



Surface alloying of Pb as a surfactant during epitaxial growth on Cu(1 1 1)

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Abstract

As an important surfactant, Pb surface alloying in surfactant-assisted epitaxy growth was studied by synchrotron radiation photoemission. As annealing causes the submonolayer Pb, distributed as two-dimensional islands on Cu(1 1 1), to form Pb–Cu surface alloy, Cu growth is also found to activate the Pb–Cu surface alloy formation on submonolayer Pb covered Cu(1 1 1). Whereas, different from the fact that the Pb–Cu surface alloy is replaced by a Pb overlayer when the Pb coverage increases up to 1.0 ML, Co deposition gives rise to the Pb–Co surface alloy even on the 1.0 ML Pb covered Cu(1 1 1) surface. In the Pb–Cu surface alloy the Pb 5d core level is shifted toward Fermi level by about 20 meV. Heating de-alloys the Pb–Co surface alloy, while the interface intermixture between Co film and Cu substrate is also enhanced at the same time.

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1. Introduction

For miscible metals, when one kind grows on the other surface, the atoms near the interfaces will interdiffuse and form alloy, which will affect the properties of the grown films. More interestingly,

for the immiscible metals a kind of surface alloy formation is found under some conditions. For example, a study with scanning tunnelling microscopy (STM) showed that Au deposited on Ni(1 1 0) replaces Ni at the surface layer and forms a surface Au–Ni alloy layer [1]. Another high-resolution photoemission study showed that when the Na atoms are situated in different surface alloy structure on Al(1 1 1), the 2p core level binding energies of both Na and Al are shifted with different

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values [2]. The Pb/Cu is also an immiscible metal system extensively studied. Henrion and Rhead [3] investigated Pb deposition on the three low index Cu surfaces, and found a $c(4 \times 4)$ superstructure on the Cu(100) surface which was later regarded as a surface Pb–Cu alloy [4]. Meyer et al. found an incommensurate dense Pb submonolayer on the Cu(111) surface whose parameter varies continuously with increasing Pb coverage [5]. The surface alloying of ultra-thin Pb on single crystal Cu surface was first verified by Nagl et al. with STM [6]. The Pb atoms were observed to replace Cu atoms and be embedded in the surface layer of Cu(111), forming the Pb–Cu surface alloy [6]. A Monte-Carlo simulation for the Pb/Cu(100) surface superstructure shows that the surface alloy $c(4 \times 4)$ structure is more stable due to the presence of Pb and Cu in the same plane [7].

Recently, the inactive Pb was found to be able to promote the 2D layer-by-layer growth [8–13] during the surfactant-assisted epitaxy growth. As a surfactant inducing layer-by-layer growth mode in epitaxy, at first, it should have a most fundamental property, i.e., always floating on the surface during epitaxy growth, which requires it to have smaller surface free energy and be immiscible with the grown film. Secondly, it should possess one or both of the following functions: effectively reducing adatom's intralayer diffusion, or enhancing interlayer diffusion. However, the potential surface alloying during the growth may have an important influence on the activation behaviour of the surfactant. So, the surface alloying phenomenon of Pb as a surfactant during the epitaxy growth becomes an important research subject.

Previously, we studied the growth of ultra-thin Pb and surface alloy on Cu(111) [14,15]. As in Refs. [5,6], submonolayer Pb was found grow first as 2D close-packed islands with an increasing lattice constant, and is surface alloyed with Cu by annealing. In this paper, we report our studies on Pb surface alloying as a surfactant in the Cu and Co growth on Cu(111) by synchrotron radiation photoemission. Our results reveal that, as annealing, the growth of Cu film causes the submonolayer Pb to form Pb–Cu surface alloy on Cu(111). Furthermore, Pb–Co surface alloy was also observed during the surfactant-assisted Co

film epitaxy growth on Cu(111) by using 1.0 ML Pb as a surfactant. Heating de-alloys the Pb–Co surface alloy but also enhances the intermixture between Co film and Cu substrate.

2. Experiments

Experiments were performed in an ultra-high vacuum multichamber system equipped with auger electron spectroscopy (AES) and low energy electron diffraction (LEED), as well as electron energy analyzers, with a base pressure better than 3×10^{-10} mbar. The synchrotron radiation source was the 4B9B beam line at the Beijing Synchrotron Radiation Facility in Beijing Electron Positron Collider National Laboratory. A spherical grating monochromator was used to disperse the synchrotron radiation. An angle-resolved hemispherical analyzer and an angle-integral energy analyzer made by VSW Inc. in Britain were used to detect the photoemission energy. The azimuthal orientation of the Cu(111) sample was established by LEED. For the photoemission from the valence band, the incident angle of the beam was chosen to be 70° , so the measurements were done with about 90% **p**-polarized light. The analyzer was normal to the Cu(111) surface, and the normal combined energy resolution was 0.2 eV. For the photoemission from Pb 5d core level, the energy resolution was about 0.1 eV determined by measuring the Fermi edge of Au at the photon energy of 43.6 eV, and the take-off angle of the photoelectron was 40° .

The Cu(111) sample was cleaned by several cycles of Ar^+ ion bombardment and annealing at 700°C , until no contamination could be detected with AES and a bright LEED pattern for Cu(111) was obtained. High purity Pb, Cu and Co were thoroughly outgassed prior to evaporation, and deposited from three resistively heated alumina crucibles with water cooling at rates of about 0.2 ML (monolayer)/min, 0.8 ML/min and 0.3 ML/min, respectively, at room temperature (RT). The coverages of Pb, Co and Cu were controlled by the evaporation times, and determined further by the AES signal ratios of Pb (94 eV) and Co (716 eV) to Cu (60 eV) and Cu (920 eV)

to Co (716 eV) (here, a clean Co(0001) sample was used), respectively. The pressure during evaporation was below 1×10^{-9} mbar.

3. Results and discussion

3.1. Surface alloying and de-alloy of Pb–Cu

The Pb growth and surface alloying on clean Cu(111) were first studied by measuring its 5d core level spectra, excited by an incident beam of 43.6 eV, with the take-off angle 40° of the photo-

electron. Fig. 1(a) shows the Pb 5d_{5/2} core level dependence on Pb coverage when Pb grows on clean Cu(111) at RT. With increasing Pb coverage, the 5d_{5/2} core level is shifted to the higher binding energy. At 3.0 ML, the binding energy has already been closed to that of bulk Pb. The core level shift indicates that there may exist charge transfer from Cu to Pb. From 0.4 ML to 1.0 ML, the small shift of about 20 meV means that the variation of the chemical surroundings of Pb is not large: According to others [5] and our previous discussions [14,15], with Pb coverage changing from submonolayer to saturate monolayer, only the atomic density in the 2D close-packed islands is changed a little. Recently, it was found that the (4 × 4) superstructure for the saturated 1 ML Pb overlayer is vertically buckled, inducing the under Cu layer modified, even with a larger buckling amplitude [16]. The buckle may be the reason to shift the Pb core level.

Fig. 1(b) shows the Pb 5d_{5/2} core level spectra with Pb coverage and annealing at 0.4 ML Pb deposition. Obviously, annealing shifted the level by about 20 meV toward Fermi level, but did not change the level intensity, indicating that annealing changed the chemical surroundings of the grown Pb although they remain on the top of surface. The Pb atoms replace the Cu atoms and are embedded in the first layer of Cu(111) forming Pb–Cu surface alloy, and therefore, the Cu number round each Pb atom is increased.

When depositing more Pb to 1.0 ML on the alloying surface, the Pb 5d_{5/2} core level binding energy is shifted back [Curve c in Fig. 1(b)], and is closed to that of Curve b in Fig. 1(a). This indicates that in this case, the chemical surroundings of Pb atoms becomes similar to that with 1.0 ML Pb deposited without annealing, that is, the Pb–Cu surface alloy disappears, indicating the de-alloying of the surface alloy when Pb coverage increases to 1.0 ML. This is in good agreement with Nagl's observation with STM [6]. The Pb–Cu surface alloy exists only when Pb distributed density is low enough. When 1.0 ML Pb was grown, the density reaches the maximum and even larger than the bulk value of Pb. The higher atomic distributed density is attributed to the reason that the Pb–Cu is de-alloyed.

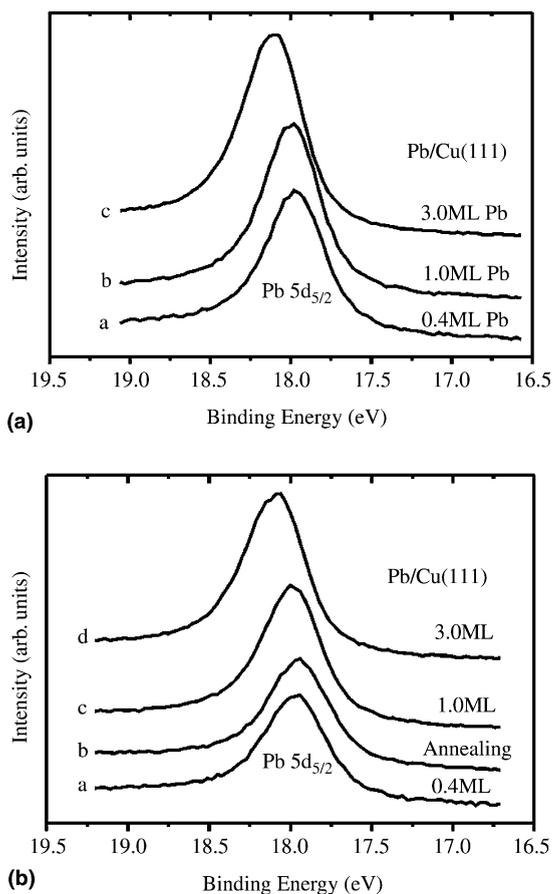


Fig. 1. (a) Pb 5d_{5/2} core level spectra with Pb coverage on Cu(111) at RT. (b) Pb 5d_{5/2} core level spectra with Pb coverage and annealing on Cu(111).

3.2. Surface alloying during Cu growth on Cu(111)

In the surfactant-assisted epitaxy growth by using Pb as a surfactant, Pb surface alloy may form, affecting the growth process. The possible alloying was studied by measuring the angle-resolved electron energy distribution curves (AREDCs) at the $\bar{\Gamma}$ point in the surface Brillouin zone (SBZ) of Cu(111) with Pb and Cu growth at RT. 0.3 ML Pb was first deposited to be the surfactant before Cu growth. The AREDCs are shown in Fig. 2(a). Curve a is for the clean Cu(111) surface, the peak SS, whose binding energy is 0.4 eV below Fermi level, is the $\bar{\Gamma}$ point surface state [17,18], and peaks A and B represent the emission from the bulk Cu 3d band. When 0.3 ML Pb was deposited on the Cu(111) surface, the SS intensity decreases correspondingly. But when 3.0 ML or more Cu was grown on the 0.3 ML Pb covered Cu(111), surprisingly, the decreased SS was found vanish almost completely.

Two possible reasons account for the SS disappearance in this case. One is that there exist lots of probable steps on the Cu(111) surface because of the 3D island growth mode of Cu [9], which de-

creases the Cu(111) surface area and thus also the SS. The other is that the 0.3 ML Pb atoms are activated by the kinetic energy of the deposited Cu atoms and dispersed on the Cu(111) surface, forming Pb–Cu surface alloy. To confirm the possible reason, the change of $\bar{\Gamma}$ point SS on clean Cu(111) with Cu growth is presented in Fig. 2(b). The SS intensity unexpectedly holds the same with Cu growth. This means that the 3D island mode of Cu film grown on Cu(111) does not affect the SS intensity significantly. So, the first reason is excluded and the most possible is that the 0.3 ML Pb atoms are dispersed all over the surface forming Pb–Cu surface alloy.

3.3. Surface alloying during Co growth on Cu(111)

The surface alloying and de-alloying during Co growth on Cu(111) by using 1.0 ML Pb as the surfactant are also studied with synchrotron radiation photoemission spectra. Fig. 3 shows the binding energy of Pb 5d_{5/2} core level with the increase of Co coverage on the 1.0 ML Pb covered Cu(111) surface at RT. For comparison, the result for another case, that 5.0 ML Co was first deposited and then 1.0 ML Pb on the Cu(111) surface, is

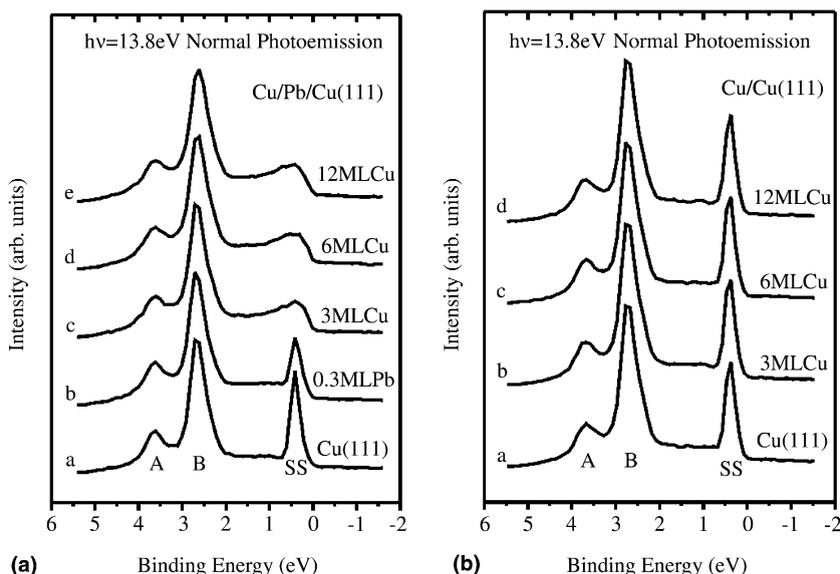


Fig. 2. (a) AREDCs at the $\bar{\Gamma}$ point in the SBZ of Cu(111) with Cu deposition on a 0.3 ML Pb Covered Cu(111) surface at RT. (b) AREDCs at the $\bar{\Gamma}$ point in the SBZ of Cu(111) with Cu deposition on a clean Cu(111) surface at RT.

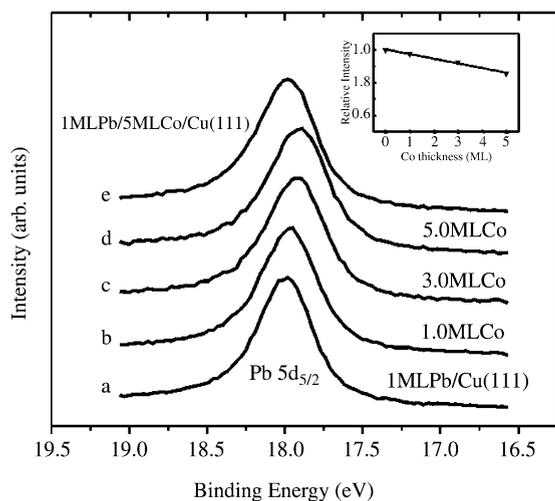


Fig. 3. Pb $5d_{5/2}$ core level spectra with Co growth on 1 ML Pb Covered Cu(111). The inset shows the relative intensity of Pb $5d_{5/2}$ peak with Co coverage.

also presented by the top Curve e in Fig. 3. The inset shows the intensity variation of Pb $5d_{5/2}$ core level peak with Co coverage. The fact that the intensity of Pb $5d_{5/2}$ core level peak drops very weakly when the Co thickness increases from 1.0 ML to 5.0 ML, reveals that almost all Pb atoms are always floated on the sample surface, only a few got buried, during Co growth. The binding energy in Curve e is only 20 meV lower than that in Curve a because of the close characters of Co and Cu atoms and the electronegativity of Co being a little less than that of Cu. With increasing Co thickness, from Curve a to d in Fig. 5, the Pb $5d_{5/2}$ core level binding energy is shifted to Fermi level gradually. When the Co thickness reaches 5.0 ML (Curve d), it is even lower than that of the case of Curve e by 80 meV. If all the Pb atoms are floated on the Co film for the case of Curve d, then the Pb $5d_{5/2}$ core level binding energy should be equal to that of Curve e. But their difference is up to 80 meV. On one hand, the buried Pb atoms may account for such big difference. On the other hand, considering the few number of them, the buried Pb atoms are not the single cause. We explain it as follows: During Co deposition, most of the Pb atoms remain on the surface but a few got buried in Co

film. On the other hand, most Co atoms go down under the Pb overlayer and nucleate into Co terrace, however, some cannot incorporate into the Co terrace but be embedded in the intervals among Pb atoms, increasing the Co atom number around each Pb atom and thus decreasing the Pb $5d_{5/2}$ binding energy. The thicker of the Co film deposited, the more are the Co atoms embedded. The Pb atoms form Pb–Co surface alloy with the embedded Co atoms around. The existence of Pb–Co alloy means that a bonding strength needs to be overcome both for the Co diffusion under Pb layer to form 2D terraces or for the floating of Pb atoms onto the surface. This may be the main reason why some Pb atoms are buried in the Co film during the growth: Some Pb atoms in the Pb–Co alloy have no enough time to break the bonding before they are covered by the deposited Co atoms. The buried Pb atoms may be the reason why the efficient Pb surfactant is often more than 1 ML [8,10]. With film growth, some Pb are buried and thus the original Pb overlayer is decreased. If the original Pb overlayer is more than 1 ML, then the decreased overlayer may keep not less than 1 ML during the whole film growth.

Once the deposited Co atoms diffuse into under the pre-deposited 1.0 ML Pb layer, their intralayer diffusion over the Cu(111) surface is suppressed, which effectively increases the Co island density at the initial stage, which is favorable to the layer-by-layer growth [19]. On the other hand, with Co deposition, the Co atom number embedded in the intervals among Pb atoms increases, indicating that the 1.0 ML Pb may hinder the interlayer diffusion of the Co atoms. This is unfavorable to the layer-by-layer growth [19].

3.4. Pb–Co de-alloying by heating

During the study on the Pb surfactant-assisted Cu homoepitaxy growth on Cu(111), Camarero et al. enhanced the interlayer diffusion of Cu atoms by heating the sample [9]. But in the heteroepitaxy growth of multilayers or superlattices, such as Co/Cu, it may be unfavorable to enhance the interlayer diffusion of the adatoms by heating, for meanwhile it will enhance the intermixture of the Co and Cu atoms at the interfaces.

The enhancement effect in the interlayer diffusion of the Co atoms by heating the sample for two minutes was also investigated. The 5d core level of Pb in 5 ML Co/1 ML Pb/Cu(111) with heating temperature is presented in Fig. 4. The corresponding 5d level signal intensity is shown in the inset. With increasing temperature, the Pb 5d core level is obviously shifted back to the higher binding energy. This reveals that the Co atomic number around each Pb atom is decreased at this moment, thus indicating that the interlayer diffusion of the Co atoms, embedded in the intervals among Pb atoms, into Co terrace takes place, i.e., the de-alloying process of Co–Pb alloy takes place with the increase in temperature. Correspondingly, the intensity of the Pb 5d core level also increases a little as shown in the inset of Fig. 4, indicating that the covered Pb atoms have diffused out of the Co films.

The 3p core level angle-integral photoemission spectra of the Cu(111) substrate taken with photon energy of 260 eV with the growth of Pb layer, Co layer and subsequent heating were also measured and shown in Fig. 5(a). The corresponding $3p_{3/2}$ photoemission signal intensity variations are presented in Fig. 5(b). With the growth of Pb and Co layers at RT, the signal of Cu 3p core level is decreased. From RT to about 55 °C, the signal intensity keeps the same. But when the tempera-

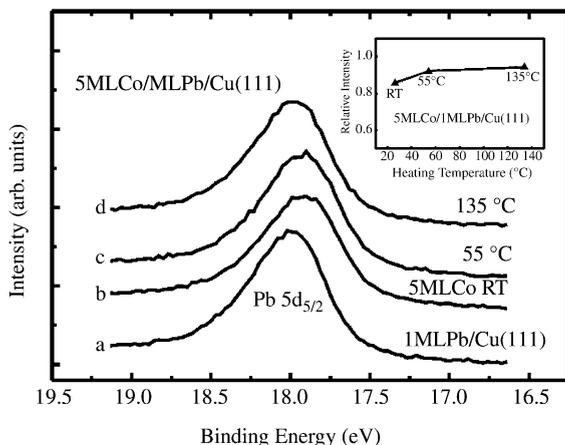
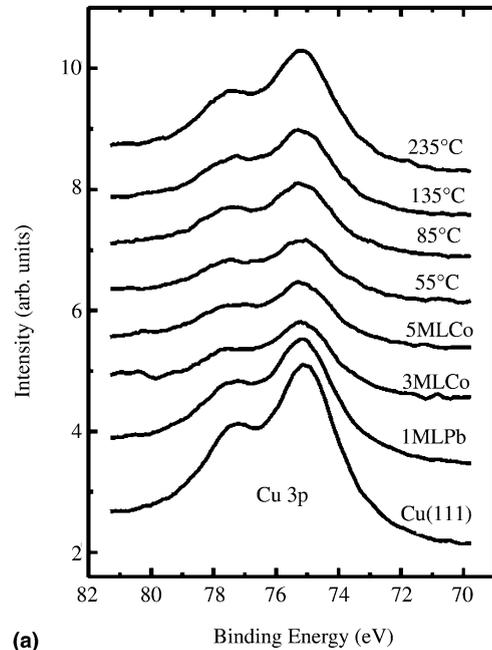
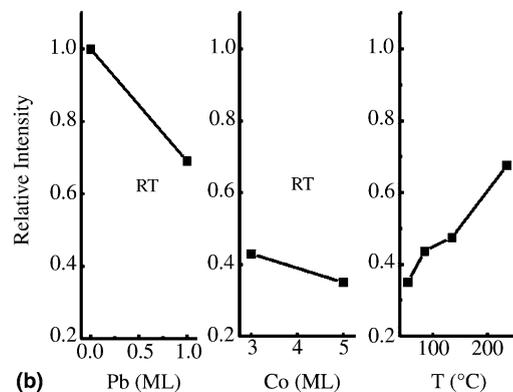


Fig. 4. Pb 5d core level spectra in 5 ML Co/1 ML Pb/Cu(111) with heating temperature. The corresponding $5d_{5/2}$ level signal intensity is present in the inset.



(a)



(b)

Fig. 5. (a) Cu 3p core level spectra of the Cu(111) substrate with the growth of Pb and Co layers, and the post-heating temperature. (b) Cu $3p_{3/2}$ core level signal intensities corresponding to the cases in Fig. 5(a).

ture is increased to about 80 °C or higher, the 3p signal intensity is seen increased. This obviously shows, in this case, that the Cu atoms in the substrate started to diffuse onto the Co film, and the Co atoms diffused into the Cu substrate. That is, the intermixture at the Co/Cu(111) interface has already started at the temperature about 80 °C. With increasing the temperature continuously, the interlayer diffusion is enhanced accordingly.

When the temperature is up to 235 °C, the Cu 3p signal has increased back to the case that only 1.0 ML Pb covers the clean Cu(111) surface but without Co deposition. In fact, we found that when the temperature is up to 235 °C, the 5d binding energy of Pb also comes back to the value (not shown here) that no Co was deposited. Both reveal that all the Co atoms have diffused deep into the Cu substrate at 235 °C.

So, the shift back to the higher binding energy of the Pb 5d core level with the temperature in Fig. 4 is mainly caused by the de-alloying of Pb–Co, by which the Co atoms embedded in the intervals among Pb atoms diffuse into the finished Co terrace. At the same time, because of the interdiffusion of Co and Cu atoms, the number of Co atoms underneath the Pb layer decreases until they are replaced completely by Cu atoms, which shifts the Pb 5d core level back to the initial value when the 1.0 ML Pb was deposited on the clean Cu(111) surface. Considering the interdiffusion of Co and Cu at the interface and the de-alloying of Pb–Co may take place at the same time, heating is not an effective method to de-alloy when Co film is grown on Cu(111) with Pb as a surfactant.

4. Conclusion

In conclusion, Pb surface alloying in surfactant-assisted epitaxy growth were studied by synchrotron radiation photoemission. The submonolayer Pb deposited at room temperature are distributed on the Cu(111) surface as two-dimensional islands. Annealing gives rise to Pb–Cu surface alloy formation. Pb–Cu surface alloy shifts the Pb 5d core level toward Fermi level by about 20 meV. At the Pb coverage of 1.0 ML, the Pb–Cu surface alloy is entirely replaced by a Pb overlayer. On submonolayer Pb covered Cu(111), Cu growth activates the formation of Pb–Cu surface alloy. While Co deposition causes to the Pb–Co surface alloy even on the 1.0 ML Pb covered Cu(111) surface. This is unfavorable for the surfactant-assisted epitaxy growth. Heating can de-alloy the Pb–Co

surface alloy, at the same time, the interface intermixture between Co film and Cu substrate is also enhanced.

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References

- [1] L. Pleth Nielsen, F. Besenbacher, I. Stensgaard, E. Lægsgaard, C. Engdahl, P. Stoltze, K.W. Jacobsen, J.K. Nørskov, *Phys. Rev. Lett.* 71 (1993) 754.
- [2] J.N. Anderson, M. Qvarford, R. Nyholm, J.F. van Acker, E. Lundgren, *Phys. Rev. Lett.* 68 (1992) 94.
- [3] J. Henrion, G.R. Rhead, *Surf. Sci.* 29 (1972) 20.
- [4] C. Nagl, E. Platzgummer, O. Haller, M. Schmid, P. Varga, *Surf. Sci.* 333 (1995) 831.
- [5] G. Meyer, M. Michailov, M. Henzler, *Surf. Sci.* 202 (1988) 125.
- [6] C. Nagl, O. Haller, E. Platzgummer, M. Schmid, P. Varga, *Surf. Sci.* 321 (1994) 237.
- [7] S. Tan, A. Ghazali, J.-C.S. Levy, *Surf. Sci.* 377–379 (1997) 15.
- [8] J. Camarero, L. Spendeler, G. Schmidt, K. Heinz, J.J. de Miguel, R. Miranda, *Phys. Rev. Lett.* 73 (1994) 2448.
- [9] J. Camarero, J. Ferron, V. Cros, L. Gomez, A.L. Vazquez de Parga, J.M. Gallego, J.E. Prieto, J.J. de Miguel, R. Miranda, *Phys. Rev. Lett.* 81 (1998) 850.
- [10] M.C. Xu, H.J. Qian, F.Q. Liu, K. Ibrahim, W.Y. Lai, S.C. Wu, *Chin. Phys. Lett.* 17 (2000) 595.
- [11] J.E. Prieto, Ch. Rath, S. Muller, L. Hammer, K. Heintz, R. Miranda, *Phys. Rev. B* 62 (2000) 5144.
- [12] L. Gomez, J. Ferron, *Phys. Rev. B* 64 (2001) 033409.
- [13] D. Farias, M.A. Nino, J.J. de Miguel, R. Miranda, J. Morse, G. Bozzolo, *Appl. Surf. Sci.* 219 (2003) 80.
- [14] M.C. Xu, H.J. Qian, F.Q. Liu, K. Ibrahim, W.Y. Lai, S.C. Wu, *Chin. Phys. Lett.* 17 (2000) 49.
- [15] M.C. Xu, H.J. Qian, F.Q. Liu, K. Ibrahim, W.Y. Lai, S.C. Wu, *Solid State Commun.* 117 (2001) 327.
- [16] S. Muller, J.E. Prieto, C. Rath, L. Hammer, R. Miranda, K. Heinz, *J. Phys.: Condens. Matter* 13 (2001) 1793.
- [17] P.O. Gartland, B.J. Slagsvold, *Phys. Rev. B* 12 (1975) 4047.
- [18] F. Baumberger, A. Tamai, M. Muntwiler, T. Greber, J. Osterwalder, *Surf. Sci.* 532 (2003) 82.
- [19] S. Esch, M. Hohage, T. Michely, G. Comsa, *Phys. Rev. Lett.* 72 (1994) 518.