Ostwald ripening is a well-known physicochemical phenomenon in which smaller particles, characterized by high surface energy, dissolve and feed the bigger ones that are thermodynamically more stable. The effect is commonly observed in solid and liquid solutions, as well as in systems consisting of supported metal clusters or liquid droplets. Here, evidence is provided for the occurrence of Ostwald ripening in an oxide-on-metal system which, in this case, consists of ultrathin iron monoxide (FeO) islands grown on Ru(0001) single-crystal support. The results reveal that the thermally-driven sintering of islands allows altering their fine structural characteristics, including size, perimeter length, defect density and stoichiometry, which are crucial, for example, from the point of view of heterogeneous catalysis.

1. Introduction

The understanding of physicochemical phenomena that determine the size, structure and properties of nanomaterials is crucial for their rational design. One of the interesting groups of nanomaterials are the 2D transition metal oxides, such as ultrathin islands and films grown on metal substrates.[1,2] Thanks to their low-dimensionality and the interaction with the underlying support, such systems often exhibit unique physicochemical properties that predispose them for applications in nanoelectronics/spintronics, energy storage/conversion and heterogeneous catalysis. Low-dimensional metal-supported oxide islands may also constitute well-defined model systems for performing fundamental studies on “inverse” catalysts,[3] as they resemble many structural features of real catalysts, such as oxide species of different size and stoichiometry, low-coordinated transition metal atoms (present at the perimeter of oxide islands and within internal defects), as well as exposed noble metal support regions.

Depending on the application, it may be desirable to maximize the number of specific structural features within an oxide-on-metal system, such as certain crystal facets, edge sites, defects or exposed substrate regions.[4] This is usually done by optimizing the oxide’s growth method. However, the structure of the system may also evolve under varying environmental conditions, for example, in response to high pressures of gases or elevated temperatures. In this respect, controlling the structure of metal-on-metal and metal-on-oxide systems, and predicting their behavior in different environments, is much more trivial, as the mechanisms governing the growth and structural evolution of metals under oxidizing and reducing conditions are well-understood. For example, thermal treatments under reducing conditions are known to lead to supported metal particles sintering and, thus, the change in the ratio between the facet and edge sites. The process usually proceeds through one of the two mechanisms: coalescence,[5] that is, Brownian-like motion of particles and their merging upon collision, or Ostwald ripening.
Ostwald ripening,\cite{5,6} in which smaller particles dissolve and feed the bigger ones. This behavior is related to a much higher surface energy of smaller particles and higher thermodynamic stability of the bigger ones. Oxidizing treatments, on the other hand, lead to the formation of surface and bulk oxides. In the case of metal-supported oxide species, the situation is much more complex, as the structural transformations critically depend on the physicochemical properties of a specific oxide (e.g., redox potential of constituent metal elements, as well as the interaction of the oxide with the metal support on which it is grown).

It is, thus, crucial to carry out fundamental studies aimed at identifying the possible transformations occurring in oxide-on-metal systems under oxidizing and reducing conditions, and elucidating the corresponding physicochemical mechanisms.

Here, on the example of ultrathin FeO islands grown on Ru(0001),\cite{7,8} we show that Ostwald ripening can also occur in an oxide-on-metal system. The islands sinter in response to high temperature annealing in ultra-high vacuum (UHV), leading to the change in their average size and total perimeter length, as well as the number of internal defects and the exposed substrate area. The process is accompanied by the transformation of FeO into an O-poor Fe$_x$O (1 $<$ x $\leq$ 2) phase, which can be potentially reoxidized back to FeO, while preserving the newly-established morphology.

### 2. Results and Discussion

**Figure 1.** STM images of a) pristine FeO/Ru(0001) and the system after annealing at 950 K for b) 10 and c) 20 min in UHV. d) The island height histogram. e,f) The structural defects within an extended island observed in STM and STS $dI/dV$ mapping modes, respectively. g) STM image showing the lack of defects following annealing at 950 K for 10 min. h,j) LEED patterns obtained for a pristine and an annealed sample, respectively. STM: $V_{\text{sample}}$ = +1.0 V; $I_\text{t}$ = 0.7 nA (all images, including STS $dI/dV$ maps); Image sizes: (a–c) 500 $\times$ 500 nm$^2$, (e–g) 50 $\times$ 50 nm$^2$. LEED: 64 eV.

Figure 1a shows a scanning tunneling microscopy (STM) image of pristine FeO islands grown on Ru(0001) by Fe deposition and post-oxidation in 1 $\times$ 10$^{-6}$ mbar O$_2$ at 950 K, while Figures 1b and 1c show the system after annealing at 950 K in UHV for 10 and 20 min, respectively. Pristine islands are well-dispersed, having different sizes and growing both at the regular terrace sites and at the step edges of the substrate.\cite{7–9} They have a height of $\approx$5 Å, indicating that they are composed of two FeO layers, and exhibit a Moiré superstructure with 21.6 Å periodicity (originating from the lattice mismatch between the oxide (a$_{\text{FeO(111)}}$ = 3.04 Å) and the Ru(0001) support (2.71 Å). The observed growth mode and structure are characteristic for the preparation conditions used.\cite{7,8} Bigger islands are formed through merging of smaller ones, which results in the appearance of characteristic line defects within the islands (Figure 1e).\cite{7–9} The distribution of defects may be traced using scanning tunneling spectroscopy (STS) $dI/dV$ mapping mode with a bias voltage value of +1.0 V (Figure 1f). Following annealing at 950 K in UHV for 10 min, the number of islands decreases, while the average island size increases, with the total coverage staying the same (within an accuracy of 5%). Moreover, the island edges become sharper, running along the crystallographic directions of the ruthenium support. Annealing for additional 10 min at the same temperature leads to further growth of bigger islands at the expense of smaller ones and the visible change in the islands shape towards the equilibrium one, that is, truncated triangle (or—ultimately—hexagonal). A significant decrease in the number of internal structural defects is also observed, $\approx$80% of which vanish after the first annealing and almost none are left after the second one (Figure 1g). The total edge length decreases by $\approx$20% after the first annealing and stays more or less the same after the second one. Most
importantly, the height profiles taken across both structures (Figure S1, Supporting Information) reveal that the annealed islands are by ≈0.5 Å lower than the pristine ones (4.45 ± 0.15 Å (annealed) vs 5.0 Å (pristine)). This indicates that sintering is accompanied by a transition to a structure with a lower apparent height. The structural evolution takes place gradually, as evidenced by the histogram shown in Figure 1d. Notably, the annealed islands are characterized by a virtually-identical Moiré structure as pristine FeO (compare Figures 1e and 1g), indicating that the new phase is structurally similar to FeO.

The low energy electron diffraction (LEED) pattern obtained for a pristine sample, shown in Figure 1h, reveals the presence of Ru(0001)-(1 × 1) and FeO(111)-(2 × 2) spots that can be assigned to O atoms chemisorbed on the exposed substrate regions and forming either 120°-rotated (2 × 1) domains or a (2 × 2) structure.[9] The diffraction pattern of the annealed sample (Figure 1i) exhibits reflexes located at similar positions, which indicates that there are no significant changes in the atomic or Moiré periodicities of iron oxide. Thus, the results further confirm the structural similarity of pristine and annealed islands. The only visible difference is the increased intensity of the spots related to the formation of larger ordered iron oxide regions.

The observed sintering of the islands could be explained either by coalescence or Ostwald ripening. To clarify this issue, we used low energy electron microscopy (LEEM) which allows real-time monitoring of structural changes that occur at solid surfaces during thermal or chemical treatments. Figure 2a shows the pristine FeO/Ru(0001), while Figures 2b and 2c show the system after annealing in UHV at 1050 K for 45 s and 2 min, respectively. The movie showing the transformation (at adjusted speed) can be found in the online Supporting Information. The higher temperature used in LEEM studies was dictated by the slow dynamics of the process at 950 K, with the thermodynamic driving force being the same, regardless of the temperature. During the annealing, the smallest islands (marked with yellow and blue circles in Figures 2a and 2b, respectively) disappear and, after some time, the bigger ones start to grow laterally in size (Figure 2d–f). This kind of behavior is characteristic for the Ostwald ripening process. The diffusion of the decomposed material across the surface was, unfortunately, not visible due to instrumentation limits. The growing parts of the islands show different contrast in LEEM when imaged with certain instrument parameters (Figure 2d), which confirms that they are characterized by a structure that is different than that of the original islands. During a prolonged annealing, the contrast within the islands equalizes toward that of the newly-grown part (Figures 2h,i), which is in agreement with the gradual nature of the process observed with STM (Figure 1d).

To determine the difference in the structure of pristine FeO and the phase formed during the annealing, synchrotron radiation was utilized for recording X-ray photoemission electron microscopy (XPEEM) images of a partially transformed sample (similar state to the one shown in Figure 2d). A series of images corresponding to the energy range in which the Fe 3p photoelectron signals are expected to appear was collected, and the signal-versus-intensity (IV) curves were locally plotted from the regions corresponding to the original and the growing parts of an exemplary island (Figure 3). The results indicate that the new phase hosts iron in a lower oxidation state than the original one (the edge of the curve is shifted towards lower binding energy values). The maximum of the signal recorded for the original structure, ≈54.5 eV, lies in between the ones expected for Fe2+ (53.7 eV) and Fe3+ (55.6 eV).[11] This is in agreement with our recent studies which indicated mixed valency of iron (Fe2+/Fe3+) in bilayer FeO on Ru(0001) (the islands have an O−Fe2+−O−Fe2+÷Ru structure, that is, the top iron layer is sandwiched in-between two oxygen layers, which leads to the Fe3+ oxidation state, while the bottom one, located in between an oxygen layer and the Ru(0001) support, is in the Fe2+ state).[9] The signal recorded from the growing parts, on the other hand, indicates the dominant contribution from iron in the Fe2+ oxidation state (the structure can be described as Fe2+−O2−Fe2÷Ru, which is related to the removal of the top oxygen layer). A similar trend is observed in the recorded X-ray photoelectron spectroscopy (XPS) Fe 3p (Figure S2a, Supporting Information) and Fe 2p (Figure S2b, Supporting Information) spectra, which show a gradual shift of both signals to lower binding energies following brief and prolonged annealing. Moreover, the Fe 2p data correlated with the O 1s signals (not shown) allowed determining the change in the Fe-O ratio before and after the complete structural transformation. For this purpose, the total area under the signals was integrated and divided by the proper atomic sensitivity factors. Taking into account the initial and final FeO coverage (with their local fluctuations on different sample regions), as well as the fact that the remaining part of the surface is covered by chemisorbed oxygen forming (2 × 1) domains (and probably also less densely-packed (2 × 2) after annealing), the stoichiometry of the new phase is determined to be roughly “Fe2O”. The precise stoichiometry could not be established due to potential partial diffusion of iron and oxygen into the substrate, local changes of oxygen concentration on Ru(0001) (partial transformation of the (2 × 1) structure into the (2 × 2)) and the possibility that the transformation was not fully completed for all the islands. Thus, the results reveal that the islands formed following a thermally-driven sintering represent an O-poor Fe2O (1 < x ≤ 2) phase.

In order to get more insight into the structure of the newly-formed iron oxide phase, density functional theory (DFT) calculations were performed. The information obtained from experimental studies, that is, the atomic and superstructure periodicities similar to that of pristine FeO(111) (deduced from STM and LEED results), the ≈0.5 Å lower height (determined with STM), the lower oxidation state of iron (from XPEEM and XPS) and the Fe-O ratio (from XPS), allowed limiting the number of investigated systems to three differently stacked layers with Fe2O stoichiometry: Fe−O−Fe/Ru, Fe−Fe−O/Ru and O−Fe−Fe/Ru. The large unit cell of the FeO/Ru(0001) Moiré superstructure and the necessity to include three atomic layers forming the oxide (two layers of Fe and one layer of O), as well as five layers of the Ru substrate (with the bottom three fixed in bulk positions and the top two allowed to relax), made the size of the computational cell challenging. To make computations feasible, separate calculations were carried out for different high-symmetry regions (HSRs) of the Moiré supercell, that is, top, fcc and hcp. Such an approach was found to reproduce the crucial structural
features of FeO grown on a different single-crystal substrate: Pt(111).\textsuperscript{[12]} Here, only the results obtained for the fcc HSR (which was found to be the most energetically-stable one) and the laterally iron oxide compressed to the Ru(0001) lattice constant ($a_{\text{Ru(0001)}} = 2.73 \text{ Å}$—as determined from the preliminary calculations), are discussed. The results obtained for other HSRs are presented in Figure S3, Supporting Information. The analysis of the stability shows that the Fe–O–Fe/Ru and O–Fe–Fe/Ru stackings are the energetically most preferred ones, being very close in total energy values (with the Fe–O–Fe/Ru as the most preferred one by 0.35 eV (Figure 4a)). The Fe–Fe–O/Ru system with oxygen atoms at the interface is energetically unfavored (the total energy is by 13.11 eV higher than that of the most stable configuration). The calculations also reveal that the atomic planes in the relaxed structures remain uncorrugated within a single HSR. The estimated layer thickness for the Fe–O–Fe/Ru configuration is 5.05 Å (Figure S3, Supporting Information), which is only \textasciitilde 15% lower than that obtained for bilayer FeO (6.08 Å\textsuperscript{[13]}. The calculations performed using the surface lattice constant of FeO (substrate atoms laterally expanded to 3.04 Å).

Figure 2. LEEM images obtained for a) pristine FeO/Ru(0001) and d–i) the system at different time intervals of annealing at 1050 K. Due to the thermal drift, the field of view shifted to the left between (c) and (d) (the islands seen on the right-hand-side in (c) are visible on the left-hand-side in (d)). The observed structural transformation can be divided into three phases: a–c) disappearance of small FeO islands, d–f) growth of bigger islands, with the new parts exhibiting different contrast, and g–i) unification of the structure towards the newly-grown parts. Scale bar: 500 nm. LEEM energy: 20 eV.
Fe–O–Fe/Ru stacking of the Fe2O layers seems reasonable, as the experimentally determined height difference is only 10%, the height measured with STM may be altered by electronic effects, especially when measuring the height between the oxide and the metal. Notably, the order of the first three layers (looking from the substrate) is the same for the most energetically-stable FeO and Fe2O configurations, with FeO having an additional O layer on top. Since the Fe–O–Fe/Ru and O–Fe–Fe/Ru stackings are almost degenerate in energy, additional studies, aimed at their distinguishment, were performed. The calculated work function values of both structures were found to be 4.65 and 765 eV, respectively (as obtained for the fcc HSR; for other HSRs, see Table S1, Supporting Information), which is related to their different surface dipole. The value obtained for the most stable FeO stacking (O–Fe–O–Fe/Ru), on the other hand, is ≈78 eV. Thus, the difference between the work function of FeO and the new phase can be the guide for the FeO stacking determination. From the recorded LEEM-IV curves (Figure S5, Supporting Information), it is evident that the work function of the newly-grown phase is by about 0.95 eV lower than the one of pristine FeO (in LEEM-IV, the work function difference can be determined from the mutual position of characteristic signal intensity drops observed at low energies). All these suggest that even though the Fe–O–Fe/Ru and O–Fe–Fe/Ru are very close in total energy, their calculated and measured work function values favor the former as the one observed experimentally.

To investigate the influence of the FeO-to-Fe2O transformation on the shape of XPS Fe 3p line, the core-levels were calculated using an all-electron code (full-potential local-orbital scheme code, FLPO\textsuperscript{16}) and the density of states (DOS) of Fe 3p orbitals of both structures was determined. The results were correlated with Fe 3p XPEEM and XPS spectra obtained experimentally. As can be seen from Figure 4b and Figure S6, Supporting Information, the Fe 3p states of the Fe2O phase are more widely spaced and shifted towards lower binding energies compared to those of FeO, which is in agreement with the experimental observations. The Fe 3p spectra of both structures consist of superimposed contributions originating from iron atoms in both, that is, top and bottom, layers. Each Fe site provides six 3p states, the configuration of which depends, inter alia, on spin-orbit coupling and spin polarization (see Figure S7, Supporting Information).\textsuperscript{14–16} Thus, the chemical shift of 3p states results from charge redistribution caused by the rearrangement of chemical bonds (reduction of iron oxide).\textsuperscript{34}

The calculated magnetic moments and Mulliken charges on atoms, presented in Table S2, Supporting Information, reveal that the most significant changes are observed for the outer (top) iron layer. The decrease in the value of the spin magnetic moment from −4.21 to −3.55 μB on Fe top atoms causes a narrowing of the 3p spectrum. On the other hand, the decrease in the positive charge on the atoms (from +0.96 to +0.39) leads to the shift of the spectrum towards lower binding energies, which provides a route for the widening of the total Fe 3p signal (Fe\textsubscript{top}+Fe\textsubscript{bottom}). The widening and shift in the Fe 3p spectra between FeO and Fe2O is, thus, a consequence of the changes in magnetic moments and charges on Fe atoms in the top FeO layer.

The origin of the Ostwald ripening process and the FeO-to-Fe2O transformation is believed to be related to energy minimization, that is, preferred reduction of the number of FeO/Ru edge sites, as well as the structural characteristics of the FeO/Ru(0001) system. First of all, the oxide on this particular
substrate preferably grows in the bilayer (O–Fe–O–Fe) form, and not as a monolayer (O–Fe) like on most single-crystal supports (e.g., Pt(111))\(^{[17]}\). The monolayer can be stabilized, however, only within a limited range of oxygen pressures.\(^{[18]}\) Second, the top FeO layer hosts Fe\(^{3+}\) ions,\(^{[19]}\) which have a much higher standard reduction potential to Fe\(^{2+}\) than the Fe\(^{2+}\) to metallic Fe. This opens a relatively simple route for the thermal reduction of the top FeO layer. Following such a reduction, the surface free energy of the island would change due to the modification of the surface termination.\(^{[18]}\) Finally, the oxide is polar when grown in the [111] direction,\(^{[7]}\) so any charge redistribution within the system may lead to significant restructuring (due to increased contribution of the electrostatic energy to the surface energy\(^{[16]}\)). Thus, the initial reduction of the top layer could start a kind of a “chain reaction” that leads to the complete structural decomposition of the island. The resulting material (most probably metallic iron) would then diffuse across the surface, binding to the encountered still-existing large iron oxide islands that are thermodynamically more stable than the small ones. It could then become oxidized by O atoms present on Ru(0001), which constitute an oxygen “reservoir”. The final structure partially results from the vicinity of pristine FeO with its original layers stacking, that is, O–Fe–O–Fe/Ru,\(^{[7]}\) and atomic periodicity (the growing part would try to adopt the stacking and follow the atomic period of the neighboring FeO), as well as the limited amount of available oxygen, that disallows the full reconstruction of the FeO structure.\(^{[8]}\)

It is important to mention that the observed sintering mechanism—being the classical Ostwald ripening process—is different than the one observed by the authors of Ref. [20] for VO\(_x\) islands on Rh(111). In their case, sintering was only observed under specific reaction conditions, with the islands initially moving towards each other and ultimately coalescing via the so-called polymerization-depolymerization mechanism. Thus, the process is driven by a chemical reaction and not a simple evaporation-condensation mechanism like in our case.

In summary, it is shown that UHV annealing leads to sintering of FeO islands grown on Ru(0001), which affects the general structural characteristics of the system: the average island size, perimeter length, number of internal defect and the stoichiometry of the oxide phase. The process occurs via the Ostwald ripening mechanism (the small islands decompose, the material diffuses across the surface and feeds the encountered large ones), which has not been observed for an oxide-on-metal system so far. Even though the annealed islands represent the “Fe\(_2\)O\(_3\)” phase, they could be potentially reoxidized after annealing, thus regaining the FeO stoichiometry, however, without becoming dispersed again. The work constitutes an important step towards understanding of complex physico-chemical processes occurring in oxide-on-metal systems under varying environmental conditions.

### 3. Experimental Section

The experiments were performed in two different UHV chambers (base pressures in the 10\(^{-10}\) mbar range) equipped with sample preparation (Ar sputter guns, e-beam heating stages, Fe evaporators, O\(_2\) lines) and characterization facilities: STM/STS and LEED in one chamber and LEEM/XPEEM, as well as XPS with synchrotron radiation in the other (UE49 SMART beamline at BESSY II\(^{[21,22]}\)). Ru(0001) single crystal was cleaned by repeated cycles of Ar\(^+\) sputtering, annealing in O\(_2\) and in UHV. Ultrathin FeO islands were grown by Fe deposition at room temperature and post-oxidation. The islands were annealed in UHV, with the temperature being monitored using infrared pyrometers. The structural changes were studied in real time with LEEM and by using STM/STS, LEED, XPEEM and XPS.

Theoretical calculations on the structure and energetics of FeO and Fe\(_2\)O films were performed in a 3 x 3 computational cell using spin-dependent DFT and projector-augmented-wave (PAW) method,\(^{[23,24]}\) as implemented in the Vienna ab initio simulation package (VASP)\(^{[25–27]}\). The Perdew–Burke–Ernzerhof (PBE) form\(^{[28]}\) of the generalized gradient approximation (GGA) functional and the Hubbard U correction were used.\(^{[29]}\) The Fe 3p electronic states, magnetic moments and Mulliken charges on atoms were calculated using the FPLO code ver. 18.00-52.\(^{[30]}\) The relaxed geometries obtained from VASP constituted an input for FPLO, while the use of an all-electron code allowed going beyond the limitations of VASP in describing the electronic core-level states.

A detailed description of experimental and computational methods is provided in the Supporting Information.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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### Conflict of Interest

The authors declare no conflict of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

iron oxide, Ostwald ripening, oxide-on-metal system, ruthenium

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