Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 85 (2016) 12 – 19

Physics Procedia

EMRS Symposium: In situ studies of functional nano materials at large scale facilities: From model systems to applications, EMRS Spring Meeting

Initial stages of the growth of mixed iron-cobalt oxides on Ru(0001)

Laura Martín-García[a], Adrian Quesada[b], Lucas Pérez[c,d], Michael Foerster[e], Lucía Aballe[e], Juan de la Figuera[a,*]

[a]*Instituto de Química Física "Rocasolano", Madrid E-28006, Spain*
[b]*Instituto de Cerámica y Vidrio, CSIC, Madrid E-28049, Spain*
[c]*Dpto. de Física de Materiales, Universidad Complutense de Madrid, Madrid E-28040, Spain*
[d]*Unidad Asociada IQFR(CSIC)-UCM,Universidad Complutense de Madrid, Madrid E-28040, Spain*
[e]*Alba Synchrotron Light Facility, CELLS, Barcelona E-08290, Spain*

Abstract

Mixed iron-cobalt oxides have been grown on a Ru(0001) single crystal substrate by reactive molecular beam epitaxy. The growth has been followed by low-energy electron microscopy and diffraction. Chemical characterization has been performed by selected area x-ray absorption spectroscopy. As previously known, iron grows into a wetting layer of FeO. In contrast, cobalt grows into three-dimensional islands of CoO, of either with a (111) -most common- or a (100) orientation. For mixed compositions, flat 2D growth is regained. Depending on temperature, either segregation into two FeCo compositions or a single phase is detected. In all cases the structure corresponds to an in-plane expanded (111)-oriented halite one. When only one phase is observed or for the Co-rich phase in the two phase film, its crystal structure is rotated by 30° relative to the Ru substrate, unlike the Co-poor phase which appears aligned with the substrate.
© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the organizing committee of the EMRS Spring Meeting 2016

Keywords: cobalt monoxide, iron monoxide, reactive molecular beam epitaxy, low-energy electron microscopy, selected area x-ray absorption, photoemission electron microscopy

1. Introduction

Cobalt and iron oxides have many similarities. The divalent oxides, CoO and FeO, both have the rocksalt structure (halite) with very similar lattice spacings. They are Mott insulators with antiferromagnetic order and Néel temperatures of 290 and 200 K respectively. One difference is that FeO, wüstite, is non-stoichiometric in bulk form. Iron oxides have long been grown in thin film form[1, 2] either by sequential deposition of metal layers followed by oxidation, or by single step reactive molecular beam epitaxy (r-MBE), i.e. depositing the metal in a background pressure of an oxidizing agent. In both cases, molecular oxygen is the most common oxidizing agent, although NO_2 or O_3 have also been used. Such approach is useful to grow thin films on either oxide substrates, or metallic substrates that are more difficult to oxidize than iron. Through such approach, it has long been observed that iron oxide growth

* Corresponding author. Tel.: +34-91-745-9517.
E-mail address: juan.delafiguera@csic.es

1875-3892 © 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Peer-review under responsibility of the organizing committee of the EMRS Spring Meeting 2016
doi:10.1016/j.phpro.2016.11.075

proceeds through a Stranski-Kranstanov growth mode on most metal substrates, albeit one where the wetting layer has a monoxide composition while the three dimensional islands correspond to the spinel phase, magnetite. The reasons for such mode are not straightforward, as FeO is not expected thermodynamically in the ranges of oxygen pressure and substrate temperature typically employed in reactive MBE[3]. In any case, the wetting character of initial FeO growth affords a way to grow ultrathin FeO films, films which are atomically flat and can be as thin as a single FeO layer, i.e. one iron layer with one oxygen layer. The FeO layers have an hexagonal arrangement, corresponding to the FeO(111) rocksalt structure. These FeO films have been discovered to have catalytic activity[4, 5, 6]. Cobalt oxides have been less studied on substrates such as Pt(111)[7]. A rather complete work of cobalt oxides on Ir(001)[8, 9, 10, 11, 12, 13, 14] highlights the complexities of ultrathin oxide films. These growth experiments, performed by sequential deposition and oxidation, determined that the preparation procedure could select different orientations of the same CoO structure[15]. The similar lattice spacing, structure and chemical characteristics of CoO and FeO suggests that they should form mixtures. The Fe-Co-O phase diagram[16] confirms the existence of $Fe_xCo_{1-x}O$ in a wide range of experimental conditions, although for most of the composition range it coexists with the spinel phase. In this work we show that the initial stages of growth of iron, cobalt and mixed cobalt-iron oxides on Ru consist of only the halite phase, although with significant differences in the growth mode.

1.1. Experimental Methods

The experiments have been performed at the CIRCE beamline of the Alba synchrotron. The station[17] comprises a preparation chamber and the main chamber which houses the low-energy electron microscope (LEEM[18]) with energy analysis capabilities. The instrument, an Elmitec III microscope, can be used in low-energy electron mode to provide real-space observations of the growth front during molecular beam epitaxy. It can also provide low-energy electron diffraction patterns of selected areas of the sample as small as a fraction of a micrometer, and can obtain dark-field images of the surface by selecting a diffracted beam to form an image. In photoemission mode (PEEM) and coupled to the Alba synchrotron, it provides selected area x-ray absorption spectroscopy without the need to transfer the sample after growth. The kinetic energy of the electrons in LEEM and PEEM mode is given by the start voltage, which is the potential difference between the sample on one side and the electron source and energy analyzer on the other side. The sample temperature is measured with a WRe thermocouple attached to a washer below the sample.

The substrates are Ru(0001) single crystals cleaned by repeated annealing to 1500 K, with annealing in oxygen at 1100 K to remove carbon. The oxide growth conditions are adequate for removing carbon segregating to the surface from the near-surface region. The Co and Fe dosers are electron-bombardment ones with solid rods of Fe or Co within a water jacket. We define one atomic layer (ML) as that with the same density as the Ru(0001) surface. Typical rates are 10^{-2} atomic layers per second (ML/s). The calibration of the Co doser is performed by depositing a complete metallic layer on Ru(0001) at 600 K, while the iron is calibrated using FeO growth[19]. To grow the oxides a typical pressure of 10^{-6} mbar of molecular oxygen is maintained in the LEEM chamber. Growth is performed under observation in LEEM. After growth the sample is cooled down to room temperature in oxygen until the temperature reaches 600 K and in vacuum afterwards.

1.2. Results and Discussion

We have previously studied the influence of both pressure and temperature in the nucleation rate of the FeO islands[19]. Depending on the pressure, the growth proceeds by either bilayer islands, or monolayer islands, where a monolayer of FeO refers to a single Fe layer covered by a single oxygen layer. In the films presented in this work, the pressure is 10^{-6} mbar, which should give rise to bilayer islands. A typical morphology for a growing film of FeO is shown in the snapshots of Figure 1a, selected from a sequence acquired during deposition of iron on the Ru(0001) substrate, at a substrate temperature of 1150 K. After the initial nucleation stage, the islands grow in size until they coalesce forming a continuous bilayer. That the islands grow as a bilayer is already indicated as the coverage corresponding to 1.2 ML_{Fe} (which corresponds to ~1.7 ML_{FeO}) does not cover completely the substrate. The electron reflectivity is another way of characterizing the surface: the reflectivity is very different for monolayer islands, bilayer or oxygen-covered Ru[20]. Here the electron reflectivity from the islands shows the typical spectrum from bilayer-height islands[19] (not shown). If the growth is interrupted before completing the layer, the islands tend to have a triangular shape with two opposite orientations on each terrace (Figure 1b). The two orientations correspond

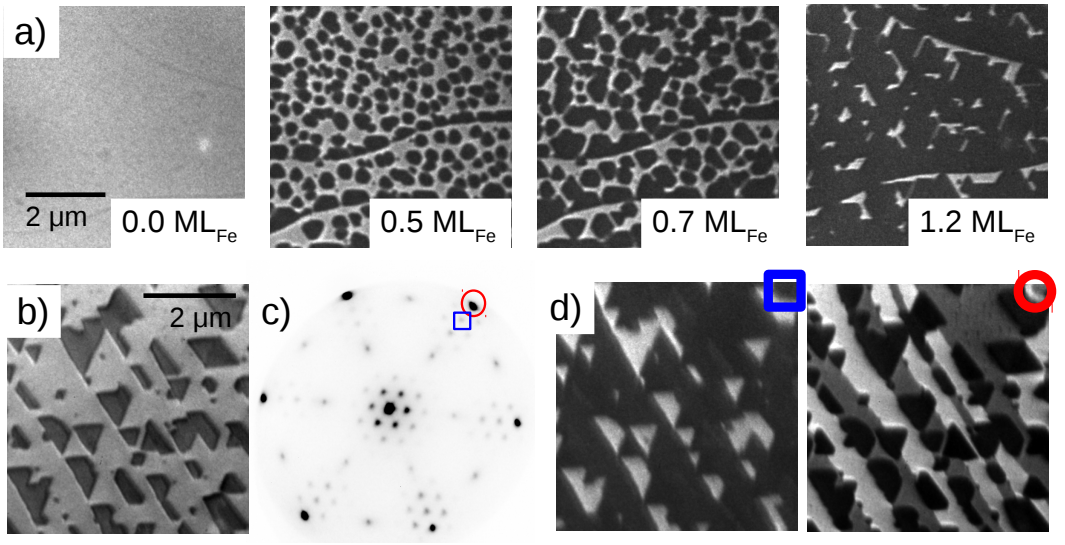

Fig. 1. (a) Frames selected from a sequence of images acquired (at a start voltage of 19 V) during the growth of FeO on Ru(0001) at 1150 K at a background pressure of $2 \cdot 10^{-6}$ mbar of molecular oxygen. The frames correspond to 0, 0.5, 0.7 and 1.2 ML of Fe respectively. (b) Incomplete film showing triangular islands. (c) LEED of the surface imaged in (b), acquired with a start voltage of 36 V. The red circle marks one of the first order Ru diffracted beams, while the blue square marks one of the first order FeO ones. (d) dark-field image using the marked beams in (c) with either a blue square (left image) or a red circle (right image), using the same start voltage of 36 V.

to twin stacking sequences relative to the substrate, and have already been detected in monolayer islands by scanning tunneling microscopy[21]. The ultrathin FeO layers present a moiré pattern due to the different in-plane lattice spacing of the film and the substrate. Such moiré pattern is reflected in the low-energy electron diffraction pattern (Figure 1c) which shows satellite spots around the FeO spots, which in turn form an hexagonal pattern aligned with the Ru(0001) one. The hexagonal layers in FeO on Ru(0001) present a simple hexagonal arrangement with a lattice spacing of 0.32 nm for the first two layers. Acquiring images with one of the FeO diffracted beams, i.e. dark-field imaging, shows the same image with only the FeO islands appearing bright (left frame of Figure 1d). If one of the Ru diffracted beams is used instead, it is the one of the two hcp Ru substrate terminations[22] that is imaged bright (right frame of Figure 1d). In summary, FeO growth proceeds by the nucleation of bidimensional islands, that wet the oxygen-covered Ru substrate and grow until they complete the bilayer. This 2D growth mode takes place in a wide range of temperature and occurs on other metal substrates such as Pt or Au[2].

Cobalt oxide can be grown in the same way on Ru(0001). A sequence of images acquired during growth are presented in Figure 2a. In contrast with the case of FeO, deposition of one ML of Co only makes small islands which nucleate around the substrate steps, even if the substrate temperature, pressure and deposition rate is similar to the FeO case. In fact, the islands have not grown much upon further deposition, indicating a strong 3D growth. Thus, instead of 2D islands, cobalt oxide grows on Ru(0001) in the Volmer-Weber one: three dimensional islands nucleate from the first stage. Lowering the temperature does not change the growth mode: in Figure 2b we show the surface after growing at 950 K for 4 ML Co. The cobalt oxide islands are seen to have a triangular shape with two opposite orientations. Additionally, much less common islands have a rectangular shape. The diffraction pattern of such a surface is shown in Figure 2c. The brightest spots, marked with red circles, correspond to the first order Ru diffracted beams. Oxygen on the bare Ru substrate gives rise to additional diffracted beams with a 2×2 periodicity (not marked). In addition there are two new patterns: a 30° rotated pattern (marked with blue triangles), and a square pattern marked with green boxes. There is no moiré pattern as observed in FeO growth. Instead, we attribute the blue hexagon spots to the triangular islands, as discussed for the mixed case of Fe and Co below (although some intensity can also be due to diffraction from the oxygen covered Ru). And the square pattern arises from the rectangular islands. The lattice spacing of the triangular islands is 0.31 ± 0.02 nm, slightly larger that the Ru(0001) value of 0.27 nm. We note that such a simple hexagonal pattern strongly suggests a simple (111)-oriented halite phase for the triangular islands: an

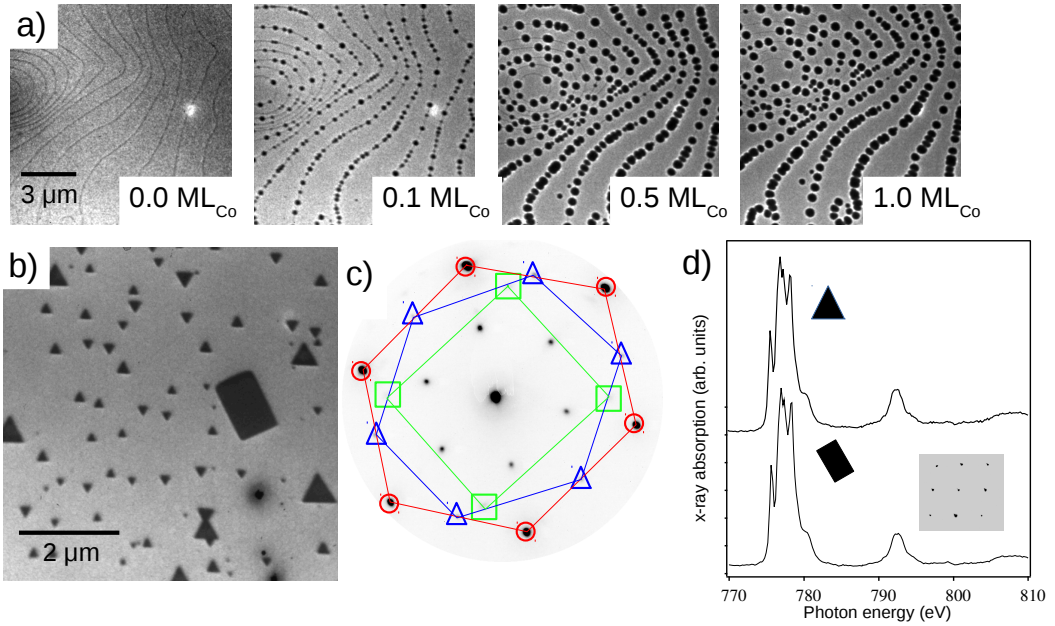

Fig. 2. (a) Frames of a sequence of images acquired during the growth of CoO on Ru(0001) at 1200 K in a background oxygen pressure of $2 \cdot 10^{-6}$ mbar. The images correspond to a cobalt dose of 0, 0.07, 0.5 and 1.0 ML respectively. The start voltage is 5 V. (b) LEEM image of a film after the growth of 4 ML of Co at 950 K in $1.5\dot{1}0^{-6}$ mbar, with clearly defined triangular and rectangular islands. (c) LEED pattern on the same area, acquired at a start voltage of 47 V. (d) Selected-area x-ray absorption spectroscopy spectra acquired respectively on one of the triangular islands, and on the rectangular one. Both spectra have been acquired with circular polarized light. In the latter, the inset shows the LEED diffraction pattern, acquired also at 47 V.

unreconstructed spinel phase would appear as a structure with a 2×2 periodicity due to the twice-as-large unit cell within a (111) plane[20]. Likewise, a corundum structure would show additional spots at $\sqrt{3} \times \sqrt{3}$R30° positions[1]. The square pattern, in contrast, corresponds to a lattice spacing of 0.20 nm, and has an angle of 10° with the triangular islands diffraction pattern. To clarify the phase of the two types of islands we have measured the x-ray absorption near the L_3 and L_2 Co absorption edges, from a triangular and a rectangular island respectively as shown in Figure 2d. To do so we have measured the local intensity from a sequence of images collecting the electrons with low kinetic energy while scanning the photon energy through the Co $L_{3,2}$ adsorption edges. The two spectra are the same, and have the typical structure arising from CoO. In fact, they are indistinguishable from published reference spectra[23]. Thus both types of islands, triangular and rectangular, are composed of CoO. The triangular islands correspond to (111) oriented islands, with the LEED pattern in reasonable agreement with the expected hexagonal arrangement with a lattice spacing in real space of 0.31 nm. The rectangular island, instead, has a square diffraction pattern (inset in bottom of Figure 2d). This suggests the rectangular island has a (001) orientation, although the observed lattice spacing is not close to a 1×1 structure. We suggest it corresponds to a 2×2 reconstruction, although further work is needed to confirm this assignment. We note that ceria on Ru(0001) has also been found to nucleate into islands with the same structure and presenting both the (001) and the (111) orientation, and in the former case a reconstructed 2×2 structure has been reported[24]. In addition, it is known that the preparation procedure can select a different oxide orientation for CoO grown on Ir(001)[15]. Apart from the coexistence of two different orientations, of which one of them comprises the majority of the islands, the 3D growth is quite unexpected: given the much lower surface free energy of oxides when compared with metals, it is usually considered that oxides wet metal substrates, while metals tend to grow three-dimensional on top of oxides. This behavior is more puzzling given the known propensity of FeO to grow in the form of extremely flat layers in a wide temperature range[19].

So while iron oxide grows as FeO wetting the Ru substrate in either monolayer or bilayer flat islands with (111) orientation and aligned with the substrate, cobalt grows as CoO in three dimensional mode. Next, mixed compositions

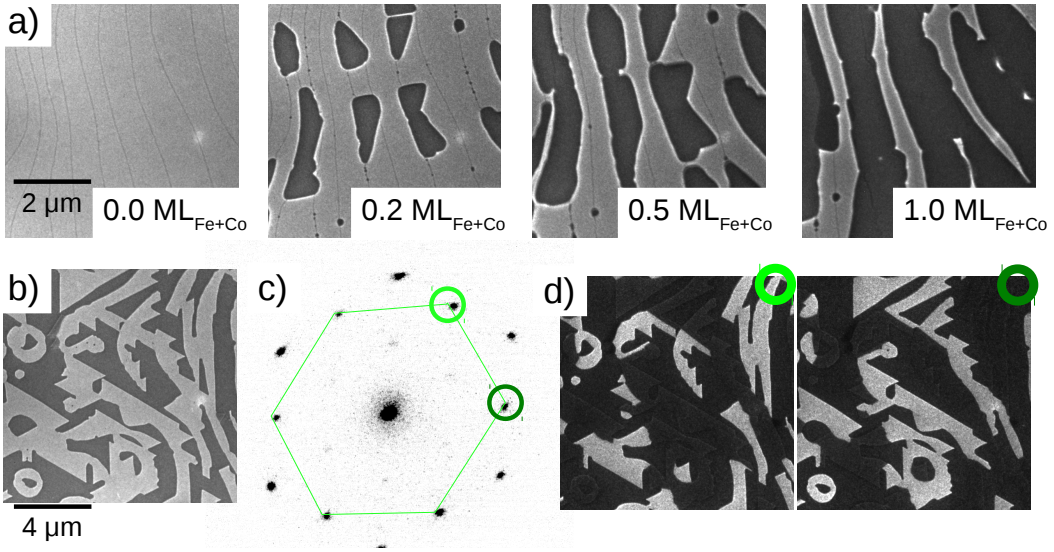

Fig. 3. (a) Frames of a sequence of images acquired during the growth of Fe and Co on Ru(0001) in $9 \cdot 10^{-7}$ mbar oxygen. The substrate temperature is 1035 K, and cobalt and iron ratio is Co:Fe ratio is 0.8:1. The start voltage is 19 V. (b) LEEM image showing the resulting film (in a different area) at a start voltage of 35 V (bright areas correspond to the mixed-oxide areas). (c) LEED pattern of the same surface at a start voltage of 35 V. (d) dark-field images acquired with the beams marked by the same symbols shown in the LEED pattern (c).

of iron and cobalt were deposited on the surface by simultaneously depositing Fe and Co in an oxygen background pressure of 10^{-6} mbar. Figure 3a showns snapshots from such a growth experiment. The conditions are similar to the previous experiments, but instead of dosing either Co or Fe, the two dosers were run at conditions where the ratio of Co:Fe was 0.8:1. As in the previous cases, most of the islands nucleate at the step edges. But unlike the cobalt case, for the mixed deposition the growth appears to be 2-dimensional, as suggested by the rate at which the islands fill the surface. Thus, a mixture of iron and cobalt oxide wets again the Ru surface as did FeO. A larger view of the deposited film is shown in Figure 3b. The covered area is in reasonable agreement with the asumption of bilayer growth. At the particular start voltage employed (35 V), the mixed-oxide islands appear brighter that the oxygen-covered substrate. The diffraction pattern from the film is shown in Figure 3c and has the same 30° rotated pattern already detected for the CoO film, in addition to the Ru substrate beams and the 2×2 from oxygen on Ru. Dark-field imaging (shown in Figure 3d) confirms that all rotated spots come from the mixed oxide. In fact, two regions are detected depending on which first order beam is chosen, suggesting that two stacking sequences are present within each substrate terrace. The diffraction pattern can be interpreted as a simple halite structure along the (111) orientation (as in the CoO only growth) with a lattice spacing is 0.31 nm, and the lack of other spots again strongly hints at a halite (monoxide) phase. XAS spectra (not shown) confirm that the areas contain both iron and cobalt. Thus, the islands should have a $Co_{0.45}Fe_{0.55}O$ composition.

Growing at a slightly lower temperature brings an unexpected feature. Such a growth sequence is shown in Figure 4a. There seems to be two types of islands with different reflectivity (i.e. gray level in the images), most clearly seen in the second frame. A similar film is shown in Figure 4b, where the LEEM image was acquired at a start voltage of 40 V where the contrast between islands is more evident. All the islands have a clear triangular shape. Furthermore, all the islands with a given reflectivity have two possible orientations, with each of one a mirror image of the other (as was previously noted for FeO islands[21]). But when comparing islands with different reflectivity, there is a 30° rotation between the two families, as marked in Figure 4b. The easiest explanation for the different orientation is that the crystal structure on each type of island is rotated itself by the same amount. This relationship between island orientation and crystal structure has been long used in thin films, and usually arises from kinetic effects for atoms diffusing around the islands. To confirm such idea in our case, we resort to dark-field imaging. First, the low-energy electron diffraction pattern is acquired from the surface, as shown in Figure 4c. This pattern has some common elements when

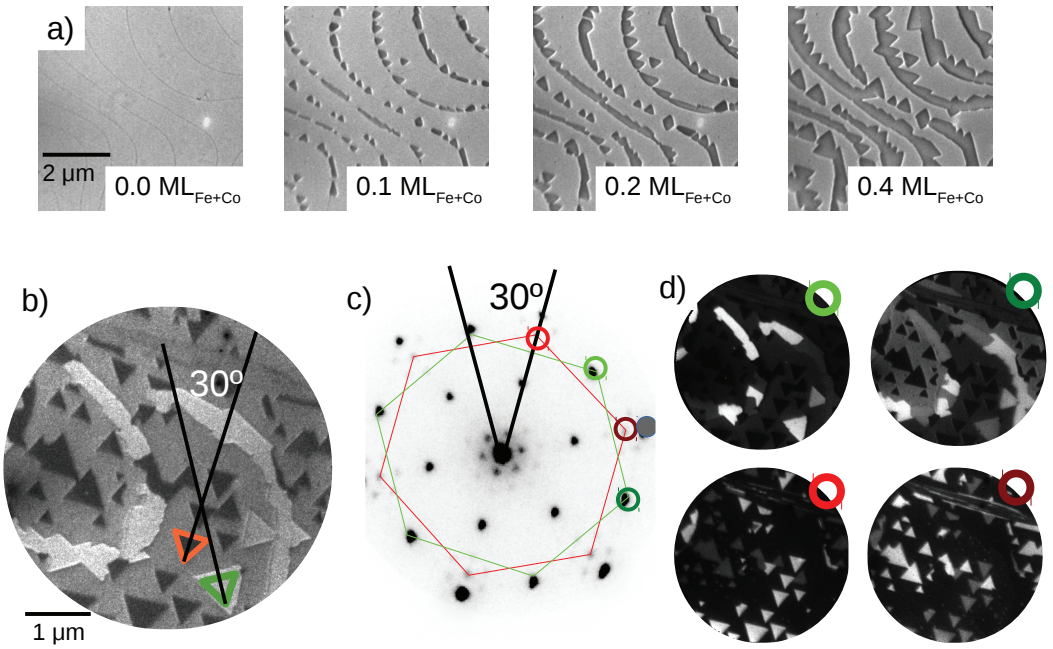

Fig. 4. (a) Frames of a sequence of images acquired during the codeposition of Co and Fe on Ru(0001) in a $2 \cdot 10^{-6}$ mbar of oxygen. The substrate temperature is 1000 K, and cobalt and iron ratio is Co:Fe ratio is 0.8:1. The start voltage is 19 V. (b) LEEM image showing in detail the two types of islands. The start voltage is 40 V. The field of view is 5 μm. (c) LEED pattern of the same surface, acquired at a start voltage of 35 V. (d) dark-field images acquired with the beams marked by the same symbols shown in the LEED pattern (c).

compared with the higher temperature mixed growth (Figure 3c). First, it shows the Ru diffracted beams, one of which is marked by a grey circle. Then there is a 2×2 lattice pattern, already seen before and arising from exposed areas of Ru covered with oxygen. Then there are the spots marked by a green hexagon. Those beams are at positions that can be attributed to a structure rotated by 30° with a lattice spacing of 0.31 nm. But in contrast with the previous experiment, and close to the Ru beams, there is the same pattern of beams and satellites that have been previously observed for FeO (Figure 1c). They can be attributed in the same way to a moiré pattern of an hexagonal structure with a lattice spacing close to 0.31 nm, and aligned with the underlying Ru substrate. Clearly, there is a strong suggestion that the "white" islands, whose shape is rotated by 30°, have the rotated diffraction pattern, while the "dark" islands correspond to the unrotated (moiré) pattern. In Figure 4d several dark-field images are shown. Confirming the previous argument, one set of islands appears bright when diffracted beams corresponding to the moiré pattern are employed. In line with the assumption of different stacking sequence for islands pointing in opposite directions, each orientation respectively appears brighter/darker for each first order beam used (see bottom two images marked with red circles in Figure 4c). When acquiring dark field images with the diffracted beams belonging to the green hexagon in the LEED pattern, the islands oriented at 30° of the previous ones appear bright. So the link between orientation and crystal structure is established.

Thus, codeposition of Fe and Co in oxygen at a slightly lower temperature gives rise to flat islands with the same orientation and crystal structure of pure FeO on Ru(0001), and to islands with a rotated structure. Both seem to have a similar height from reflectivity measurements (not shown). Nevertheless, their structure is the same: it corresponds to a simple hexagonal unit cell with a 0.31 nm lattice spacing. That structure and lattice spacing are compatible with a rocksalt structure of either FeO or CoO with a (111) orientation, considering a similar lattice spacing to the experimentally observed for ultrathin FeO. Given that no rotated structure has ever been observed on pure FeO on Ru(0001)[25, 26], it is clear that the rotated structure is due to the addition of Co. In fact, for CoO-only growth, we have already shown triangular islands with the same rotated orientation. So it is tempting to assume that the different

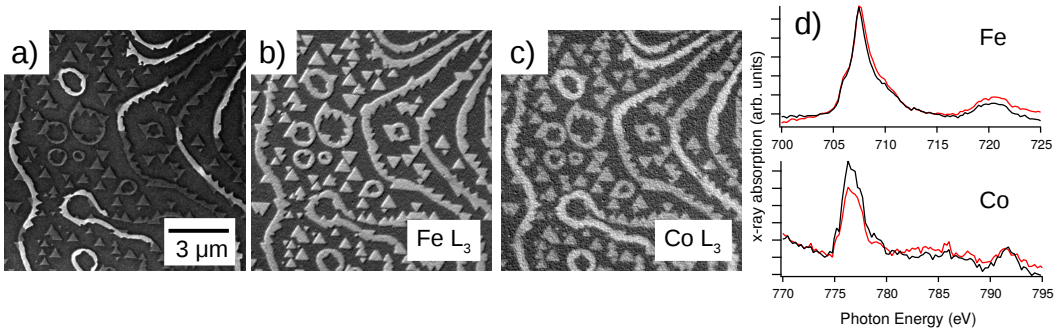

Fig. 5. (a) LEEM image of codeposition of Fe and Co of 0.5 ML (Co:Fe 0.8:1) at a substrate temperature of 990 K and an oxygen pressure of $0.9 \cdot 10^{-6}$mbar, acquired at a start voltage of 2.7 V. (b) Difference image between images acquired at photon energies corresponding to the Fe L_3 peak and 5 eV below, respectively. Each image corresponds to a start voltage of 1 V. (c) Difference image, corresponding to the Co L_3 edge photon energy and 5 eV below, respectively. (d) Selected-area spectra acquired from dark-gray islands of image (a) in red, and of bright ribbons decorating the substrate steps in black.

orientation is related to the islands composition, where the two types of islands would then reflect a segregation into two compositions.

To confirm or disprove that the island composition is related to the island orientation, we show XAS images and spectra acquired from the islands. For comparison, a LEEM image of the same area is shown in Figure 5a. In the next two frames difference images, acquired at the L_3 absorption edge of either Co or Fe and their pre-edge intensity, are shown. The same general topography is observed in the LEEM and the XAS images, with triangular islands nucleated in the substrate terraces as well as islands decorating the substrate steps. In the LEEM image the two different types of islands, rotated and aligned with the substrate, are clearly distinguished. Most of the bright islands are decorating the step edges, something that was already apparent in Figure 4b. The Fe XAS image does not indicate any difference between the two regions. The full spectra acquired at the two type of areas is also similar (Figure 5d, top). But a difference in cobalt content is clear in the Co XAS image (Figure 5c). The same is observed in the selected area spectra of Figure 5d, bottom. This result clearly indicates that the rotated islands are enriched in cobalt, confirming the hypothesis that related their composition with their orientation. Both types of islands, however, are not either iron or cobalt monoxide, but rather correspond to mixed compositions.

1.3. Summary

We have followed the initial stages of iron, cobalt and mixed iron-cobalt oxides grown by reactive molecular beam epitaxy while observing the growth front in real time and real space by low-energy electron microscopy. Further characterization has been performed by low-energy electron diffraction and x-ray absorption. In all cases, monoxide phases have been detected. For iron, FeO grows wetting the substrate and forming flat FeO islands of bilayer height. CoO in contrast forms three dimensional islands, most of which have a (111) orientation, but with occasional ones of (100) orientation. Mixtures grow again wetting the substrate. At higher temperatures, a single phase film is obtained with a rotated orientation. For a lower temperature range segregation is observed into Co-rich islands, which present a lattice structure rotated by 30° relative to the Ru substrate, and Co-poor islands that have the lattice oriented in the same way as the underlying Ru.

Acknowledgements

This work is supported by the Spanish Ministry of Economy and Competitiveness through Projects No. MAT2015-64110-C2-1-P, MAT2015-64110-C2-2-P and MAT2013-48009-C4-1-P. These experiments were performed at the CIRCE beamline of the ALBA Synchrotron Light Facility with the collaboration of ALBA staff.

References

[1] W. Weiss, W. Ranke, Surface chemistry and catalysis on well-defined epitaxial iron-oxide layers, Prog. Surf. Sci. 70 (2002) 1–151.

[2] G. S. Parkinson, Iron Oxide Surfaces, Surf. Sci. Rep. 71 (2016) 272–365. doi:10.1016/j.surfrep.2016.02.001.

[3] G. Ketteler, W. Weiss, W. Ranke, R. Schlogl, Bulk and surface phases of iron oxides in an oxygen and water atmosphere at low pressure, Phys. Chem. Chem. Phys. 3 (2001) 1114–1122.

[4] Y. Sun, Z. Qin, M. Lewandowski, E. Carrasco, M. Sterrer, S. Shaikhutdinov, H. Freund, Monolayer iron oxide film on platinum promotes low temperature CO oxidation, J. Cat. 266 (2009) 359–368.

[5] Q. Fu, W. Li, Y. Yao, H. Liu, H. Su, D. Ma, X. Gu, L. Chen, Z. Wang, H. Zhang, B. Wang, X. Bao, Interface-Confined ferrous centers for catalytic oxidation, Science 328 (2010) 1141–1144. doi:10.1126/science.1188267.

[6] L. Xu, Z. Wu, W. Zhang, Y. Jin, Q. Yuan, Y. Ma, W. Huang, Oxygen Vacancy-Induced Novel Low-Temperature Water Splitting Reactions on FeO(111) Monolayer-Thick Film, J. Phys. Chem. C 116 (43) (2012) 22921–22929. doi:10.1021/jp307104a.

[7] M. De Santis, A. Buchsbaum, P. Varga, M. Schmid, Growth of ultrathin cobalt oxide films on Pt(111), Phys. Rev. B 84 (12) (2011) 125430. doi:10.1103/PhysRevB.84.125430.

[8] W. Meyer, D. Hock, K. Biedermann, M. Gubo, S. Mueller, L. Hammer, K. Heinz, Coexistence of rocksalt and wurtzite structure in nanosized CoO films, Phys. Rev. Lett. 101 (1) (2008) 016103. doi:10.1103/PhysRevLett.101.016103.

[9] K. Biedermann, M. Gubo, L. Hammer, K. Heinz, Phases and phase transitions of hexagonal cobalt oxide films on Ir(100)-(1x1), J. Phys. Cond. Mat. 21 (18) (2009) 185003. doi:10.1088/0953-8984/21/18/185003.

[10] M. Gubo, C. Ebensperger, W. Meyer, L. Hammer, K. Heinz, Substoichiometric cobalt oxide monolayer on Ir(100)-(1x1), J. Phys. Cond. Mat. 21 (47) (2009) 474211. doi:10.1088/0953-8984/21/47/474211.

[11] C. Ebensperger, M. Gubo, W. Meyer, L. Hammer, K. Heinz, Substrate-induced structural modulation of a CoO(111) bilayer on Ir(100), Phys. Rev. B 81 (23) (2010) 235405. doi:10.1103/PhysRevB.81.235405.

[12] M. Gubo, C. Ebensperger, W. Meyer, L. Hammer, K. Heinz, Structural elements in the oxidation process of a single cobalt layer on Ir(100)-(1x1), Phys. Rev. B 83 (7) (2011) 075435. doi:10.1103/PhysRevB.83.075435.

[13] C. Troeppner, T. Schmitt, M. Reuschl, L. Hammer, M. A. Schneider, F. Mittendorfer, J. Redinger, R. Podloucky, M. Weinert, Incommensurate Moire overlayer with strong local binding: CoO(111) bilayer on Ir(100), Phys. Rev. B 86 (23) (2012) 235407. doi:10.1103/PhysRevB.86.235407.

[14] K. Heinz, L. Hammer, Epitaxial cobalt oxide films on Ir(100)the importance of crystallographic analyses, J. Phys. Cond. Mat. 25 (17) (2013) 173001. doi:10.1088/0953-8984/25/17/173001.

[15] M. Gubo, C. Ebensperger, W. Meyer, L. Hammer, K. Heinz, F. Mittendorfer, J. Redinger, Tuning the Growth Orientation of Epitaxial Films by Interface Chemistry, Phys. Rev. Lett. 108 (6) (2012) 066101. doi:10.1103/PhysRevLett.108.066101.

[16] W.-W. Zhang, M. Chen, Thermodynamic modeling of the CoFeO system, Calphad 41 (2013) 76–88. doi:10.1016/j.calphad.2013.02.002.

[17] L. Aballe, M. Foerster, E. Pellegrin, J. Nicolas, S. Ferrer, The ALBA spectroscopic LEEM-PEEM experimental station: layout and performance, J. Sync. Rad. 22 (3) (2015) 745–752. doi:10.1107/S1600577515003537.

[18] E. Bauer, Surface Microscopy with Low Energy Electrons, Springer Berlin Heidelberg, 2014.

[19] I. Palacio, M. Monti, J. F. Marco, K. F. McCarty, J. d. l. Figuera, Initial stages of FeO growth on Ru(0001), J. Phys. Cond. Matt. 25 (48) (2013) 484001. doi:10.1088/0953-8984/25/48/484001.

[20] M. Monti, B. Santos, A. Mascaraque, O. Rodríguez de la Fuente, M. A. Niño, T. O. Mentes, A. Locatelli, K. F. McCarty, J. F. Marco, J. de la Figuera, Magnetism in nanometer-thick magnetite, Phys. Rev. B 85 (2) (2012) 020404.

[21] H. Zeuthen, W. Kudernatsch, L. R. Merte, L. K. Ono, L. Lammich, F. Besenbacher, S. Wendt, Unraveling the edge structures of Platinum(111)-supported ultrathin FeO islands: The influence of oxidation state, ACS Nano 9 (1) (2015) 573–583. doi:10.1021/nn505890v.

[22] J. de la Figuera, J. Puerta, J. Cerda, F. El Gabaly, K. McCarty, Determining the structure of Ru(0001) from low-energy electron diffraction of a single terrace, Surf. Sci. 600 (9) (2006) L105–L109.

[23] T. J. Regan, H. Ohldag, C. Stamm, F. Nolting, J. Lüning, J. Stöhr, R. L. White, Chemical effects at metal/oxide interfaces studied by x-ray-absorption spectroscopy, Phys. Rev. B 64 (21) (2001) 214422. doi:10.1103/PhysRevB.64.214422.

[24] J. I. Flege, J. Hcker, B. Kaemena, T. O. Menteş, A. Sala, A. Locatelli, S. Gangopadhyay, J. T. Sadowski, S. D. Senanayake, J. Falta, Growth and characterization of epitaxially stabilized ceria(001) nanostructures on Ru(0001), Nanoscale 8 (20) (2016) 10849–10856. doi:10.1039/C6NR02393B.

[25] G. Ketteler, W. Ranke, Heteroepitaxial growth and nucleation of iron oxide films on Ru(0001), J. Phys. Chem. B 107 (18) (2003) 4320–4333.

[26] B. Santos, E. Loginova, A. Mascaraque, A. K. Schmid, K. F. McCarty, J. de la Figuera, Structure and magnetism in ultrathin iron oxides characterized by low energy electron microscopy, J. Phys. Cond. Matt. 21 (2009) 314011. doi:10.1088/0953-8984/21/31/314011.