



# Significant surface flattening effect by Au addition for Cu growth on $\text{Cu}_3\text{Au}(001)$



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## ABSTRACT

To prepare a flat surface of Cu film on  $\text{Cu}_3\text{Au}(001)$ , we utilized the effect of Au addition to Cu, and investigated the dependence of the growth mode on the amount of Au added. We grew  $\text{Cu}-x\%\text{Au}$  ( $x = 0-20$ ) films on  $\text{Cu}_3\text{Au}(001)$  underlayers by co-deposition and observed the surface morphology by scanning tunneling microscopy. For Cu film without Au addition, three-dimensional islands were observed on the surface while flat two-dimensional surfaces were observed for Cu film with only 2.5% Au addition. This difference in the growth mode was found to be due to surface segregation of Au revealed by *in situ* Auger electron spectroscopy. It was considered that the Au atoms acted like a surfactant and avoided three-dimensional island growth by suppression of the accumulation of epitaxial strain in  $\text{Cu}-x\%\text{Au}$  films. However, the terrace size decreased with  $x$ . This decrease was thought to be due to an increase in an effective Ehrlich–Schwoebel barrier. The surface flattening effect by addition of another element would be obtained in other systems as well by employing a suitable element.

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## 1. Introduction

Artificially structured materials often show novel and interesting properties, particularly ultrathin films and multilayer films, which have been intensively studied for the purposes of fundamental investigation and new device development. For instance, non-existing materials in thermal equilibrium such as  $\text{L}_{10}\text{-FeAu}$  [1] and  $\text{hcp-CoRu}$  [2] can be fabricated epitaxially by using particular deposition techniques. The electronic and magnetic properties of such materials are very sensitive to their structure (thickness, strain, substrate material, etc.). Novel functional materials consisting of only 3d elements such as  $\text{L}_{10}\text{-FeCo}$  [3] and  $\text{L}_{10}\text{-FeNi}$  [4] have attracted attention, mainly in the field of magnetics. These materials have a large uniaxial magnetic anisotropy and should form a perpendicularly magnetized film. In order to investigate systematically physical properties of such alloys, samples should be precisely deposited on suitable underlayers. A Cu surface is appropriate for such deposition because it has good lattice matching to 3d alloys. However, preparing Cu film with sufficient surface flatness is very difficult, and there have been few reports on the preparation of such a flat Cu film [5,6]. Therefore, development of a growth process for obtaining a sufficiently flat Cu film is an important issue.

In most metal-on-metal epitaxy, interlayer surface diffusion from an upper terrace to a lower one is harder than diffusion on a terrace due to the presence of an additional energy barrier to diffuse across a step edge, so-called Ehrlich–Schwoebel (ES) barrier [7,8]. This results in the nucleation of new islands on other islands and consequently in the

formation of mound (or pyramid)-type islands [9]. The ES barrier ( $E_{ES}$ ) is described as a diffusion barrier descending over a step edge ( $E_{ds}$ ) minus the diffusion barrier on the terrace ( $E_d$ ). Some of surfactant elements have been shown to reduce  $E_{ES}$  by increasing  $E_d$ . This enhances the layer-by-layer growth. Such surfactants include Sb in the growth of Ag on Ag(111) [10], Pb in the growth of Cu on Cu(111) [11], and Bi in the growth of Co on Au(111) [12]. Theoretical calculations have recently indicated that co-deposited impurities also affect the growth morphology [13–15]. In the study reported here, we obtained a two-dimensional flat surface by adding Au during Cu growth on  $\text{Cu}_3\text{Au}(001)$  and investigated the dependence of the growth mode on the amount of Au added.

## 2. Experiments

All the films were deposited in an ultrahigh vacuum molecular beam epitaxy system with a base pressure of  $1 \times 10^{-8}$  Pa. Atomically flat  $\text{Cu}_3\text{Au}(001)$  underlayers were prepared by deposition of Cu (50 nm) at 500 °C on a Au (20 nm)/Fe (1 nm)/MgO(001) substrate [16].  $\text{Cu}-x\%\text{Au}$  ( $x = 0-20$ , atomic percent) films with a thickness of 50 nm were grown on the  $\text{Cu}_3\text{Au}(001)$  layer by co-deposition using Knudsen cells. The growth temperature was set at 100 °C to achieve both promotion of surface diffusion and avoidance of significant interlayer diffusion between the growth film and the  $\text{Cu}_3\text{Au}$  [17]. The alloy compositions were estimated from the deposition rates of the Cu and Au, and their validity was confirmed from the lattice parameters estimated by using *ex situ* X-ray diffraction and Vegard's law. The deposition rate of Cu was fixed (0.119 Å/s) for all films, and the rate of Au was adjusted to be between 0.004 Å/s (Cu–2.5% Au) and 0.043 Å/s (Cu–20% Au). The growth mode in the primary stage was monitored by intensity oscillation of

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reflection high-energy electron diffraction (RHEED). After finishing the growth of a Cu- $x\%$ Au film, low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) were performed *in situ* to investigate the surface structure and morphology. The chemical composition of each surface was investigated by *in situ* Auger electron spectroscopy (AES) using a 3-keV electron beam directed perpendicular to the film surface. The surface composition was estimated from the peak-to-peak height ratio of Au *NOO* (239 eV) and Cu *LMM* (915 eV) using a relative sensitivity factor ( $S_{\text{Au},239/\text{Cu},915}$ ), which was determined by AES measurements of pure Au and pure Cu films and consideration of the backscattering factors [18,19].

### 3. Results

Fig. 1 shows the RHEED intensity oscillations during the primary stage of Cu- $x\%$ Au growth. Intensity  $I$  was normalized by  $I_0$ , the intensity before shutter opening. The Cu growth without Au addition showed 10 periods of RHEED oscillation as shown in Fig. 1(a). This indicates that the growth mode changed from layer-by-layer to three-dimensional (3D) after disappearance of the oscillation. The Cu-2.5%Au growth showed longer oscillation (Fig. 1(b)). The oscillation duration increased with the amount of Au added (Fig. 1(c)–(e)). Since the amplitude of RHEED oscillation changes with even a slight change in the incidence angle [20,21], a comparison of the amplitudes between these oscillations is meaningless.

Epitaxial growth was confirmed by RHEED for all films. Fig. 2 shows LEED patterns.  $(1 \times 1)$  patterns of fcc-(001) were observed for the pure Cu and Cu-20%Au films (Fig. 2(a) and (e)) while superstructure spots appeared for the Cu-2.5%Au, Cu-5%Au, and Cu-10%Au films (Fig. 2(b), (c), and (d)). The crystal orientation and distance between spots indicate that the superstructure spots originated from  $c(2 \times 2)$  surface structures.

Fig. 3(a)–(e) shows STM images of surfaces of Cu- $x\%$ Au films with a thickness of 50 nm. 3D islands were observed on the Cu film without Au (Fig. 3(a)) while two-dimensional (2D) flat surfaces were observed on the Au-added Cu films (Fig. 3(b)–(e)). Fig. 3(f) shows the dependence of the root mean square (RMS) of the surface roughness on the amount of added Au. The RMS roughness was estimated from several STM images for different regions in the  $195 \times 195 \text{ nm}^2$  scan area. The addition of even only 2.5%Au dramatically changed the surface morphology and flatness. However, the terrace sizes decreased with an increase in the Au amount, which led to an increase in the surface roughness.

Surface segregation often affects the growth morphology, and Au atoms tend to segregate on the surface of Cu–Au alloys [22] due to the low surface energy of Au. Thus, surface segregation of Au probably

occurred during our deposition and led to the formation of 2D flat surfaces. Fig. 4(a) shows the Au composition of the Cu- $x\%$ Au films estimated from AES measurements, i.e., the average composition near the surface depending on the escape depth of Auger electrons. The experimental value was larger than the nominal composition, indicating surface segregation of Au. Foiles theoretically calculated that Cu- $x\%$ Au(001) with  $x = 0.01$  to 3 forms a  $c(2 \times 2)$  structure with a 1/2 monolayer of Au at room temperature in thermal equilibrium [23]. This agrees with the result of our LEED observation and supports the occurrence of Au segregation in our Cu- $x\%$ Au films. On the assumption that the Au composition of the topmost layer ( $x_s$ ) is 50% and that those of the other layers are equal to  $x$ , we simulated the Au composition ( $C_{\text{AES},\text{sim}}$ ) using the calculated AES intensities ( $I_{\text{Au}}, I_{\text{Cu}}$ ) by following equations:

$$I_{\text{Au}} \propto \int_0^t x \exp\left(-\frac{z}{\lambda_{\text{Au}}}\right) dz = \int_0^1 x_s \exp\left(-\frac{z}{\lambda_{\text{Au}}}\right) dz + \int_1^t x \exp\left(-\frac{z}{\lambda_{\text{Au}}}\right) dz, \quad (1)$$

$$I_{\text{Cu}} \propto \int_0^t (100-x) \exp\left(-\frac{z}{\lambda_{\text{Cu}}}\right) dz = \int_0^1 (100-x_s) \exp\left(-\frac{z}{\lambda_{\text{Cu}}}\right) dz + \int_1^t (100-x) \exp\left(-\frac{z}{\lambda_{\text{Cu}}}\right) dz, \quad (2)$$

$$C_{\text{AES},\text{sim}} = \frac{\lambda_{\text{Cu}} I_{\text{Au}}}{\lambda_{\text{Cu}} I_{\text{Au}} + \lambda_{\text{Au}} I_{\text{Cu}}} \quad (3)$$

where  $t$  is the thickness of the Cu- $x\%$ Au films,  $z$  is the depth from the top of the surface, and  $\lambda$  is the escape depth of electrons ( $\lambda_{\text{Au}} = 3.3$  monolayers at a kinetic energy of 239 eV, and  $\lambda_{\text{Cu}} = 6.1$  monolayers at 915 eV [24]). The  $C_{\text{AES},\text{sim}}$  was estimated with correction of escape depths as described in Eq. (3) to compare it to the experimental data corrected using the relative sensitivity factor including the difference in escape depths. The  $C_{\text{AES},\text{sim}}$  was in acceptable agreement with the experimental composition despite the simple calculation. In order to verify the simulation, we also calculated  $x_s$  by using Eqs. (1)–(3) and using the Au composition experimentally estimated by AES; this composition was substituted into  $C_{\text{AES},\text{sim}}$  in Eq. (3). As shown in Fig. 4(b), the calculated  $x_s$  was around 50% except  $x = 0$ . Somewhat larger values of  $x_s$  than 50% for  $x \geq 5$  are probably attributed to a larger Au composition than  $x$  in the subsurface layers. This Au enriched subsurface may not have energetically favored a  $c(2 \times 2)$  surface structure for  $x = 20$  (see Fig. 2(e)) as a  $c(2 \times 2)$   $\text{Cu}_{50}\text{Au}_{50}$  surface is on a pure Cu subsurface in  $\text{Cu}_3\text{Au}(001)$  [25]. Therefore, the Au composition of the topmost layer of Cu- $x\%$ Au films probably was close to 50%. This segregation apparently changed the growth mode and the surface flatness.

### 4. Discussion

For the growth of Cu without Au on  $\text{Cu}_3\text{Au}$ , the 3D island growth apparently started after the layer-by-layer growth of about 10 monolayers to relieve the strain energy resulting from the large lattice mismatch of  $-3.3\%$  (Stranski–Krastanov growth).

In contrast, no 3D islands were observed for the Cu-2.5%Au film despite a slight difference in the lattice parameter compared to that of pure Cu film. This indicates that the change in the growth mode was caused by Au segregation.

Camarero et al. investigated the atomistic mechanism of the surfactant effect of Pb in homoepitaxy on Cu(111) by using a combination of experiments and simulations [11]. They found that deposited Cu adatoms quickly get buried and then diffuse under the Pb layer by exchanging sites with other Cu atoms constituting the substrate. Suppressing faster hopping diffusion on terraces and promoting slower exchange diffusion under the Pb layer effectively increase the diffusion barrier on a terrace ( $E_d$ ), and thus the ES barrier ( $E_{\text{ES}} = E_{\text{ds}} - E_d$ ) is reduced and the layer-by-layer growth is enhanced. An increase in  $E_d$  also induces a high nucleation density [26] which is thought to easily

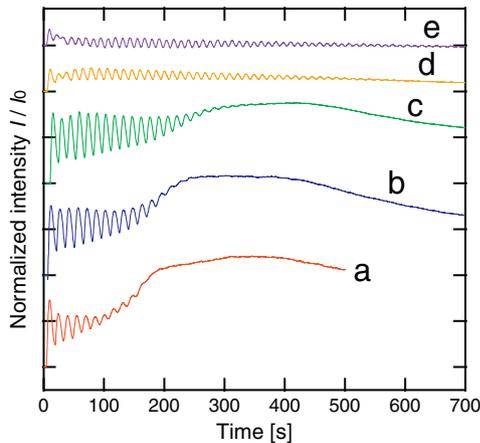
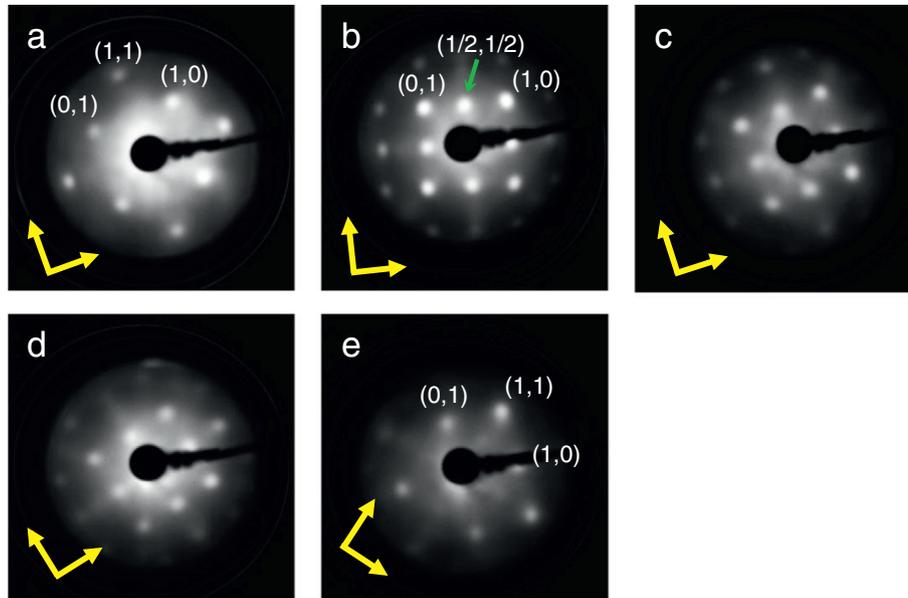
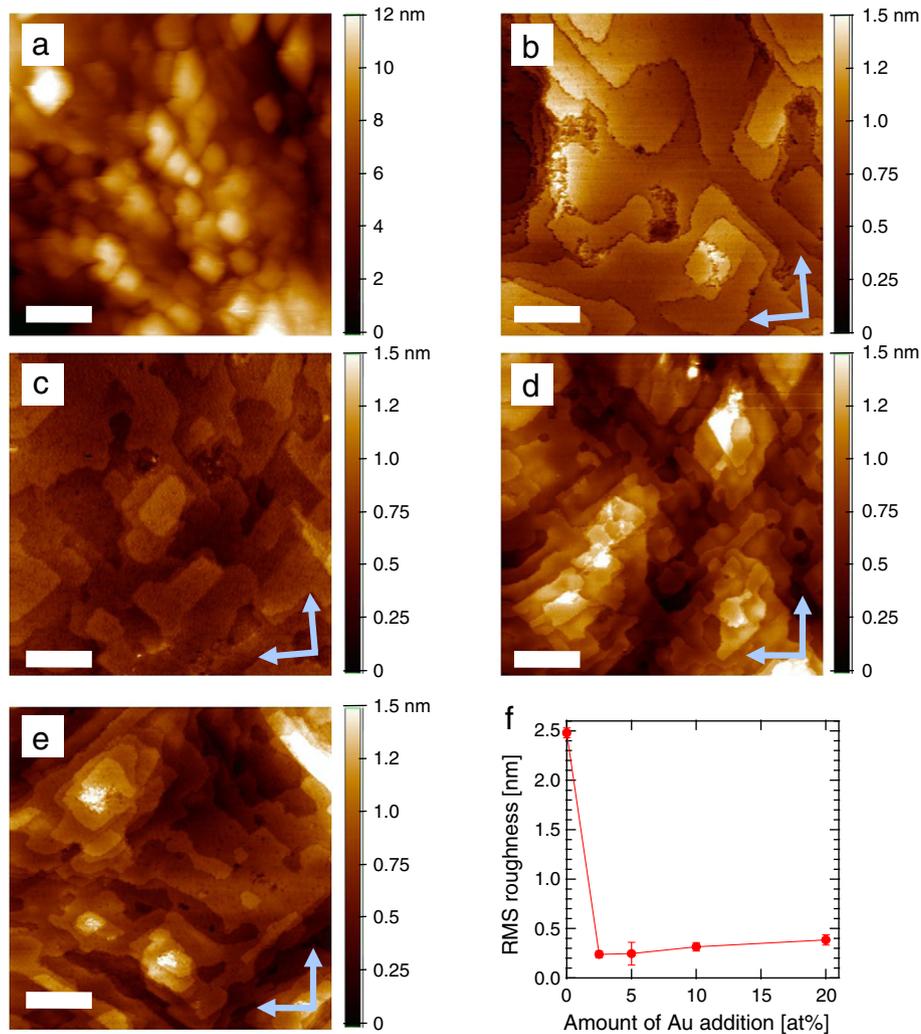


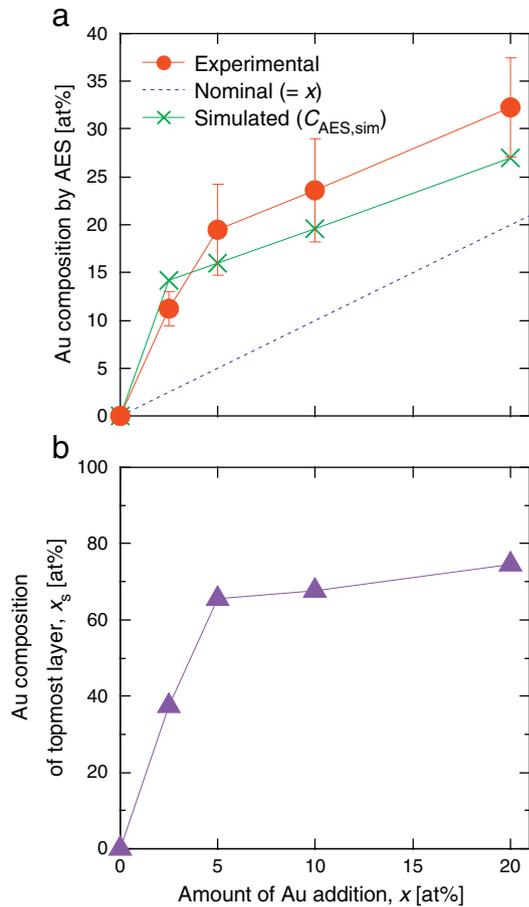
Fig. 1. RHEED intensity oscillations during primary growth stage: (a) Cu, (b) Cu-2.5%Au, (c) Cu-5%Au, (d) Cu-10%Au, and (e) Cu-20%Au. Each division on vertical axis corresponds to 1.



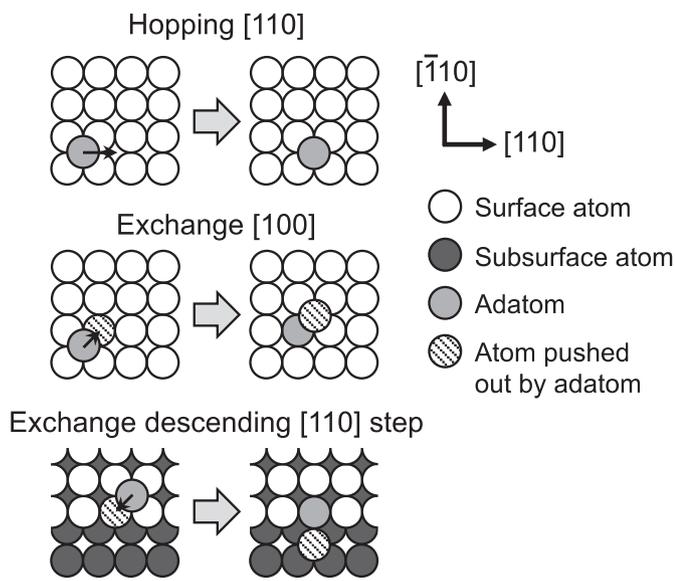
**Fig. 2.** LEED patterns after 50-nm-thick growth: (a) Cu, (b) Cu–2.5%Au, (c) Cu–5%Au, (d) Cu–10%Au, and (e) Cu–20%Au. Double arrows represent crystal orientations of [100] and [010] on fcc-(001) surface. Reciprocal space indices next to spots are based on  $p(1 \times 1)$  of fcc-(001). Incident beam energies were (a) 125.4 and (b)–(e) 113.5 eV.



**Fig. 3.** Typical STM images of top of surface after 50-nm-thick growth: (a) Cu, (b) Cu–2.5%Au, (c) Cu–5%Au, (d) Cu–10%Au, and (e) Cu–20%Au. (f) Dependence of RMS roughness on amount of Au added. Scan area was  $195 \times 195 \text{ nm}^2$ . Scale bars in STM images correspond to 40 nm; double arrows represent [100] and [010] directions, which were roughly determined by eye from geometry between samples and scanner. RMS roughness was estimated from several STM images for different areas.



**Fig. 4.** (a) Au composition estimated by AES measurements in Cu- $x$ %Au films after 50-nm-thick growth (circles with line). Dashed line shows nominal composition corresponding to amount of Au addition ( $x$ ). Crosses with line show simulated values ( $C_{AES,sim}$ ) as estimated from AES intensities on assumption that Au composition is 50% for only topmost layer and that it is equal to  $x$  for all other layers. (b) Au composition of topmost layer ( $x_s$ ) calculated from experimental values plotted in (a).



**Fig. 5.** Schematic illustration of typical diffusion processes on fcc-(001) surface. Hopping in [110] direction (top) and exchange in [100] direction (middle) are diffusions on a terrace. Close-packed [110] step is energetically favorable, and diffusion descending over step edge is taken place by exchange process (bottom). Exchange occurs due to adatom pushing out a neighboring atom under the adatom.

**Table 1**

Calculated activation energy barriers (eV) for diffusion of Au adatoms on Au(001) and Cu(001) surfaces as extracted from reports by Kim et al. [28]. Terrace diffusion barriers for hopping process in [110] direction and exchange process in [100] direction and diffusion barrier for exchange process descending over [110] step edge are shown. Barrier on Cu(001) was calculated only for terrace diffusion with [110] hopping.

Terrace diffusion		Exchange descending [110] step
Hopping [110]	Exchange [100]	
0.531 (on Au)	0.388 (on Au)	0.515 (on Au)
0.554 (on Cu)		

introduce a misfit dislocation when the coalescence occurs. Kamiko et al. reported that Bi surfactant enhanced the layer-by-layer growth of Co on Au(111) and that an in-plane lattice parameter of Co decreased immediately after starting the growth compared to growth without Bi surfactant [12]. This indicated that the Bi surfactant increased  $E_d$  and nucleation density and that the epitaxial strain was substantially suppressed by introducing a misfit dislocation during the initial growth stage.

These reports indicate that Au atoms acted like a surfactant in our study and suppressed the accumulation of epitaxial strain in the Cu- $x$ %Au ( $x \neq 0$ ) films, and thus 3D island growth did not start. However, no surfactant effect was indicated for the pure Cu growth although there were Au atoms in the Cu<sub>3</sub>Au underlayer; this is considered to be due to stability of an ordered Cu<sub>3</sub>Au phase [27].

Furthermore, the reduction in terrace size with the Au amount can be explained by energy barriers for diffusion processes. The findings of Camarero et al. [11] suggest that deposited Cu atoms slowly diffused under the Au-segregated topmost surface with a small ES barrier and that the Au atoms diffused on the surface in the Cu- $x$ %Au growth. In general, for an fcc-(001) surface, hopping in the [110] direction and exchange in the [100] direction (not the same process as exchange diffusion under a Pb layer [11]) are typical diffusion processes on a terrace. The step energetically favors a close-packed [110] edge compared to a [100] edge, and the exchange process is dominant for a descending step edge. These diffusion processes are illustrated in Fig. 5, and the diffusion barriers for these processes for Au atoms as calculated by Kim et al. [28] are shown in Table 1. On the assumption that Au atoms at the top of the surface hardly take place the exchange with the Cu atoms under the Au atoms due to the surface segregation tendency of Au, Au atoms are considered to diffuse on a Cu–Au terrace by the hopping and by the exchange with other Au atoms. The barrier for exchange of Au is smaller than those for hoppings of Au on Cu(001) and Au(001). This indicates that an effective ES barrier increased with  $x$  in Cu- $x$ %Au films because increases in the amounts of deposited Au adatoms and of the subsurface Au atoms enhance the contribution of the exchange process to the terrace diffusion of Au, and that consequently the terrace size decreased.

## 5. Conclusions

We performed the addition of Au during the growth of Cu films on Cu<sub>3</sub>Au(001) underlayers and investigated the dependence of the growth mode on the amount of Au added. For Cu film growth without Au addition, although 10 periods of RHEED oscillation were observed during the initial growth, large 3D islands were observed by STM after 50-nm-thick growth, indicating the Stranski–Krastanov growth due to the large lattice mismatch between Cu and Cu<sub>3</sub>Au. In contrast, flat 2D surfaces were observed in STM images for Cu film growth with only 2.5% Au addition. This change in the growth mode was found to be due to the segregation of Au, as revealed by LEED and AES. It was considered that the Au atoms acted like a surfactant and suppressed the accumulation of

epitaxial strain by introducing a misfit dislocation during the initial growth stage, so 3D island growth did not start. However, the terrace size decreased with the Au amount. This is probably attributed to an increase in an effective ES barrier, resulting from the enhancement of the contribution of the exchange terrace diffusion of Au atoms to the surface diffusion processes due to increases in the amounts of deposited Au adatoms and of subsurface Au atoms. The addition of a suitable element would probably lead to the formation of a flat 2D surface in other systems as well.

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