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Behavior of Ni atoms on the Cu(111) surface: A study by high-resolution electron-energy-loss spectroscopy

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The temperature-dependent behavior of vapor-deposited Ni atoms on the Cu(111) surface has been studied by HREELS. Submonolayer coverage of Ni atoms are vapor-deposited on this surface in ultrahigh vacuum in the temperature range of 140–600 K. CO is used to monitor the structure of the Ni-covered Cu(111) surface at various Ni-deposition temperatures. For submonolayer Ni deposition at $T=140$ K, no significant diffusion of Ni atoms is observed. Above 150 K, Ni atoms begin to diffuse on the Cu(111) surface to form two-dimensional islands. At $T>260$ K, atomic exchange with the substrate atoms occurs and a mixed Ni-Cu monolayer is formed. Above 600 K, Cu atoms segregate to the surface and Ni atoms disappear completely from the top surface layer.

I. INTRODUCTION

In the past two decades diffusion of metal atoms on metal surfaces has been investigated to understand the thermodynamic and kinematic behavior of surface atom transport.[1] Although most experimental results are consistent with the well-accepted hopping diffusion mechanism, i.e., migration occurs by a series of hoppings over the saddle points of the potential-energy barrier between adjcent binding sites, there are some exceptions. In systems such as Ir/Ir(001), Ir/Ir(110), Pt/Pt(001), Pt/Ni(110), W/Pt(110), W/Ir(110), and Re/Ir(001), etc., an atomic-exchange mechanism occurs at low temperature and it dominates the diffusion process.[2] These experiments are mostly done with the field ion microscope. Here we report a high-resolution electron-energy-loss spectroscopy (HREELS) study of the temperature-dependent behavior of vapor-deposited Ni atoms on the Cu(111) surface.

In the Ni-Cu system, Cu has a lower surface free energy than Ni. Thermodynamically, Cu atoms tend to come out to cover the surface.[3] The objective of this study is to determine the overlayer structure of these vapor-deposited Ni atoms and diffusion of Ni atoms on the Cu(111) surface. Of particular interest is whether or not atomic exchange occurs in the Ni-Cu system, and if it does, then at what temperature.

In this paper, the chemical and thermal properties of CO adsorption on Ni-covered Cu(111) surfaces[4] are also studied to help determine the structure of the deposited Ni layer at various temperatures.[5]

II. EXPERIMENTAL PROCEDURES

The experiments were carried out in an UHV chamber equipped with a model LK-2000R HREELS of LK Technologies and a quadrupole mass spectrometer. The base pressure of the chamber was about 1×10^{-10} Torr. The Cu(111) surface was cut from a single crystal of Cu of 10 mm in diameter and 3 mm in thickness (Technisch Co.) and polished within 0.5° of the desired orientation and checked by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) in another UHV system before being loaded into the chamber. The surface was carefully cleaned by cycles of Ar^+ sputtering (2.2 kV) and annealing (800 K). After transferring to the HREELS system, the sample was cleaned again with the same procedures. The cleanliness of the surface is checked by AES in the preparation chamber, then with EELS in the experimental chamber. The EELS spectrum [curve (*a*) of Fig. 1] with a magnification of 10^3 com-

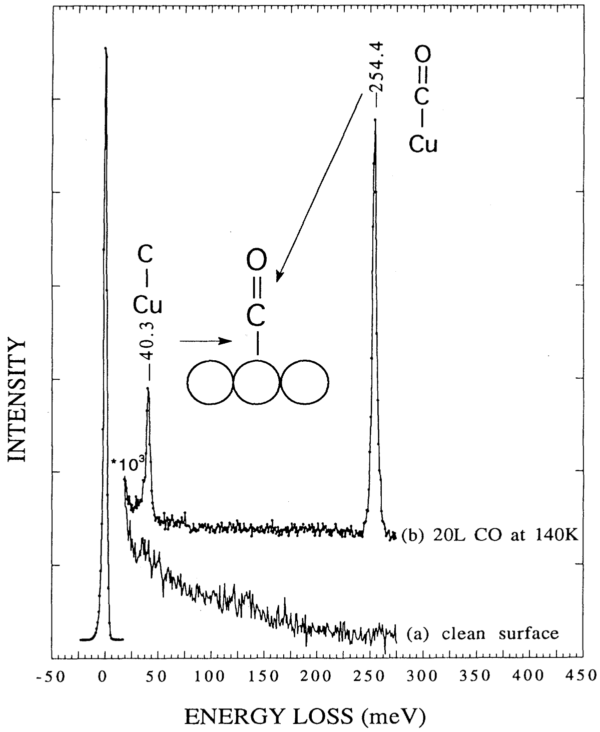

FIG. 1. High-resolution electron-energy-loss spectra of CO chemisorption on a Cu(111) surface at 140 K.

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pared to the elastic beam were free of any dipole loss due to contamination by C, O, or S. The EELS spectrum [curve (*b*) of Fig. 1] taken following CO (99.98%) exposure on the surface at 140 K shows only characteristic vibrational loss of Cu-CO at 254.4 meV and Cu-C at 40.3 meV , further ensuring the cleanliness of the Cu(111) surface.

Nickel atoms are vapor deposited on the Cu(111) surface which is kept at a temperature in the range 140–600 K by heating a Ni-wire filament. Unfortunately small amounts of C contamination were usually detected by EELS following the Ni deposition. The Ni coverage is controlled by varying the deposition time while maintaining a constant Ni partial pressure (0.5×10^{-12} Torr) in the QP mass spectrometer.

Following the Ni deposition, a saturated coverage dose of CO is exposed to the Ni-covered Cu(111) surface while it is kept at 140 K. The gas dosing is performed by backfilling the chamber with CO through a variable leak value with a tube directed at the sample 3 cm in front of the surface. The amounts of CO are also monitored by keeping the CO partial pressure constant at 2×10^{-8} Torr in the quadrupole mass spectrometer during the period of gas dosing.

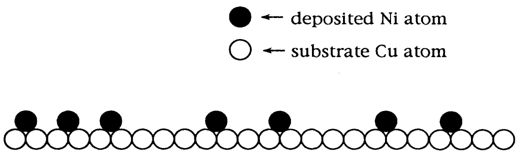
EELS is used to determine the adsorption site of chemisorbed CO at 140 K on the Cu(111) surface. This enables us to distinguish the single Ni atoms from Ni islands grown on the Cu(111) surface with an experimental resolution of about 3.7 meV full width at half maximum. EELS itself also provides an independent method to determine the submonolayer Ni coverage as discussed in Sec. III B. All EELS spectra are recorded in the specular direction with an incident angle of 70° off-normal and an impact energy of 2.0 eV. The counting rate of the specularly scattered elastic beam from the cleaned Cu(111) surface is usually in the $(3-5)\times10^5$ counts/s range.

III. RESULT AND DISCUSSIONS

A. Dispersion of Ni atoms on the Cu(111) surface

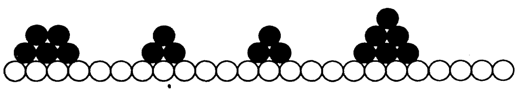
When a submonolayer of Ni atoms is deposited on a Cu(111) surface, four possible structures of the Ni atoms can be expected as illustrated in Fig. 2. Ni atoms may condense on the surface without any mobility, thus resulting in random distribution of single adatoms [Fig. 2(a)] with only a small fraction of them forming islands or clusters. Nickel atoms may have sufficient mobility at the given temperature, thus all these nickel atoms will combine into two-dimensional islands [Fig. 2(b)] or three-dimensional clusters of different sizes [Fig. 2(c)]. Nickel atoms may also exchange with Cu atoms to form a Ni-Cu alloy layer with Cu atoms on the surface [Fig. 2(d)]. From the vibrational behavior of CO adsorption on the Cu(111), Ni(111)[6], and Ni-covered Cu(111) surfaces, summarized in Table I, we will be able to find the dispersion behavior of vapor-deposited Ni atoms on the Cu(111) surface. For the convenience of our discussions, let us first present our data taken at 140 K, which is the lowest temperature we can reach with this system at the present time.

We find that at 140 K, the deposition of a submonolayer of Ni on the Cu(111) surface is dominated by single Ni atoms [Fig. 2(a)]. The lack of diffusion of Ni atoms at 140 K is evidenced by the fact that the bridge-site CO stretching mode (236 meV) is very small at a small Ni coverage. In Figs. 3(a)–3(c), the Ni bridge-site stretching signals (236 meV) are very small if one considers the very large dynamical dipole moment of this mode.[6] Also even in random deposition without diffusion, a fraction of Ni atoms can already have nearest-neighbor Ni atoms. As shown in Fig. 3(c) (at $\theta_{\mathrm{Ni}}\sim0.14$), the two strong loss peaks at 49.5 and 252.5 meV arise from the stretching vibration of CO molecules chemisorbed on the top site of single Ni atoms. A set of EELS spectra with various Ni coverage (the determination of Ni coverage will be discussed in Sec. III B) are collected; only some of them are shown in Fig. 3. For $\theta_{\mathrm{Ni}}<0.1$ [Figs. 3(a) and 3(b)], stretching vibration of terminal CO on both Cu and Ni atoms is observed at 40.3 (Cu-C), 49.5 (Ni-C), 252.5 (Ni-CO), and 254.4 meV (Cu-CO). For $0.2<\theta_{\mathrm{Ni}}$ [Figs. 3(d) and 3(e)], the peak of the bridge-bound CO (236 meV) starts to grow in intensity. For $\theta_{\mathrm{Ni}}\sim1$ (not shown here), the EELS spectrum, which is dominated by vibrational modes of the bridge-bound CO (Ni-C at 49.5 meV and bridge-bound CO at 236 meV) is almost the same as that obtained from a Ni(111) surface. In Figs. 3(a)–3(d), the small vibrational loss peak at 55.8 meV may arise from carbon contamination during Ni deposition and those CO adsorbed on the Ni atoms which sit on defects sites of the Cu(111) surface.

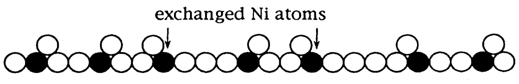


(a) single Ni atoms deposited

(b) 2D Ni islands formed



(c) 3D Ni clusters formed



(d) surface Ni atoms exchanged with substrate Cu atoms

FIG. 2. Four possible structures of submonolayer Ni atoms deposited on the Cu(111) surface.

TABLE I. Vibrational loss peaks for terminal CO and bridge-bounded CO on Cu(111), Ni(111), and Ni-covered Cu(111) surfaces (units in meV).

	Terminal CO				Bridge-bounded[a] CO			
	C-Cu	C-Ni	CO-Cu	CO-Ni	C-Cu	C-Ni	CO-Cu	CO-Ni
Cu(111)	40.3		254.4					
Ni(111)[6]		49.6		254.2		49.6		236.8
Single Ni on Cu(111)		49.5		252.5		49.5		
Island Ni on Cu(111)		49.5		252.5		49.5		236
Exchanged Ni on Cu(111)	42.1	59.5	255.3	246.6				

[a] Since our sample temperature cannot be lowered below 140 K, no bridge-bound CO can be expected on the Cu(111) surface.

B. Determination of Ni coverage

We use EELS signal intensities to determine the Ni coverage. At $T = 150$ K, most CO desorbs from the Cu(111) surface, but CO will not desorb from the Ni(111) surface at $T < 180$ K.[4] Owing to this difference in their thermodyamic behavior, the peak at 252.5 meV (from terminal CO on Ni atoms) can be separated from the peak at 254.4 meV (from terminal CO on Cu atoms). The latter vanishes when the sample temperature is raised above 150 K. As shown in Fig. 4, vibrational loss peaks of CO chemisorption on both Cu and Ni atoms are observed [curve (*a*) of Fig. 4]. The vibrational loss peak at 254.4 meV consists really of two components, one from terminal CO on Cu atoms and one from terminal CO on Ni atoms. By raising the sample temperature to 150 K, CO molecules desorb from the Cu atoms of the Cu(111) surface, resulting in the disappearance of the vibrational loss peak of Cu-C bond (40.3 meV) and Cu-CO bond (254.4 meV) [curve (*b*) of Fig. 4]. Since the peak at 254.4 meV [Fig. 4(a)] is overlapped with the peak at 252.5 meV, the peak centered around 254.4 meV does not disappear at $T = 150$ K, but reveals the hidden peak at 252.5 meV. The peak intensities (normalized to elastic peak) of the terminal-CO chemisorption on single Ni atoms (252.5 meV) are plotted as the circular points as function of the Ni deposition times and are shown in Fig. 5.

In order to relate the deposition time to the Ni coverage, a computer simulation is carried out to simulate the deposition of Ni atoms on the Cu(111) surface. In this computer simulation, two assumptions are made: one is that the deposited Ni atoms will not diffuse on the

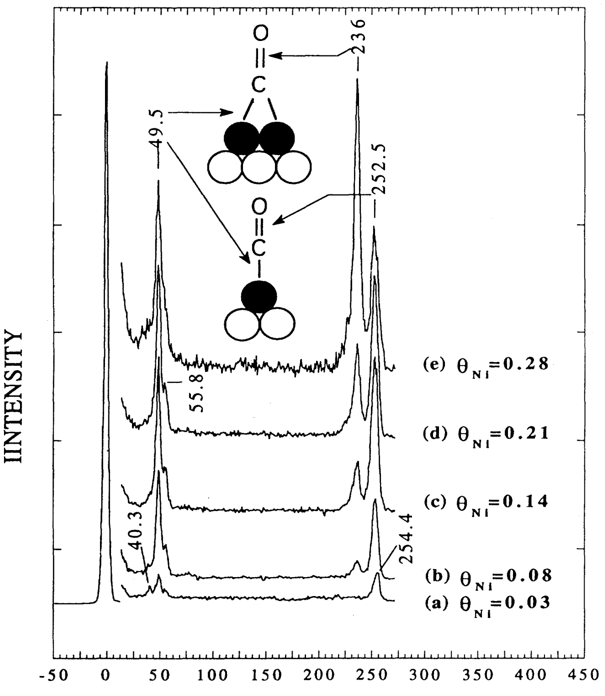


FIG. 3. EELS spectra of CO adsorption at different Ni coverages of Cu(111) surface at 140 K.

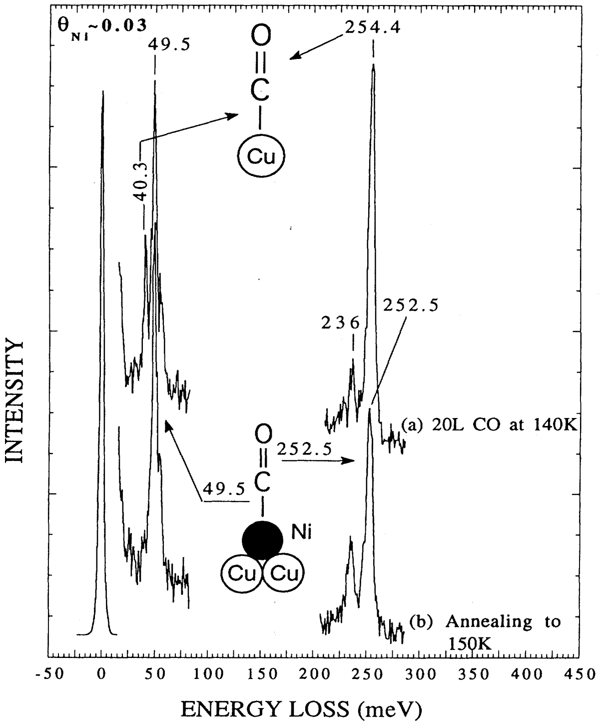


FIG. 4. CO adsorption on a 0.03-monolayer Ni-covered Cu(111) surface. (a) 20-L CO adsorption at 140 K. (b) Annealing the sample to 150 K to desorb CO from the top sites of Cu atoms, then cooling it down again to 140 K.

Cu(111) surface at this temperature; the other is that the growth of Ni islands is restricted to be two dimensional, or if a Ni atom condenses on a site which is already occupied by another Ni atom, it will settle into a nearest site. The result is plotted as the solid line in Fig. 5. In this figure, at low Ni coverage ($\theta_{\mathrm{Ni}} < 0.2$), the experimental result can be fitted very well until the single Ni atom site is saturated. Beyond the saturation of single Ni atoms, the Ni-covered Cu(111) surface becomes rough with the formation of many two-dimensional Ni islands which makes the normalization of the vibrational loss peak to the elastic peak incorrect. Using this calibration method, the Ni coverage is related to the deposition time to be 0.22 monolayer/1600 s.

C. Temperature dependence of Ni deposition on the Cu(111) surface

A set of EELS spectra taken at various temperatures is shown in Fig. 6. During the Ni deposition, the sample was held at the indicated temperature and then allowed to cool, all spectra [except Figs. 6(d) and 6(e)] were recorded after exposing to CO to a saturated coverage at 140 K.

The spectroscopic changes observed in Fig. 6 can be roughly divided into two temperature ranges. At temperatures between 150 and 250 K [Figs. 6(a)–6(c)] one observes the gradual conversion of terminal CO (252.5 meV) into bridge CO (236 meV). This indicates that Ni atoms can already diffuse on the Cu(111) surface in this temperature range. When they condense on the surface they can diffuse on the surface to form two-dimensional Ni islands; the structure is already illustrated in Fig. 2(b).

However, a reverse conversion, i.e., the conversion of bridge CO (236 meV) back into terminal CO (252.5 meV) can occur at higher temperatures ($T > 260$ K). In fact, at 500 K, the bridge CO is completely converted into terminal CO (the Ni-CO at 246.6 meV) as shown in Fig. 6(d). In Fig. 6(d), the energy-loss peaks are identified as the vibrational stretching of Ni-C at 59.5 meV and Ni-CO at 246.6 meV. The shift in the energy-loss peaks as shown in Fig. 6(d) from those shown in Figs. 6(a)–6(c) arises from a structure change of the nickel-covered copper surface: from the two-dimensional nickel layer to a Ni-Cu mixed layer. Or at 500 K, many of the condensed Ni atoms already exchange and alloy with the substrate Cu atoms. The mixing of Ni and Cu atoms on the outmost surface layer can also be evidenced from the result of Fig. 6(e). In Fig. 6(e), terminal-site stretching of CO on both Ni and Cu atoms are observed when reexposing a small amount of CO (0.3 L) to the "exchanged" and alloyed surface [Fig. 6(d)] after cooling the sample temperature to 140 K.

The temperature dependence of these various conversion processes are more clearly seen in Fig. 7. The ratio

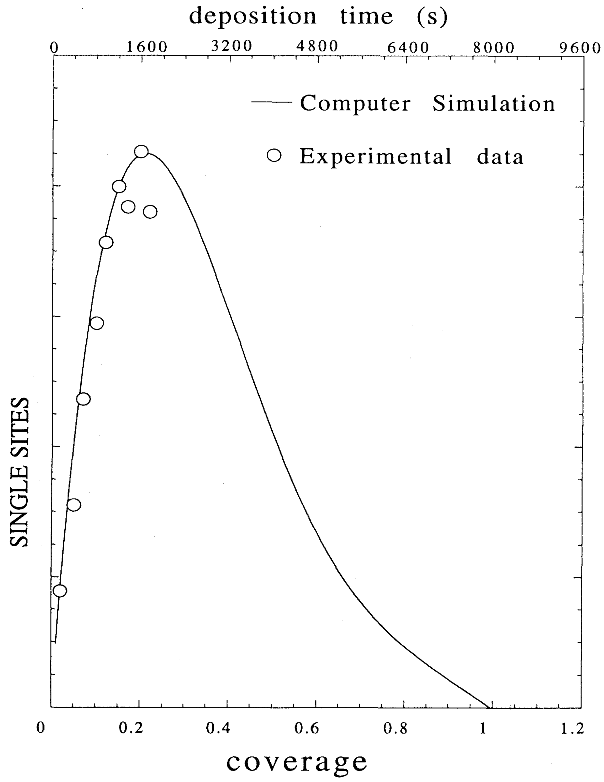


FIG. 5. The number of single Ni atoms as a function of Ni coverage (in monolayers) from a computer simulation. The circles refer to the spectral intensities of the energy-loss peaks at 252.5 meV.

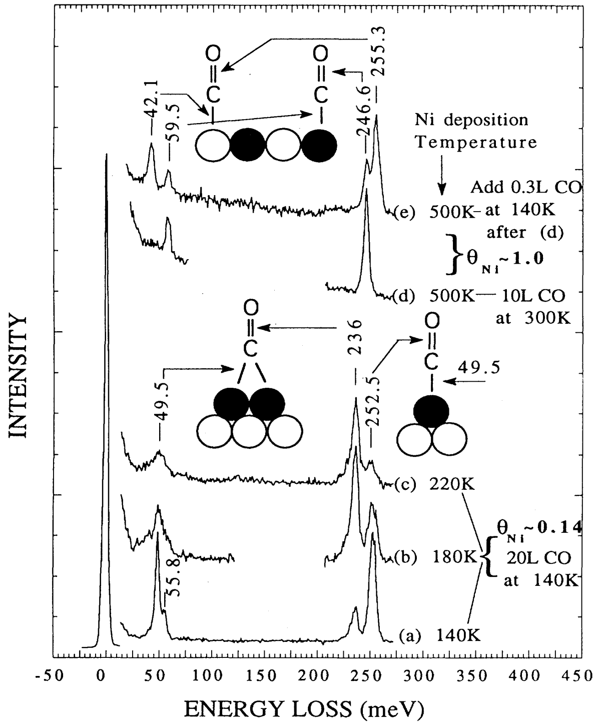


FIG. 6. Temperature-dependent behavior of Ni atoms on the Cu(111) surface. (a)–(c) After the Ni deposition ($\theta_{\mathrm{Ni}}=0.14$) at the indicated temperature, the sample is cooled down to 140 K and it is then exposed to 20 L of CO. (d) and (e) Ni deposition ($\theta_{\mathrm{Ni}}=1$) at 500 K then (d) 10-L CO exposure at 300 K; (e) add 0.3-L CO after cooling down to 140 K.

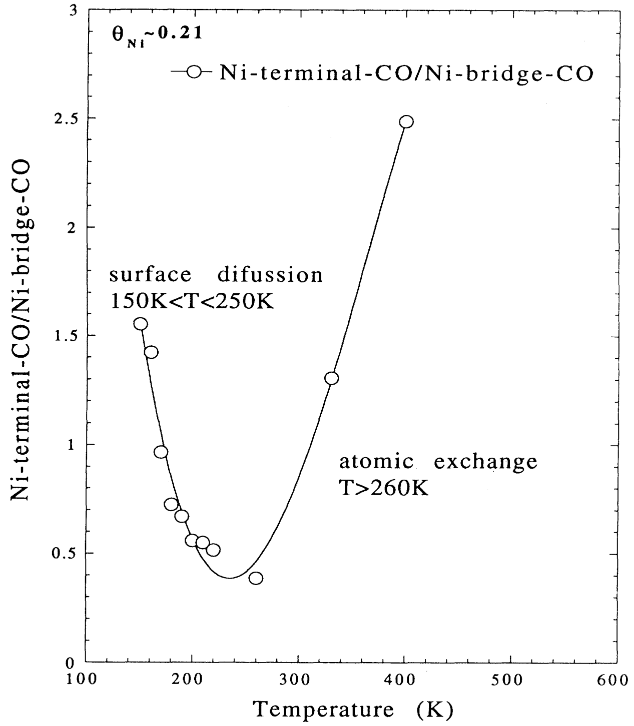
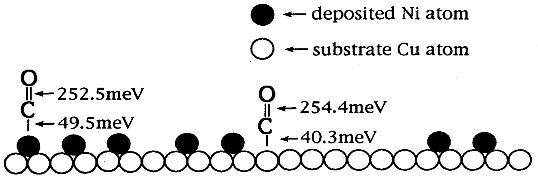
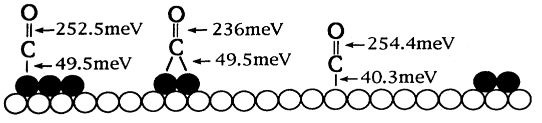


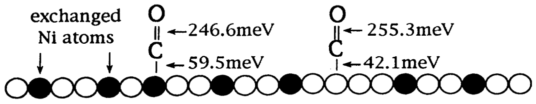
FIG. 7. The intensity ratio of the peaks at 252.5 meV (Ni-terminal-CO) and 236 meV (Ni-bridge-CO) as a function of the Ni-deposition surface temperature.



(a) T=140K, The surface structure is dominated by single Ni atoms



(b) T>150K, surface diffusion of Ni atoms on Cu(111) surface occurs



(c) T>260K, surface Ni atoms will exchange with substrate Cu atoms

FIG. 8. Experimental results at different Ni-deposition surface temperatures.

of the peak intensity (Ni-terminal-CO/Ni-bridge-CO) is about 2:1 deposition at 140 K where the surface structure is dominated by single Ni atoms. The ratio decreases dramatically to about 0.5:1 at 250 K, which is dominated by two-dimensional Ni islands on the surface. This ratio then increases to about 1:1 at 350 K, which is dominated by a mixed Ni-Cu surface. The disappearance of the two-dimensional Ni islands with the reappearance of single Ni and Cu atoms can be explained by a direct exchange of surface Ni atoms with substrate Cu atoms. Above 600 K, Cu atoms come to the surface to replace all the surface Ni atoms to form a pure Cu layer, or Cu atoms segregate to the surface and cover the entire surface; only loss peaks of CO adsorption on the Cu(111) surface can be found. Our observations therefore indicate that surface diffusion of Ni atoms on Cu(111) surface occurs at $T > 150$ K. At $T > 260$ K, deposited Ni atoms can exchange with substrate Cu atoms to form a Ni-Cu mixed layer or alloying of Ni and Cu occurs on the Cu(111) surface at $T > 260$ K.

IV. CONCLUSIONS

From the result and discussions presented above, the following conclusions, illustrated in Fig. 8, can be drawn concerning the behavior of vapor-deposited Ni atoms on the Cu(111) surface.

(1) Surface diffusion of Ni atoms on the Cu(111) surface occurs at a temperature above 150 K.

(2) Even at 140 K, the growth of Ni islands on the Cu(111) surface is two dimensional because of the large affinity between Ni and Cu atoms.

(3) Exchanges of Ni atoms with substrate Cu atoms on the Cu(111) surface can occur at $T > 260$ K.

(4) Above 600 K, the surface is completely covered with Cu atoms again because of surface segregation effects.

We would like to mention that our result and conclusions are remarkably similar to a recent STM study by Chambliss, Wilson, and Chiang.[7] They find that Au deposition of 0.5 monolayer at 300 K on the Cu(100) surface produces intermixing of Au and Cu atoms to form a monolayer of CuAu $c(2\times2)$ alloy. Deposition of Au at 110 K does not form such an alloy layer. That vapor deposited atoms can exchange with substrate atoms to form a monolayer of alloy at a temperature at or slightly below 300 K will have a profound effect on the structure and morphology of vapor phase grown ultrathin films. This is a subject of considerable current interest.[8]

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[1] See, for example, articles in *Surface Mobilities on Solid Materials,* Vol. 86 of *NATO Advanced Study Institute, Series B: Physics,* edited by V. T. Binh (Plenum, New York, 1982); A. G. Naumovets and Yu. S. Vedula, Surf. Sci. Rep. **4**, 365 (1985); R. Gomer, Rep. Prog. Phys. **53**, 917 (1990); Y. L. He, J. K. Zuo, G. C. Wang, and J. J. Low, Surf. Sci. **255**, 269 (1991); D. E. Sander and A. E. Depristo, *ibid.* **254**, 341 (1991); T. T. Tsong, Rep. Prog. Phys. **51**, 759 (1988).

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