Quasicrystalline Epitaxial Single Element Monolayers on Icosahedral Al-Pd-Mn and Decagonal Al-Ni-Co Quasicrystal Surfaces

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Single element quasicrystalline monolayers were prepared by deposition of antimony and bismuth on the fivefold surface of icosahedral $Al_{71.5}Pd_{21}Mn_{8.5}$ and the tenfold surface of decagonal $Al_{71.8}Ni_{14.8}Co_{13.4}$. Elastic helium atom scattering and low energy electron diffraction of the monolayers show Bragg peaks at the bulk derived positions of the clean surfaces, revealing highly ordered quasicrystalline epitaxial films. Their adatom densities of $(0.9 \pm 0.2) \times 10^{15}$ cm^{-2} and $(0.8 \pm 0.2) \times 10^{15}$ cm^{-2} on Al-Pd-Mn and Al-Ni-Co, respectively, correspond to roughly one adatom per Al atom of the quasicrystalline substrate surfaces.

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Quasicrystals are intermetallic alloys of aperiodic long-range order which often exhibit crystallographically forbidden rotational symmetries such as five-, eight-, ten-, or twelvefold axes. Their unusual symmetries as well as their outstanding physical properties have induced great interest in this class of materials [1]. Quasicrystals provide the opportunity to revisit many basic concepts in solid state physics in which the effect of long-range order has been discussed predominantly in the framework of periodic structures. Thus, new insights have been gained regarding the stabilization of thermodynamic phases [1], transport properties [2], plasticity [3], and the formation of electronic bands [4]. Most of these have been related to bulk properties of quasicrystals.

In the study of quasicrystalline surfaces and interfaces, the field is rapidly approaching the point where similarly profound insights are within reach. Recently, significant progress has been made in the preparation and characterization of high symmetry five- and tenfold surfaces of icosahedral and decagonal quasicrystals [5–8]. These surfaces have been found to exhibit flat terraces with a quasicrystalline structure compatible with surface atom positions given by appropriate truncations of the respective bulk lattice structures [9]. Beyond the characterization of clean surfaces, knowledge is yet very limited. For example, it has been an open question whether quasicrystalline adsorbate phases and ultrathin films can be stabilized by a quasicrystalline surface. Single element films would be of particular interest as they would provide an opportunity to study the impact of quasicrystallinity independently of the complex alloy composition of thermodynamically stable bulk phases.

At submonolayer coverage, preferential adsorption sites as well as adatom clusters with fivefold symmetry were observed on five- and tenfold quasicrystalline surfaces [8,10,11]. However, no quasicrystalline phases with long-range order were found. All efforts to grow films on quasicrystalline surfaces have so far resulted in amorphous or polycrystalline films with domains of common periodic bulk structures. Frequently, the domains align along the n-fold degenerate high symmetry directions of the substrate and the film yields a pseudo-n-fold diffraction pattern [12–14]. The only quasicrystalline films reported are complex decagonal epilayers on the fivefold Al-Pd-Mn surface induced by ion bombardment and annealing. While Bolliger *et al.* observed a thin film (20 Å) of $Al_{22}Pd_{56}Mn_{22}$ composition [15], Naumovic *et al.* recently reported a surface layer of several hundred angstroms thickness consisting of the stable decagonal $Al_{69.8}Pd_{12.1}Mn_{18.1}$ bulk phase [16].

In this Letter, we report on the epitaxial growth of quasicrystalline single element bismuth and antimony monolayers on the fivefold surface of icosahedral Al-Pd-Mn and the tenfold surface of decagonal Al-Ni-Co.

The experiments were performed by He atom scattering (HAS). HAS is ideally suited for the study of quasicrystalline surfaces and thin films, as it is absolutely surface sensitive and directly probes the reciprocal space of the surface corrugation [17]. Moreover, the extreme sensitivity of the He scattering intensity on defects and adatoms provides an excellent monitor for film growth and for the structural quality of the surface layer. In the He atom scattering apparatus, a monoenergetic beam of neutral He atoms is produced by supersonic expansion into the vacuum (typical kinetic energy: 8–40 meV, $\Delta E/E \approx 3\%$). The He beam is scattered from the surface of the sample and detected by a mass spectrometer under a fixed total scattering angle of 90°. Diffraction spectra are recorded by rotating the sample along the axis normal to the scattering plane.

Single grain $Al_{71.5}Pd_{21}Mn_{8.5}$ and $Al_{71.8}Ni_{14.8}Co_{13.4}$ quasicrystals were grown by the Czochralski method [18,19]. The icosahedral Al-Pd-Mn was annealed for three months at 820 °C, cut, and polished perpendicular to

the fivefold axis. The decagonal Al-Ni-Co sample was oriented perpendicular to the tenfold axis. In the He atom scattering chamber (base pressure 2×10^{-10} mbar), the single crystal surfaces were prepared by ion bombardment (Ne^+, 1–5 keV) and annealing at 650 °C and 850 °C, respectively. Antimony and bismuth were deposited by *e*-beam evaporation.

The film growth was studied by monitoring the intensity of the specular (reflected) He atom beam during deposition at constant adsorbate flux. Bi and Sb growth on GaAs(110) served as a reference system [20,21]. At elevated temperatures (100–300 °C) deposition curves on all three substrates fall off steeply, pass through a minimum, and saturate at a monolayer coverage [as in Fig. 1(b)].

For the coverage calibration of the quasicrystalline monolayers, deposition curves were recorded at suitably low substrate temperatures (Fig. 1) to limit diffusion and ensure a random distribution of the adatoms, as verified by the uniform exponential intensity decrease [22]. The slope reflects the He scattering cross section of a single adatom which has been shown to be nearly independent of the specific substrate [17]. Consequently, in the region of the exponential decrease, a common coverage scale (adatoms per unit area) can be achieved by rescaling the x coordinate to yield identical slopes. In order to gain an absolute coverage scale, the deposition curves were fitted by a simple solid-on-solid growth model and calibrated to the known coverage of the Bi monolayer on GaAs(110) (0.82×10^{15} cm^{-2}, Refs. [20,21,23]). The model incorporates reduced sticking and increased diffusion for adatoms in the second and higher layers. The specular intensity is calculated from the sum of effective amplitudes associated to the individual lattice sites, reflecting the local adatom configuration [22]. This basic simulation can reproduce the experimental data perfectly. The analysis of Bi and Sb deposition curves at various beam energies and sample temperatures yields adsorbate-independent coverages of $(0.9 \pm 0.2) \times 10^{15}$ cm^{-2} and $(0.8 \pm 0.2) \times 10^{15}$ cm^{-2} for monolayers on Al-Pd-Mn and Al-Ni-Co, respectively. This adatom density is very similar to that of the Bi and Sb monolayers on GaAs(110).

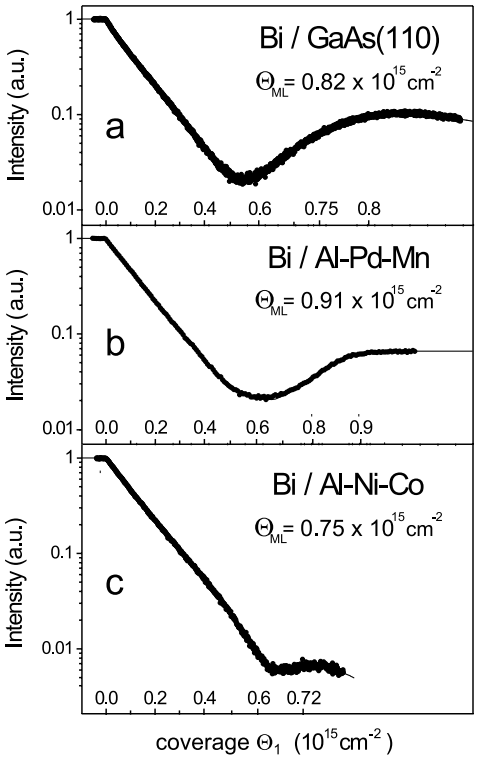

FIG. 1. Evolution of the intensity of the specular He atom beam for Bi deposition on (a) GaAs(110), (b) the fivefold surface of Al-Pd-Mn, and (c) the tenfold surface of Al-Ni-Co. The coverages in the first layer Θ_1 determined by the model calculations (thin curves, see text) are shown on the horizontal axis. Θ_{ML} is the resulting coverage of the completed monolayer. Sample temperatures were 20 °C, 150 °C, and −50 °C, respectively. The beam energy was 15 meV.

To relate this adatom density to the quasicrystalline substrates, we recall that the tenfold Al-Ni-Co surface is perpendicular to the periodic direction and all bulk truncations are equivalent and consist of atoms in a single plane with a total density of 1.5×10^{15} cm^{-2} and a partial aluminum density of 1.1×10^{15} cm^{-2} (Ref. [24]). In contrast, the possible Al-Pd-Mn bulk truncations perpendicular to the fivefold axes show a considerable variety in density and stoichiometry. Of these, terminations with a buckled surface layer in which one-third of the atoms are retracted by 0.4 Å are representative of the sputter/annealed surface [9]. They have an atom density of 1.4×10^{15} cm^{-2} and an aluminum density of 1.0×10^{15} cm^{-2}. Thus, the adatom density of the monolayers roughly matches the density of the Al atoms in the two quasicrystalline substrate surfaces.

The trends in the thermal stability of adlayer and multilayers are very similar to those reported for Sb and Bi on GaAs(110). Highly ordered epitaxial monolayers are formed by Sb and Bi deposition on GaAs(110) at room and slightly elevated temperature [20]. The Sb monolayer on GaAs(110) is stable up to 550 °C, whereas additional layers desorb at 250 °C. The respective temperatures for Bi on GaAs are somewhat lower. On the aluminum-rich quasicrystal surfaces, we observe an even higher stability of the monolayers with desorption temperatures of 750 °C and 400–600 °C for Sb and Bi, respectively. The desorption temperatures reveal that the Sb and Bi layers are characterized by strong chemical bonds to the substrate and much weaker bonds between the adsorbates. The adsorbate-adsorbate interaction is, however, strong enough to induce limited island formation of Bi on Al-Ni-Co in the submonolayer regime when the sample temperature is high enough to allow diffusion. The varying degree of island formation is evident in the sample temperature dependence of the Bi deposition curves.

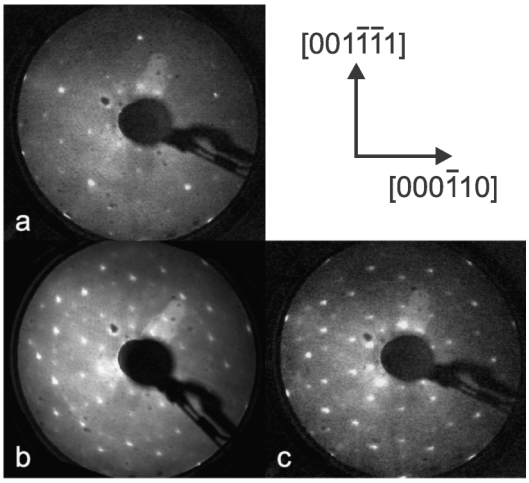

FIG. 2. LEED images from the fivefold Al-Pd-Mn surface with electron energy of 63 eV: (a) clean surface, (b) Sb monolayer, and (c) Bi monolayer. Although the patterns from the monolayers (b),(c) appear tenfold, different electron energies confirm a fivefold symmetry. Indexing follows Ref. [27].

For their structural characterization, high quality monolayers were prepared by deposition at 300 °C, i.e., above the multilayer desorption temperature. Sb monolayers were subsequently annealed at 550 °C. Low energy electron diffraction (LEED) patterns from the monolayers show the same symmetry and peak positions as those from the respective clean surfaces [25,26], illustrating the quasicrystalline epitaxial structure of the monolayers (Fig. 2). The larger number of diffraction peaks observed from the monolayers does not point to a superstructure, as it would for a periodic surface. Instead, the higher electron scattering cross section of the heavy Sb and Bi adatoms allows detection of a larger number of diffraction peaks in the hierarchy of densely spaced bulk derived peaks.

These observations are confirmed quantitatively by He atom scattering. The clean surfaces of Al-Pd-Mn and Al-Ni-Co exhibit diffraction peaks that can be indexed according to the bulk reciprocal lattice structure. The diffraction spectra from the Sb and Bi monolayers reveal diffraction peaks at these same bulk derived positions (Fig. 3). As the He atoms are reflected well above the surface, this unambiguously demonstrates the quasicrystalline structure of the monolayers. The diffraction spectra show the characteristic τ scaling ($\tau = 1.618\ldots$, golden mean) arising from the fivefold symmetry. The high diffraction intensity from the monolayers reveals highly ordered films with a very low defect density. In addition, the extreme similarity of the diffraction spectra from Bi and Sb on the same substrate points towards a common atomic structure [28].

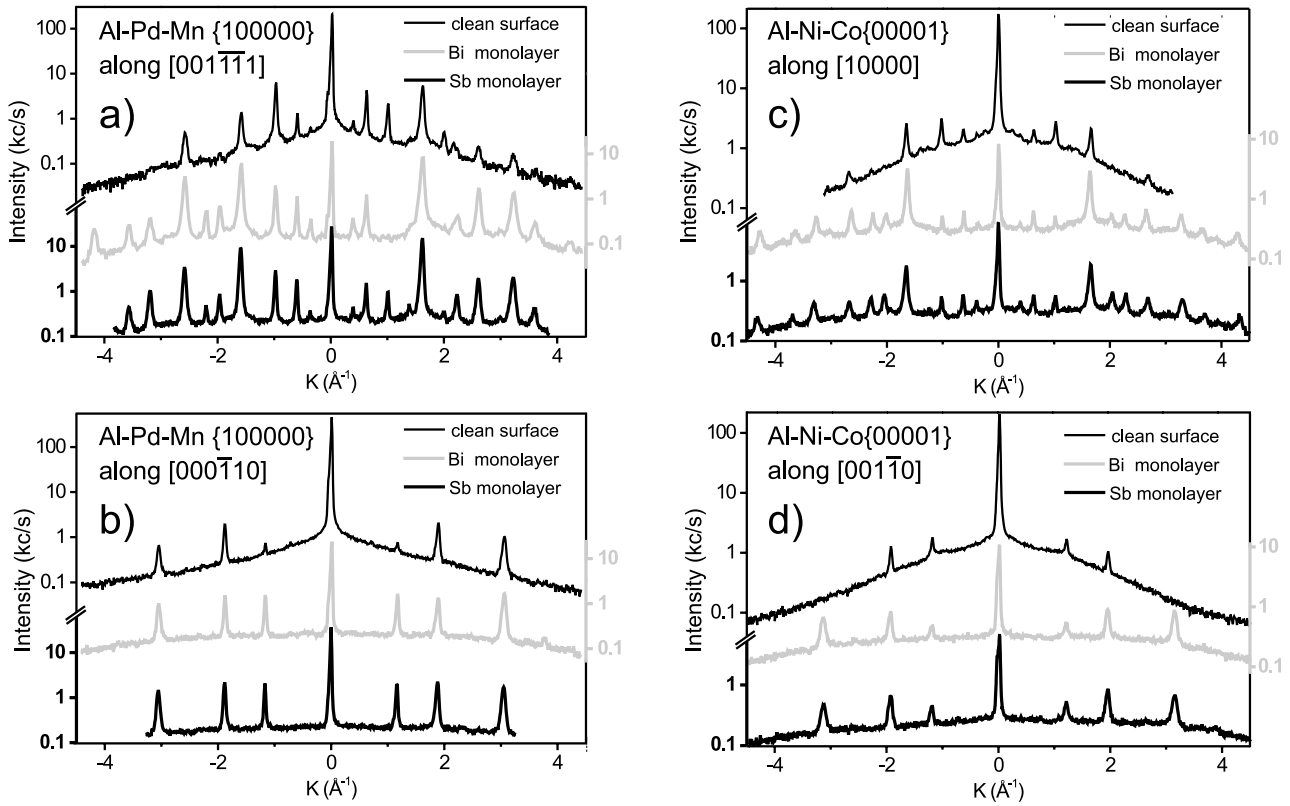

FIG. 3. He atom diffraction from the clean surface and the Sb and Bi monolayers on the fivefold surface of Al-Pd-Mn (a),(b) and the tenfold surface of Al-Ni-Co (c),(d) with 15 and 22 meV kinetic energy, respectively. In each panel the spectra from top to bottom are of the clean surface (scale on the left-hand side), Bi monolayer (scale on the right), and Sb monolayer (scale on the left). Note the logarithmic scale. Indexing as in Fig. 2 and Ref. [27].

The intensity distribution of the diffraction peaks is a measure of the surface corrugation [17]. With increasing corrugation, the intensity shifts from the specular into diffraction peaks at higher momentum transfer. Thus, the diffraction data reveals that the Al-Pd-Mn surface is more strongly corrugated than the Al-Ni-Co surface, in agreement with the atomic structure of the bulk truncations discussed above. The monolayers have an even larger corrugation. On Al-Pd-Mn they are slightly more corrugated than on Al-Ni-Co, as expected on a more corrugated substrate.

The diffraction spectra also provide information on the length scale of the surface corrugation. This is illustrated in the spectra from Al-Ni-Co [Figs. 3(c) and 3(d)]. On the clean surface the intensities fall off rapidly with increasing momentum transfer. From the monolayers, however, the diffraction peak with $K = 1.65$ Å^{-1} in the [10000] direction strongly dominates the 2D diffraction pattern (note the logarithmic scale). This **K** vector corresponds to a real space modulation with a period of $2\pi/K = 3.8$ Å which is on the order of a typical adatom nearest-neighbor distance expected for the measured monolayer coverage.

In conclusion, single element quasicrystalline monolayers have been observed for Sb and Bi on the fivefold surface of icosahedral $Al_{71.5}Pd_{21}Mn_{8.5}$ and the tenfold surface of decagonal $Al_{71.8}Ni_{14.8}Co_{13.4}$. Elastic helium atom scattering and low energy electron diffraction revealed quasicrystalline epitaxial monolayers of high structural quality and very low defect density. The coverage of the monolayers was determined by a direct comparison with Sb and Bi monolayers on GaAs(110), yielding adatom densities reflecting a closed film.

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