Structures of (001) Surface of Cu–Au Alloy as Observed by LEED

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The (001) surfaces of the Cu–Au alloy with various compositions have been prepared by depositing gold onto the surface of copper and by subsequent heating. The surface structures have been studied by LEED and compared with those of the bulk alloy crystals obtained by previous researchers.

By the present vaporization and heating method a series of the LEED patterns in the order of hexagonal, streak, $(1 \times 1)_I$, $c(2 \times 2)$ and (1×1) , have been observed with decreasing gold content. The $c(2 \times 2)$ structure corresponds to the surface structure of the bulk ordered Cu_3Au crystal, while the hexagonal structure is a new structure observed on the alloy surface.

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I. Introduction

There have been many low energy electron diffraction (LEED) studies on the surface structures of elements and simple compounds, and on the gas-adsorbed and metal-deposited surfaces. However, only a few studies were done on the surface of alloys in which an extensive solid solution forms^{(1)~(4)}. Recently the surface structure of the alloys was investigated in a wide range of the surface composition by a vaporization and heating (V. H.) method and many characteristic surface structures have been found⁽⁵⁾⁽⁶⁾. In the present study, the V. H. method for making the alloy surface was applied to the study of a Cu–Au (001) surface. Although the V. H. method has the advantage of preparing the alloy surface with various compositions, comparison of the surface structures obtained by this method with those of a bulk alloy crystal has not been made for many substances because the data of the latter are quite few. There have been several LEED studies on the (001) surface structures of the bulk Cu–Au alloy^{(2)~(4)}. In the present study the (001) alloy surfaces of the Cu–Au system were prepared by the V. H. method and their structure was investigated by LEED and Auger electron spectroscopy (AES), and the results were compared with those of the bulk alloy surfaces.

II. Experimental Procedure

The LEED system used in this study was a conventional display type having four grids in front of a fluorescent screen. Auger spectra were obtained using LEED grids as a retarding field analyzer. The accelerating voltage of primary electron beam for AES was 2.5 kV. Modulation of 6 V_{pp} was applied to obtain sufficient collector current.

A copper single crystal was grown from the melt, which was 99.998% pure. After determination of a crystal orientation by X-ray diffraction a sample with the (001) surface was prepared by spark cutting. The surface was mechanically polished by the finest emery paper and then electropolished⁽⁵⁾.

To clean the surface, argon ion bombardment was carried out at 600–1000 V and $\sim 50 \text{ mA/m}^2$ for longer than 1.2 ks (20 min). The sample was then heated by an electron bombardment from backside. Gold of 99.99% purity was evaporated from a tungsten basket which was previously out-gassed. The amount of the deposited gold was monitored by a commercial quartz crystal oscillator. The sample temperature was determined by Pt–PtRh thermocouple and thermospotmeter. Since deposited gold grew epitaxially on the (001) copper surface at room temperature the substrate was usually kept at room temperature during the deposition. The mean surface composition was determined by AES, using the peak signals from gold at 70 eV and copper at 60 eV. The heights

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of these peaks were compared with the standard peak from the pure element. It was not possible, however, to obtain a pure gold signal from the surface in this experiment, even after gold was deposited as thick as 100 nm on the copper surface. A method of correction to get a standard gold signal was applied⁽⁵⁾.

The other experimental arrangements and the method of the determination of the surface composition are the same as those in a previous study⁽⁵⁾.

III. Results

1. LEED observation and AES analysis

When gold was deposited to a thickness of more than 1.0 nm onto the (001) copper surface, LEED patterns were observed in the order of hexagonal, streak, (1×1) I, $c(2 \times 2)$ and (1×1) structures after successive heat treatments. Table 1 shows a series of heat treatments after depositing gold to a thickness

Table 1 A series of surface structures and mean surface compositions on the (001) surface of Cu-Au alloy.

	Treatment	Surface structure	Mean surface composition (at% Au)
a	before deposition	(1×1)	0
b	after deposition	hexagonal	53
	423 K 0.3 ks (150°C 5 min)	hexagonal	53
c	423 K 0.6 ks (150°C 10 min)	streak	50
	423 K 1.2 ks (150°C 20 min)	streak	31
d	423 K 2.4 ks (150°C 40 min)	(1×1) I	25
	423 K 4.8 ks (150°C 80 min)	(1×1) I	
	423 K 9.6 ks (150°C 160 min)	$c(2 \times 2)$	14
	473 K 0.6 ks (200°C 10 min)	$c(2 \times 2)$	
e	523 K 0.6 ks (250°C 10 min)	$c(2 \times 2)$	10
	573 K 0.6 ks (300°C 10 min)	$c(2 \times 2)$	
	673 K 0.6 ks (400°C 10 min)	$c(2 \times 2)_w + (1 \times 1)$	4
f	773 K 0.6 ks (500°C 10 min)	(1×1)	3

of 3.3 nm, the observed LEED pattern as well as the mean surface composition. It is shown that gold content of the alloy surface is decreased as the heat treatment proceeds and the LEED pattern changes with changing surface composition.

In the following the experimental results obtained from the sample with 3.3 nm thick gold are described in detail. Photograph 1 shows a series of LEED patterns and Fig. 1 shows AES spectra corresponding to them. When gold was deposited onto the clean (001) copper surface (Photo. 1(a)), a hexagonal pattern shown in Photo. 1(b) was obtained. Diffraction spots due to the (1×1) structure from the substrate disappeared. This fact means that the (001) substrate is covered with the surface having a hexagonal structure. The mean surface composition is 53 at% Au. After heating at 423 K (150°C) for 0.9 ks (15 min) the hexagonal pattern changed into a streak pattern shown in

Fig. 1 A series of Auger spectra on the (001) surface of Cu-Au alloy and the mean surface composition. Notations of (a)-(f) correspond to those of (a)-(f) in Photo. 1, respectively.

Photo. 1 A series of LEED patterns on the (001) surface obtained after deposition of gold to a thickness of 3.3 nm and subsequent heat treatments. Accelerating voltage is 130 V. (a) Clean surface; (b) hexagonal pattern after depositing gold; (c) streak pattern, after heating at 423 K for 0.9 ks (15 min); (d) $(1 \times 1)_I$, after heating at 423 K for 4.5 ks (75 min); (e) $c(2 \times 2)$, after successive heating at 423 K for 18.9 ks (315 min), 473 K for 0.6 ks (10 min) and 523 K for 0.6 ks; (f) after further successive heating at 573 K for 0.6 ks, 673 K for 0.6 ks and 773 K for 0.6 ks.

Photo. 1(c). The streaks run parallel to the $\langle 10 \rangle^*$ direction. The mean surface composition is 50 at% Au. After heating at 423 K for 4.5 ks (75 min) in total, a pattern with a $(1 \times 1)_I$ structure resulted as shown in Photo. 1(d). Although the periodicity of the structure is in agreement with that of the pure (001) copper surface the mean surface composition is 25 at% Au. Successive heatings at 423 K for 10.8 ks (3 h), at 473 K for 0.6 ks (10 min) and at 523 K for 0.6 ks changed the LEED pattern into that shown in Photo. 1(e). It represents a $c(2 \times 2)$ structure. The mean surface composition is 10 at% Au. After further successive heatings at 573 K for 0.6 ks, at 673 K for 0.6 ks and at 773 K for 0.6 ks, the $\{1/2 \ 1/2\}$ extra spots of the $c(2 \times 2)$ pattern disappeared and the pattern again became a (1×1) type as shown in Photo. 1(f). The mean surface composition is 3 at% Au. After final heating at

973 K for 0.6 ks the gold signal disappeared and the LEED pattern of the (1×1) type corresponding to that of a pure (001) copper surface was obtained.

2. Influence of the thickness of deposited gold

The surface structures formed on the (001) surface are shown in a diagram in Fig. 2 as functions of the thickness of the deposited gold and the mean surface composition. Since a pure gold surface was not obtained even by the deposition of gold as thick as 10 nm, the surface structure in the gold rich region could not be investigated. The hexagonal pattern was observed in the composition range between 40 and 60 at% Au. When gold was deposited to a thickness of less than 1.0 nm, it was not possible to observe the hexagonal pattern, probably because the gold content in the alloy was insufficient. The $c(2 \times 2)$ structure was stable in

Fig. 2 Surface structures on the (001) surface as functions of the thickness of deposited gold and the mean surface composition. The composition range in which the bulk ordered phases Cu_3Au , CuAuI and CuAuII form is shown.

the composition range between 4–15 at% Au. The diagram shows that the appearance of the (001) surface structures of the Cu–Au alloy obtained by means of the V. H. method depends only on the surface composition and is independent of the thickness of deposited gold.

3. Influence of the substrate temperature and deposition rate on the LEED pattern

In a previous study⁽⁵⁾, when gold was deposited to a thickness of 3.3 nm onto a (111) or (110) copper surface at room temperature, nothing could be observed in the fluorescent screen for the LEED observation. It was necessary to raise the substrate temperature. In the present study, when gold was deposited onto the (001) surface to a thickness of 3.3 nm and 1.1 nm in the temperature range of 623 ~ 433 K, LEED patterns were observed in the order of $(1 \times 1) \text{I} \rightarrow c(2 \times 2) \rightarrow (1 \times 1)$ and the hexagonal and streak patterns were not observed. This is thought to be due to an insufficient gold content to form the hexagonal and the streak structures, because the deposited gold in this case has diffused into the substrate crystal kept at high temperature.

A series of the surface structures mentioned above were not influenced by the deposition rate which ranged between $2 \times 10^{-12} \sim 2.3 \times 10^{-11}$ m/s (0.12–1.4 nm/min). Thus, the appearance of the structures on the (001) Cu–Au

alloy surface seems to be only influenced by the surface composition and little influenced by the substrate temperature and the deposition rate.

IV. Discussion

1. LEED patterns

(1) Hexagonal pattern

The surface structure corresponding to the hexagonal LEED pattern seems to be that of a (111) section of the *fcc* crystal with a random substitution of copper atoms by gold atoms. The ratio of the interatomic distances in the hexagonal structure and the (1×1) structure is determined by measuring the distances between the diffraction spots in Photo. 1(a) and (b) to be $a_{\text{hex}}/a_{(1 \times 1)}$ is 1.075 ± 0.019 . If we assume that the lattice constant of the (1×1) surface structure is equal to that of the pure bulk copper crystal, it turns out to be $a_{\text{hex}}/a_{\text{fccCu}}$. While the ratio of the interatomic distances of pure gold and copper in bulk state $a_{\text{fccAu}}/a_{\text{fccCu}}$ is 1.128, i.e. $a_{\text{Au}} > a_{\text{hex}} > a_{\text{Cu}}$. This means that alloying of gold into copper in the hexagonal structure takes place.

The LEED pattern shown in Photo. 1(b) is thought to be a result of the superposition of two equivalent domains of the hexagonal structure rotated by $\pi/2$ rad with each other as shown in Fig. 3. The orientation relationship of the domains with the (001) copper substrate is as follows: $[10]_{\text{hex}}//[10]_{\text{Cu}(001)}$ and $[10]_{\text{hex}}//[01]_{\text{Cu}(001)}$. Confirmation of the existence of the

Fig. 3 Equivalent hexagonal net domains on the (001) surface. The large solid circles represent the hexagonal net and the small open circles represent the (001) net of the *fcc* substrate.

Photo. 2 Hexagonal LEED patterns obtained after depositing gold onto the (001) copper surface. LEED patterns of (a) and (b) were observed in different areas of the sample (150 V). (c) and (d) were observed in different areas of another sample (130 V).

domains is made by another experiment, shown in Photo. 2. The LEED patterns shown in Photo. 2(a) and (b) were obtained from the different areas of the same sample (the accelerating voltage: 150 V). The two patterns show that the diffraction spots along the inner circle in the latter are seen to be alternately weak. It seems that the one type of the domain is predominant within the irradiated area of the incident beam. We sometimes observed LEED patterns shown in Photo. 2(c) and (d) in the different area of the sample (the accelerating voltage: 130 V). The pattern in Photo. 2(d) is due to one type of the domain.

The (5×1) or (20×5) structure obtained on a pure (001) gold surface has been interpreted as monolayer of a distorted hexagonal structure on the (001) surface^{(7)~(9)}. Similar hexagonal structure was obtained on a gold overlayer on the copper (001) surface⁽⁹⁾. But the hexagonal structure on the alloy surface obtained in the present work does not have the distorted hexagonal symmetry. In addition,

the hexagonal structure seems to be formed by more than several layers with hexagonal symmetry, because the influence from the substrate of the (001) plane of the *fcc* structure cannot be observed in the LEED pattern. Thus, the hexagonal structure is a different type from those obtained on the pure gold surface and the gold overlayer on the Cu(001) surface.

In the case of film growth in ultrahigh vacuum, epitaxial growth of a few *fcc* metals with the (111) orientation was observed on alkali-halide crystals cleaved parallel to (001)⁽¹⁰⁾. At the initial stage the deposited metals remain in discontinuous island state. Although the hexagonal LEED pattern shows the same symmetry of the (111) orientation of the *fcc* metal on the (001) surface, the diffraction spots due to the substrate are not observed in the LEED pattern shown in Photo. 1(b). The hexagonal structure must therefore be the surface structure covering all over the (001) copper surface, although non-uniform growth

of the hexagonal structure might take place on the surface.

(2) Streak pattern

The broad streaks observed in Photo. 1(c) resemble to those observed in a LEED pattern of the (110) Cu–Au surface⁽⁵⁾. On the (110) surface the streak pattern was explained by considering the existence of a furrowing which was disordered and embryonic⁽¹¹⁾. However, on the (001) surface, it is difficult to consider such a three-dimensional furrowing state during the two-dimensional transformation from the hexagonal structure to the (1×1) I structure. Further study will be required to clarify the phenomena.

(3) (1×1) I pattern

Diffraction spots of the (1×1) I pattern shown in Photo. 1(d) are broad. The appearance of this ill-defined LEED pattern may be due to the non-uniform small mosaic domains which are formed during the transformation from the hexagonal structure to the (1×1) I structure. The periodicity of the structure is the same as that of the clean copper surface. The structure can be explained assuming a random substitution of copper by gold atoms.

(4) $c(2 \times 2)$ pattern

The surface structure of $c(2 \times 2)$ for the (001) surface corresponds to the section of the bulk crystal in which the ordered Cu_3Au ($L1_2$ -type) structure forms. The range of the mean surface composition exhibiting this surface structure, however, is shifted to the copper rich side compared with that of the ordered structure of the bulk crystal. We believe that the $c(2 \times 2)$ structure corresponds to the section of the ordered Cu_3Au structure of the bulk crystal by the following reasons; (1) on the (110) and (111) surfaces of the Cu–Au system, surface structures corresponding to the section of the ordered structure of the bulk crystal have been observed in the copper rich region compared with the composition exhibiting the bulk ordered structure⁽⁵⁾, (2) the LEED pattern of the $c(2 \times 2)$ structure has been observed for the bulk Cu_3Au crystal^{(2)~(4)}.

2. Influence of the thickness of deposit, the deposition rate and the substrate temperature on the LEED pattern

It has been shown that the appearance of the characteristic surface structures is little influenced by the thickness of the deposited gold and the deposition rate. From this fact we can expect that similar surface structure of alloy crystal will be formed as a function of only the surface composition.

When gold was deposited onto a (110) or (111) surface of copper at room temperature it did not grow epitaxially⁽⁵⁾. On the other hand, it grows epitaxially on the (001) surface of copper as shown in the present work. It may be noted that, according to Palmberg and Rhodin⁽⁹⁾, appreciable ordering also occurs on the (001) surface at room temperature. These facts suggest that ordering kinetics on the surfaces is dependent on the surface orientation.

3. Comparison of the surface structures obtained by means of the V. H. method and the ordinary method

There have been several LEED studies on the (001) surface structure of the bulk Cu–Au alloy crystal^{(2)~(4)}. Surface structures obtained from the bulk crystal and those obtained by the present V. H. method are shown in Table 2. For the bulk alloy crystal the surface structures have been obtained at the stoichiometric composition. On the other hand, in the present work the surface structures are obtained in the wide range of the composition, although the gold rich region remains unexamined. Accord-

Table 2 Surface structures on the (001) surface of Cu–Au alloy which is prepared by the ordinary method in the previous work and the V.H. method in the present work.

	Previous works	Present work
Au	(5×1) , (20×5)	
CuAu_3	(1×1)	hexagonal streak
CuAu		(1×1) I
Cu_3Au	$c(2 \times 2)$	$c(2 \times 2)$
Cu	(1×1)	(1×1)

ing to Table 2 the $c(2 \times 2)$ structure appears in the both columns and it seems to arise from an identical surface structure. The $c(2 \times 2)$ LEED pattern was also observed on the alloy crystal obtained by depositing gold onto a single crystal film of copper and by subsequent annealing⁽⁹⁾, i.e. the $c(2 \times 2)$ structure is stable on the (001) surface of Cu–Au alloy independent of the method for preparing the alloy sample. On the other hand, the hexagonal structure obtained by the V. H. method has not been found on the surface of the bulk crystal. Since no investigation has been carried out on the bulk crystal in the composition range where the hexagonal structure is formed, it is necessary to confirm the existence of the hexagonal structure in the bulk crystal.

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