Quantum Size Effects in Metal Thin Films Grown on Quasicrystalline Substrates

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We have investigated by scanning tunneling microscopy the growth of Bi and Ag thin films on the fivefold surface of $Al_{63}Cu_{24}Fe_{13}$ and $Al_{72}Pd_{19.5}Mn_{8.5}$ quasicrystal, respectively. For both systems, we observe the formation of islands with magic height, corresponding to the stacking of a specific number of atomic layers. We interpret this unusual growth morphology in terms of quantum size effects, arising from the confinement of the electron within the film. The magic island heights are thus a direct manifestation of the electronic structure of the quasicrystalline substrates.

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Materials with reduced dimensions, comparable to the electron Fermi wavelength, can have their properties modified by quantum size effects (QSE) [1,2]. This occurs in ultrathin metal films grown on semiconductor substrates and on certain metal surfaces, where the conduction electrons are confined by the vacuum barrier on one side and the substrate interface on the other side. The electronic confinement leads to the formation of discrete energy levels—the quantum well states—affecting the electronic structure of the film. Because the energy of these quantum well states depends on the film thickness t, the physical properties of the film also vary with t. This is true also for the film stability, because the electronic contribution to the total energy of the film depends on t [3,4]. As a result, films or islands of specific thicknesses can have an enhanced stability over other thicknesses due to QSE effects [3–8]. More precisely, preferred films or islands thicknesses with enhanced stability are those for which the energies of the quantum well states are well below the Fermi level [4–8]. Other film thicknesses leading to quantum well states close to the Fermi level will have an enhanced density of states at the Fermi level, increasing the electronic energy of the film, and will therefore be less stable.

This phenomenon is interesting both for scientific and technological reasons. QSE could be used to obtain specific film morphology, with uniform film thickness, which could have important technological applications such as lasing devices, sensors, or magnetic layer systems to name a few. The QSE has been observed in a number of systems, including Ag, Pb, or Bi on Si(111) [9–11] or Ag on GaAs (110) [12]. But the QSE has also been observed in metal heterostructures like Pb on Cu(111) or Ag on Fe(100) [4,5]. In fact, the necessary condition for QSE is that the film interfaces act as a confinement barrier for the motion of the electrons, in the direction perpendicular to the surface. At the film/substrate interface, an electron can only be confined in the film if its energy lies in a band gap of the substrate; in which case it cannot propagate into the substrate and is reflected at the film/substrate interface [1,2]. Therefore, the substrate does not need to be a semiconductor but can also be a metallic system presenting a relative band gap in the direction perpendicular to the surface. Confinement can even be produced by a relative "symmetry gap" [2]. This occurs, for example, if the film valence electrons close to the Fermi level have sp character and the substrate sp partial density of states (DOS) has a gap at the Fermi level.

Typically, such "electronic growth" is not observed upon deposition at room temperature but at lower substrate temperature. In this Letter, we shall present experimental evidences of QSE affecting the morphology of metal thin films grown at room temperature or above. The substrates we are using are quasicrystalline surfaces, presenting a structural and chemical order of higher complexity than simple metal or semiconductor systems. The QSE manifests itself by the formation of islands with "magic height" that we observe by scanning tunneling microscopy (STM). The observations are made for two different metals deposited on two different quasicrystalline systems, suggesting that the QSE may be quite common for quasicrystalline substrates.

Both Al-Cu-Fe and Al-Pd-Mn substrates are Al-rich quasicrystalline phases with icosahedral symmetry [13]. They are well-ordered structures like regular crystals, but they lack periodicity. Their diffraction pattern shows sharp Bragg peaks that distribute in reciprocal space according to the icosahedral symmetry. Both systems are almost isostructural and are described by the same model [13,14]. Their unique atomic structure correlates with unexpected electronic properties, different from both amorphous and crystalline alloys [15]. For example, low values of the electrical conductivity σ are typical in Al-based quasicrystals, and σ increases with increasing temperature, contrary to the usual metallic behavior. The electronic structure of quasicrystals is characterized by a deep minimum in the electronic density of states located at the Fermi level, called a pseudogap, due to both structural and *sp-d* hybridization effects [16].

In our experiments, we used two single grains with nominal compositions $Al_{63}Cu_{24}Fe_{13}$ and $Al_{72}Pd_{19.5}Mn_{8.5}$ cut perpendicularly to a fivefold axis within ±0.25° and mechanically polished using diamond paste down to 0.25 μm. Clean surfaces were prepared in UHV (base pressure $<1 \times 10^{-10}$ mbar) by repeated cycles of ion sputtering (Ar^+, 1–3 keV, 30 mn) and annealing (up to 940 K for Al-Pd-Mn and 1020 K for Al-Cu-Fe, total annealing time up to 22 h). Such a surface preparation method leads to a step-terrace surface morphology, with a chemical composition of the near-surface region similar to the bulk. The structural quality of the fivefold surface can be checked down to the atomic scale by STM and compared to bulk structural models, as described elsewhere [17,18]. It is found that the exposed surface planes correspond to Al-rich dense terminations of the quasiperiodic bulk structure, with no chemical segregation or surface reconstruction, except for some interlayer relaxation. The detailed atomic structures of the surface planes exposed by both Al-Cu-Fe and Al-Pd-Mn are isostructural, although the chemical decoration is of course slightly different.

Bi and Ag were evaporated from Knudsen cells and the pressure was kept in the low 10^{-9} mbar during deposition. The deposition temperature was 300 K for Bi on Al-Cu-Fe and 365 K for Ag on Al-Pd-Mn. Flux calibration of the sources is achieved by measuring the coverage directly from the STM images at low coverage. In the case of Bi, the flux was cross-checked by calculating the thickness of a Bi thin film deposited on Pd(111) from the intensity of the photoemission core-level spectra. The estimated values are 3.4×10^{-2} ML s^{-1} for Bi and about 10^{-3} ML s^{-1} for Ag. The two systems—Bi and Ag thin films—were studied in two different chambers, both equipped with a scanning tunneling microscope (STM). The STM data were acquired at the same temperature as the deposition temperature. In the case of Bi, the thin film growth was also characterized by reflection high-energy electron diffraction (RHEED).

In the case of Bi deposited on the fivefold Al-Cu-Fe surface, a wetting layer is formed first, followed by the growth of large Bi islands for larger coverages. Figure 1(a) shows an STM image (40×30 nm^2) of a single terrace of the surface dosed with approximately 0.35 ML of Bi. It is partly covered with dots of bright contrast that correspond to isolated Bi adatoms. Whereas we observed limited island formation for deposition at 523 K in the submonolayer regime, this is clearly not the case at room temperature and terrace diffusion must be inhibited. This suggests a rather strong binding between Bi and substrate atoms, trapping the adatoms in adsorption sites close to their landing position. Several facts suggest that the structure of the Bi wetting layer is quasiperiodic. First, the distribution of the adatoms should naturally be influenced by the substrate structure in a strong binding scheme, and indeed, local configurations with fivefold symmetry are frequently observed [Fig. 1(b)]. Second, the fast-Fourier transform (FFT) of the STM image is still a tenfold symmetric pattern [Fig. 1(c)]. By applying an appropriate height threshold to the raw STM image, it is also possible to generate a binary image where dots reflect the positions of Bi adatoms. The FFT of this image still shows the tenfold symmetry. Finally, the RHEED pattern characteristic of the clean quasiperiodic surface is not modified by the presence of the wetting layer. This observation is also consistent with the previous report by Franke *et al.* on the growth of an epitaxial Bi monolayer on the isostructural fivefold Al-Pd-Mn substrate [19]. In their experiment, the substrate temperature during deposition was held at 523–573 K, a temperature which is above the multilayer desorption temperature, such that only a single atomic layer of Bi could adsorb. The quasiperiodic structure of the monolayer was demonstrated by low energy electron diffraction (LEED) and helium atom scattering (HAS) [19].

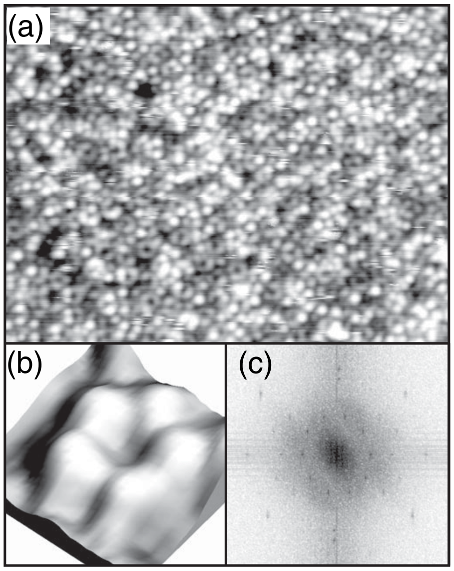

FIG. 1. (a) STM topography (40×31 nm^2) of the fivefold $Al_{63}Cu_{24}Fe_{13}$ surface dosed with 0.35 ML of Bi. (b) 3D view of a local pentagonal motif formed by 5 Bi adatoms (2.9×2.9 nm^2). (c) Fast-Fourier transform of the image in (a).

For coverages larger than 1 monolayer, once the first Bi wetting layer has been completed, the formation of islands with sharp edges and smooth tops is observed. An example is shown in Fig. 2 for a surface dosed with 4.5 ML of Bi. The island density is rather low and their growth shape is rectangular. We recall that Bi has a rhombohedral structure, which can be considered as a slightly distorted simple cubic structure [20]. It is only poorly metallic, with a low carrier density, and its surface energy is rather low ($\gamma_{Bi} = 0.54$ J/m^2). The Bi islands adopt five preferred orientations relative to the substrate, which are rotated from each other by multiples of $2\pi/5$. This fivefold twinning of Bi islands can be deduced from angles between preferred

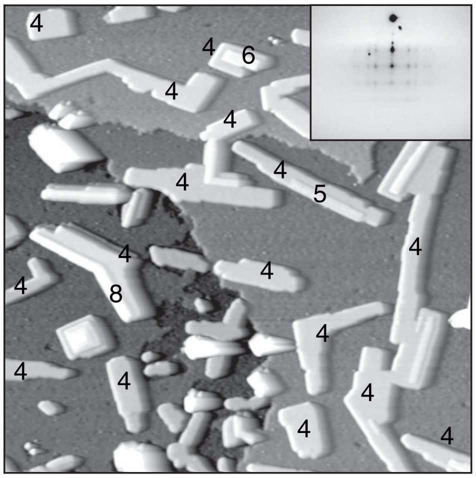

FIG. 2. STM topography (400×400 nm^2) of the fivefold $Al_{63}Cu_{24}Fe_{13}$ surface dosed with 4.5 ML of Bi. Island heights are indicated in units of monolayer. The inset shows a typical RHEED pattern observed for the Bi thin film.

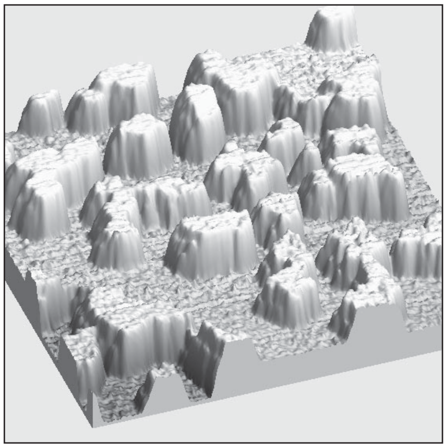

FIG. 3. 3D view of an STM image of the fivefold $Al_{72}Pd_{19.5}Mn_{8.5}$ surface dosed with 1 ML of Ag at 365 K (243×243 nm^2).

growth directions measured directly in the STM images but more precisely from the RHEED analysis. A typical RHEED pattern of the Bi film is shown in the inset of Fig. 2. The pattern consists of diffraction spots (not streaks) aligned along straight lines, indicating transmission-reflection diffraction through the 3D Bi islands. The distribution of spots shows that the film grows with a pseudocubic (001) orientation. The small spots size also shows the good crystallinity of the islands. The same diffraction pattern is observed when the sample is rotated *in situ* azimuthally by $2\pi/5$. This further demonstrates that the epitaxial relationship within the surface plane is defined by the alignment of a crystallographic axis of the Bi islands with one of five equivalent directions of the Bi wetting layer.

Height profiles taken across the Bi islands show that the Bi crystallites have a thickness of $\sim$13 Å or a multiple of this height. The interlayer spacing along the pseudocubic [100] direction is $d_{100} = 3.28$ Å and therefore the islands have a thickness corresponding to the stacking of four atomic layers, or a multiple of this height. In Fig. 2, the island heights are indicated in units of monolayers. In a few cases, 6.5 Å (2-layer) island heights could also be observed immediately after deposition, but these islands had irregular shapes and tended to disappear with time, suggesting that such islands are less stable. In any case, one layer thick Bi islands were never observed. The occurrence of ''magic'' height reveals a special stability associated with islands of specific thickness.

Figure 3 shows an STM image of the fivefold Al-Pd-Mn surface dosed with 1 ML of Ag at 365 K. In this case, flattop islands grow directly onto the bare quasiperiodic substrate, without formation of a first wetting layer. The mobile Ag adatoms nucleate into islands either on terraces or at step edges. The islands are irregularly shaped, unlike the Bi islands. For coverages below 0.3 ML, most islands have a height corresponding to 1 or 2 atomic layers ($\sim$ 2.2 and 4.4 Å). Above this coverage, more than 80% of the islands are either 4- or 5-layer high. One-, 2-, and 3-layer high islands can be observed, but they represent less than 20% of the total population of Ag islands. Therefore, in a way similar to the Bi on Al-Cu-Fe system, it appears that the formation of Ag islands of specific height is also favored in this system.

We reported earlier a study of Ag thin films grown on the same surface at room temperature [21]. At 300 K, islands nucleate by capture of Ag adatoms at specific quasilattice trap sites and then start growing vertically, appearing as ''needles'' which are up to 4 and 5 atoms high at 1 ML coverage, implying an easy uphill motion of the Ag adatoms. This suggests that the thermal energy of the adatoms at room temperature is sufficient to overcome the energy barrier associated with the uphill diffusion, E_{up}, but not the barrier associated with leaving the adsorption well formed by the trap sites, E_{ad}. At 365 K or above, however, both E_{up} and E_{ad} can be overcome by the adatoms, and the film can reach its stable state by forming well-defined 3D Ag islands with magic height.

As mentioned in the introduction, uniform island height selection during metal thin film growth has been observed recently in several systems and interpreted in terms of quantum size effects. Typically, these electronic effects are observed on semiconductor or metal substrates upon deposition below room temperature. This is because the energy difference between N-layer high islands compared to $N \pm 1$-layer high islands due to the electronic contribution must be of the same order of magnitude as the thermal energy kT; otherwise electronic effects will be smeared out [4]. In this work, we have presented two examples where a metal thin film grown on a quasiperiodic substrate develops this unusual morphology, with islands having steep edges, flattops, and uniform heights corresponding to the stacking of a specific number N of atomic layers.

Magic layer thickness in Bi ultrathin films on Si(111) was reported recently [11,12]. It was found that even-number layer films are prominently stable [11]. The mechanism that induces the magic thicknesses was ascribed either to the QSE [11] or to large atomic relaxation which paired each two neighboring layers and avoids dangling bonds [22]. In the latter case, the pairing of the layers occurs independently from the nature of the substrate. However, 2-layer high islands are expected to be the most stable in this model, whereas we observe that such islands are unstable are reshaped into 4-layer high islands. Furthermore, we have deposited Bi on Pd(111) and found no evidence of magic thicknesses or layer pairing effect. Therefore, we believe that the mechanism that induces the magic thickness in the Bi/Al-Cu-Fe system is rather due to the QSE.

The interpretation of our results in terms of quantum size effects implies that the film/substrate interface acts as a confinement barrier for the motion of the electron. The valence band of Bi and Ag metals being dominated by sp bands around the Fermi level, the confinement can only occur if the energy of the Bi or Ag sp electrons lies in a band gap of the substrate, or at least in a gap of the partial sp density of states of the substrate.

The bulk electronic structures of the Al-Cu-Fe and Al-Pd-Mn quasicrystals have been investigated both experimentally and theoretically [see [16] and references therein]. The Cu d (Pd d) band lies well below the Fermi level—at about 4 eV—whereas the Fe d (Mn d) band maximum lies around 1 to 2 eV below E_F. The total DOS shows a deep minimum at the Fermi level, termed the pseudogap, due to both structural and hybridization effects. In particular, the sp states are strongly hybridized with the transition metal d states, leading to the formation of a strong suppression of the sp density of states at the Fermi level. Several experiments have shown that the pseudogap is maintained up to the first layers of the sputter-annealed surface [23]. The pseudogap in the partial sp DOS could thus be the origin of the electronic confinement within the metal thin films. Therefore, our observation of magic island height on quasicrystalline substrates is a direct manifestation of the electronic structure associated with quasiperiodicity.

In summary, we have presented new and unexpected examples of electronically controlled growth of metal thin films on quasicrystalline surfaces. This constitutes a dramatic example of the influence of the pseudogap in the electronic structure associated with these complex alloys. Our study opens the possibility to grow metallic overlayers on quasicrystals, at room T or above, with control of thickness down to the atomic level. Further work is needed to study the electronic structure and stability of these atomically uniform islands, and possibly films, which could have implications in engineering of stable materials and devices with nanometer-scale dimensions.

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