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

M.C. Xu [a,*], H.J. Qian [b], F.Q. Liu [b], K. Ibrahim [b], W.Y. Lai [c], H.J. Gao [a]

[a] *Nanoscale Physics and Device Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*
[b] *Synchrotron Radiation Laboratory, Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100039, China*
[c] *State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

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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.

Keywords: Surface alloy; Surface state; Core level shift; Surfactant-assisted epitaxy; Lead; Copper; Cobalt

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

* Corresponding author. Tel.: +86 10 82648048; fax: +86 10 62556598.
E-mail address: mcxu@aphy.iphy.ac.cn (M.C. Xu).

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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 × 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(1 1 1) 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(1 1 1), forming the Pb–Cu surface alloy [6]. A Monte-Carlo simulation for the Pb/Cu(1 0 0) surface superstructure shows that the surface alloy c(4 × 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(1 1 1) [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(1 1 1) 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(1 1 1). Furthermore, Pb–Co surface alloy was also observed during the surfactant-assisted Co film epitaxy growth on Cu(1 1 1) 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(1 1 1) 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(1 1 1) 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(1 1 1) 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(1 1 1) 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)