Ordering of Si atoms on the fivefold Al-Pd-Mn quasicrystal surface

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Silicon atoms are found to form an ordered overlayer on the fivefold surface of the icosahedral Al-Pd-Mn quasicrystal. Using scanning tunneling microscopy, the adsorption site is identified as the center of truncated clusters which are building blocks of the bulk structure. Comparison with theoretical models suggests that this site is favored because of bonding to Mn atoms.

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Quasicrystals are metallic alloys which possess long-range order without translational symmetry.[1] They have been found to possess many novel physical, chemical, and tribological properties, such as extremely low electrical conductivities, unusual optical conductivities, low coefficients of friction, and low surface energies.[2–4] Many attempts have been made to understand whether these properties are due to their nonperiodic but well-ordered structures, or whether they originate in their very specific chemical stoichiometries. Such attempts are much more complicated by the multielement nature of these materials.

In the past couple of years the use of surfaces as growth templates has emerged as a realistic route to the formation of systems of reduced chemical complexity. Several systems have been found where the adsorbing species adopts the structure of the substrate to form unusual monolayers and thin films.[5–7] Such behavior has so far been confined to the situation where the adsorbing element is metallic.[8] Attempts to form ordered molecular structures have been relatively unsuccessful.[9]

The formation of a single-element quasiperiodic system using a semiconducting adsorbate has up to now not been achieved. Such systems would be attractive not only to study the relationship between quasiperiodic structure and physical properties but also because of the possibility of unusual electronic behavior due to the interplay of the quasicrystalline pseudogap of the substrate and the semiconducting band gap of the adsorbate. In this Brief Report we show that up to monolayer coverages, Si atoms order quasiperiodically on the Al-Pd-Mn surface as a consequence of preferential adsorption on identical quasiperiodically distributed sites.

The $Al_{70}Pd_{21}Mn_9$ sample provided by Ames Laboratory was prepared according to a well-established process described in detail elsewhere.[10,11] In ultrahigh vacuum (base pressure 1×10^{-8} Pa), the surface preparation consisted of cycles of sputtering and annealing to 920 K for several hours. The chemical composition and the structure of the surface were checked by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED), respectively. An Omicron variable-temperature scanning tunneling microscope (VTSTM) was used to assess the quality of the surface preparation. For these studies the preparation was considered complete when the surface exhibited large terraces of micrometer dimensions and an overall roughness (Z_{rms}) below 0.4 Å.

The deposition of Si on the fivefold Al-Pd-Mn surface was achieved by an Omicron EFM 3 evaporator. The purity of the crystalline Si rod (length 45 mm, diameter 2 mm) was 99.999%. The source-to-sample distance was 45 mm. The source was equipped with a flux monitor and the deposition rate was kept constant throughout the experiment. The coverage was determined using STM by calculating the area of the surface covered by successive Si depositions. The base pressure during deposition did not exceed 5×10^{-8} Pa. All measurements were done at room temperature and the sample was checked by AES, LEED, and STM after each Si deposition.

We first present an overview of the adsorption system. Figure 1(a) shows the distribution of Si atoms across terraces at a coverage of 0.25 ± 0.03 monolayers (ML). Step edges are not preferentially decorated in this system. As the coverage is increased to 0.75 ± 0.09 ML [Fig. 1(b)], individual Si atoms and small clusters coexist on the surface. At 3.6 ± 0.5 ML, the three-dimensional (3D) character of the growth mode is evident. LEED patterns are not observed at this coverage. The roughness in Fig. 1(c) is calculated at 1.77 Å (Z_{rms}). Figure 1(d) shows the peak-to-peak ratio of Si_{LVV} (92 eV) and Al_{LVV} (68 eV) Auger peaks versus the coverage in ML. The monotonic increase in the Si-Al peak-to-peak ratio procludes the formation of a Si-Al alloy. The Si overlayers are found to desorb or diffuse into the bulk by annealing the dosed sample to 600 K for 5 min. STM measurements reveal a surface comparable to the one prior to Si deposition, with a sharp LEED pattern.

We now concentrate on the submonolayer regime and in particular on the 0.25 ± 0.03 ML coverage. Figure 2 shows a STM image obtained after Si deposition (0.25 ML). Si atoms appear as bright protrusions with an average monatomic height measured at 2.13 ± 0.10 Å. The quasicrystal substrate remains well resolved and the pentagonal "dark stars," which are the pentagonal hollows that are prominent in images of the clean surface,[12,13] are still distinguishable.

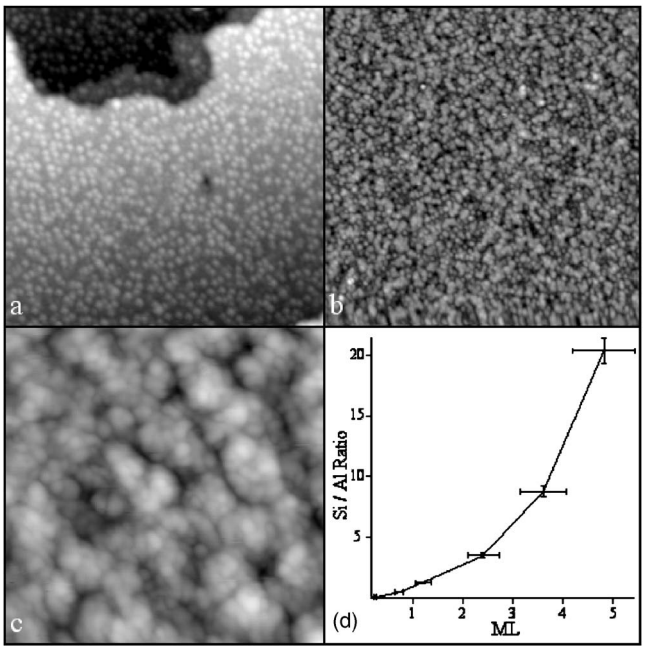

FIG. 1. (a) 650×650 Å^2 STM image recorded after 0.25 ML of Si adsorbed on the fivefold Al-Pd-Mn surface. (b) The coverage is increased to 0.75 ML (640×640 Å^2). (c) The 3D nature of the growth mode is evident at 3.6 ML (330×330 Å^2). (d) The ratio of the peak-to-peak intensity of the Si_{LVV} (92 eV) and Al_{LVV} (68 eV) Auger peaks is plotted against the coverage in ML.

Using a procedure first described by Schaub *et al.*[12] it is possible to form a Fibonacci pentagrid from the quasicrystal surface by drawing lines connecting the edges of the dark stars. Because these dark stars can still be resolved in this image, this method has been used here to generate the sequences of lines shown in Fig. 2. The arrangements of the spacings between the lines form the sequences *LSLSLL* and *LSLSLLSL* with *L* and *S* measured at 7.35 ± 0.20 and 11.90 ± 0.20 Å, respectively, which is in agreement with the values derived by Schaub *et al.*[12]

It is apparent from Fig. 2 that there is a remarkable degree of alignment between these lines and the large protrusions representing the Si atoms: the majority of the protrusions are bisected by the lines. The alignments along the other directions not indicated in Fig. 2 can be observed by viewing the figure at an oblique angle. These observations indicate that at this coverage Si atoms are predominantly quasiperiodically spaced across the Al-Pd-Mn surface.

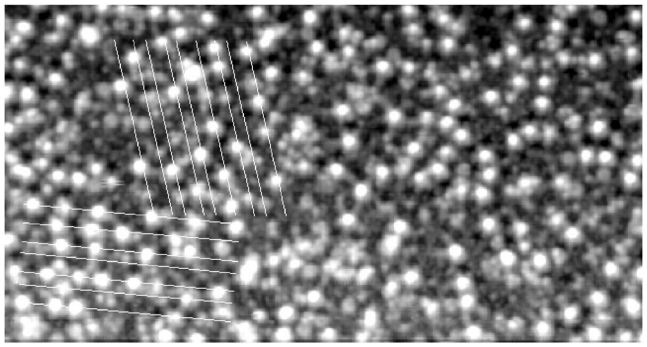

FIG. 2. 403×218 Å^2 STM image for a Si coverage identical to Fig. 1(a). Two 1D Fibonacci sequences have been drawn following the method of Schaub *et al.* (Ref. 12). Si atoms appear as white protrusions and sit on these Fibonacci lines.

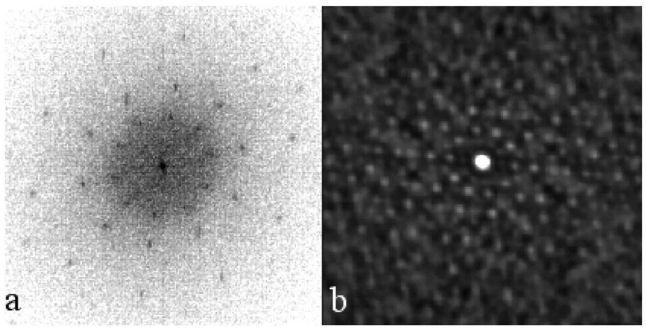

FIG. 3. (a) Fast Fourier transform calculated when only Si atoms (0.25 ML coverage) are selected by a thresholding procedure over an area equal to 388 100 Å^2. (b) 138×138 Å^2 autocorrelation function obtained from Si atoms.

The formation of an ordered quasiperiodic array of Si atoms is confirmed by the tenfold fast Fourier transform (FFT) calculated from Fig. 1(a). This was done by applying a threshold filter to the STM image to select only the Si atoms. The FFT, which displays three rings of spots whose radii are related to each other by powers of the golden ratio $\tau=(1+\sqrt{5})/2$, is shown in Fig. 3(a). A similar FFT, although less intense, is obtained from Fig. 1(b) at 0.75 ML coverage. In both cases, the positions of the spots are commensurate with those calculated from images of the clean Al-Pd-Mn surface. A two-dimensional autocorrelation function [Fig. 3(b)] has also been calculated from the thresholded STM image (0.25 ML coverage). Correlation maxima indicate a spatial correlation of the Si atoms over distances of at least 130 Å.

We now turn to the identification of the adsorption site. The icosahedral Al-Pd-Mn quasicrystal has a geometric cluster substructure consisting of the 33-atom Bergman cluster and the 51-atom pseudo-Mackay cluster.[14,15] The Bergman clusters are distributed at the odd vertices of the 3D Penrose tiling. Equatorial truncations of the Bergman and pseudo-Mackay clusters produce distinctive motifs in high-resolution STM images where they have been labeled "dark stars" and "white flowers," respectively, in a previous publication.[16,17]

Figure 4(a) represents a portion of the clean Al-Pd-Mn surface prior to Si deposition. The larger circle in this image encloses a white flower; the smaller circle encloses a dark star.[11] Figure 4(b) is a segment of a plane from an established geometrical model[11] which corresponds closely to the image in Fig. 4(a). Figure 4(c) shows a Si atom adsorbed on the surface. The resolution of the image is such that the Si atom can be seen to sit in a white flower. Despite the presence of the adsorbed silicon atom, some of the surrounding dark stars can also be resolved. Thus the adsorption site is therefore identified as being at the center of a truncated pseudo-Mackay cluster.

This conclusion is supported by other considerations. The truncated Bergman clusters or dark stars were the sites iden-

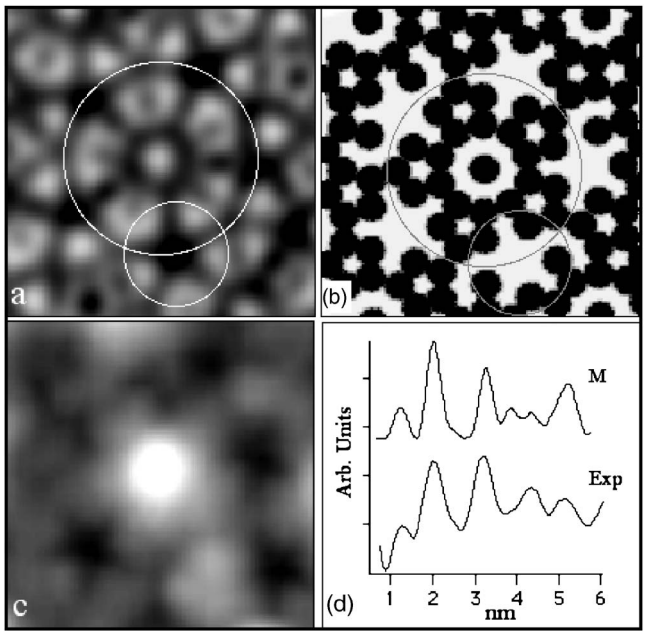

FIG. 4. (a) 33×33 Å^2 STM image of the clean Al-Pd-Mn surface. A white flower corresponding to a truncated pseudo-Mackay cluster is indicated by the large circle, and a dark star corresponding to a truncated Bergman cluster is shown by the smaller circle. (b) Theoretical model of the surface (Ref. 11), with circles again representing truncated pseudo-Mackay and Bergman clusters. (c) STM image of a single Si atom adsorbed on the surface. The dimensions are identical for (a), (b), and (c). (d) Radial distribution functions calculated from autocorrelation functions. The top curve labeled *M* is a simulation calculated for Si atoms adsorbing in the center of the truncated pseudo-Mackay cluster. The bottom curve represents the radial distribution function calculated from the experimental data at 0.25 ML coverage.

tified for adsorption in all previous cases. In this study, they can be excluded. First, the shortest distance between adsorbed Si atoms and the centers of still visible dark stars is measured at 10.5 ± 0.5 Å [from Fig. 4(c)]; this does not correspond to either of the nearest separations measured on clean surfaces between two dark stars which are 7.8 and 12.5 Å. Second, a high density of dark stars is still visible on the quasicrystal surface (see Fig. 2), and if the Si atoms were adsorbing in these sites, the combined density of filled and unfilled truncated Bergman clusters would be too high compared with the highest known values from planes of the bulk model.

Figure 4(d) (bottom) shows a radial distribution function calculated from the experimental autocorrelation pattern in Fig. 3(b). This is compared with a simulated radial distribution function calculated for adsorption in the truncated pseudo-Mackay site presented in Fig. 4(d) (top). The closest Si-Si distance observed is 12.6 Å and matches the closest distance between the centers of the truncated pseudo-Mackay clusters. The pattern agrees well at other distances out to 40 Å also. On the basis of the above measurements and this simulation, this site emerges as the only possible site on Al-Pd-Mn for Si atoms at 0.25 ML coverage.

The number of truncated pseudo-Mackay clusters available is estimated at 0.2 nm^{-2} from the modified Katz-Gratias-Elser bulk model.[11] This is comparable with the density of Si atoms measured on Fig. 2. Above this number, the lack of available sites leads to disorder in the overlayer evidenced by the progressive loss of the diffraction pattern with the formation of small Si clusters [see Fig. 1(b)]. At the 0.25 ML coverage, a small number of Si atoms do not sit on the Fibonacci lines drawn using the Schaub methodology.[12] This is consistent with what is expected from a consideration of the planes of the theoretical model,[11] where not every pseudo-Mackay cluster is found at the intersecting points of the Schaub pentagrid; alternatively this may be due to the saturation of the pseudo-Mackay cluster sites and the beginning of the occupation of other sites.

Recent theoretical studies provide understanding of why Si atoms adsorb in the centers of truncated pseudo-Mackay clusters, rather than in the truncated Bergman clusters as was found for Al,[18] Cu,[6] and C_{60}.[13] *Ab initio* density functional methods have been used to investigate the structural and electronic properties of the fivefold Al-Pd-Mn surface.[19] It emerges from these calculations that valence charge maxima are located around Mn atoms within the surface layer which correspond to the centers of the truncated pseudo-Mackay clusters. This is also consistent with the *ab initio* full-potential linear augmented plane wave calculations of Zijlstra and Bose[20] where the Mn atoms are found to have a large negative valence.

This charge density maximum around Mn atoms could account for the tendency of Si atoms to bond in these sites. The atomic orbitals of Si hybridize to an sp^3 configuration and hence Si tends to form directional covalent bonds, rather than occupy sites of maximal coordination such as the truncated Bergman clusters, which coincide with a minimum in the valence charge density.[19] This interpretation is consistent with the relatively large apparent diameter and the brightness of the protrusions corresponding to the Si atoms observed in this study (see Fig. 2), although a tip-sample convolution could also cause this effect. A core-level photoemission study could help to clarify this point.

In conclusion, it has been shown that Si atoms form a quasiperiodic array on the fivefold surface of *i*-Al-Pd-Mn by adsorption in previously unidentified adsorption sites. This work extends the range of single-element quasiperiodic surface structures to include semiconductors and opens up the possibility of observing unusual electronic behavior in these systems.

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[1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
[2] C. Janot, *Quasicrystals, A Primer*, 2nd ed. (Clarendon, Oxford, 1994).
[3] *Physical Properties of Quasicrystals*, edited by Z. M. Stadnik, Springer Series in Solid State Sciences Vol. 126 (Springer-Verlag, Berlin, 1999).
[4] *Quasicrystals: Structure and Physical Properties*, edited by H. -R. Trebin (Wiley-VCH, Berlin, 2003).
[5] K. J. Franke, H. R. Sharma, W. Theis, P. Gille, P. Ebert, and K. H. Rieder, Phys. Rev. Lett. **89**, 156104 (2002).
[6] J. Ledieu, J. T. Hoeft, D. E. Reid, J. A. Smerdon, R. D. Diehl, T. A. Lograsso, A. R. Ross, and R. McGrath, Phys. Rev. Lett. **92**, 135507 (2004).
[7] H. R. Sharma, M. Shimoda, A. R. Ross, T. A. Lograsso, and A. P. Tsai, Phys. Rev. B **72**, 045428 (2005).
[8] V. Fournée and P. A. Thiel, J. Phys. D **38**, R83 (2004).
[9] J. T. Hoeft, J. Ledieu, S. Haq, T. Lograsso, A. R. Ross, and R. McGrath, Philos. Mag. **86**, 869 (2006).
[10] J. Ledieu, C. A. Muryn, G. Thornton, R. D. Diehl, T. A. Lograsso, D. W. Delaney, and R. McGrath, Surf. Sci. **472**, 89 (2001).
[11] Z. Papadopolos, G. Kasner, J. Ledieu, E. J. Cox, N. V. Richardson, Q. Chen, R. D. Diehl, T. A. Lograsso, A. R. Ross, and R. McGrath, Phys. Rev. B **66**, 184207 (2002).
[12] T. M. Schaub, D. E. Bürgler, H. J. Güntherodt, and J. B. Suck, Phys. Rev. Lett. **73**, 1255 (1994).
[13] J. Ledieu and R. McGrath, J. Phys.: Condens. Matter **15**, S3113 (2003).
[14] G. Kasner, Z. Papadopolos, P. Kramer, and D. E. Bürgler, Phys. Rev. B **60**, 3899 (1999).
[15] D. Gratias, F. Puyraimond, M. Quiquandon, and A. Katz, Phys. Rev. B **63**, 024202 (2000).
[16] Z. Papadopolos (private communication).
[17] In Ref. 11 the white flower is labeled "wF" and the dark star "dS."
[18] T. Cai, F. Shi, Z. Shen, M. Gierer, A. I. Goldman, M. J. Kramer, C. J. Jenks, T. A. Lograsso, D. W. Delaney, P. A. Thiel, and M. A. Van Hove, Surf. Sci. **495**, 19 (2001).
[19] M. Krajčí and J. Hafner, Phys. Rev. B **71**, 054202 (2005).
[20] E. Zijlstra and S. Bose, Philos. Mag. **86**, 717 (2006).