6$ eV). An Omicron EA 125 hemispherical analyzer was used for the energy analysis. The geometry of the photoemission measurement was the same as that in a published work.⁵ We measured ultraviolet photoemission spectra at the polar angle of $\theta = 25^\circ$ and x-ray photoemission spectra at $\theta = 0^\circ$ (normal emission). The acceptance angle of the analyzer was set to be $\pm 8^\circ$. We determined the Fermi level in the ultraviolet photoemission spectra by measuring the Fermi edge of the Cu(111) substrate. The energy resolution was estimated to be ~ 30 meV also from the Fermi edge. The base pressure in the measurement chamber was 7×10^{-11} Torr.

Figure 1 shows the valence-band photoemission spectra of Ni adatoms on Cu(111) (a) and those of CuNi 2D alloys (b) taken at the polar angle of $\theta = 25^\circ$. The Cu(111) spectrum shown at the bottom is almost identical to that in Ref. 5. Since the sharp Shockley surface state does not appear below E_F and the Cu-4*s* spectrum near E_F is practically flat, one can observe a small spectral change near E_F induced by a small deposition at this polar angle. The sharp structures between ~ 2 and ~ 4 eV are assigned to bulk Cu-3*d* bands.¹³ For each sample we have also measured x-ray photoemission spectra and have estimated the deposition amount from the intensity ratio of Ni-2*p*_{3/2} and Cu-2*p*_{3/2} levels as noted in the figure.¹⁴ All the spectra have been normalized to the Cu-3*d* intensity integrated from 1.95 to 4.60 eV. As the deposition amount increases from the bottom to the top in the figure, a Ni-3*d* derived state just below E_F gradually overlaps the flat Cu-4*s* state. It appears clear even on this energy scale that the peak position of the Ni-3*d* derived state is closer to E_F in Ni adatom systems than in CuNi 2D alloys.

Since the spectra in Fig. 1 were normalized to the intensity of the substrate, one can cancel out the Cu-4*s* contribution near E_F by subtracting the spectrum of Cu(111) from

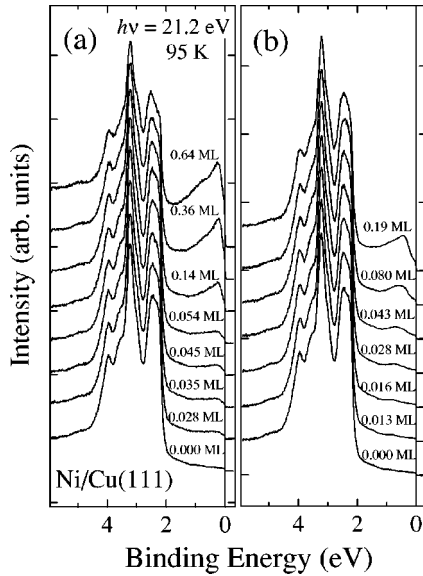


FIG. 1. Valence-band photoemission spectra of Ni/Cu(111) measured at 95 K with the photon energy of $h\nu = 21.2$ eV. Ni atoms have been deposited at 95 K (a) or at room temperature (b).

that of Ni/Cu(111). We have thus extracted the Ni-3*d* component near E_F as shown in Fig. 2. Here, the peak area increases linearly with the deposition amount and the area for the adatom systems is identical to that for the 2D alloys when the deposition amount is the same. This means that scattering of the Cu(111) surface state by the Ni atoms to the

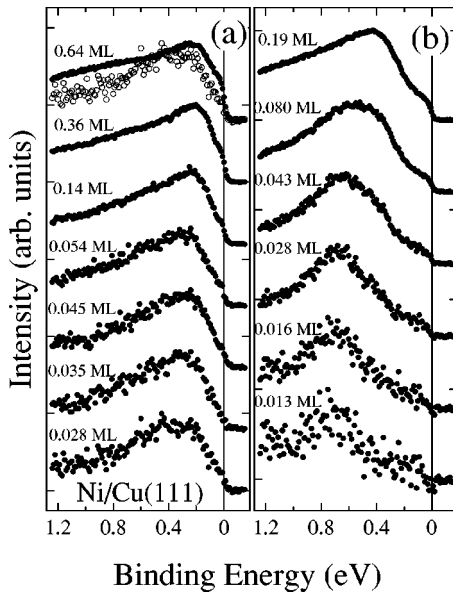


FIG. 2. Difference spectra between Ni adatom systems and Cu(111) (a) and those between CuNi 2D alloys and Cu(111) (b). The spectral intensity has been normalized to the peak maximum. The data corresponding to the thinnest (0.013 ML) and the second thinnest (0.016 ML) samples in the right panel are the average of the measurements on two independently prepared samples, respectively. The difference spectrum of the 0.028-ML Ni adatom system is shown also by open circles overlapping the spectrum of the 0.64-ML sample in the left panel.

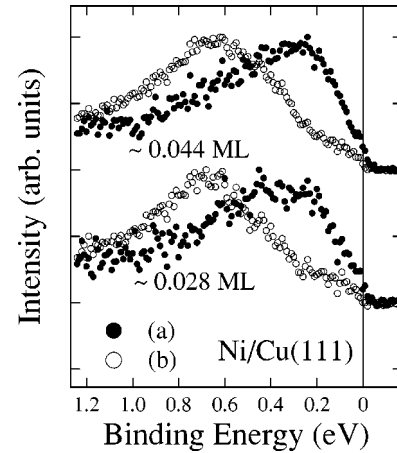


FIG. 3. Top two curves: difference spectra at ~ 0.044 -ML deposition. Bottom: difference spectra at ~ 0.028 -ML deposition. The filled circles (a) represent the difference between Ni adatom systems and Cu(111) and the open circles (b) represent the difference between CuNi 2D alloys and Cu(111).

emission direction is negligibly small compared with the Ni-3*d* intensity. The spectra of adatom systems are shown in the left panel and those of 2D alloys are shown in the right panel of the figure. At the top in panel (a) we compare the spectrum of 0.64 monolayer (ML) Ni adatoms with that of 0.028-ML adatoms. The Ni-3*d* spectrum of the 0.64-ML sample shows a clear Fermi edge and a long tail to the higher binding energy side. Since the Ni-3*d* states of Ni metal distribute from E_F to ~ 2 eV in the angle-integrated photoemission spectrum taken with the photon energy of $h\nu = 21.2$ eV,¹⁶ the widely spread 3*d* spectrum of the 0.64-ML sample would indicate a finite interaction between Ni atoms at that deposition. As the Ni amount decreases the Ni-3*d* spectral intensity at E_F is gradually reduced and becomes almost zero around 0.05 ML. However, except for the gradual change in the peak width, the deposition dependence of the Ni-3*d* spectrum is relatively small for Ni adatom systems within the deposition range studied here. This means that the observed line shape at low depositions would show an individual adatom spectrum. On the other hand, the Ni-3*d* peak position of CuNi 2D alloys is very sensitive to a small change in the Ni amount as shown in panel (b) of the figure. Such a strong deposition dependence in CuNi 2D alloys, which is absent in Ni adatom systems at the similar depositions, would be due to a Cu-mediated Ni-Ni interaction through a larger Δ in CuNi 2D alloys.

In Fig. 3 we have selected two sets of the difference spectra to compare the Ni-3*d* spectrum of adatom systems with that of 2D alloys at similar depositions, where the effect of the Ni-Ni interaction is relatively small as visible in Fig. 2. We note here that the spectral intensity at E_F is very small but is finite in these spectra. This means that the Ni atoms in these samples are mixed valent: If the valence of Ni atoms is an integer, the onset of the Ni-3*d* spectrum is separated from E_F like core levels with higher binding energies. Assuming that the 3*d* electrons in the surface Ni impurities are still in a 3*d*⁹-3*d*¹⁰ mixed-valent configuration as in bulk CuNi alloys, the photoemission peak near E_F can be assigned to the

$3d^{10} \rightarrow 3d^9$ process from the viewpoint of ionic configurations. Based on a large degeneracy approach of AIM, the $3d^{10} \rightarrow 3d^9$ photoemission peak near E_F in mixed-valent Ni impurities could be described analytically for $U = \infty$ and to lowest order in $1/N_d$, where U is the Coulomb interaction between $3d$ electrons and N_d is the degeneracy of the $3d$ level.^{17,18} The peak position δ which is measured from E_F is given by

$$\delta = B \exp\left(-\frac{\pi \varepsilon_d^0}{N_d \Delta}\right), \quad (1)$$

where B is the conduction-band width above E_F , ε_d^0 is the bare d ($3d^9 \rightarrow 3d^{10}$) level ($\varepsilon_d^0 > 0$), and \bar{n}_d is the d -hole occupancy. According to Eq. (1) the peak binding energy δ decreases monotonously as the hybridization strength Δ is reduced. Therefore the observed peak shift from 0.6–0.7 eV in the 2D alloys to 0.2–0.3 eV in the adatom systems can be attributed to a decrease in Δ if one assumes that the bare Ni- $3d$ level is not changed very much between the two morphologies.

We now compare the photoemission spectra of Ni/Cu(111) with those of bulk CuNi alloys. Since Δ would be

larger in bulk CuNi alloys than in surface alloys, the Ni- $3d$ peak position should appear further away from E_F in bulk alloys according to Eq. (1). However, a larger Δ may cause a stronger indirect Ni-Ni interaction, which may shift the Ni- $3d$ peak again towards E_F as the deposition dependence of Fig. 2(b) shows. Bosch *et al.* measured the photoemission spectrum of a bulk dilute alloy Cu_{0.95}Ni_{0.05} with the photon energy of $h\nu = 21.2$ eV and found a Ni- $3d$ derived peak at 0.78 eV,⁶ close to the peak position of the 0.043-ML 2D alloy in Fig. 2(b). This would mean that the Cu-mediated Ni-Ni interaction is still large in dilute bulk CuNi alloys even at the Ni concentration of 5%. Thus one can state that the transition-metal single-impurity effect, which would be smeared by a strong intersite effect in bulk dilution systems, may appear itself clearly in adatom systems.

In conclusion, we have resolved the narrow $3d$ spectral line shape of a Ni adatom, where the peak appears 0.2–0.3 eV below E_F . The Ni- $3d$ peak has been shifted by ~ 0.4 eV away from E_F in 2D surface alloys, reflecting an increase in the impurity-host hybridization strength in surface alloys.

T.S. was financially supported by the Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Encouragement of Young Scientists.

-
- ¹V. Madhavan, W. Chen, T. Jamneala, M.F. Crommie, and N.S. Wingreen, *Science* **280**, 567 (1998).
- ²J.J. Yeh and I. Lindau, *At. Data Nucl. Data Tables* **32**, 1 (1985).
- ³A. Schiller and S. Hershfield, *Phys. Rev. B* **61**, 9036 (2000).
- ⁴O. Újsághy, J. Kroha, L. Szunyogh, and A. Zawadowski, *Phys. Rev. Lett.* **85**, 2557 (2000).
- ⁵T. Susaki, T. Komeda, and M. Kawai, *Phys. Rev. Lett.* **88**, 187602 (2002).
- ⁶A. Bosch, H. Feil, G.A. Sawatzky, and J.A. Julianus, *J. Phys. F: Met. Phys.* **14**, 2225 (1984).
- ⁷H.H. Hsieh, Y.K. Chang, W.F. Pong, J.Y. Pieh, P.K. Tseng, T.K. Sham, I. Coulthard, S.J. Naftel, J.F. Lee, S.C. Chung, and K.L. Tsang, *Phys. Rev. B* **57**, 15 204 (1998).
- ⁸We have studied only the $3d^{10} \rightarrow 3d^9$ peak just below E_F here: To observe a $3d^9 \rightarrow 3d^8$ signal, which appears at ~ 6 eV in the case of Ni metal (Ref. 9), would be very difficult since a bulk Cu- $3d$ band is overlapped (Ref. 10) and it is further broadened due to an atomic term splitting.
- ⁹S. Hüfner, *Photoemission Spectroscopy* (Springer-Verlag, Berlin, 1995).
- ¹⁰D. van der Marel, G.A. Sawatzky, and F.U. Hillebrecht, *Phys. Rev. Lett.* **53**, 206 (1984).
- ¹¹Y.-R. Tzeng, H.T. Wu, K.-D. Shiang, and T.T. Tsong, *Phys. Rev. B* **48**, 5549 (1993).
- ¹²The intensity maximum shifts away from E_F with time, possibly due to a gradual diffusion of the Ni atoms.
- ¹³R. Courths and S. Hüfner, *Phys. Rep.* **112**, 53 (1984).
- ¹⁴We have considered the photoionization cross section (Ref. 2) photoelectron escape depth (Ref. 15), and E_{kin}^{-1} -form efficiency of the electron analyzer as in Ref. 5. The estimation has been confirmed by monitoring an evaporation flux with an ion collector. The nominal thickness of Ni thus estimated has been converted into monolayer (ML) with the relation of 1 ML = 2.03 Å, the interlayer spacing of Ni(111).
- ¹⁵S. Tanuma, C.J. Powell, and D.R. Penn, *Surf. Interface Anal.* **17**, 911 (1991).
- ¹⁶I. Abbati, L. Braicovich, A. Fasana, C.M. Bertoni, F. Manghi, and C. Calandra, *Phys. Rev. B* **23**, 6448 (1981).
- ¹⁷O. Gunnarsson and K. Schönhammer, *Phys. Rev. B* **28**, 4315 (1983).
- ¹⁸O. Gunnarsson and K. Schönhammer, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, and S. Hüfner (Elsevier Science Publishers B.V., New York, 1987), Vol. 10, p. 103.