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Abstract

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Comments

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Morphology of Sn Films Grown on the Fivefold Surface of Icosahedral $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ Investigated by Scanning Tunneling Microscopy

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ABSTRACT

Sn film growth on the fivefold surface of icosahedral $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ has been investigated by employing scanning tunneling microscopy. For about monolayer coverage, the deposited Sn forms a layer of monoatomic height. A Fourier transform of the layer's structure reveals quasicrystalline long range order. At higher coverage, flat-topped clusters of uniform heights are formed. The clusters preferentially grow at the step edges.

INTRODUCTION

Despite their complex atomic structure and lack of periodicity, quasicrystals yield highly ordered surfaces under suitable preparation. The surfaces usually retain the surface projected symmetry of the underlying bulk which can include the unusual fivefold or tenfold rotational symmetries. The success in the surface preparation and characterization has opened up an opportunity to perform thin film growth studies on these surfaces with unconventional symmetries. Indeed, there have been many investigations on a wide range of materials (for example, metals [1-7], semimetals [8,9], nonmetal [10], organic molecules [11-12]) deposited mainly on the fivefold surface of icosahedral (*i*) and the tenfold surface of decagonal (*d*) quasicrystals. Considerable progress has been made in growing stable single element quasicrystalline films [6-9] as well as in understanding the nature of nucleation and growth [3-5]. Single element quasicrystalline films are of a great interest as they could provide an insight into the origin of quasicrystals and their anomalous physical properties.

One focus in the study of thin film growth on quasicrystal surfaces has been that of surfactant mediated growth. These studies have shown that elements with low surface free energy, especially indium, can act as surfactants promoting two-dimensional growth of a more noble metal on the tenfold surface of *d*-Al-Ni-Co or on the fivefold surface of *i*-Al-Pd-Mn [1,2]. These studies were carried out mainly by reflection high-energy electron diffraction (RHEED) and X-ray photoemission diffraction (XPD), which provide information about the average structure. In order to achieve an atomic scale understanding of the surfactant effect in noble metal film growth on quasicrystalline surfaces, we employed scanning tunneling microscopy (STM) on these systems. This paper reports on the first results of this study. A full report of the investigation will be presented elsewhere. Here, we present STM investigation of Sn films grown on the fivefold surface of *i*- $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$. Sn has very low surface free energy [13] close to that of indium and thus has promise to also constitute a surfactant.

In addition to the surfactant effect, investigation of Sn film is of another interest. It was recently shown that quasicrystalline monolayer of Sn can be formed on the tenfold surface of *d*-Al-Ni-Co by surface diffusion [7]. In this experiment, Sn coated on the rear side of the sample was allowed to diffuse onto the sputtered surface by annealing the sample. Upon annealing, Sn starts to diffuse onto the surface prior to the full recovery of quasicrystalline order and saturates below the temperature that is required to yield a well-ordered structure on the surface. This makes it difficult to obtain STM images with atomic scale resolution. It should be noted that sputtering yields a very rough surface and destroys the quasicrystalline order [14,15, and references therein]. To restore a fine structure with quasicrystalline order, the sputtered surface needs to be annealed at sufficiently high temperature [15]. To overcome the difficulties apparent in the diffusion experiment, for the present work we first obtained a well-ordered substrate surface and subsequently grew the Sn films by vapor deposition. With this method, we examined the possibility of forming a quasicrystalline monolayer of Sn on the fivefold surface of *i*-Al₆₃Cu₂₄Fe₁₃.

EXPERIMENTAL

The single grain Al₆₃Cu₂₄Fe₁₃ sample [16] was cut perpendicular to the fivefold axis and mechanically polished using diamond paste down to 0.25 μm. The sample was fixed on a molybdenum holder using strips of tantalum foil and inserted into the preparation chamber (base pressure 1×10^{-10} mbar) for further surface treatment. Repeated cycles of Ar⁺ sputtering (1-3 keV) and annealing (up to 740 °C) were performed to prepare the surface. The temperature was measured by an optical pyrometer (emissivity $\epsilon = 0.35$). The cleaning process was repeated until no oxygen was detectable by X-ray photoemission spectroscopy (XPS).

Sn was deposited in a separate UHV chamber by using a liquid-nitrogen-cooled evaporator with a tungsten basket (flux 0.1-0.2 ML/s, ML: monolayer). The temperature of the sample was kept at 300-350 °C during deposition. We investigated the surface at different coverages. The surface was sputter-annealed prior to each new deposition. After deposition, Sn could be removed completely from the surface by sputtering. However, upon annealing Sn reappears on the surface. This is possibly due to a scenario that the Sn collected on the sample holder and/or on the tantalum foils during deposition diffuses onto the surface upon annealing. Hence, except for the first deposition, the surface contains a small amount of Sn (less than 0.05 ML) prior to the deposition. The reappearance of Sn makes it impossible to exactly achieve a desired coverage by deposition of a well known amount of Sn. However, the amount of Sn on the surface could be estimated by measuring the Sn 3d core level photoemission intensity. We determined the coverage by a combination of STM data at the submonolayer regime and XPS Sn 3d intensity.

For this study, we used an Omicron room temperature STM. Images were recorded at constant current mode. The sample could be transferred into the STM chamber from the preparation and evaporation chambers without exposing it into the air.

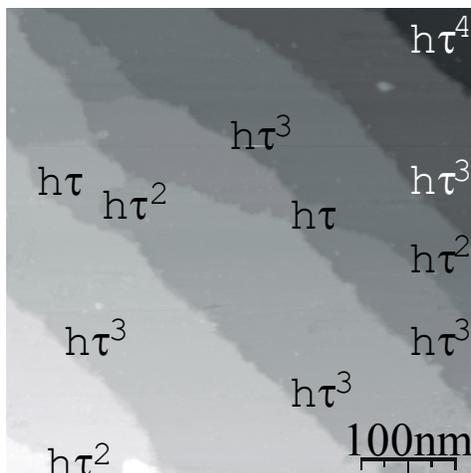


Figure 1. STM image of the clean fivefold $i\text{-Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ surface (Area $A = 500 \times 500 \text{ nm}^2$, bias voltage $V = 2 \text{ V}$ and tunneling current $I = 0.2 \text{ nA}$). The step heights are indicated in the image.

RESULTS AND DISCUSSION

Clean surface

Scanning tunnelling microscopy of the fivefold $i\text{-Al-Cu-Fe}$ surface has been reported earlier [17-19]. Here we present STM images to give an overview of the clean surface used for Sn deposition. STM images reveal flat terraces separated by rough steps of different heights (Figure 1). Among the observed step heights, the three smallest heights are about $h \approx 0.25 \text{ nm}$, $h\tau \approx 0.40 \text{ nm}$, and $h\tau^2 \approx 0.65 \text{ nm}$, where $\tau = 1.618\dots$, a scaling factor related to the pentagonal or decagonal geometry. Other step heights of about 0.95 nm and 1.6 nm correspond to $\approx h\tau + h\tau^2 (= h\tau^3)$ and $\approx h\tau^2 + h\tau^3 (= h\tau^4)$, respectively. The step heights of 0.40 nm , 0.65 nm , and 0.95 nm appear more frequently than the others. This observation differs from the previous results on the same surface [17] as well as those on the five fold surface of $i\text{-Al-Pd-Mn}$ [20,21], another widely investigated icosahedral system possessing bulk structure similar to that of $i\text{-Al-Cu-Fe}$. These reports found that the steps of height close to 0.25 nm , 0.40 nm , and 0.65 nm are frequently observed.

Monolayer coverage surface

A representative STM image of the surface with approximately 1ML of Sn is shown in Figure 2a. The height distribution of the image (frequency of the measured z values) is represented by a histogram in Figure 2b. The peak-to-peak distance in the histogram corresponds to the separation of the respective terraces. On the basis of the peak separation, the observed step height distribution is illustrated in a schematic diagram (Figure 2c). The step heights of $\approx 0.16 \text{ nm}$ and $\approx 0.50 \text{ nm}$ do not appear in the clean surface. The 0.16 nm height is close to a half of the lattice constant of the tetragonal Sn along the c -direction ($c/2$), while the step height of $\approx 0.50 \text{ nm}$ is approximately equal to $(h\tau^2 - c/2)$. Note that the bulk lattice parameters of tetragonal Sn are $a = b = 0.58318 \text{ nm}$ and $c = 0.31819 \text{ nm}$ [22]. Assuming a stacking of Sn along the c -direction, the terraces marked by '4' and '7' represent single layers of Sn, whereas the terraces '3' and '6' correspond to the uncovered part of the substrate. All other terraces are completely covered by a single layer of Sn.

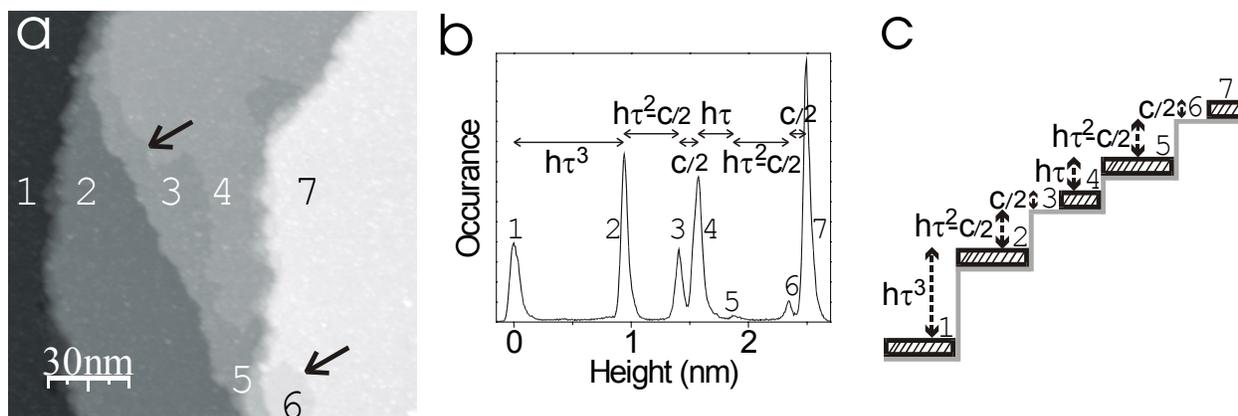


Figure 2. (a) STM image of the Sn covered fivefold $i\text{-Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ surface for about a ML coverage ($A = 150 \times 150 \text{ nm}^2$, $V = 2.8 \text{ V}$, and $I = 0.2 \text{ nA}$). The steps of 0.16 nm ($c/2$) height are indicated by arrows. (b) Height distribution of the image (a). Peaks corresponding to each terrace are denoted by numbers 1, 2, (c) Schematic view of the step height distribution of the image (a). The black hatched strips represent monolayers of Sn, while the substrate top layer is denoted by gray.

Further information on the monolayer film is gained by analyzing its structure. A close-up view of an STM image is given in Figure 3a. In this image, the upper and lower terraces, which are separated by a 0.16 nm high step, are the monolayer of Sn and the substrate, respectively. It is clearly seen that the Sn film exhibits a rough structure as compared to the substrate. The Sn film exhibits many pentagonal-shaped features of identical size and orientation. The Fourier transform of the Sn monolayer displays sharp spots with a near tenfold symmetry (Figure 3b). The sharpness of the spots suggests an excellent long range order of the layer. The spots are located on rings with radii of about 4.0 nm^{-1} and 2.5 nm^{-1} (the given values are the average of largest and shortest radii of the distorted circles). The radii have a ratio of $\approx 1:\tau$, reflecting the quasicrystalline order of the Sn layer.



Figure 3. (a) Close-up view of the Sn layer demonstrating pentagonal-shaped features enclosed by circles ($A = 46 \times 22 \text{ nm}^2$, $V = 1.2 \text{ V}$, and $I = 0.2 \text{ nA}$). (b) Fourier transform of the upper terrace.

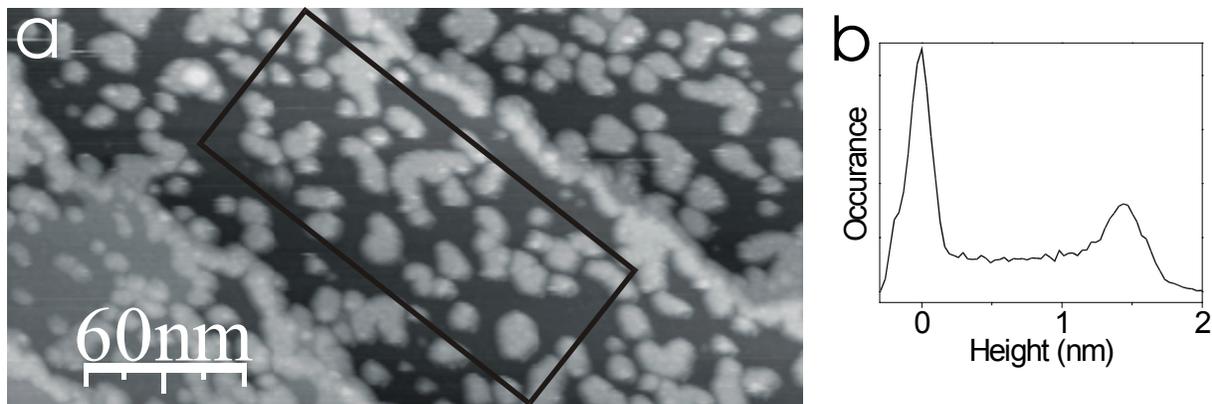


Figure 4. (a) STM image of the Sn covered fivefold $i\text{-Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ surface for about 5 ML coverage ($A = 300 \times 150 \text{ nm}^2$, $V = 2.5 \text{ V}$, and $I = 0.20 \text{ nA}$). (b) Height histogram of the selected area of the terrace marked by the frame.

Higher coverages

An STM image for about 5 ML coverage is given in Figure 4a. The brighter features on the terraces correspond to Sn clusters. The height histogram of the selected area of the terrace marked by the frame is given in Figure 4b. The histogram shows two distinct peaks revealing that the clusters have a uniform height approximately equal to 1.5 nm, the peak separation. Assuming a stacking along the c -direction, the cluster height corresponds to about 10 ML. The clusters preferentially nucleate at the step edges; however the terraces also exhibit a considerable density of clusters. The preferential growth at the step edges has been observed in the growth of metals on periodic substrates in a number of systems. Palladium growth on the oxide substrates serves as such an example [23-24].

Due to the large corrugation associated with Sn clusters, it was necessary to keep the STM tip far from the surface to avoid a tip crash during scanning. This is achieved by employing high sample bias voltages and low currents (typically 2.5 V and $I = 0.2 \text{ nA}$). As the applied bias voltage is higher than those typically used to yield atomic-scale resolution on metal surfaces, it is not possible to resolve the atomic structure of the clusters or the terraces. Only based on these images, it would be unfounded to conclude that dark part of the terraces is covered by a Sn layer. However, considering the layer growth at monolayer coverage, we speculate that the clusters are formed atop the monolayer covered surface. Then the associated growth mode would correspond to Stranski-Krastanov type (layer-plus island growth).

CONCLUSION

We used scanning tunneling microscopy to investigate Sn film growth on the fivefold $i\text{-Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$ surface at elevated temperatures by vapor deposition. The surface was studied at different coverages. At about 1ML coverage, the deposited Sn forms a layer with a height corresponding to a monolayer of Sn. A Fourier transform of the layer reveals a long range quasicrystalline order. For higher coverages, flat-topped clusters of uniform height are observed. The clusters are found to grow preferentially at step edges.

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REFERENCES

1. M. Shimoda, J.Q. Guo, T.J. Sato, A.P. Tsai, Surf. Sci. **482-485**, 784 (2001); Jpn. J. Appl. Phys. **40**, 6073 (2001); Surf. Sci. **507-510**, 276 (2002).
2. M. Shimoda, T.J. Sato, A.P. Tsai, J.Q. Guo, J. Alloys and Comp. **342** (2002) 441.
3. T. Cai, J. Ledieu, R. McGrath, V. Fournée, T. Lograsso, A. Ross, A.P. Thiel, Surf. Sci. **526**, 115 (2003).
4. V. Fournée, T.C. Cai, A.R. Ross, T.A. Lograsso, J.W. Evans, P.A. Thiel, Phys. Rev. B **67**, 33406 (2003).
5. V. Fournée, A.R. Ross, T.A. Lograsso, J.W. Evans, P.A. Thiel, Surf. Sci. **537**, 5 (2003).
6. J. Ledieu, J.T. Hoefl, D.E. Reid, J. Smerdon, R.D. Diehl, T.A. Lograsso, A.R. Ross, R. McGrath, Los Alamos National Laboratory, Preprint Archive, Condensed Matter, arXiv:cond-mat/0307131, 1 (2003).
7. M. Shimoda, J.Q. Guo, T.J. Sato, A.P. Tsai, J. Non Crys. Solid, in press.
8. K.J. Franke, H.R. Sharma, W. Theis, P. Gille, Ph. Ebert, K.H. Rieder, Phys. Rev. Lett. **89**, 156104 (2002).
9. W. Theis, H.R. Sharma, K.J. Franke, K.H. Rieder, in *Quasicrystals, Structure and Physical Properties*, edited by H.-R. Trebin (Wiley-VCH, Weinheim, 2003).
10. J. Ledieu, V.R. Dhanak, R.D. Diehl, T.A. Lograsso, D.W. Delaney, Surf. Sci. **512**, 77 (2002).
11. R. McGrath, J. Ledieu, E.J. Cox, S. Haq, R.D. Diehl, C.J. Jenks, I. Fisher, A.R. Ross, T.A. Lograsso, J. Alloys Compd. **342**, 432 (2002).
12. J. Ledieu, C.A. Muryn, G. Thornton, R.D. Diehl, T.A. Lograsso, D.W. Delaney, R. McGrath, Surf. Sci. **472**, 89 (2001).
13. L. Vitos, A. Ruban, H.L. Skriver, J. Kolla, Surf. Sci. **411**, 186 (1998).
14. P.A. Thiel, A.I. Goldman, C.J. Jenks, in *Physical Properties of Quasicrystals*, edited by Z.M. Stadnik (Springer, Berlin, 1999), p. 327.
15. R. McGrath, J. Ledieu, E.J. Cox, R.D. Diehl, J. Phys.: Condens. Matter **14**, R119 (2002).
16. C.J. Jenks, P.J. Pinhero, Z. Shen, T.A. Lograsso, D.W. Delaney, T.E. Bloomer, S.L. Chang, C.M. Zhang, J.W. Anderegg, A.H.M.Z. Islam, A.I. Goldman, P.A. Thiel, in *Quasicryst.*, (Proc. Int. Conf., 6th, 1998), p. 741.
17. 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, M.A. Van Hove, Surf. Sci. **495**, 19 (2001).
18. T. Cai, V. Fournée, T. Lograsso, A. Ross, P.A. Thiel, Phys. Rev. B **65**, 140202 (2002).
19. R.S. Becker, A.R. Kortan, F.A. Thiel, H.S. Chen, J. Va. Sci. Technol. B **9**, 867 (1991).
20. L. Barbier, D. Le Floc'h, Y. Calvayrac, D. Gratias, Phys. Rev. Lett. **88**, 085506 (2002).
21. Z. Shen, C.R. Stoldt, C.J. Jenks, T.A. Lograsso, P.A. Thiel, Phys. Rev. B **60**, 14688 (1999).
22. V.T. Deshpande, D.B. Sirdeshmukh, Acta Cryst. **14**, 355 (1961).
23. C. Xu, X. Lai, G.W. Zajac, D.W. Goodman, Phys. Rev. B **56**, 13464 (1997).
24. R.A. Dixon, R.G. Egwell, Surf. Sci. **452**, 207 (2000).