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Structural transformations at the surface of the decagonal quasicrystal $Al_{70}Co_{15}Ni_{15}$

M. Zurkirch, B. Bolliger, and M. Erbudak
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

A. R. Kortan
Bell Laboratories, Lucent Technologies, Murray Hill, New Jersey 07974

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By using Auger electron spectroscopy and secondary-electron imaging, we show that, as a result of bombardment with 1.5-keV Ar^+ ions, Al is preferentially sputtered and the surface structure of a decagonal $Al_{70}Co_{15}Ni_{15}$ quasicrystal transforms to body-centered cubic. Annealing the sample at 700 K restores the Al concentration at the surface and, thereby, the quasicrystalline structure. Real-time observations establish the orientational relationship between the quasicrystalline and cubic surface structures, which we use to propose an atomic model of their interface. [S0163-1829(98)03246-9]

The term quasicrystal (QC) is used to describe a material with long-range quasiperiodic order, in analogy with quasiperiodic mathematical functions, and long-range orientational order. The decagonal quasicrystalline phase represents an intermediate state between icosahedral and crystalline phases, consisting of periodically stacked planes of tenfold-symmetric atomic arrangements.

The decagonal quasicrystal $Al_{70}Co_{15}Ni_{15}$ (Al-Co-Ni) has been the focus of a number of studies from which several structural models have emerged. These models are based on a periodic double-layered structure with a repeat unit of 0.41 nm along the tenfold axis. Studies using the structure-refinement method based on x-ray single-crystal data[1,2] or high-resolution transmission electron microscopy[3–5] (TEM) share the same quasilattice structure in the aperiodic plane, but differ in their chemical ordering. Secondary-electron imaging (SEI), on the other hand, is sensitive to the local order and can critically examine the short-range properties of the proposed models.[6]

Shortly after the discovery of QC's, it was recognized that the structure of icosahedral Al-Mn undergoes a phase transition when exposed to irradiation with energetic particles.[7] Similar phenomena for decagonal QC's were reported after stable samples became available. Most studies have focused on determining whether the structure of quasicrystalline Al-Cu-Co transforms into a body-centered-cubic[8] (bcc) or a face-centered-cubic structure[9] at the surface upon bombardment with 400-keV electrons. By contrast, results of a TEM study revealed that a twin-related crystalline surface layer was induced by bombardment with 4-keV Ar^+ ions and that misfit dislocations occurred at the interface.[10] Similar work has dealt with phase transformations in Al-Co-Ni induced by 120-keV Ar^+-ion irradiation.[11] According to these results, the decagonal QC is transformed into a bcc phase and, upon increasing the Ar^+-ion dose, to an ordered CsCl structure.

In this paper, we report the observation of a structural transformation occurring at the *surface* of decagonal Al-Co-Ni which can be repeated reproducibly. The changes from a tenfold-symmetric quasicrystalline to a bcc structure upon sputtering and from bcc to decagonal structure upon annealing are monitored by means of SEI and x-ray photoelectron spectroscopy (XPS). The orientational relationship between these two phases is determined and a structural model for the epitaxial growth at the interface is presented, as has recently been proposed for icosahedral $Al_{70}Pd_{20}Mn_{10}$.[12]

The experiments were performed in an ultrahigh-vacuum chamber with a total pressure in the lower 10^{-10}-Torr range. In addition to the quasicrystalline sample of area $8\times 4\ \mathrm{mm}^2$, we have also used polycrystalline samples of pure Al and Ni to calibrate the XPS measurements. XPS has been applied to determine the cleanliness of the surface of the specimen at the beginning of the experiment and its chemical composition at different stages of treatment. Chemical information in XPS was obtained by measuring the intensity of photoemitted electrons that are element specific, i.e., the core electrons of the alloy components. For this purpose, the ratio of the Ni $2p$ and Al $2p$ peak intensities was determined in the QC and compared to the corresponding value obtained using pure metals. The information depth in XPS is approximately 1–1.5 nm, determined by the mean free path of photoelectrons excited by Al K_α radiation. The escape depth of electrons used to generate the SEI patterns may be slightly longer and one can safely assume that the information originates in both cases from a surface layer of approximately the same thickness.[13]

As the details of the apparatus and the principles of the SEI technique can be found elsewhere,[14] only a short description of the experimental method is given here. SEI involves the excitation of the surface with a beam of electrons having an energy of 2000 eV. The quasielastically backscattered electrons are imaged on a hemispherical phosphorescent screen. Since elastic forward scattering dominates at energies above a few hundred eV, the scattered electrons are channeled along chains of atoms.[15] Therefore, the pattern observed on the screen represents a central projection of the atomic arrangement in real space, so SEI reproduces local structural features with angular fidelity. If the sample is rotated around an appropriate axis, the observed patterns provide three-dimensional views of the structure. In the case of structural transformations, as reported here, besides clearly identifying the surface structures before and after the transition, one can unambiguously observe the correspondence of the symmetry axes of these structures.

Figure 1 shows an SEI pattern obtained from Al-Co-Ni with the electron beam directed along the tenfold-symmetry

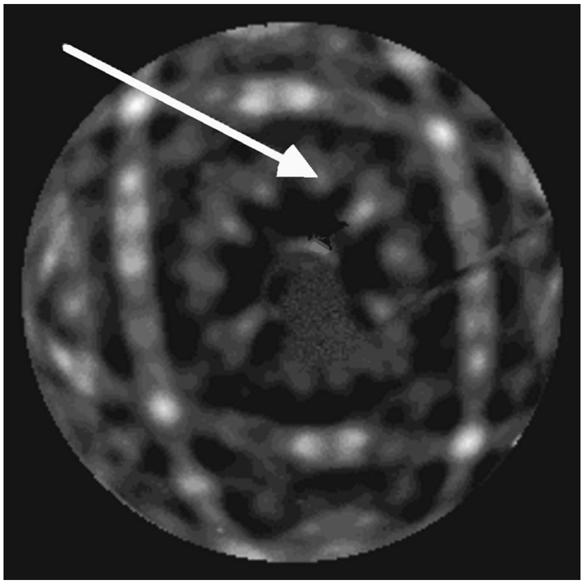

FIG. 1. A secondary-electron pattern obtained from the bulk decagonal quasicrystalline alloy $Al_{70}Co_{15}Ni_{15}$ after bombarding its surface with Ar^+ ions (1500 eV, 10^{-8} A/mm^2). The orthogonal symmetry of the pattern signals the existence of the cubic units in the (110) orientation. The portion of the pattern containing the [110] direction is obscured by the shadow of the electron gun used for the excitation. There are remnants of decagonal symmetry around the central portion of the pattern, one of which is marked by an arrow. A chemical analysis of the surface indicates a composition close to $Al_{50}(CoNi)_{50}$.

axis. The sample had previously been sputtered for 30 min with Ar^+ ions at normal incidence having a kinetic energy of 1500 eV at a current density of 10^{-8} A/mm^2. The only features with decagonal symmetry are those located on a small circle with an opening angle of 18°. One such feature is marked with an arrow. Other features of the pattern show precise *orthogonal* symmetry. Recently, a similar SEI pattern was interpreted by a direct projection of the vectors in a hemisphere connecting the nearest-neighbor atoms to a reference atom in a bcc structure with the [110] direction oriented normal to the surface.[12] In Fig. 1, the angles between the high-symmetry directions were measured and identified as those of the cubic lattice. Then, the two bright patches, which lie approximately 70° apart at the top right and bottom left of the pattern, represent the $[\overline{111}]$ and [111] directions, respectively.[16] The [010] (top left) and the [100] (bottom right) directions are separated by 90°. Hence, the overall symmetry is cubic, suggesting that a bcc layer or islands with cubic symmetry have developed at the surface. Additionally, rotation of the sample produces different views of the surface atomic structure which confirm the existence of the bcc phase. While successful imaging of the surface by SEI implies the existence of perfect orientational order in these layers, the absence of low-energy electron diffraction indicates that there is no translational long-range order.

Beneath the top few atomic layers imaged by SEI the quasicrystalline structure is still perfectly intact, which was established by reflection Laue x-ray diffraction. This means that the specimen is a bulk decagonal quasicrystal covered with a layer of bcc units, all of which must possess the identical orientation to generate the SEI pattern shown in Fig. 1. The lower limit for the thickness of the bcc layer corresponds to the information depth of SEI, which is of the order of 2 nm.[13] This layer is still thin enough to transmit the decagonal features observed at 18° which originate from the bulk quasicrystalline structure. Interestingly, XPS measurements revealed a surface composition of $Al_{50}(CoNi)_{50}$, i.e., there is a strong depletion of Al in a near-surface region caused by preferential sputtering. In fact, AlNi, AlCo, and Al_2NiCo are all well known to have the CsCl structure with a lattice constant of 0.28–0.29 nm. This is consistent with our observations, because SEI cannot differentiate the different atoms and can therefore not distinguish between bcc and CsCl structures.

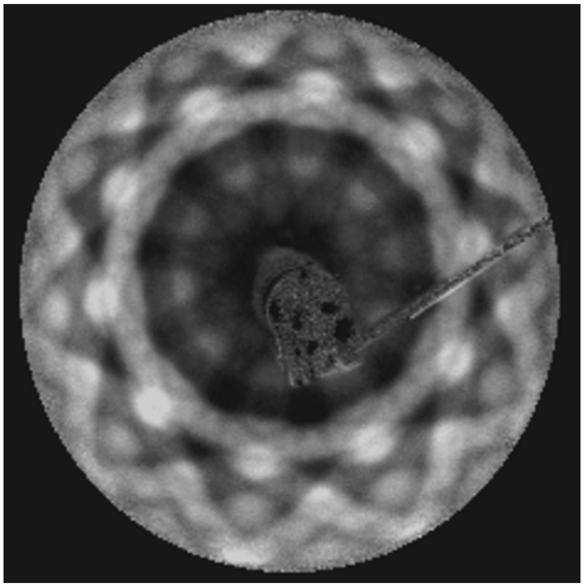

FIG. 2. A secondary-electron pattern at a primary-electron energy of 2000 eV obtained from the same quasicrystal after a heat treatment at 700 K. Bright patches of perfect tenfold symmetry are observed, proving that the decagonal quasicrystalline structure is restored at the surface.

The quasicrystalline surface can be recovered gradually upon annealing the sample for approximately 90 min at 700 K. Figure 2 shows the SEI pattern obtained from the recovered surface. As a comprehensive description of this pattern has already been presented,[6] we only point out that a perfect decagonal structure has emerged at the surface. Moreover, the chemical composition equals the nominal bulk composition of $Al_{70}Co_{15}Ni_{15}$, thus suggesting a segregation of Al atoms to the surface upon annealing. This sputtering/annealing cycle can be repeated reproducibly, which indicates that the quasicrystalline phase is thermodynamically the more stable.

The orientational relationship between the decagonal structure of the quasicrystalline surface and the cubic units on the Ar^+-bombarded surface can be obtained with confidence by determining the corresponding directions in the patterns shown in Figs. 1 and 2 and in those taken on a surface perpendicular to the twofold-symmetry axis.[6] A [110] axis of the bcc phase is clearly oriented parallel to the tenfold-symmetry direction. For the twofold-symmetry axes, denoted A2D and A2P (using the nomenclature of Ref. 11),

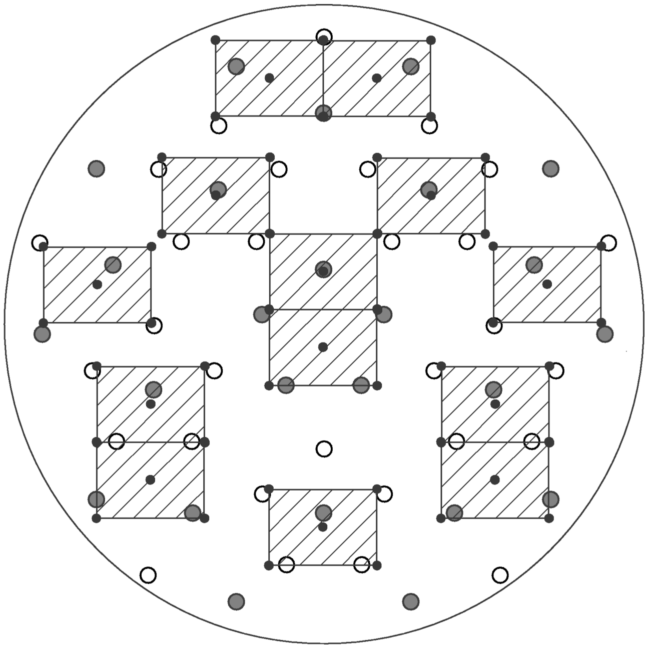

FIG. 3. An atomic model representing the interface between the (110) surface of a bcc structure and the surface of the decagonal Al-Co-Ni. Filled circles denote transition metal and empty circles Al atoms, while small circles represent the atoms on the (110) surface of the bcc lattice. The atomic distances for the crystalline surface is 0.28 nm, as given in the crystal data for AlCo or AlNi, and the coordinates for the quasicrystal are taken from Burkov (Ref. 17).

the following relationship was found: A2P$||\langle 110\rangle$ and A2D$||\langle 111\rangle$ and $\langle 110\rangle$. While this correspondence is accurate to within experimental error,[16] there is an expected mismatch of ±0.75° between the A2D and the [111] directions. Similar results have also been reported for thin films of AlCoNi,[11] but as this study was not performed on a bulk material, there is no interface with a quasicrystalline substrate locking the cubic structure into a specific position.

We conjecture that the junction between the bulk quasicrystal and the cubic units at the surface is an atomically abrupt interface. To analyze the atomic structure at this interface, a few (110) planes of the bcc structural unit are superimposed onto an atomic model suggested for AlCoNi by Burkov,[17] as shown in Fig. 3. The orientation of the (110) planes with respect to the substrate is chosen according to the SEI patterns presented in Figs. 1 and 2. Interestingly, there is satisfactory agreement between the cubic phase and most of the Al and transition-metal atoms, with only a small mismatch. This mismatch is negligible along the [100] direction (along the short edge of the rectangles), but on the overall surface it can cause strains between the bcc units and so prevent the growth of long-range ordered crystalline surface layer. This interpretation is consistent with the lack of a low-energy electron-diffraction pattern.

The question of why the cubic structure does not develop in islands rotated by multiples of 72° around the [110] axis cannot yet be answered. There cannot be an influence on the local symmetry from sputtering, since the direction of ion incidence was carefully kept normal to the specimen surface. It is certain that the answer lies in the structure of the decagonal quasicrystal. It must have elements that do appear tenfold, yet make the cubic overlayers predominantly grow in a preferred and predetermined alignment. Hence, one of the important results of the present investigation is the existence of a preferential direction within the ''tenfold'' symmetric structure. At present, it cannot be decided with certainty whether the bulk structure of our specimen contains a 5_1 screw axis which could affect the symmetry of the surface structure.

A similar question is why the bcc units grow in this one particular direction. The presence of some remaining structural defects when the cubic phase is annealed would explain this observation. These defects, not detectable to SEI, are sufficiently effective to lock the cubic units to the particular orientation on the quasicrystalline surface. Another possible cause for the preferred alignment of the cubic units can be due to a minute deviation of the surface normal from the decagonal axis. This will create steps with a preferred orientation on the surface, and preferential nucleation of islands of single orientation along these step edges can occur.

Note that the pattern shown in Fig. 2 can also be created by superimposing five bcc lattices by rotating each by 72° with respect to each other around the common [110] axis. Since forward scattering of electrons is responsible for the formation of the SEI images, the experimental patterns can be simulated by a simple central projection. Hence, structural models can easily be tested for their ability to reproduce the experimentally observed spots. To ensure that the real decagonal surface has been fully recovered, central projections of five such bcc lattices tilted by 90° have been studied and compared to SEI patterns taken along the twofold-symmetry axis of the decagonal structure. No agreement has been found between the experimental results and the simulations using the structure assembled by five bcc units, thus confirming that no twinning of bcc units occurs at the surface upon annealing. By contrast, the experimental pattern completely overlaps with the projection of the quasicrystalline structure proposed recently.[6]

To summarize, the decagonal surface of Al-Co-Ni has been observed to transform into a surface with cubic symmetry upon bombarding with Ar^+ ions at room temperature. This transformation is caused by removing the Al atoms from the decagonal structure, thus resulting, with only a small lattice mismatch, in a bcc structure. The reverse structural transition can be induced by annealing the sample and is caused by the resulting segregation of Al to the surface where the bcc units act as a seed for the formation of the original quasicrystalline structure. A similar structural transformation at the surface of icosahedral $Al_{70}Pd_{20}Mn_{10}$ has recently been accounted for by the same mechanism.[12]

These observations are supported by the fact that almost all the quasicrystalline phase-forming systems known so far exhibit a closely related approximant phase in a bcc-type structure. The structural transformation between the bcc and the quasicrystalline phase occurs favorably at the surface. We conjecture that at the proper surface, in this case the (110), the mismatch between the periodic and the quasiperiodic lattices is sufficiently small that only different atomic concentrations determine which phase is thermodynamically more stable.

Because of the two-dimensional character of the problem and the lack of a proper phase diagram, an atomistic approach is required to relate the complicated quasicrystalline structure with the crystalline counterpart. Some time ago, a construction scheme was proposed for three-dimensional QC's starting with a CsCl unit as a seed.[18] The observations presented here prove the coexistence of these structures and the schematic drawing for the atomic arrangement at the crystal/quasicrystal interface (Fig. 3) demonstrates their mutual affinity, which should be regarded as an encouragement to such theories.

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