

Self-Assembled Nano-Structures on the Icosahedral Al-Pd-Mn Quasicrystal

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Abstract

A quasicrystal is a solid with an aperiodic atomic distribution, but displaying discrete diffraction pattern. At an interface where an ordinary crystal and a quasicrystal intersect, the lack of commensurability between the structures leads to misfits on atomic scale resulting in a wealth of novelties. Here, we present experimental observations on three essentially different cases: Al, Fe, and Si ultra-thin layers grown in vacuum on the pentagonal surface of an icosahedral Al-Pd-Mn quasicrystal. In all three cases, the growing layer decays into nm-size islands. Al is the major alloy component of the substrate material and provides a natural tool to investigate the surface structure. Fe offers an insight into nano-scale magnetism. Si is a classical candidate to explore quantum-confinement effects.

Key Words: crystal, quasicrystal, interface, size selection, self-assembly, epitaxy, Debye temperature, magnetic anisotropy, quantum dots, electron diffraction.

1. Introduction

Atoms occupy periodic lattice points in crystals, which show structural invariance for 2-, 3-, 4-, or 6-fold rotations. Rotations through $2\pi/n$, where n is 5, 8, 10, and 12, are forbidden in crystals as a consequence of periodicity; solids that have such exceptional orientational order are called quasicrystals. They are not periodic, nevertheless show extraordinarily sharp diffraction peaks in electron- and x-ray scattering signaling the presence of long-range order [1]. Low-energy electron diffraction (LEED) patterns, which correlate with the Fourier transform of a surface structure, obtained from quasicrystalline surfaces display a large number of spots, depending on experimental conditions, because reciprocal space is densely filled with discrete Bragg peaks. In contrast, a periodic solid surface generates only few Bragg peaks characteristic of the size and shape of its unit cell. The quasicrystalline ordering and the origin of its stability still awaits an atomistic clarification.

Beside exploring the bulk properties, there is a fair amount of research effort concentrated on quasicrystal surfaces. Some groups scrutinize the atomic structure mainly using scanning tunneling microscopy, while others investigate interfaces formed between a quasicrystalline surface and atomic layers of an ordinary crystal grown on it. In such cases, epitaxial growth conditions are only satisfied in a very limited region of the surface, beyond which adjacent domains are formed. Thus, due to this size-selecting mechanism, islands on the surface usually remain in nm size. In this work, we outline our efforts in this line of research giving three relevant examples of overlayer material grown on the pentagonal surface of $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ (Al-Pd-Mn). The adsorption of Al provides some knowledge about the averaged quasicrystalline surface structure. The growth morphology of Al follows the quasicrystalline surface texture. We were able to extract some bulk information, like concentration of vacancies and diffusion constants. For ferromagnetic materials, the decrease in domain size usually results in a decrease in magnetic anisotropy, until clusters

become superparamagnetic. Fe clusters of well-defined sizes might render possible the study of magnetic order in nanometric scale. Finally, quantum confinement in three dimensions has attracted considerable interest scientifically and technologically. However, these results sometimes are hampered by the large inhomogeneity of the size distribution of clusters which we attempt to overcome with our method of film growth.

In Section 2, we briefly outline our experimental techniques and emphasize their significance in extracting averaged structural information about surfaces. In Section 3, we present our results, and in Section 4, we draw conclusions on what has been done so far and present our forecast for further research.

2. Experimental

A single-grain Al-Pd-Mn sample with dimensions $7 \times 5 \times 1 \text{ mm}^3$ was oriented by means of the x-ray Laue method with an accuracy of $\pm 0.5^\circ$ along the pentagonal symmetry axis, cut, and polished mechanically to an optical finish [2]. After insertion into the ultrahigh-vacuum chamber operating in the lower 10^{-9} -mbar region, the quasicrystalline surface was cleaned by cycles of heat treatment (700 K for 30 minutes) and sputtering with Ar^+ ions (1.5 keV, $4.5 \times 10^{-7} \text{ A/mm}^2$). This surface treatment has proven to result in surface structures with excellent quality, as determined by LEED. Diffraction spots are generated by directing a monochromatic beam of electrons in the energy range of 30 – 300 eV onto the specimen surface and recording the backscattered electrons. The result is a projection of the surface atomic distribution in reciprocal space. In crystals, the observed pattern shows the size and symmetry of the unit cell at the surface. The angular dimensions of diffraction spots are used to extract information about the extent of regions on the surface that contribute coherently to pattern formation [3]. Also for quasicrystals, the size of real-space regions at the surface, in which scatterers are found in structural coherence, is a measure of structural quality. Patterns of surfaces with improved quality therefore contain an increasing number of detectable spots.

Figure 1 shows a LEED pattern obtained from a pentagonal surface of Al-Pd-Mn at a primary-electron energy of 120 eV. If we group the diffraction spots according to their intensity, we observe that sets of spots with comparable intensity are systematically distributed in pentagonal rotational symmetry. The electron gun, used for the excitation, and its holder are seen as a shadow running vertically towards the center of the pattern.



Figure 1. Diffraction pattern from a prepared pentagonal surface of Al-Pd-Mn quasicrystal. The electron energy is 120 eV. The immense number of spots with decreasing intensity is a measure of the size of surface region with correlated scatterers in which the quasicrystalline perfection prevails.

The chemical composition in a near-surface region of the sample was determined by means of Auger electron spectroscopy (AES) during sample preparation and film growth. This task was achieved using an electron gun operating at 2.4 kV and a beam current of $\approx 3 \mu\text{A}$ in conjunction with a single-pass cylindrical mirror energy analyzer with a resolution of $\Delta E/E = 0.5\%$. Pure elements were evaporated onto the sample from an atomic-beam source comprising a Mo crucible indirectly heated by electron bombardment to an adequately high constant temperature. The deposition rates (4 pm/s for Al, 1 pm/s for Fe, and 1.5 pm/s for Si) were calibrated in separate experiments by measuring the relevant Auger transitions during deposition on a polycrystalline Cu sample. In-plane magnetic ordering at the surface was detected using the longitudinal magneto-optical Kerr effect (MOKE). The experimental setup allowed monitoring *during* the growth of Fe.

3. Results

3.1. Growth of Al

We have first studied the thermodynamical stability of crystalline Al layers on the pentagonal surface of Al-Pd-Mn quasicrystal by evaporating thin Al films. The film thickness decreases due to diffusion of Al into the bulk at elevated temperatures. This decrease, and consequently the amount of Al absorbed by the bulk, is monitored as a function of time at substrate temperatures T using AES. The amount of Al that diffuses from the surface into the bulk can be represented as an analytic function depending on the square root of time in order to extract the diffusion coefficient D related to the absorption process for a given temperature. For a thermally activated diffusion process, a plot of D vs. $1/T$ is called Arrhenius plot, the slope of which represents the activation energy $Q(T)$ for diffusion and the ordinate intersection gives the pre-exponential factor D_0 [4]. The values of $Q(T)$ and D_0 are characteristic of the type of diffusion. The activation energy around 100 kJ/mol ≈ 1 eV/atom together with the relatively large pre-exponential factor imply that the absorption of Al is governed by a fast vacancy-mediated diffusion mechanism as it is known for non-transition metals.

At finite temperatures, each atom fluctuates about its equilibrium position. The mean-square displacement can be related to the intensity of a LEED spot. The attenuation of the intensity as a function of increasing temperature is described by the Debye-Waller factor, which is used to determine the Debye temperature, θ_D . The latter reflects the structural stability, the strength of bonds, and the occurrence of defects and vacancies in the material. Since bonding properties of surface atoms are vastly different than those of bulk atoms, the normal modes of vibration are different going from surface to the bulk. Consequently, it is common that θ_D of a surface is 1.5 – 2 times lower than the corresponding bulk value [5]. For the quasicrystalline surface, which results in a LEED pattern shown in Figure 1, we have obtained $\theta_D = 298 \pm 7$ K [6]. This value, however, is very close to the bulk value of 312 K [7] which implies that the quasicrystalline bulk closely resembles the surface with regard to their elastic properties. A by-product of these measurements is the determination of the thermal expansion coefficient of atomic layers. We find $(24 \pm 2) \times 10^{-6} \text{ K}^{-1}$ for the pentagonal surface assuming that the quasicrystalline structure consists of planes like ordinary crystals do. This value is very close to that of bulk Al.

The fast diffusion of Al into the bulk gives the opportunity to increase the rigidity of the quasicrystalline solid by quenching vacancies. To this end, we have evaporated Al in steps up to 20 nm onto the pentagonal surface of Al-Pd-Mn, kept at 770 K, providing efficient diffusion of Al into the bulk. As a result of the diffusion process, θ_D at the surface gradually increases and reaches ≈ 400 K, which corresponds to a decrease of the thermal vibrational amplitude by more than 20 %, without affecting the quasicrystalline order. Indeed, the structural order is well preserved and no changes in the Al and Pd AES intensities could be measured during and after evaporation. Assuming a homogeneous distribution of Al, we can give 1 – 2 % as an upper limit for the concentration of vacancies that are quenched by Al in this process. We conjecture that Al diffuses following the Al subnetwork and, hence, the vacancies involved in this process are concentrated at Al sites. We conclude that although the quasicrystalline structure is thermodynamically stable, its bulk and surface are porous with an appreciable amount of vacancies, which can be filled. In this way, the elastic properties of the bulk can be noticeably improved by the addition of Al [6].

We have investigated the growth and structure of vapor-deposited Al textures on the pentagonal surface of Al-Pd-Mn as a function of the substrate temperature between 200 and 300 K so that diffusion of Al into

the bulk is impeded to a great extent. In order to achieve a layer-by-layer growth [8] we have kept the ratio of temperature to evaporation rate relatively large. Vacuum deposition up to 0.5 nm of Al causes a decrease of LEED spot intensities. For thicker coverages additional diffraction spots appear which are characteristic of crystalline Al. Quasicrystalline and crystalline patterns coexist up to 1.5 nm after which only a crystalline pattern is observed without any further change. The observation for submonolayers can be understood in terms of epitaxial and continuous growth of Al on the pentagonal surface of Al-Pd-Mn. At this initial stage of growth, the resulting morphology is probably governed by kinetic effects. A crucial factor influencing the (kinetic) growth process is the energy barrier of an Al atom that is trapped at surface vacancies. This will impede the surface diffusion and create a seed for the growth of Al. Regardless of the affinity of Al to an Al-Pd-Mn surface, in all heteroepitaxial systems some strain is always involved. This strain is first concentrated at those sites where nucleation occurs and changes with film thickness. When the Al film gradually adopts its bulk lattice properties, strain relaxes. Thus, strain influences the nucleation kinetics in a layer-dependent way and a competition between the epitaxy-imposed ordering versus the stable bulk phases of the film is encountered.

We observe in LEED the evolution of a new surface structure as the Al coverage increases. At a substrate temperature of 300 K, the pattern depicted in Figure 2a is obtained at an electron energy of 61 eV. With increasing electron energy, the spots converge to directions tilted away from the surface normal. This observation implies that the film consists of crystalline textures exposing surfaces, which are inclined with respect to the fivefold-symmetry surface. Detailed analyses show that the surface structure consists of 5 Al crystalline domains exposing their (110) surfaces aligned in such a way that two $\langle 111 \rangle$ and one $\langle 100 \rangle$ visible axes coincide with threefold- and twofold-symmetry directions of the quasicrystal, respectively. In this orientation, the $[0, 1, \tau]$ direction of the domains is aligned parallel to the surface normal of the substrate, where τ is the golden mean [9].

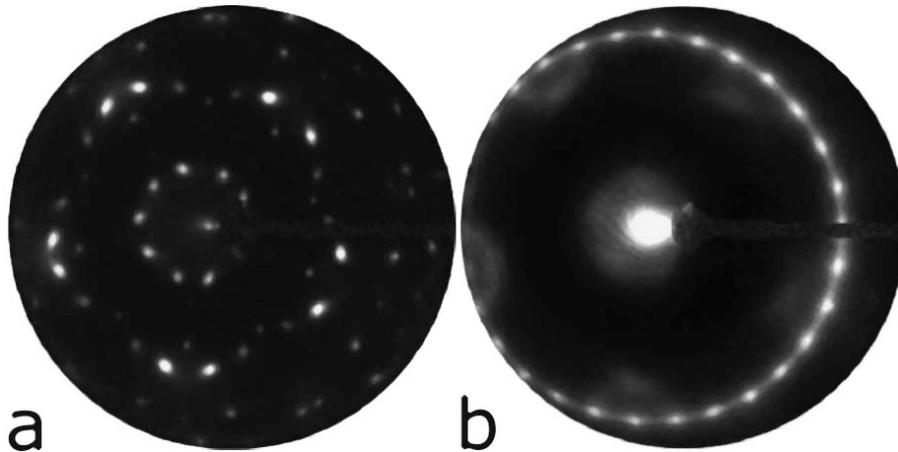


Figure 2. LEED patterns at 61 eV observed from the 1.1-nm Al-covered pentagonal surface kept at (a) 300 and (b) 200 K during deposition. Observe that the sample normal is tilted to the left-hand side by a few degrees.

If the substrate temperature is lowered below ≈ 250 K, a distinctly different growth mode is observed. As shown in Figure 2b ($T = 200$ K), a ring of 30 diffraction spots appears that converges towards the surface normal as the electron energy is increased. In this case, we have the formation of five Al domains in the face-centered cubic structure exposing their (111) faces parallel to the substrate surface. These domains are azimuthally oriented in 72° steps which is consistent with the average pentagonal symmetry of the substrate. This observation represents a layer-by-layer growth mode of Al in which the detailed morphology is strongly influenced by the quasicrystalline substrate structure. For Al deposited at intermediate temperatures, in addition to 30 spots observed for low-temperature evaporation, also features typical of the high-temperature growth are discernible. We observe that, in the high-temperature regime, three-dimensional Al islands develop in contrast to layer-by-layer growth observed at low temperatures. The reason for this growth mode is essentially the low surface energy of the quasicrystalline substrate compared to the corresponding values

for Al and the interface.

Hence, during growth of Al on Al-Pd-Mn, two different alignments of nano-crystals below and above 250 K are observed. These alignments decide upon the macroscopic structure in which the crystallites evolve. Generally, both kinetics and thermodynamics influence the interface formation in the initial stage of growth. In particular, diffusion along and into the substrate surface as well as intermixing and subsequent alloying have to be considered in the first stage of interface formation.

3.2. Growth of Fe

In general, the magnetic anisotropy energy prevents spontaneous changes in magnetization direction. When the anisotropy energy decreases for microscopically small domains, magnetic order is gradually lost. This fact puts a natural limit for miniaturization of magnetic storage devices and calls for strategies to extend the superparamagnetic limit. One obvious solution is to enhance the magnetocrystalline contribution to the anisotropy energy by reducing the crystal-field effects in transition-metal d -bands and their hybridization with other states. This goal can be achieved by reducing the coordination of atoms by producing still smaller, i.e., nanometric clusters.

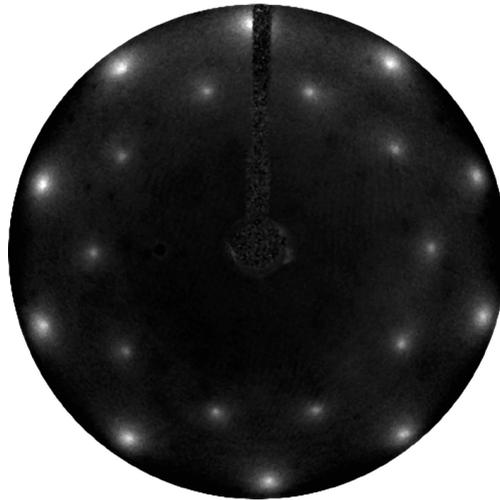


Figure 3. LEED pattern obtained at 162 eV from the pentagonal surface of the quasicrystal, covered with 8 AL of Fe.

In order to explore the possibility of producing small Fe clusters with a homogeneous size distribution, we have deposited Fe on the pentagonal surface of Al-Pd-Mn and monitored its growth by observing the LEED pattern. The intensities of LEED spots decrease markedly and spots show some broadening as soon as minute amounts of Fe (≈ 20 pm) are deposited on the quasicrystalline surface. This amount of Fe corresponds to 0.1 atomic layers (AL). After evaporating 2 AL, no spots originating from the quasicrystalline substrate are discernible anymore. Similar observations have been made during growth of Fe on Al and were interpreted as evidence for strong diffusion of Fe into the bulk crystal [10]. Also in the present case, the obliteration of diffraction spots can be taken as intermixing of Fe with the quasicrystalline substrate by diffusion processes during this early stage of growth which is verified by observing the changes of elemental concentrations at the surface during Fe deposition. A new LEED pattern originating from a different surface structure appears for an Fe deposition of 4 AL. A corresponding LEED pattern recorded after deposition of 8 AL is shown in Figure 3.

In Figure 3, the positions of the diffraction spots reveal that there are five discrete cubic domains present on the surface, azimuthally rotated by 72° with respect to each other. Each domain exposes its (110) face. This distribution suggests that the quasicrystalline substrate acts as a symmetry template for the rotational alignment of Fe crystallites. The widths of diffraction spots indicate domain sizes in the range of

3 – 4 nm, resulting from the degree of lattice mismatch between Fe crystals and the substrate structure. For Fe coverages thicker than 4 AL, MOKE measurements show an in-plane magnetic ordering in the film [11].

In summary, at the initial stage of Fe growth on Al-Pd-Mn quasicrystal, there is a strong intermixing in the absence of crystalline and quasicrystalline order. This situation prevails for films as thick as 2 AL. The initial layer forms an intermediate stage between the quasicrystal and the final Fe crystalline textures for thicker coverages. It is interesting that although the intermediate layer does apparently not show any structural ordering, the quasicrystalline properties are transmitted through this layer and limit the growth of Fe to nm-size islands. Also interesting is the fact that those Fe islands have an azimuthal distribution dictated by the symmetry of the quasicrystal. Our proposed method of nano-structured island growth by self-assembly thus seems to be successful. The outcome, however, yet remains to be tested by methods of nano-magnetism.

3.3. Growth of Si

Quantum confinement of carriers in all three dimensions produces a discrete energy-level spectrum for electrons and holes. This issue is widely known as quantum dots in connection with quantum-information processing and requires fabrication of photonic nano-structures. In practice, common growth techniques do not warrant for a homogeneous size distribution of clusters.

Al and Fe growth modes of nano-structures are largely determined by diffusion and alloying properties of involved elements, respectively. For metals chemically not interacting, energetic considerations, i.e., kinetic control, decide upon the morphology of the growing film. The low-temperature deposition of Al is an example to this growth mode. This argument is in agreement with the fact that metal bonds have no distinct directionality that would influence neighbor interactions in the growing film. The assembly of silicon atoms, on the contrary, represents the opposite case of structure formation. By virtue of the symmetry in the electronic sp^3 hybrid states, Si crystallizes in diamond structure with the rigid tetrahedral bond angle of 109.5° . Unlike for metals, the bond angle in Si is relatively stiff and lends limited elasticity in fitting the diamond structure to the quasicrystalline substrate during the initial stages of growth. Hence, considerations used to describe metal-atom epitaxy can only be applied to Si with reservation.

We have deposited Si onto the pentagonal surface of Al-Pd-Mn, kept at a mildly elevated temperature of 400 K, using a sufficiently low deposition rate in order to achieve layer-by-layer growth. This temperature, which is about 100 K higher than that for Al films, is chosen to avoid diffusion of Si into the quasicrystal. For films as thick as 20 AL, we have not detected any structural order using LEED. The lack of any indication for structural order signals the growth of amorphous or polycrystalline Si without any preferential texture. Experiments at higher substrate temperatures allowing for moderate diffusion of silicon into the quasicrystalline substrate could induce the formation of an intermediate layer, as witnessed in the case of Fe growth on the same surface, and facilitate crystalline growth. These efforts are under way.

4. Conclusions

We have presented results of thin-film growth dominated by the aperiodic nature of the pentagonal surface of the Al-Pd-Mn quasicrystal, which, as a substrate, only offers a limited region of commensurability for growing adsorbate layers. Crystalline domains are formed which are confined to these regions and act as seeds for nano-structured self-assembly of surface textures. The azimuthal distribution of the domains is yet another consequence of the aperiodic substrate, which acts as a symmetry template and aligns the domains in mutually pentagonal order. Although this method seems to be attractive for fabricating nano-crystallites with homogenous size distribution, preparation of quasicrystalline surfaces prior to domain fabrication is not straight-forward to date and may therefore impede the utilization of quasicrystals as such magical substrates.

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