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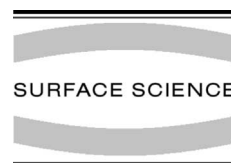
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Surfactant-mediated growth of AuAl_2 film on a decagonal $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal

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Abstract

In an effort to produce an epitaxial quasicrystalline film of simple substances, Au was deposited on the quasiperiodic surface of a decagonal $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal. In the case of a submonolayer deposition, the Au layer is crystallized with annealing and transformed into a multiply twinned AuAl_2 crystalline layer with (1 1 0)-oriented surface. This was not the case for multilayer Au. However, predeposition of In on the quasiperiodic surface affected the behavior of the Au overlayer significantly. It was found that In acted as a surfactant and promoted the epitaxial crystallization of the Au overlayer, giving rise to the formation of multiply twinned AuAl_2 crystals with annealing. © 2001 Elsevier Science B.V. All right reserved.

Keywords: Photoelectron diffraction; Reflection high-energy electron diffraction (RHEED); Surface structure, morphology, roughness, and topography; Gold; Indium; Growth; Crystallization

1. Introduction

Recently, we have found that the depositions of submonolayer Au onto the quasiperiodic surface of a decagonal $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal and subsequent annealing give rise to a selective alloying with Al in the substrate and form an epitaxial layer of multiply twinned AuAl_2 crystals [1]. Each domain of the crystalline layer has a (1 1 0)-oriented surface and the azimuthal orientation corresponding to the tenfold symmetry of the substrate. (Note that we stretch the meaning of “epitaxy” to describe the phenomenon in which

films grown on a quasiperiodic substrate maintain the directional order of the substrate.) The decagonal $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ is known to be a two-dimensional quasicrystal with well-defined quasiperiodic planes perpendicular to the tenfold axis [2]. As already reported, the surface exposing the quasiperiodic plane (tenfold surface) is thermodynamically stable and has the same quasiperiodic structure as in the bulk [3–5].

Depositions on the quasiperiodic surface of an $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal were originally attempted to create quasicrystalline films of various materials, such as pure metals, oxides and organic compounds, since the formation of quasicrystals with desired combination of elements was expected to yield several novel phenomena or properties. Indeed, the properties of quasicrystals reported so far are quite unique. The electric conductivity is

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extraordinarily low in comparison with usual metallic alloys. It increases with increasing temperature and decreases when the structural perfection is improved. The heat conductivity is unusually low, while the hardness is very large. These properties originate from significantly modified electronic structures, such as a pseudo-gap near the Fermi level, due to the quasiperiodic order [6]. So far, however, quasicrystals have been discovered only as alloys with limited combinations of elements under restricted conditions, which suggests that the formation of quasicrystals in a desired combination of elements is thermodynamically impossible with conventional means. This is the reason why we attempted the epitaxial growth. Although we were unable to obtain the desired quasicrystalline layer of Au in a previous experiment [1], the formation of an epitaxial crystalline film of multiply twinned AuAl₂ shows that heteroepitaxy is possible, even on quasicrystal surfaces. This leaves us with the following questions. What would happen if the deposited Au layer is thicker? And what kind of layers would be formed if other elements are deposited?

In the present paper, we report the results of multilayer depositions of Au on two different surfaces, i.e. a clean tenfold surface of Al₇₂Ni₁₂Co₁₆ and a tenfold surface covered by a submonolayer In prior to the Au deposition (In-predeposited surface). In the latter case, we found that In acted as a surfactant and promoted the crystallization of the Au layer with annealing.

2. Experimental

A slice of a sample with the quasiperiodic tenfold surface was cut from a large single-grained Al₇₂Ni₁₂Co₁₆ quasicrystal, which was prepared by the floating-zone method and confirmed to be of excellent quality [7]. After mechanical polishing, the sample was transferred to a vacuum chamber, where the stable quasiperiodic surface was prepared by several cycles of sputtering (30 min bombardment of 5 keV Ar⁺ ions) and annealing (~700 K).

Au was deposited at room temperature from a liquid-nitrogen-cooled evaporator with a tungsten

basket. A quartz crystal oscillator was used as a thickness monitor. The thickness of the Au film was estimated to be ~10 ML (in the closed-packed (111) structure). The In-predeposited surface was prepared at ~700 K during the final annealing cycle of the cleaning process. The amount of In was estimated to be ~0.3 ML. The structure was investigated by reflection high-energy electron diffraction (RHEED), which is highly sensitive to long-range orders, and X-ray photoelectron diffraction (XPD), sensitive to short-range orders [8].

3. Results and discussion

Au depositions on the clean tenfold surface of Al₇₂Ni₁₂Co₁₆ yielded nothing more than a polycrystalline film. The RHEED pattern from this surface showed concentric rings regardless of the direction of the incident electron beam, which is typical of polycrystalline films. Even with increasing temperature this film did not change until re-evaporation of Au took place, which means that no structural changes occurred in the Au film. Considering the fact that, in the case of submonolayer depositions, the Au layer was transformed into the AuAl₂ crystalline layer, the growth mode of Au on the clean tenfold surface was two-dimensional at the beginning and then transformed to cluster growth, i.e. a Stranski–Kratonov type growth mode.

On the other hand, the In-predeposited surface gave rise to a significant effect on the behavior of the Au film. Although Au depositions at room temperature yielded a polycrystalline layer on the In-predeposited surface, the RHEED pattern changed drastically with subsequent annealing at 350–400 K. The appearance of clear diffraction spots indicated that the Au overlayer was recrystallized (Fig. 1(a)). Moreover, the annealing gave rise to a significant change in the XPS spectrum. As shown in Fig. 2, the Al2s peak submerged by the multilayer Au deposition became visible again. In addition, the XPS spectrum of the Au 4f emission exhibited a chemical shift of ~1.7 eV. Since no signals from Co and Ni were detected, a chemical analysis based on the relative intensity between Au 4f and Al 2s peaks would provide the

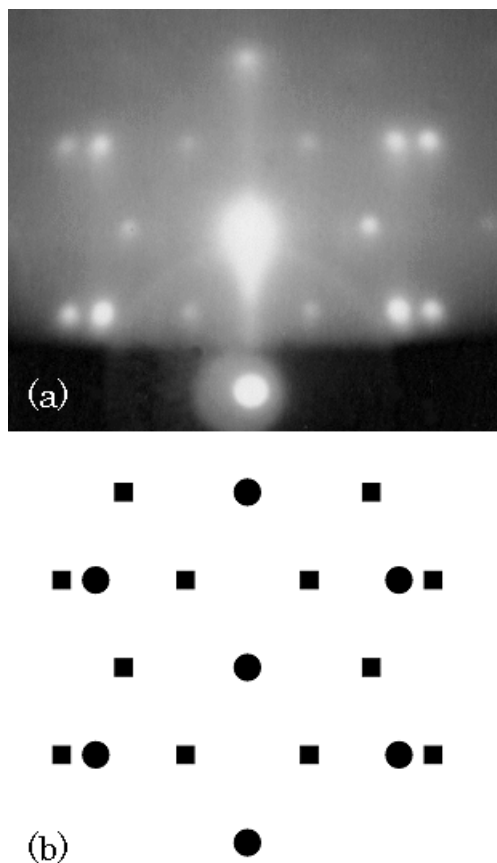


Fig. 1. (a) RHEED pattern from the Au overlayer on the In-predeposited surface of the $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal after annealing. The direction of the incident electron beam is parallel to the A2D axis, one of the twofold axes. (b) Schematic pattern of diffraction spots from an fcc crystal with the (110)-oriented surface for [001] (●) and $[-1\ 1\ 2]$ (■) incidence.

average composition of the overlayer; the Au–Al ratio was estimated to be $\sim 1:2$. These findings indicate the formation of an Au–Al alloy.

At this point, we should resolve two major questions: (1) the structure of the overlay after annealing and (2) the role of the predeposited In. Information from RHEED patterns provides us an answer to the first one. The RHEED pattern in Fig. 1(a) is observed along the A2D axis of the $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal [9] (one of the twofold axes which are perpendicular to the tenfold axis). This pattern is interpreted as a superposition of two different patterns; one is diffraction spots from an fcc crystal with the (110)-oriented surface for

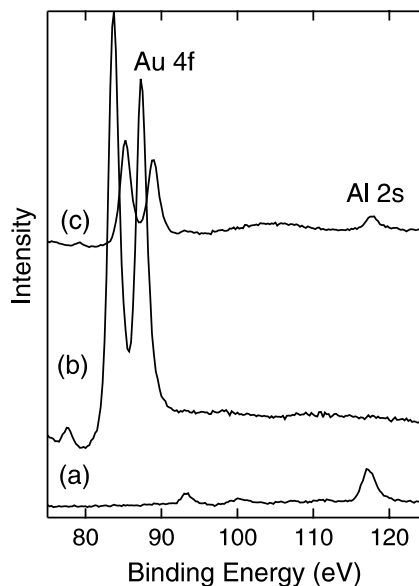


Fig. 2. XPS spectra of Au 4f and Al 2s emissions from the In-predeposited tenfold surface of the $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal: (a) before Au deposition, (b) after the deposition of ~ 10 ML Au, and (c) after the Au deposition and subsequent annealing at 350–400 K.

the [001] incidence and the other is from the same surface for the $[-1\ 1\ 2]$ incidence (Fig. 1(b)). Since the angle between [001] and $[-1\ 1\ 2]$ is very close to 36° (35.26° , to be exact), this superposition could be generated by twin-related fcc crystals with the (110)-oriented surface and different azimuthal orientations corresponding to the tenfold symmetry of the substrate. Note that, since there are 10 equivalent A2D axes perpendicular to the tenfold axis, this pattern can be observed every 36° by rotating the sample around the tenfold axis. The lattice constant estimated from the pattern is ~ 0.6 nm, which is much larger than the 0.408 nm for the fcc Au crystal and very close to the 0.5998 nm for the CaF_2 -type AuAl_2 [10,11]. XPD images of the Au 4f and Al 2s emissions show a tenfold symmetric pattern, which is consistently explained with the epitaxial layer model of multiply twinned AuAl_2 crystals [1] (Fig. 3). On the basis of these findings, we conclude that an epitaxial layer of multiply twinned AuAl_2 crystals with the (110)-oriented surface was formed, as was the case for

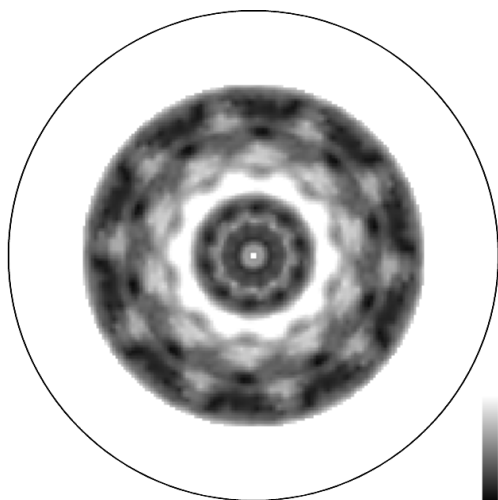


Fig. 3. Stereographic projection of the XPD image of the Au 4f emission from the Au multilayer on the In-predeposited tenfold surface after annealing. This image has been modified so as to enhance both the peak positions and the tenfold symmetry. The region of 0–360° in azimuthal angle and 0–70° in polar angle is shown in a linear gray scale. The outer circle represents the directions corresponding to the 90° in polar angle.

the submonolayer Au on the clean tenfold surface of $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$.

The other question regards the role of predeposited In. It is clear that In acts as a surfactant and induces the recrystallization. A surfactant effect of In has been observed in the homoepitaxial growth of Si(111), where In enhances the diffusivity of Si [12]. It is also known that the existence of submonolayer In induces layer-by-layer growth and suppresses the formation of twin crystals in the homoepitaxial growth of Cu(111) [13].

In the present case, the substrate is quasiperiodic. Two-dimensional growth of a crystalline phase on a quasiperiodic surface could cause an epitaxial recrystallization due to a local lattice matching between the overlayer and the substrate. Even in that case, twinning is inevitable, because the periodicity of crystals is not consistent with the quasiperiodicity. Therefore, the role of In is the suppression of cluster formation and the promotion of two-dimensional growth of Au with annealing. In other words, the existence of In changes the growth mode from Stranski–Krastanov type to Frank–van der Merwe type.

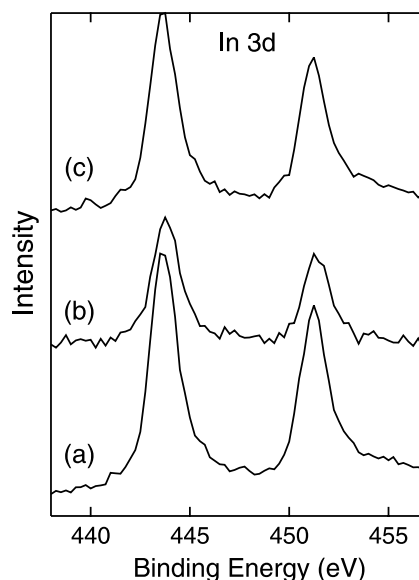


Fig. 4. XPS spectra of the In 3d emission from the In-predeposited surface of the $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal: (a) before the Au deposition, (b) after the deposition of ~ 10 ML Au, and (c) after the Au deposition and subsequent annealing at 350–400 K.

As shown in Fig. 4, the intensity of the In 3d peak decreased only a little even after the Au deposition. This is a clear contrast to the elements of the substrate (Al, Ni and Co), which became invisible in the XPS spectra due to the thick Au overlayer. Moreover, the intensity of the In 3d peak was restored to the initial value with annealing. These findings suggest that In diffused in the Au overlayer even at room temperature and emerged on top of the sample. This high diffusivity, which was due to the lower surface energy of In, could be one of the driving forces as a surfactant.

4. Conclusion

We performed multilayer depositions of Au on the tenfold surface of a decagonal $\text{Al}_{72}\text{Ni}_{12}\text{Co}_{16}$ quasicrystal in an attempt to grow quasicrystalline Au films. Although the desired film was not obtained on the clean tenfold surface, Au deposition on the In-predeposited surface and subsequent

annealing yielded an epitaxial layer of multiply twinned AuAl₂ crystals, where In acted as a surfactant and promoted two-dimensional growth of the overlayer with annealing.

Acknowledgements

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