



Interface-dependence of Nucleation and Self-Assembly of Ultrathin Iron Oxide Films

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Abstract

The interface-dependence of heteroepitaxial growth of iron oxide films is investigated by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). We show that the different chemical affinity to the metal substrate (Ru vs. Pt) and the step density (basal vs. vicinal Pt) significantly influence nucleation, heteroepitaxial crystal growth, and adhesion. Repeated Fe deposition-oxidation cycles lead to a Stranski-Krastanov growth mode on all substrates. On Ru(0001), metastable FeO(111) layers with strongly expanded lattice constants with a thickness up to 4 monolayers (ML) can be obtained by one-minute oxidation of the corresponding amount of Fe. Homogeneous nucleation of self-assembled, periodic Fe₃O₄(111) nanodomains embedded in an ultrathin FeO(111) film occurs on Ru(0001) in ~4 ML thick FeO(111) films. Nucleation of Fe₃O₄(111) islands below 4 ML on Ru(0001) occurs preferentially at substrate step edges while on Pt(111), no influence of surface defects was observed. On a vicinal Pt substrate, the terrace width and step height triplicates under influence of the wetting FeO(111) film. Differences in the growth behavior are discussed in terms of the involved surface and interface free energies.

Introduction

Oxide compounds are used in a vast variety of applications, for example as magnetic devices, ionic superconductors, catalysts, surface coatings, etc. Iron oxides occur in different oxidation states and crystal structures with different properties and are utilized, e.g., in magnetic storage media or as heterogeneous catalysts for the dehydrogenation of ethylbenzene [1,2].

The intrinsic characteristics of such compounds are strongly modified when the length scales determining these properties become of the order of the spatial extent of the system. Some properties of compounds are mainly due to surface effects such as the catalytic activity, or are altered due to the reduced atomic coordination at a surface such as the magnetic properties [3]. Ultrathin films may differ from the thermodynamically expected bulk phases and interface-stabilized phases may form [4-6]. Also the adhesion between two materials is strongly influenced by the chemical interaction at an atomic scale.

Differences in the adhesive behavior of two materials can be rationalized by considering the energies associated with the change of surface area to interface area when an interface between two materials is formed [7]. The energy balance $\Delta\gamma = \gamma_f + \gamma_{in} - \gamma_s$ determines the growth mode of a deposited material (γ_f , γ_s : surface free energy of the deposited film and a substrate, respectively; γ_{in} : interface free energy). For $\Delta\gamma > 0$, the formation of compact islands (Volmer-Weber growth mode) is anticipated while $\Delta\gamma < 0$

leads to wetting layers with a high surface and interface area (Frank-Van der Merwe growth mode). Generally, the surface free energy of oxides is higher than of metals, therefore most metals tend to form compact particles on oxide substrates whereas oxide films are dispersed on metal substrates. However, the dispersion of different metals on the same oxide substrate may differ significantly [8,9], and it has recently been demonstrated that Co films can be forced to wet an alumina substrate after hydroxilation [10]. These effects are determined by specific interactions at the interface such as the chemical affinity, strain due to a lattice mismatch, etc, and thus the interface free energy γ_{in} . For $\gamma_{in} < 0$, even dissolution and formation of an interface alloy is expected [14]. The interaction of interface layers (interfacants) [11,12] or surfactants [13] which lower the interface or surface free energy, respectively, may also lead to otherwise unexpected wetting films. On the other hand, a high lattice mismatch may generate oxide islands on a metal substrate although the surface free energies would favor a layer-by-layer growth [15,16].

Surface irregularities such as steps or kinks lead to a higher contact area of the film with the substrate, and thus a low interface energy may lead to a preferential nucleation at these sites when the condition $\gamma_{in} < \gamma_s + \gamma_f$ is fulfilled [7]. Finally, also growth kinetics has to be considered, as high deposition rates or low temperatures lead to an insufficient mobility of surface atoms for equilibration, so that continu-

ously multilayers may form from a supersaturated precursor (pseudo-Frank-Van der Merwe growth mode).

To summarize, modifications of the interface energetics by the growth conditions or by a modification of the interface region may have decisive influence on the preferential nucleation site, the growth morphology and adhesion between two compounds. This is discussed in this article for the growth of iron oxide films on different metal substrates.

Experiment

Iron oxides were grown on single-crystalline Ru(0001), Pt(111) and Pt(9 11 11) substrates. The Pt crystals were cleaned by repeated cycles of Ar-sputtering and annealing to 1300 K. Ru crystals were annealed at higher temperatures (1450 K). A vicinal Pt crystal was created by cutting a Pt(111) single crystal by 5.2° along the $[\bar{2} 11]$ direction. Iron was evaporated from an iron wire wrapped around a resistively heated tungsten filament. Scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) measurements were performed in an ultrahigh vacuum chamber which is part of a multi-chamber system [17]. The chamber contains facilities for gas dosage, Ar-

sputtering, a combined backview LEED and AES optics and a STM head (Burleigh). STM measurements were performed in the constant current mode with electrochemically etched tungsten tips.

Results

1. Growth of ultrathin iron oxide films

On various substrates, iron oxides grow in form of ultrathin FeO(111) films with a thickness of a few monolayers (ML). On Ru(0001) and Pt(111), quite different coincidence structures are formed as shown in fig. 1. Details of both structures can be found in previous publications [18,19]. FeO(111) films on Ru(0001) grow with a thickness of up to 4 ML and are perfectly aligned with the atomic rows of the substrate and coincidence is achieved by locking either 6 or 7 FeO units on 8 Ru atom sites with a concomitant lattice constant expansion to 3.58 or 3.08 Å (bulk FeO: 3.04 Å), respectively (fig. 1a) [18]. On Pt(111), a maximum FeO(111) thickness of 2.5 ML can be obtained. The lattice constant of the FeO(111) films is less strongly expanded and a thickness-dependent coincidence is achieved by a slight rotation of the films (fig. 1d) [19].

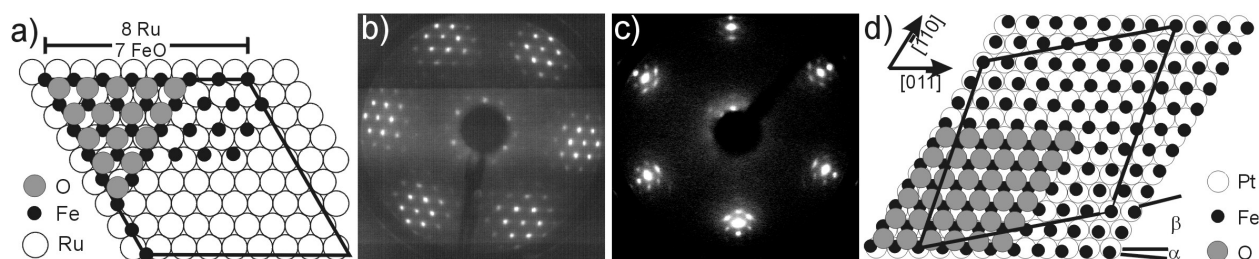


Figure 1: Coincidence structures and corresponding LEED patterns of FeO(111) monolayer films on Ru(0001) (a,b) and Pt(111) (c,d).

As similar growth conditions have been used on both substrates, the different coincidence structures should be caused by the different interaction at the interface. On both substrates the FeO(111) film is spatially clearly separated from the substrate, therefore γ_{in} is positive in both cases. However, the interface energy γ_{in} in the case of FeO/Ru very likely is lower than for FeO/Pt. Despite the slightly larger lattice mismatch (14% on Ru(0001), 11% on Pt(111)), simple, unrotated “6 on 8” or “7 on 8” coincidence structures are observed on Ru(0001), even if this requires a tremendous lattice constant expansion. On Pt(111), the FeO(111) film does not align with the atomic rows of the substrate but rather seems to “float” on the substrate indicating a weaker interaction. Further, these films are less stable than on Ru(0001) where thicker FeO(111) films can be obtained. Remarkably, also on a Pt(100) substrate FeO films grow with the polar (111) termination, even though the hexagonal reconstruction of the clean Pt(100) does not form under influence of a growing FeO film, and thus hexagonal FeO(111) films form on a substrate with square symmetry [20]. Shaikhutdinov et al. suggested therefore that the lattice mismatch between substrate and film is of minor importance for the growing iron oxide film. However, this might not be true for more strongly interacting substrates where the growing oxide film aligns with the substrate atoms.

2. Nucleation and Growth of Fe₃O₄(111) islands

On Ru and Pt substrates, a Stranski-Krastanov-type growth mode of Fe₃O₄(111) islands on a FeO(111) wetting layer occurs when the growth is thermodynamically controlled, i.e., by successive deposition and oxidation of iron [16]. High oxide deposition rates can be realized by depositing large amounts of iron and short oxidation times (however,

long enough to ensure stoichiometric conversion to the corresponding iron oxide). On Ru(0001), this approach leads to a homogeneous nucleation of self-assembled, periodically arranged Fe₃O₄ nanodomains embedded in an FeO(111) Moiré structure when ~4ML Fe are deposited and oxidized (fig. 2) [18]. On Pt(111), no difference was reported using either repeated deposition-oxidation cycles [15] or one-minute-oxidation of 3 ML Fe deposited in one turn [21].

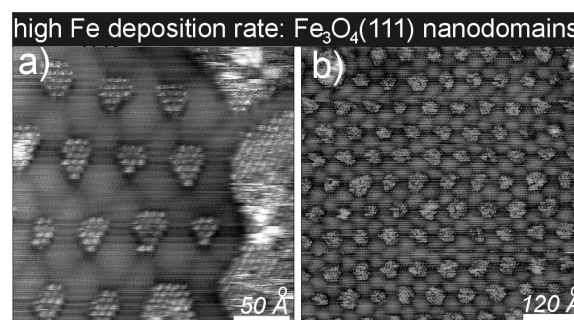


Figure 2: Periodically arranged Fe₃O₄(111) nanodomains after one-turn deposition of ~4 ML Fe and subsequent oxidation. (a) 250x250 Å² STM image of atomically resolved Fe₃O₄(111) domains embedded in a FeO(111) film. (b) 600x600 Å² region of an extended terrace.

Again, these differences should be caused by the different chemical interaction at the interface with both metals. Generally, a layer-by-layer growth of FeO(111) on both substrates is expected from the high surface free energies of the metals and the low surface free energy of FeO, respectively (Pt: 2.3 J/m²; Ru: 2.9 J/m²; FeO: 0.6 J/m² [16]). However, the island growth mode of Fe₃O₄ ($\gamma_f = 0.4$ J/m²)

can only be explained by a high interfacial energy due to the lattice mismatch with both substrates.

On Ru(0001), the homogenous nucleation of Fe_3O_4 nanodomains occurs when the critical thickness for Fe_3O_4 nucleation is exceeded [16]. For a stoichiometric conversion, this requires a thickness of at least 4 ML FeO. As FeO(111) films are polar, thick films should not be stable [22,23]. However, as discussed in a previous publication, these films are stabilized electrostatically by a strong lattice constant expansion due to the strong interaction with the Ru substrate so that, unlike on Pt substrates, even thicker FeO(111) films can be stabilized [18]. Details on the growth on both substrates can be found in previous publications [15,16,18].

3. Influence of the substrate step morphology

As discussed in the introduction, increased contact areas and diffusion characteristics on stepped or kinked surfaces may affect nucleation and growth. In heterogeneous catalysis, one has long become aware of a different chemical reactivity due to altered adsorption properties of defective or complex surfaces, often responsible for the so-called 'material gap' [24]. We have thus turned to investigations of the influence of substrate steps to growth and adhesion.

On Pt(111), no influence of substrate defects on the Fe_3O_4 island formation was observed and a homogeneous nucleation was assumed [15]. This is different from growth on Ru(0001), where a preferential nucleation of Fe_3O_4 islands at step edges has been observed (fig. 3a) [16].

As outlined in the introduction, for $\gamma_{\text{in}} < \gamma_{\text{s}} + \gamma_{\text{f}}$ nucleation is expected to occur on terraces while for $\gamma_{\text{in}} > \gamma_{\text{s}} + \gamma_{\text{f}}$ nucleation should preferentially take place at steps or kinks [7]. Preferential nucleation at steps on Ru(0001) can thus be explained by the slightly higher surface free energy of Ru compared to Pt (2.93 vs. 2.34 J/m²) [16] and is also in line with the proposed lower interface energy for the stronger interacting FeO/Ru system.

Experiments on a vicinal Pt substrate, Pt(9 11 11), revealed essentially a similar Stranski-Krastanov growth mode as on Pt(111) (fig. 3b). First, the growing FeO(111) film changes the step structure of the clean Pt substrate and more kinks are formed at the substrate step edges (fig. 4a). After deposition of ~1ML FeO(111), the substrate morphology has significantly changed and triple steps separating terraces with a triplicated width (~75 Å) have formed (fig. 4). At this stage, Fe_3O_4 islands start to nucleate (fig. 3b).

It has been calculated that the surface free energies of vicinal oxide surfaces deviate considerably from the low-index surface planes ($\gamma_{\text{vicinal}}(\text{Oxide}) > \gamma_{\text{basal}}(\text{Oxide})$) due to the more localized electronic structure of partially covalent compounds when compared to vicinal metal surfaces which have a similar surface free energy as the low-index surface planes ($\gamma_{\text{vicinal}}(\text{Metal}) \approx \gamma_{\text{basal}}(\text{Metal})$) [25]. Additionally, for polar oxide surfaces, the formation of more stable facets (e.g., autocompensated FeO(100)) may become important as, for instance, has been reported for $\alpha\text{-Al}_2\text{O}_3(10\bar{1}0)$ after annealing [26]. Even if the additional energy cost for the formation of triplicated steps (or nanofacets) has to be considered, these effects cause the observed tendency for the formation of extended low-index

FeO(111) surface planes separated by nanofacets. This is similar to the previously reported restructuring of vicinal Pt surfaces due to changes in the surface free energies in reactive atmosphere (e.g., upon chemisorption of oxygen) [27,28]. Terrace width extensions of stepped oxides have been reported for MgO(100) [29] and $\alpha\text{-Al}_2\text{O}_3(0001)$ [30]. In the latter case, the terrace width was very uniform (~100nm) and this was attributed to repulsive and attractive interactions between the steps; maybe similar interactions lead to the uniform triplicated terrace width of FeO(111) films on Pt(9 11 11).

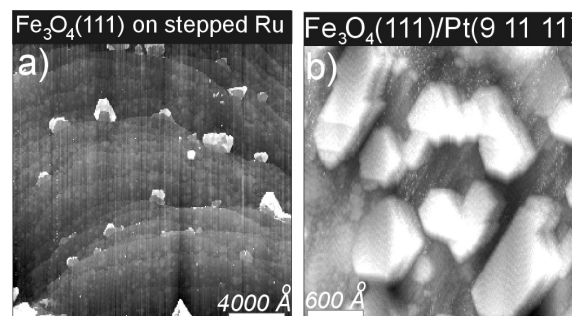


Figure 3: (a) 2x2 μm² STM image of $\text{Fe}_3\text{O}_4(111)$ islands nucleating at step edges from a closed ~3 ML FeO(111) film after extended oxidation. (b) 3000x3000 Å² STM image of $\text{Fe}_3\text{O}_4(111)$ islands grown on a Pt(9 11 11) substrate.

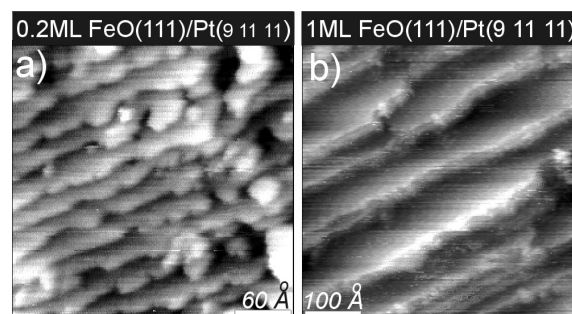


Figure 4: (a) 300x300 Å² STM image of Pt(9 11 11) after formation of ~0.2 ML FeO(111). Note the increased formation of kinks at the substrate step edges. (b) 500x500 Å² STM image after deposition of ~1 ML FeO(111). The step height and terrace width has triplicated.

Conclusions

We have investigated the interaction of thin iron oxide films with Ru and Pt substrates. We could show that the interface energy is of major importance for the structure of the growing film. The chemical (or electronic) nature in combination with the geometric structure (e.g. steps) significantly influence processes such as nucleation, crystal growth and adhesion between two materials leading to a quite different heteroepitaxy of iron oxides on Ru and Pt substrates.

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