Surface Alloying of Submonolayer Pb on Cu(111) Studied by Photoemission *

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The reactions of superthin Pb films on a Cu (111) surface with respect to the coverage of Pb and annealing have been studied by synchrotron radiation photoemission. The submonolayer Pb atoms deposited at room temperature are distributed on the Cu (111) surface as two-dimensional (2D) islands. Annealing to 200° C gives rise to Pb-Cu surface alloy formation. Analyses show that the surface alloy occurs only in the first layer of the Cu (111) surface. As a surfactant, Pb can promote 2D layer-by-layer growth of thin films on Cu (111), but the Pb-Cu surface alloying may have an unfavorable effect on the activation process.

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The alloying phenomena on solid surfaces have attracted much interest because of the importance both in fundamental theory and practical technology. During the growth of thin films for miscible metals, atoms at metal/metal interfaces can interdiffuse and form alloy, which will strongly affect the properties of thin films. During the growth of superthin Au films on a Cu (100) surface, a $c(2\times2)$ surface superstructure made up of a Cu-Au surface alloy layer was observed.[1] Au atoms were also found intermixing with the first two Ag layers when Au grew on Ag(110).[2] However, the most interesting thing is that the immiscible metals can also develop surface alloy formation. In effect, the possibility of such surface alloying was theoretically predicted in the early 1970s.[3] A study with scanning tunneling microscopy (STM) showed that Au deposited on Ni(110) replaces Ni at the surface layer and forms a surface Au-Ni alloy layer.[4] When Ag was grown on Pt(111), the monolayer-confined mixing Ag-Pt alloy at the interface was revealed.[5] Theoretical calculation demonstrated that Na replacing a surface Al atom is more favorable than its being adsorbed on the Al(111) surface.[6]

The early study of superthin Pb deposited on single crystal Cu surfaces was performed mainly by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES).[7,8] Henrion and Rhead[7] investigated in detail the conditions for Pb deposition on the three low-index Cu surfaces, and found a $c(4\times4)$ superstructure on the Cu (100) surface which was later regarded as a surface Pb-Cu alloy layer.[9] Meyer *et al.* found an incommensurate dense Pb submonolayer on the Cu (111) surface whose parameter varies continuously with increasing coverage of Pb.[10] However, the surface alloying phenomenon of superthin Pb on single crystal Cu surface was not verified until STM was used to study this system. This phenomenon was first observed by Nagl *et al.* in studying the growth of superthin Pb on Cu (111),[11] where Pb atoms replaced Cu atoms and were embedded in the surface layer of Cu (111), forming the surface Pb-Cu alloy. By STM and thermal energy atom scattering (TEAS), the Pb-Cu surface alloying phenomena were observed on all the Cu (111), (100), (110), (211) index surfaces.[9,11−15] A calculation by the tight-binding method combined with Monte Carlo simulation for half-monolayer Pb on Cu (110) surface predicted an equilibrium surface Pb-Cu alloying during the order-disorder transition of the $c(2\times2)$ phase.[16] By a Monte-Carlo simulation of the Pb/Cu (100) surface superstructure, it was also found that the surface alloy $c(4\times4)$ structure is more stable due to the presence of Pb and Cu in the same plane.[17]

The surface alloying of immiscible Pb on single crystal Cu (111) is an important research subject. On the one hand, the large lattice mismatch between Pb and Cu (Pb is 37% larger) and the closest-packed (111) surface make their surface alloying impossible. On the other hand, inactive Pb is often used as a surfactant during the growth process of thin films to promote 2D layer-by-layer growth,[18] but the surface alloying may have an unfavorable effect on the activation process. In view of the susceptibility of the surface electron state to changes in the surface structure, we have studied in detail the variation of the $\overline{\Gamma}$ point surface state at the Cu (111) surface Brillouin zone (SBZ) with different coverage levels of Pb before and after annealing. Our results reveal the change of Pb distribution on Cu (111) after annealing, whereby a Pb-Cu surface alloy is formed. We also discuss the possible effect of the surface alloying on the activation function when Pb is used as a surfactant during the growth of films.

Experiments were carried out in a UHV multichamber system equipped with AES and LEED. The base pressure was below 3×10^{-10} mbar. The syn-

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chrotron radiation source was the 4B9B beam line at the Beijing Synchrotron Radiation Facility in the Beijing Electron Positron Collider National Laboratory. A spherical grating monochromator was used to disperse the synchrotron radiation which had an energy range between 10 and 60 eV. The photoemission energy detector was an angle-resolved hemispherical analyzer made by VSW Inc. in Britain. The combined energy resolution was 0.2 eV at a photon energy of 20 eV and the 15 eV pass energy of the analyzer. The azimuthal orientation was established by LEED. The analyzer was normal to the Cu (111) surface during the experiment. The incident angle of the beam was chosen to be 70°, so the measurements were done with about 90% p-polarized light.

The Cu (111) single crystal sample was cleaned by many cycles of Ar ion bombardment and annealing at 700°C, until no contamination could be detected with AES and a bright LEED pattern with threefold symmetry Cu (111) surface diffraction spots was obtained. High purity Pb was thoroughly outgassed prior to evaporation, and was deposited on the Cu (111) surface from a resistively heated alumina crucible with water cooling at a rate of about 1 ML(monolayer)/min (1 ML is defined as a complete overlayer with Pb bulk lattice constant). The coverage of Pb was controlled by the evaporation time, and determined by the AES signal ratio of Pb (94 eV) to Cu (60 eV). The pressure during evaporation was below 1×10^{-9} mbar.

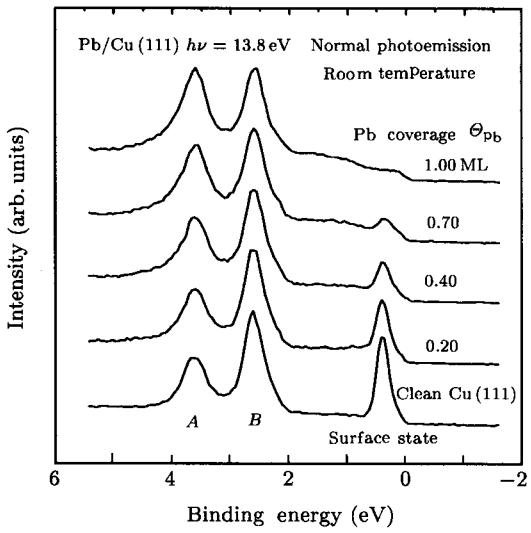


Fig. 1. ARED curves at the $\overline{\Gamma}$ point in the SBZ of Cu (111) for different coverage levels of Pb deposited on a Cu (111) surface at room temperature.

The angle-resolved electron energy distribution (ARED) curves at the $\overline{\Gamma}$ point in the SBZ of Cu (111) for the different coverage levels of Pb deposited at room temperature are shown in Fig. 1. The surface state peak is just the $\overline{\Gamma}$ point surface state whose binding energy is 0.4 eV below the Fermi level,[19] and peaks A and B represent the emission from the bulk Cu 3*d* band. One can see from Fig. 1 that the intensity of the surface state peak decreases monotonically with increasing Pb coverage Θ_{Pb} from 0.20 to 1.00 ML. As the coverage reaches 0.70 ML, the surface state peak still gives a measurable intensity. And it vanishes completely when the coverage is equal to 1.00 ML. Because the surface state can exist in a fairly small area of a clean ordered surface,[20] the above results indicate that the submonolayer Pb is distributed over the Cu (111) surface as two dimensional (2D) close-packed islands, but not distributed evenly over the surface and does not accumulate as three dimensional islands. When the coverage is about 1.00 ML, a clear $p(4\times4)$ surface superstructure is observed by LEED. These results are in good agreement with those of Beauvais *et al.* at 303 K obtained by TEAS.[12]

Given the effective radius of Pb atoms σ in the 2D close-packed island and σ_0 in bulk, then the intensity I_0 of the surface state with respect to the coverage θ of Pb can be written as

$$I_\theta = I_0 - I_0\theta(\pi\sigma^2)/(\pi\sigma_0^2) = I_0(1 - \theta\sigma^2/\sigma_0^2), \quad (1)$$

where I_0 is the intensity of the surface state peak emitted from the clean Cu (111) surface. Substituting the corresponding experimental results for I_0 into Eq. (1), one can get the effective radius $\sigma = 2.1, 2.0, 1.9, 1.75$ Å for $\theta = 0.20, 0.40, 0.70, 1.00$ ML, respectively, where $\sigma_0 = 1.75$ Å. Though the above values are slightly larger than those from the results by Meyer *et al.* who used a spot profile analyzing LEED,[10] the variation of the average Pb-Pb distance dependence on the coverage of Pb is similar. That is, the 2D lattice parameter of Pb islands decreases continuously with the increase of the coverage of Pb.[10] The difference, we consider, may result from the simplicity of our model. For instance, the region where the surface state has been destroyed may be larger than the real area of 2D Pb islands, and this difference makes the effective radius values obtained from Eq. (1) larger than the real ones.

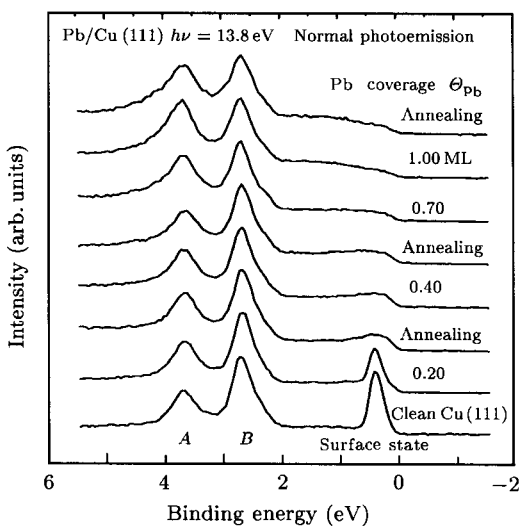


Fig. 2. ARED curves at the $\overline{\Gamma}$ point in the SBZ of Cu (111) for different coverage levels of Pb deposited at room temperature and after annealing to 200°C.

From the above discussion, our results are in good agreement with those of Meyer *et al.* as well as Beauvais *et al.* at room temperature,[10,12] but are not very similar to those of Nagl *et al.*,[11] who found that the surface alloy coexisted with 2D islands. This may be caused by the different evaporation methods used. Nagl deposited the Pb by electron beam evaporation, instead of heat evaporation as we used. Some of the Pb spurting from the electron beam evaporator consists of Pb ions, which enables the Pb atoms to intermix with Cu and form a high defect density in a small region when the sample is prepared.

Figure 2 shows the ARED curves at the $\overline{\Gamma}$ point in the SBZ of Cu (111) for the different coverage levels of Pb deposited at room temperature before and after annealing to 200°C. The annealing process strongly changes the surface state, as can be seen from the difference among the energy distribution curves in Fig. 2. At the coverage of 0.20 ML before annealing, the corresponding surface state in Fig. 2 is very similar to that in Fig. 1, and the intensity of the surface state peak is not very different from that of the clean Cu (111) surface. But after annealing to 200°C, the intensity of the surface state peak decreases sharply and the surface state almost vanishes. This indicates that the atom-flat ordered Cu (111) surface has been greatly changed after annealing, and Pb atoms are randomly dispersed on the Cu (111) surface and no longer arranged as 2D close-packed islands. There are two possible positions for the randomly dispersed Pb atoms: (a) The Pb atoms are adsorbed on the Cu (111) surface. (b) One Pb atom replaces one Cu atom on the surface forming a surface alloy with Cu. We note that, in the former case, its energy is higher than that of 2D Pb islands, so it is not realistic from the thermodynamic viewpoint. In our opinion, case (b) is more likely.

Studies by Nagl *et al.* with STM found that annealing enables Pb atoms, presenting as hexagonal close-packed 2D islands, to spread on the Cu (111) surface to form a surface alloy with Cu atoms.[11] In the surface alloy, Pb atoms replace the surface Cu atoms and thereby are embedded randomly in the first surface layer. Beauvais also found with TEAS that for high Cu substrate temperatures the submonolayer Pb is no longer present as 2D close-packed islands but has become a surface alloy.[12] Thus our photoemission results are consistent with the STM and TEAS findings.

According to the above discussion, Pb-Cu surface alloy has been formed at our single crystal sample Cu (111) surface. In Fig. 2, as the coverage increases to 0.40 ML, the weak intensity of the surface state peak decreases continuously. This shows that during the deposition at room temperature, the surface alloyed Pb atoms are so stable that they can not be activated to reaggregate to form 2D Pb islands. At 0.40 ML, the faint surface state peak vanishes completely after annealing, just like the case at 1 ML in Fig. 1. This is sufficient to demonstrate that at this stage the clean ordered Cu (111) surface, which can maintain the presence of the surface state, is destroyed completely. This just corresponds to the results of Nagl *et al.*,[11] and suggests that a maximum density of Pb-Cu surface alloy has been developed.

To investigate the annealing effect, the 5*d* core level spectra of Pb, stimulated by an incident beam of 37.4 eV, have also been studied during experiments. The core level shift upon annealing can not be distinguished due to the poor resolution of our experiment (further work will be submitted later), but the fact that the intensity of the 5*d* peak is the same before and after annealing apparently indicates that annealing can not activate the Pb atoms to diffuse into the bulk of Cu.

It is well known that inactive Pb is often used as a surfactant during the growth process of thin films.[7] Surface alloying, we think, may have an unfavorable effect on the activation process. For instance, de-alloying may leave some Cu vacancies in the substrate surface. When other kinds of atoms grow on such a surface, they will fill the vacancies and lead to interface roughness. Furthermore, whether the de-alloying is truly complete, or whether a few Pb atoms remain at the embedded sites is still controversial. The Pb atoms remaining at the embedded sites will also certainly affect the film growth, so we conclude that Pb deposited at room temperature with a heat evaporator will be favorable for Pb to perform such a surfactant activation function.

In conclusion, we have studied the reactions of superthin Pb films on a Cu (111) surface with respect to the coverage of Pb and annealing by photoemission spectroscopy, as well as AES and LEED. The submonolayer Pb deposited at room temperature is distributed on the Cu (111) surface as 2D close-packed islands. Annealing evenly redistributes the Pb atoms, and thereby the Pb-Cu surface alloy is developed, but only in the first layer of the Cu (111) surface. When Pb serves as a surfactant during the growth of thin films, surface alloying may have an unfavorable effect on the activation process.

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