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Dynamic study of a surface-confined alloy in an ultrathin Ag/Pt(111) film

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During alloy formation of the surface-confined fcc(111) systems, we demonstrate that the energy barrier of diffusion for surface atoms can be determined from a dynamic study of a surface alloy by low-energy electron diffraction. The corresponding energy barrier of 0.95 ± 0.11 eV was obtained from data consistent with the results of Monte Carlo simulations in submonolayer Ag/Pt(111) films. Ultrathin Ag film deposited at 360 K shows pseudomorphic growth. Annealing of a submonolayer ultrathin Ag film above 550 K causes formation of a two-dimensional surface alloy. After alloy formation, the vibration of surface atoms is enhanced and the enhancement could be as large as 70%. [S0163-1829(98)04228-3]

I. INTRODUCTION

The formation of alloys is an important subject in material physics. Elements that are immiscible in bulk have been found to form two-dimensional (2D) alloys confined to a single atomic layer at the surface.[1] The possibility of forming such an alloy has important applications for surface chemical processes such as a heterogeneous catalysis. Recently, a number of experimental investigations discussed the surface structure of ultrathin Ag films grown on the Pt(111) surface.[2–6] It is an excellent system for the investigation of a 2D system. Many interesting phenomena, such as dendritic growth,[2] surface stress,[3,4] and surface alloy formation,[5,6] were revealed. The energy barrier of a surface atom in the process of surface alloying is an important parameter for describing how fast the alloy forms. However, to our knowledge, a quantitative investigation has not been carried out.

In this paper, we report on the determination of the energy barrier of diffusion for surface atoms in the process of surface alloying for a surface-confined alloy system. From a dynamic study of surface alloy, this energy barrier for a submonolayer of Ag on Pt(111) surface was determined by low-energy electron diffraction (LEED).

II. INSTRUMENTATION

Experiments were conducted in an ultrahigh vacuum (UHV) chamber with a background pressure better than 3×10^{-10} Torr. The pressure was measured by an ion gauge and checked by a quadrupole mass spectrometer. The UHV chamber was equipped with four-grid video-LEED, Auger electron spectroscopy (AES), and ultraviolet photoelectron spectroscopy (UPS). The LEED spots were recorded by a computer-controlled image processor. The intensities, half-maximum widths and peak intensities of the LEED spots could be obtained from analyzing the distribution of gray levels by a computer program. The LEED experiments were performed with a specular beam with an electron energy of 66.2 eV. In this energy, the LEED should be very surface sensitive. An electron incident angle near the normal direction was chosen. The specular beam is sensitive to the surface step density.[7,8]

The platinum crystal was oriented within 0.5° of the [111] direction checked by x-ray reflection. The Pt(111) surface was cleaned by Ar ion bombardment and annealing cycles. The annealing temperature reached 1100 K. The sputtering-annealing cycles were continued until a well-ordered $p(1\times 1)$ LEED pattern with bright, sharp spots and a low background was observed. To remove the residual carbon, the sample was heated to 870 K in an oxygen pressure of 5×10^{-7} Torr before sputtering. The chemical impurity on the surface was checked by AES. A ceramic crucible, resistively heated by a Ta wire, was used to evaporate silver atoms. The purity of the silver was 99.999%. The deposition rate was 0.1 ML/min. The background pressure was about 1×10^{-9} Torr during Ag dosing. The substrate temperature was kept at 360 K to ensure that the structure of the Ag film was in compact form.[9] The Auger signals versus time (AS-t) plots and LEED intensity oscillation were used to determine the growth rate.[10] The coverage of Ag overlayer was double checked by a SYCON thickness monitor of quartz balance.

III. RESULTS AND DISCUSSION

LEED was used to investigate the surface structure of Ag adlayer on Pt(111). At any coverage of Ag below 1.5 ML, we have found that it shows a well-developed (1×1) pattern during deposition at 360 K. Ultrathin Ag film shows pseudomorphic growth. This indicates that Ag atoms accumulate on the Pt(111) surface in a compact arrangement. After annealing the film at a temperature below 750 K, LEED shows that the film retains its 1×1 structure. The LEED spots diffused at a high temperature. No additional LEED spots were observed. The annealing was limited below 750 K because Ag adatoms desorb at a higher temperature.[8,11] From investigation of scanning tunneling microscopy (STM) at submonolayer range,[9] the morphologies of a Ag film grown below 270 K are metastable. After annealing at a temperature above 300 K, all the low-temperature structures convert into a much more compact form. STM studies of 1.5 ML Ag/

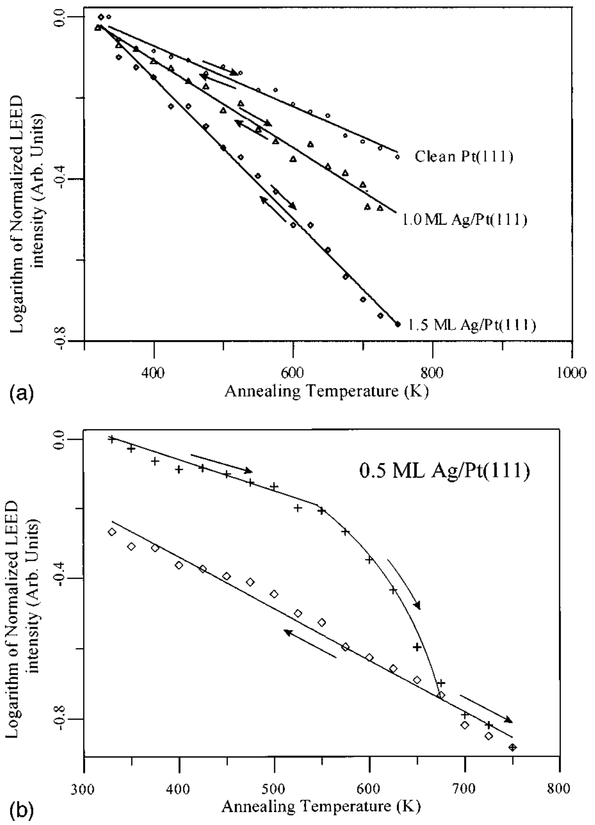

FIG. 1. The logarithm of the LEED peak intensity of the specular beam versus the surface temperature. In (a) for a clean Pt(111) surface, 1.0, and 1.5 ML Ag/Pt(111), the intensities obey the Debye-Waller effect. In (b) for 0.5 ML Ag/Pt(111), ln I decreases linearly but with an abnormal drop between 550 and 650 K during the heating up process. It increases linearly in the cooling down process irreversibly. A thermal hysteresis is observed.

Pt(111) show that the first monolayer grows in a (1×1) fashion.[12] This strain is relieved in the second Ag layer by incommensurate reconstruction. These are the reasons for the 1×1 structure in our LEED observation.

Figure 1 shows the logarithms of the LEED intensities ln(I) of the specular beams versus the surface temperature (T) for clean Pt(111), 1.0 ML and 1.5 ML Ag/Pt(111) in Fig. 1(a) and for 0.5 ML Ag/Pt(111) in Fig. 1(b). From the ln I versus T plot of clean Pt(111) surface, we can find that ln I decreases linearly as temperature increases. According to the Debye-Waller effect, the LEED intensity I should be exponentially proportional to the root-mean-square displacement $\langle u^2\rangle$ of the surface atom. In a 2D system, it can be derived as[13,14]

$$\ln I=\ln I_0-\Delta k^2\langle u^2\rangle$$
$$=\ln I_0-(12Nh^2\cos^2\phi/Mk_B\lambda^2\theta_D^2)T, \tag{1}$$

where Δk is the scattering vector during electron interaction with the surface, N is Avogadro's number; h is the Plank constant, ϕ is the incident angle, M is the atomic weight, k_B is the Boltzmann constant, λ is the wavelength of electrons, and θ_D is the surface Debye temperature. The attenuation of the specular beam for the coverage of 1.0 and 1.5 ML also obeys the Debye-Waller effect. After annealing to 750 K, the temperature is abated and the ln I versus T plots are all identical to those before annealing. They are reversible. This indicates that the surface structure remains unchanged.

From the ln I versus T plot for 0.5 ML Ag/Pt(111) sample as shown in Fig. 1(b), ln I decreases linearly with a slope of 8.72×10^{-4} for temperatures roughly below 550 K in the heating run. However for temperatures between 550 and 675 K, it drops abruptly. Roughly above 675 K, it decreases linearly again with a slope of 1.47×10^{-3}. For the cooling run, the intensity of the specular beam decreases linearly and still keeps the same slope of 1.47×10^{-3}. The linear parts are due to the Debye-Waller effect. All the linear parts in Fig. 1(b) are reversible. This indicates that the surface structure remains unchanged in these linear temperature regions. The dramatic decay between 550 and 675 K indicates a major evolution of the film morphology. This structure change is due to the formation of a 2D surface alloy.[4,6,8] The change of the surface morphology is irreversible during heating from 550 to 650 K.

The attenuation in the intensity of a diffraction spot as a function of temperature is a good technique in obtaining information about the atomic vibration in a solid. Since low-energy electrons are very surface sensitive, the intensity of the LEED specular beam reflects the perpendicular atomic vibration of surface layers. Comparing the linear fitting lines for clean Pt(111), 1.0 ML and 1.5 ML Ag/Pt(111) in Fig. 1(a), the slope increases as the Ag coverage increases. The reason is that the slope is inversely proportional to the effective mass M, which decreases as the Ag coverage increases. Fitting the linear part of the data in Fig. 1(b) where the temperature increases between 325 and 550 K, the value of the slope is between those of clean Pt(111) and 1.0 ML Ag/Pt(111) as shown in Fig. 1(a). However, the slope of the linear fitting line after alloy formation is as large as that of 1.5 ML. This is unusual. According to Eq. (1), this abnormal slope is due to the enhancement of the perpendicular vibration of the surface atoms. From the data fitting, the slopes of ln I versus T plots before and after alloy formation are 8.72×10^{-4} and 1.47×10^{-3}, respectively. Comparing these two slopes, the value of the vibration enhancement is as large as 70% at a given temperature. The first few monolayers of silver deposited on the Pt(111) bear a very great surface stress due to the charge transfer from Ag to Pt.[3,4] After alloy formation, Ag adatoms mix into the first surface layer. This causes the net charge transfer to be smaller and bonding of the Ag is reduced in the perpendicular direction. This is the reason for the enhancement of the perpendicular vibration.

To quantitatively investigate the formation of the surface alloy, the annealing effect of the system was systematically studied at a number of constant temperatures. The peak-height intensities versus time of the specular beam at temperatures between 550 and 625 K for 0.5 ML Ag/Pt(111) are shown in Fig. 2. The intensity of the specular beam decreases monotonously after annealing. The higher the annealing temperature, a faster attenuation in intensity is observed. The attenuation of intensity in this case is a direct measurement of the number of surface steps and other defects because the momentum change of the low-energy electrons in the specular beam is exactly perpendicular to the surface. This decrease in the LEED intensity implies that the annealing does not smooth out the ultrathin film; instead, it roughens the surface. Surface steps and defects are produced

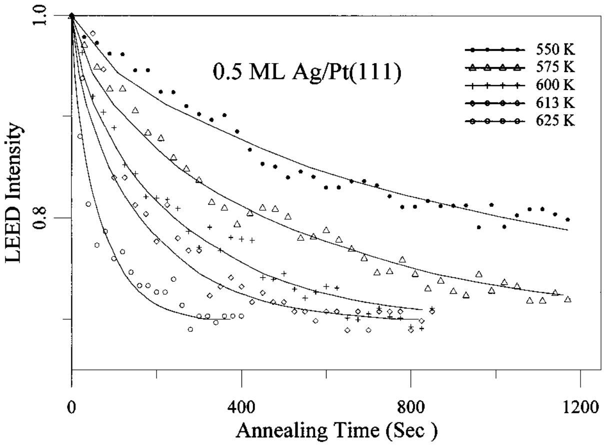

FIG. 2. The peak-height intensities versus time of the specular beam at temperatures between 550 and 625 K for 0.5 ML Ag/Pt(111). The intensities of the specular beam decrease monotonously after annealing. The higher the annealing temperature, a faster attenuation in the intensity is observed.

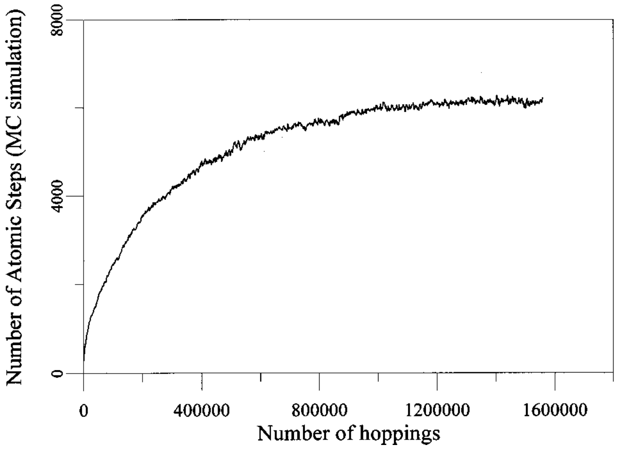

FIG. 4. The number of atomic steps versus the number of hoppings. The hopping rate R was assumed to be 1 in this figure. It saturates after 1×10^{6} hopping. According to the kinematic theory, LEED peak-height intensity is proportional to the square of the scattering area. After substituting the experimental data of LEED peak-height intensities of both the initial and final states of alloy formation, the LEED intensity versus the number of hoppings could be obtained.

in the process of alloy formation. This phenomenon was also checked at other coverages. It occurs only at the submonolayer range. From the results of STM, submonolayers of the Ag deposited on the Pt(111) mix into the first surface layer to form a 2D surface alloy upon annealing above 620 K.[4,6] This surface confined mixing provides the opportunity for the production of the surface steps and defects.

To obtain the 2D diffusion barrier of surface atoms during alloy formation, the kinetic Monte Carlo (MC) simulation was used for data consistency. The substrate is modeled as a 2D array of atoms placed along a triangular lattice. In the simulation, 64×64 substrate atoms were used. A periodic boundary condition was applied to the four extremes of the samples to reduce discontinuity. Since Ag adatoms accumulate on the Pt(111) surface in a compact arrangement, the top layer can be separated into two regions before alloy formation as shown in Fig. 3. The alloy formation of Ag-Pt surface alloy was simulated as follows. Initially, an atom on the top layer was selected randomly. This atom diffuses to one of the nearest sites with equivalent probability. The hopping rate is

$$R=R_0\exp(-E/k_BT), \tag{2}$$

where R_0 is estimated to be k_BT/h, and E is the diffusion barrier of surface atoms during alloy formation.[15,16] Because the atomic heights of Ag and Pt are different, two adjacent species produce one atomic step. The number of atomic steps (N_s) was counted along [110], [101], and [011] directions after each atomic hopping. This process was carried out until N_s was saturated. As an example, N_s versus the number of hoppings is shown in Fig. 4. To simplify the description, hopping rate R was assumed to be 1 in this figure. N_s increases as the simulation cycle increases and saturates after 1×10^{6} hopping. The behavior of N_s reflects the fact that surface roughness increases until the alloying is complete during formation of the surface alloy.

According to the kinematic theory,[17] LEED peak-height intensity is proportional to the square of the scattering area. When a surface contains defects, such as point defects, steps, and dislocations, the effective scattering area is reduced. In the simulation process, we assume that the generation of an atomic step is equivalent to the reduction of an effective scattering area A_K. For a perfect surface, LEED peak-height intensity I is proportional to the square of the scattering area from the kinematic theory, i.e., $I=A_0^2$, where A_0 is the scattering area. During alloy formation, the relationship between I and N_s can be obtained, i.e.

$$I=(A_0-N_sA_K)^2. \tag{3}$$

After substituting experimental data of I and the simulated result of N_s of both the initial and final states of alloy formation, A_0 and A_K could be obtained to be 1.008 and 2.80×10^{-5}, respectively. Then the LEED intensity versus the number of hoppings could be obtained. Now justifying the value of R and following the above procedure, the best con-

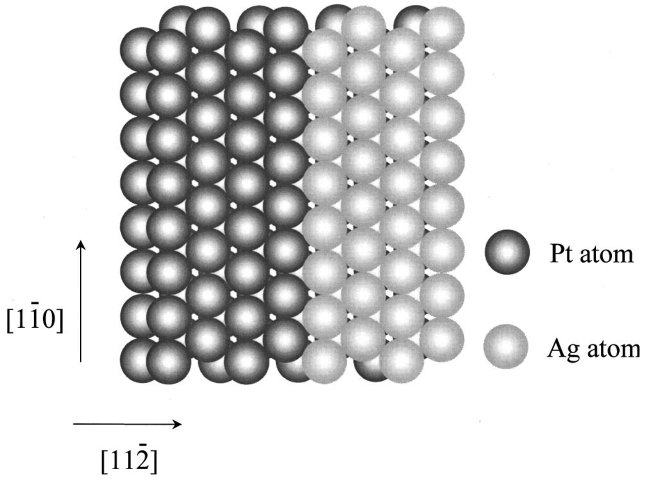

FIG. 3. Since Ag accumulate on the Pt(111) surface in a compact arrangement, the top layer of 0.5 ML Ag/Pt(111) can be separated into two regions before alloy formation.

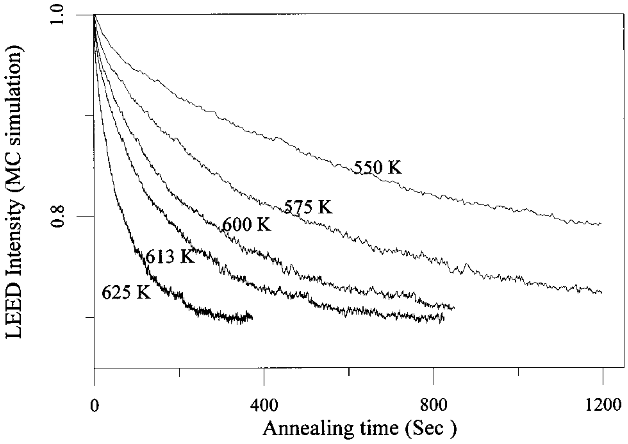

FIG. 5. After justifying the value of R, the best consistent curves for Fig. 2 could be obtained as shown in this figure. As annealing time is increased, the LEED intensities attenuate until the mixing is complete.

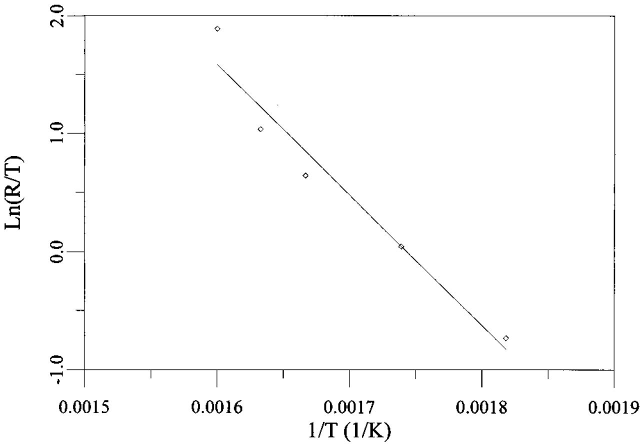

FIG. 6. From the plot of $\ln(R/T)$ versus $1/T$, we obtain the energy barrier of 0.95 ± 0.11 eV for surface atoms in the process of the formation of a 2D surface alloy.

sistent curves for Fig. 2 could be obtained as shown in Fig. 5. As the annealing time is increased, the LEED intensities attenuate until the mixing is complete. The calculated LEED intensities are very consistent with those from the experimental observation. The hopping rate R was obtained at 550, 575, 600, 613, and 625 K from Fig. 5. According to the form in Eq. (2), a plot of $\ln(R/T)$ versus $1/T$ is shown in Fig. 6. The energy barrier E can be yielded from the slope of the straight line, which is obtained from data consistency between Fig. 6 and Eq. (2). The energy barrier of 0.95 ± 0.11 eV is obtained for surface atoms in the process of formation of a 2D surface alloy.

IV. CONCLUSION

At any coverage below 1.5 ML, ultrathin Ag film shows pseudomorphic growth. After annealing the film below 750 K, LEED spots diffused at a high temperature but the film retains its 1×1 structure. At the coverage above 1 ML, the attenuation of the LEED specular beam obeys the Debye-Waller effect during annealing below 750 K. This indicates that the surface structure remains unchanged. While the submonolayer ultrathin Ag film is annealed above 550 K, a 2D surface alloy is formed. After formation of the surface alloy, the vibration of surface atoms is enhanced due to the charge transfer of Ag to Pt. The value of the vibration enhancement could be as large as 70% at a given temperature.

At submonolayer range, annealing treatment causes a mixture of Ag adatoms into the first surface layer to form a 2D surface alloy. At higher annealing temperatures, a faster mixing of surface atoms is observed. To obtain the 2D diffusion barrier for the surface atoms during alloy formation, kinetic MC simulation was applied for data consistency. The corresponding energy barrier for surface atoms is 0.95 ± 0.11 eV in the process of formation of 2D surface alloy in an ultrathin Ag/Pt(111) film.

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