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Disorder or Complexity? Understanding a Nanoscale Template Structure on Alumina

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Abstract: One strategy in creating functional nanostructures is templating where active nanoparticles are arranged on a regular nanoscale array of anchor sites on an inert substrate. An extraordinarily well ordered substrate with a 4.2 nm template periodicity is an alumina (aluminum oxide) film grown on a $Ni_3Al(111)$ metallic alloy support. Templating on the alumina film is facilitated by a dot and a network superstructure that can readily be prepared but has not yet been understood at the atomic scale. By imaging the alumina surface with dynamic scanning force microscopy (SFM) operated in the noncontact mode (NC-AFM), we reveal that the main structural element of the oxide film is a lattice of hexagons with a 0.29 nm side length that is pinned to the 0.51 nm periodicity of the substrate. The surface unit cell is defined by distinguished sites forming the *dot structure*. Pinning the oxide film to the substrate furthermore results in a honeycomb-like topographic modulation referred to as the *network structure*. These findings demonstrate how long range order is generated by the superposition of complex structures that locally exhibit apparent atomic disorder.

The understanding and fabrication of regular structures is a most important endeavor in modern nanotechnology, and the issue is often to create regular nanoscale patterns that can be used as template structures for creating nanoscale architectures. A particularly favorable strategy of template formation on surfaces is to exploit nanoscale periodic variations in the surface electronic structure induced by a reconstruction with a very large unit cell.

Surface reconstructions with large unit cells are most intriguing for alumina (aluminum oxide), a material with widespread industrial applications[1−4] and a fascinating variety of surface structures,[5] many of them at present not well understood. If an alumina film is grown on the (111) surface of a Ni_3Al substrate, the surface exhibits large atomically flat terraces with two extraordinarily regular superstructures with periodicities of 4.2 nm (*dot structure*) and 2.4 nm (*network structure*), respectively.[6] Scanning tunneling microscopy experiments revealed that both superstructures provide an excellent template for the controlled growth of monodisperse catalytically active particles.[7] The surface, however, kept its secrets regarding atomic details in contrast to another alumina film with a less distinct superstructure where atomic details could recently be revealed.[8]

Here we unveil atomic details of alumina on $Ni_3Al(111)$ with dynamic scanning force microscopy (SFM) operated in the noncontact mode (NC-AFM), a technique which has demonstrated atomic resolution on the high temperature reconstructed α-$Al_2O_3(0001)$ surface.[9] Figure 1 is a high-resolution SFM image clearly exhibiting the major structural elements of the film, namely the dot structure (unit cell shown in blue) and the network structure (unit cell shown in red) that are related to each other by a $(\sqrt{3} \times \sqrt{3})R30°$ transformation.

The distinguished sites of the dot structure appear as bright circular features with a strong contrast against six surrounding smaller dark spots while the network structure covers the entire surface with atomic scale features and contrast enhancements forming a honeycomb-like pattern. The wealth of structural details leaves a strong impression of atomic scale disorder; however, the Fourier transform power spectrum of the image shown in Figure 2A with its sharp reflexes reveals a stunningly high degree of atomic order. The inner hexagon of reflexes marked in red represents the network structure while the reflexes of the dot structure are difficult to identify in the very center. All other spots of the Fourier spectrum are arranged on a hexagonal grid with a corresponding real space lattice constant of 4.2 nm. We interpret these spots as higher order reflexes,

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(1) Woodruff, D. P. In *The Chemical Physics of Solid Surfaces - Oxide Surfaces*; Elsevier: Amsterdam, 2001.
(2) Ertl, G.; Freund, H.-J. *Phys. Today* **1999**, 32−38.
(3) Ye, P. D.; Wilk, G. D.; Yang, B.; Kwo, J.; Gossmann, H. J. L.; Frei, M.; Mannaerts, J. P.; Sergent, M.; Hong, M.; Ng, K. K.; Bude, J. *J. Electron. Mater.* **2004**, *33*, 912−915.
(4) Wilk, G. D.; Wallace, R. M.; Anthony, J. M. *J. Appl. Phys.* **2001**, *89*, 5243−5275.
(5) Renaud, G. *Surf. Sci. Rep.* **1998**, *32*, 1.
(6) Degen, S.; Krupski, A.; Kraj, M.; Langner, A.; Becker, C.; Sokolowski, M.; Wandelt, K. *Surf. Sci.* **2005**, *576*, L57−L64.
(7) Becker, C.; Rosenhahn, A.; Wiltner, A.; von Bergmann, K.; Schneider, J.; Pervan, P.; Milun, M.; Kralj, M.; Wandelt, K. *New J. Phys.* **2002**, *4*, 75.
(8) Kresse, G.; Schmid, M.; Napetschnig, E.; Shishkin, M.; Kohler, L.; Varga, P. *Science* **2005**, *308*, 1440−1442.
(9) Barth, C.; Reichling, M. *Nature* **2001**, *414*, 54−57.

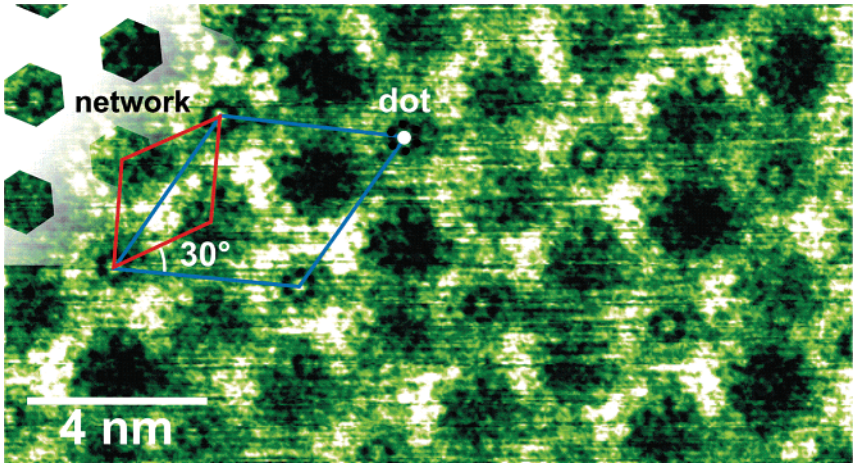

Figure 1. Dynamic scanning force microscopy (SFM) image of the alumina film grown on $Ni_3Al(111)$. The unit cells of the dot structure (blue) and the network structure (red) are highlighted. Their $(\sqrt{3} \times \sqrt{3})R30°$ relation is directly visible. Smaller scale structures are anticipated.

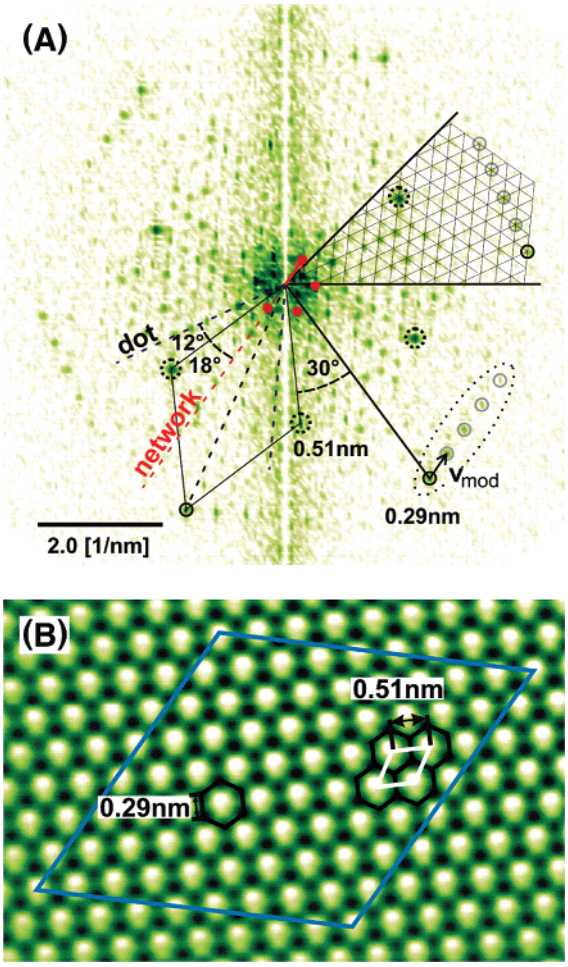

Figure 2. Fourier power spectrum of the original image exhibiting a manifold of hexagonal structures. The spots (four of them marked in red) of the inner hexagon represent the periodicity of the network structure, while the spots for the dot structure are hardly to be identified in the center of the spectrum. Additional reflexes indicate a periodicity of 0.51 and 0.29 nm. (B) The image was produced by an inverse Fourier transformation considering only the spots corresponding to the 0.51 nm periodicity and the main spots of the 0.29 nm group. It consists of a continuous net of open hexagons. The distance between the hexagons amounts to 0.51 nm.

documenting the morphologic predominance of the dot structure. However, some of the reflexes are so strong that they cannot be explained as mere high order reflexes but have to be caused by further periodicities present in the image. Very prominent are spots marked by dotted circles indicating a hexagonal periodicity of 0.51 nm. The outermost reflexes are linearly aligned groups of five spots indicating a periodicity of 0.29 nm. Comparable interatomic distances have earlier been found in scanning tunneling experiments.[10]

The axis defining the main reflexes of the group is rotated by 30° with respect to the axis of the 0.51 nm structure and by 42° with respect to the dot structure. The additional, linearly arranged spots of the outer group are satellite peaks caused by a modulation of the 0.29 nm periodicity. The modulating structure is represented by the translation vector v_{mod} between the satellite reflections. As v_{mod} corresponds to the lattice vector defining the network structure, we identify the network as the modulating structure. While the larger superstructures are clearly visible in the original image, the smaller scale structures revealed by the Fourier spectrum are not that obvious. An inverse Fourier transformation based only on the spots related to the 0.51 nm and the main spots of the 0.29 nm structure results in an artificial image visualizing the real space equivalents of these spots as shown in Figure 2B. As expected, the filtered inverse transform image consists of dark spots arranged on a regular hexagonal grid with a hexagon side length of 0.29 nm. The center points of all hexagons appear as bright spots with a lattice constant of 0.51 nm. While the filtered image reveals the fundamental structural elements of the surface, the structural subtleties causing the dot and network structures are contained in the spectral parts removed by spectral filtering.

For an analysis of the surface structural details, we use an image averaged in real space by a superposition of equivalently sized sections of the original image from Figure 1. In this averaged image shown in Figure 3A, it is possible to clearly recognize the atomic scale structures anticipated by the Fourier spectrum. The most clearly visible hexagonal structure is the one formed by six dark spots arranged around the dots of the dot structure. However, we can identify further hexagons that are primarily located in bright regions forming the network

(10) Addepalli, S. G.; Ekstrom, B.; Magtoto, N. P.; Lin, J. S.; Kelber, J. A. *Surf. Sci.* **1999**, *442*, 385−399.

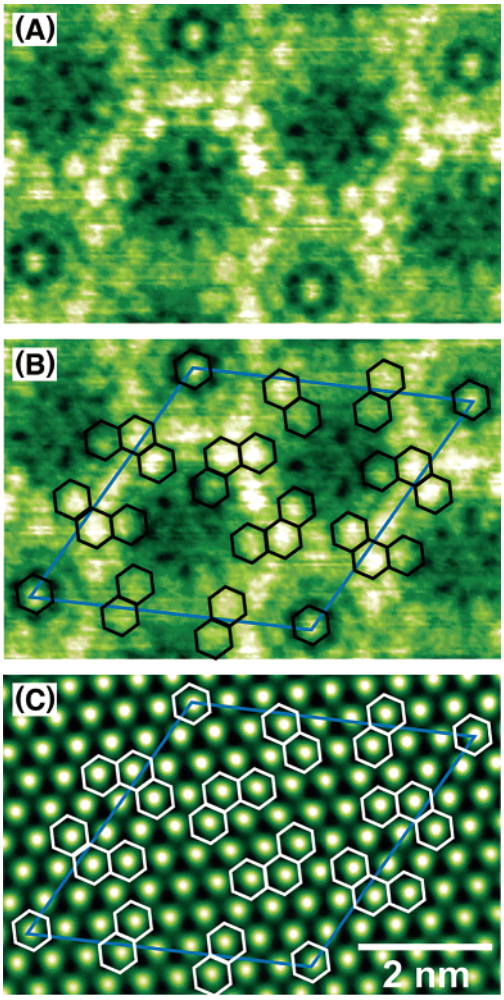

Figure 3. (A) Superposition of equally sized sections of the original nc-AFM image showing one surface unit cell. (B) The same image, but all recognizable hexagonal structures are highlighted. (C) The open hexagons are centered on a hexagonal lattice with 0.51 nm periodicity, confirming the interpretation of the FFT spectrum.

structure. The full set of hexagons that are reasonably well reproduced in the image is displayed in panel B. Although the hexagons do not form a closed hexagonal lattice comparable to the artificial image of Figure 2B, the fundamental structure is well reproduced, as the center point of each hexagon is located on the 0.51 nm grid as demonstrated in Figure 3C. This analysis reveals that both the dot and the network structure effectively yield an enhancement of contrast between bright center spots and the surrounding hexagonal arrangement of smaller dark spots in certain regions of the surface unit cell where the most pronounced contrast is found at the dot location. The modulation, on the other hand, yields a deformation of the 0.51 nm grid and, therefore, a less well pronounced regularity in the other regions of the surface.

The dominance of the 0.51 nm lattice results in the strong spots present in the Fourier power spectrum and is further underlined by the self-correlation image shown in Figure 4. Strongly enhancing the main spatial frequencies of the original image, the self-correlation image reproduces the dot, network, and 0.51 nm structures and directly establishes the relations between them. Besides the eye-catching relation of the dot and network structure, we notice a close tie between the commensurate dot and 0.51 nm structures with their unit

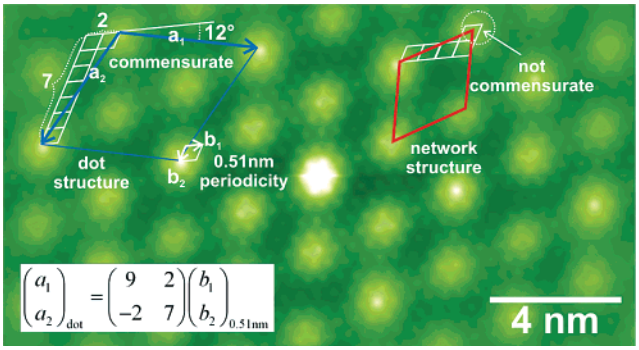

Figure 4. Self-correlation of the original SFM image from Figure 1 strongly enhancing the 0.51 nm periodicity. The unit cells of the 0.51 nm structure, the dot structure, and the network structure are highlighted in white, blue, and red, respectively. In contrast to the network structure, the dot structure is commensurate with the 0.51 nm lattice.

vectors related by the transformation:

$$\begin{pmatrix} a_1 \\ a_2 \end{pmatrix}_{\mathrm{dot}} = \begin{pmatrix} 9 & 2 \\ -2 & 7 \end{pmatrix} \begin{pmatrix} b_1 \\ b_2 \end{pmatrix}_{0.51}$$

There is no such relation between the network structure and the 0.51 nm grid. As the dots are clearly the points of highest correlation, we conclude that the surface unit cell is unambiguously defined by the dot structure as it was anticipated from the analysis of the original image.

Remarkably, the 0.51 nm periodicity found in our experiments perfectly coincides with the well-known aluminum sublattice of the Ni_3Al substrate.[6] We believe that this provides the clue to the understanding of the complex surface structure and propose that the 0.29 nm lattice is formed by aluminum atoms that are hexagonally arranged around oxygen atoms, located on top of substrate aluminum atoms forming the first interface layer. Open hexagons of aluminum atoms are a fundamental structural motif in the aluminum rich layer of α-$Al_2O_3(0001)$[11] and have also been found for alumina on NiAl-(110).[8] In previous studies of the alumina film grown on Ni_3Al-(111), spot profile analysis low-energy electron diffraction (SPA-LEED) spectra were reported that correspond well to the Fourier spectrum presented here. The existence of a hexagonal atomic surface lattice was, however, dismissed because the authors could explain their data solely based on contributions of the substrate and the dot structure.[6] In a second combined SPA-LEED and gracing incidence X-ray diffraction (GIXD) study, the spectrum of spatial frequencies was interpreted to arise from a modulated hexagonal surface layer that has similar dimensions but is rotated by 7.5° compared to the one proposed here.[12,13] Providing real space information of the topmost surface layer by scanning force microscopy, we can clearly establish the existence of a surface hexagonal lattice that is at least in parts regular.

We speculate that a complex and strong interplay between the highly ordered aluminum sublattice of the substrate and the hexagonal structure of the oxide film gives rise to the evolution of the coincidence lattice of the dot structure. The necessary reconfiguration of the oxide film to adapt to this coincidence

(11) Tepesch, P. D.; Quong, A. A. *Phys. Status Solidi B* **2000**, *217*, 377−387.
(12) Bikondoa, O. Structural properties of oxide thin films on alloys. Ph.D. thesis, Euskal Herriko Unibertsitatea, Bilbao, 2003.
(13) Wendler, F. Untersuchung der $Fe_3O_4(001)$-c(2×2)-Oberfläche und dünner Al_2O_3-Filme auf Nickelaluminium mit Oberflächenröntgenbeugung. Dissertation, Ludwig-Maximilians-Universität, München, 2004.

causes the topographic feature of the network structure. The network covers the complete surface, modulating the 0.51 nm periodicity hexagonal lattice that is the fundamental atomic scale structure. In this way, the apparent disorder turns into a complexity of the surface that can be traced back to a complicated but well ordered arrangement of hexagons. We clearly identify those structures as the origin of the reconstruction providing the nanoscale template of this extraordinary alumina surface.

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Supporting Information Available: Experimental technique and sample preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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