Kinetic asymmetry in the growth of two-dimensional Mn oxide nanostripes

T. Obermüller,1 W. Steurer,1 S. Surnev,1 G. Barcaro,2 L. Sementa,2 A. Stroppa,2 A. Fortunelli,2,* and F. P. Netzer1,*

1Surface and Interface Physics, Institute of Physics, Karl-Franzens University A-8010 GRAZ, Austria
2CNR-ICCOM, CNR-IPCF and CNR-SPIN, Consiglio Nazionale delle Ricerche, I-56124 PISA and I-67010 L’AQUILA, Italy

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Nanostructures with very high (>20) aspect ratios of a two-dimensional manganese oxide phase are grown on the Ag(100) surface using a physical vapor deposition method and thoroughly characterized via low-energy electron diffraction and scanning tunneling microscopy. Despite the square pattern of the substrate, symmetry breaking is produced by the structural anisotropy of the kinetically stabilized, metastable Mn surface oxide phase. As rationalized by a first-principles analysis, the resulting asymmetry in edge diffusion and attachment energies and the difference in adsorption energetics between Mn and Ag adatoms leads to the kinetic formation of such strikingly anisotropic structural domains: they feature nanoscale width (∼5–20 nm), mesoscopic length (up to ∼1 μm), very low defect density, and grow along the high-symmetry directions of the Ag(100) substrate.

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Anisotropic growth processes are at the basis of many bottom-up nanostructure fabrication concepts. Asymmetric growth is mediated by the uniaxial transport of atoms and molecules, the building blocks of bottom-up nanostructure formation, and/or preferential aggregation along specific directions in the growing of small nuclei, leading to anisotropic island shapes.1–3 A desired asymmetry in a particular growth direction can be promoted by various means, such as anisotropic crystal structure, anisotropic building blocks (possible in the case of molecules), template directed synthesis using patterned substrate surfaces, or symmetry breaking in the nucleation step in multiphase (e.g. vapor-liquid-solid) processes.3 Unsymmetrical lattice misfit at the film-substrate interface and anisotropic strain has also been invoked to cause anisotropic island shapes.4–6 Structural anisotropy is important in view of several applications, as it can endow the system with directional transport in wave-guides, sensors, and other nanodevice systems.7,8 Here, we describe the formation of nanostripes with very high aspect ratios of a two-dimensional (2D) manganese oxide phase on a metal surface using a physical vapor deposition method. What makes this system so peculiar with respect to previous studies is that such a strong growth anisotropy occurs for a MnO-type oxide on a Ag(100) surface, whose square pattern would suggest symmetrical surface diffusion and the growth of equilateral two-dimensional oxide islands. It will be argued that the structural asymmetry of a kinetically stabilized metastable Mn surface oxide phase, which causes an asymmetry in attachment energies and in edge mobility via unconventional diffusion mechanisms, is at the root of this nanostripe formation process.

The Ag(100) surface is a suitable substrate for the growth of epitaxial MnO(100) oriented thin films,9–12 despite the relatively large lattice mismatch (9%) between Ag(100) and MnO(100), if one takes the bulk lattice constants as a reference. This lattice misfit becomes however reduced after taking into account the shrinking of the lattice constant in ultrathin oxide layers at the 2D limit.13 MnO is antiferromagnetic as a bulk phase, but low-dimensional MnO nanostructures have been reported to display unusual magnetic behavior, such as ferromagnetism14–16 or large paramagnetic orbital anisotropy.17 In view of the interest of these structures, the investigation of MnO-type nanostructure growth on a magnetically inert metal surface is an actual scientific challenge.

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We find that the 2D MnO monolayer on Ag(100) exhibits a (2 × 1) surface structure, which is a kinetically stabilized two-dimensional metastable phase. The MnO (2 × 1) phase grows with very low defect density in stripes of mesoscopic length with very high aspect ratios (>20) along the high-symmetry directions of the Ag(100) substrate. It is proposed that this striking kinetic asymmetry in the growth process on the symmetric (100) substrate is mediated by a strong bonding and diffusion anisotropy of adatoms at the growing (2 × 1) island boundaries.

The scanning tunneling microscopy (STM) images of Fig. 1 illustrate the morphology of the Mn oxide overlayers deposited on Ag(100) for various oxide coverages. The Mn oxide deposits were prepared by reactive vaporization of Mn in oxygen followed by annealing (700–800 K) or by Mn evaporation onto Ag at room temperature followed by oxidation at 700–800 K—see Supplemental Material18 for experimental details. Figure 1(a), with a nominal oxide coverage of 0.3 ML, shows well-defined stripes of the MnO (2 × 1) structure (see below) with darker contrast following the high-symmetry (110) directions of the Ag(100) surface. Stripes running along orthogonal directions merge at 90° angles, displaying domain boundaries with somewhat brighter contrast lines. The stripes have perfectly straight, defect-free edges and a low defect density inside the stripe phase; they appear to be embedded into the Ag substrate. A number of second-layer Ag islands with bright contrast are attached to the Mn oxide stripes, with straight edges pinned to the oxide but with frizzy free boundaries; this is indicative of a high mobility of unpinned Ag step atoms at room temperature and will be further discussed below. While Fig. 1(a) has been recorded with positive sample bias, thus imaging the empty sample states, the image of Fig. 1(b) has been recorded with negative bias: we notice a contrast inversion, where the Mn oxide stripes are now imaged brighter. The domain boundaries, where orthogonal stripes meet, are again apparent with bright contrast. Figures 1(c) and 1(d) are STM images of 0.75-ML Mn oxide on Ag(100), where the geometrical regularity of the stripe pattern is clearly apparent; the stripes have very high

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aspect ratios (in many cases larger than 20) and extend over mesoscopic length scales. The inset of Fig. 1(c) shows a sharp $(2 \times 1)$ low-energy electron diffraction (LEED) pattern of this surface. At the top of Fig. 1(c), lower Ag terrace levels can be recognized, whereas at the bottom right of Fig. 1(d), two MnO $(2 \times 1)$ (minority) stripes located on top of a Ag terrace are seen. The line scans in the inset of Fig. 1(d) specify the apparent depth of the embedded MnO stripes (line scan 1) and the apparent height of the MnO on top (line scan 2) to $-0.13 \text{ nm}$ and $0.11 \text{ nm}$, respectively. These apparent heights are dependent on the bias voltage. Line scan 3 from a Ag terrace over a MnO top stripe to the next Ag terrace level is consistent with this scenario of embedded and on-top MnO stripes. It has to be mentioned at this point that, while the MnO $(2 \times 1)$ phase is by far the most dominant Mn oxide phase in the 2D monolayer regime, a couple of minority Mn oxide structures have been detected occasionally in coexistence with the $(2 \times 1)$ structure at low or high chemical potentials of oxygen; these are, however, not the topic of this paper. The MnO$(100)$ $(1 \times 1)$ phase is only observed for islands of several monolayers in height.\textsuperscript{9,19}

The STM images of Fig. 2 specify the atomic details of the MnO $(2 \times 1)$ structure. The image of Fig. 2(a) shows that the $(2 \times 1)$ structure is characterized by bright and dark lines running parallel to the long stripe direction. The bright lines consist of atomic protrusions that specify the $(2 \times 1)$ unit cell, as evident from the atom-resolved image Fig. 2(b). The corrugation along the bright lines amounts to $\sim 10 \text{ pm}$ [line scan 1, Fig. 2(c)]; across the lines (following the $(x \times 2)$ direction of the unit cell), it is $\sim 30 \text{ pm}$ [line scan 2, Fig. 2(c)]. The domain boundary, where two orthogonal stripes meet, lacks atomic order although some matching of $(2 \times 1)$ rows between the two domains can be recognized, see the inset of Fig. 2(a). The $(2 \times 1)$ Ag edge perpendicular to the $(x \times 1)$ lines displays a double row of bright blobs, as evident at the top left of Fig. 2(b). This is due to an electronic effect of the nonpolar reconstructed MnO-Ag boundary line, which is discussed below.

A structural model of the Ag$(100)$/MnO$(2 \times 1)$ phase is shown in Fig. 3(a), as obtained by locally optimizing at the density functional theory (DFT) $+ U$ level (with $U = 4.5 \text{ eV}$; see Fig. S1 in the Supplemental Material\textsuperscript{18}) a configuration.

FIG. 1. (Color online) Constant current topographic STM images of Mn oxide $(2 \times 1)$ stripes on Ag$(100)$. (a) Nominal Mn oxide coverage 0.3 ML $(V_S = +2 \text{ V}, I_T = 200 \text{ pA})$. (b) Mn oxide coverage 0.3 ML $(V_S = -1.9 \text{ V}, I_T = 100 \text{ pA})$. (c) Mn oxide coverage 0.75 ML $(V_S = +1 \text{ V}, I_T = 200 \text{ pA})$. The inset displays a LEED picture of this surface $(electron energy 120 \text{ eV})$. (d) Mn oxide coverage 0.75 ML $(V_S = +1.8 \text{ V}, I_T = 150 \text{ pA})$. The inset shows three line profiles following the lines 1–3, as indicated in the image.
KINETIC ASYMMETRY IN THE GROWTH OF TWO-...  

PHYSICAL REVIEW B 88, 235410 (2013)

FIG. 2. (Color online) High-resolution STM images of Mn oxide (2 × 1) stripes, (a) \( V_S = -1.9 \) V, \( I_T \) = 100 pA; (b) \( V_S = -1.0 \) V; \( I_T \) = 100 pA. The inset in (a) shows a domain boundary between two orthogonal (2 × 1) stripes. A (2 × 1) unit cell is indicated in image (b). (c) Line scans along the lines 1 and 2 of image (b).

taken from the homologous Ag(100)/NiO-(2 × 1) phase. As discussed in detail in the Supplemental Material, the structural details of the MnO (2 × 1) phase depend on the choice of the exchange-correlation (xc) DFT functional, whereas the energetics and simulated STM images are much more robust and insensitive to this choice. The simulated STM images always show brighter spots arranged along lines associated with the uppermost oxygen species, as illustrated in Fig. 3(a). Moreover, in close analogy with the NiO/Ag case, the (2 × 1) phase exhibits a zigzag antiferromagnetic spin arrangement (AFM3) as its most favorable configuration and is higher in energy with respect to the pseudomorphic (1 × 1) phase by 1.19 eV per MnO unit (see the Supplemental Material 18 for more details). Let us recall that, in the NiO/Ag(100) case, the thermodynamic stability of the (1 × 1) phase with respect to the (2 × 1) one has been experimentally proven. The formation of the (2 × 1) phase must then be due to a kinetic stabilization, and—again in perfect analogy with NiO/Ag case (see Fig. 8 in Ref. 20)—this is indeed what we found by comparing the energies of structural models of the early stages of the growth of a MnO monolayer on a Ag(100) step edge, see Fig. 3(b). It can be noted that the stabilization of the (2 × 1) growth with respect to the (1 × 1) growth pattern is much more pronounced than in the NiO case, and we can expect an even clearer kinetic preference for the metastable (2 × 1) monolayer—as indeed found in the experiment.

A full investigation of the growth process via a sophisticated first-principles approach such as the present DFT + \( U \) one, which is required by the complex energetics of these supported oxide ultrathin phases, is outside present computational possibilities. In the following, we focus on selected capture and diffusion processes and extract information which can provide insight into interpreting the experiment. Figure 4 shows structural models of the investigated diffusion and capture mechanisms and the associated energetics (evaluated via a DFT + \( U \) approach with \( U = 4.5 \) eV). We limit to a single Mn or Ag adatom interacting with and moving along the [110]-O and [−110]-MnO edges of the (2 × 1) phase, with the former representing the oxygen-rich side of the polar edge parallel to the direction of anisotropic growth and the latter modeling the growth front of the (2 × 1) nanostripes. In Fig. 4(a), the two local minima and saddle point between them, corresponding to adatom diffusion along the [110]-O edge, are shown, while in Fig. 4(b), only the configuration corresponding to the adatom adsorbed at the [−110]-MnO ridge is shown. Interestingly, the diffusion energy barriers are not proportional to the corresponding capture energies (summarized in Table I): capture energies are higher on the [110]-O edge because an incoming adatom interacts with two oxygen atoms rather than with only one (and in an unfavorable position) on the [−110]-MnO edge, but adatom diffusion is much faster along the [110]-O edge because the system can exploit the structural freedom at this edge to go through a saddle point structure which is highly distorted but in which bonding is still preserved to a great extent—see Fig. 4(a)—whereas the additional adatom cannot but lose all its binding to the oxide when jumping from one adsorption...
FIG. 4. (Color online) Diffusion process of a Mn adatom along the (a) [110]-O border and (b) [−110]-MnO border of a MnO (2 × 1) stripe. In (a), the two minima are shown on the right and left sides, whereas the saddle point is shown in the middle; the side profiles are also displayed to highlight the remarkable reconstruction characterizing the [110]-O border in the saddle point. In (b), only one minimum is shown, as it has not been possible to single out the single point corresponding to the diffusion process along the [−110]-MnO border; the arrow indicates the location of the first-neighbor minimum analogous to the original one.

In short, the present simulations suggest that a Mn adatom strongly interacts with but can easily diffuse along a [110]-O ridge with a mobility barrier of only 0.12 eV (implying extremely fast mobility at 700–800 K), whereas it interacts less strongly with but has a hindered mobility with a barrier practically equating its interaction energy (1.2 eV) along the [−110]-MnO ridge. A qualitatively similar conclusion is found for an Ag adatom on the same edges, which can diffuse along [110]-O exploiting a saddle point with a strongly reconstructed geometry (not shown), whereas it is less mobile on the [−110]-MnO ridge, with the crucial difference that the oxygen affinity of Ag is much lower than that of Mn, so that its adsorption energy on the [−110]-MnO ridge—and thus its diffusion barrier along the growth front—is much weaker: about 0.3 eV. Such an energy is small enough to ensure mobility of Ag adatoms on the growth front at 700–800 K and therefore the possibility for Ag to make space for incoming, much more strongly interacting Mn species. The barrier for O$_2$ dissociation at the polar [110] border on the Mn-rich side has been calculated to be negligible; at the given temperature/pressure conditions of growth, the oxygen supply thus is not a limiting factor for asymmetric growth.

This overall picture simultaneously is in tune and provides a basis for rationalizing the asymmetric, preferentially uniaxial growth of the (2 × 1) phase. The growth of deposited Mn atoms in an oxygen environment starts at Ag(100) step edges in the metastable (2 × 1) structure due to kinetic reasons. The so-formed (2 × 1) rows then continue growing in narrow anisotropic stripes as more incoming Mn atoms attach to the [110] and [−110] boundaries, but can quickly diffuse along the former, whereas they get stuck on the latter. At the same time, Ag mobility is large along both edges and on the regular Ag(100) surface at the temperatures used in beam epitaxy experiments (700–800 K): this high mobility explains why the (2 × 1) MnO stripes—although initially formed on top of the Ag(100) surface—tend to transform into an embedded phase. Ag adsorption energy on the [110] edges and the corresponding stabilization associated with Ag condensing on these polar steps are nonnegligible and will eventually give rise to Ag(100) terraces limited on one side by the MnO(2 × 1) phase and on the other side by irregular borders. A number of such “transient” Ag island structures, i.e., those involved in the process of embedding the (2 × 1) phase, is visible in the STM image of Fig. 1(a) with the bright contrast (see also Fig. S2 in the Supplemental Material).

| Adsorption and diffusion barrier energies of Mn and Ag adatoms adsorbed on the [110]-O and [−110]-MnO borders of a (2 × 1) stripe of MnO; the corresponding configurations are shown in Fig. 4. The adsorption energies are measured with respect to the adatom adsorbed on the bare (100) silver surface. |
|---|---|---|---|
| [110]-O border | Diffusion barrier (eV) | [−110]-MnO border | Diffusion barrier |
| Adsorption energy (eV) | Mn | 2.4 | 1.2 |
| | Ag | 0.2 | 0.3 |
| | Diffusion barrier (eV) | Mn | 0.12 |
| | Ag | 0.10 | – |
| | | | – |
It should be noted in passing that other possible mechanisms leading to anisotropic growth, such as in-plane 2D polarity in the [110] direction\textsuperscript{21} or strain due to mismatch,\textsuperscript{4–6} cannot rationalize the experimentally observed features. In fact, they would produce a narrow distribution of stripe widths centered around a maximum, whereas very different widths are observed in Fig. 1 and probably also nonstoichiometric MnO polar [110] edges to compensate in-plane dipole, whereas no edge roughening is observed in STM. The highly polarizable Ag support may help in the compensation of dipoles, both parallel and perpendicular to the MnO stripes. Strain is also excluded by the commensurate character of the MnO(2 $\times$ 1) surface phase.

In summary, the growth of the first 2D MnO monolayer on Ag(100) is characterized by a well-ordered (2 $\times$ 1) structure in the form of uniaxial nanostripes with very high aspect ratios running along the high-symmetry directions of the substrate over mesoscopic length scales. The MnO(2 $\times$ 1) structure is a metastable kinetically stabilized phase as revealed by DFT calculations. The observed asymmetric growth pattern is rationalized by a first-principles theoretical analysis and a scenario based on edge diffusion and attachment energies of Mn and Ag adatoms at the nonequivalent edge boundaries of the growing (2 $\times$ 1) islands. The calculations reveal that a pronounced difference in the adatom diffusion energies at the edges of the MnO(2 $\times$ 1) structure with unconventional atomistic mechanisms is at the root of this striking symmetry-breaking phenomenon. This is thus one paradigmatic case in which diffusion mechanisms entirely determine the final growth morphology of ultrathin oxide films.

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alessandro.fortunelli@cnr.it; falko.netzer@uni-graz.at

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