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Study of the early stages of growth of Co oxides on oxide substrates†

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The growth of Cobalt oxides by reactive thermal evaporation of metallic Cobalt in an oxygen atmosphere on a series of oxide substrates, namely SiO_2, Al_2O_3 and MgO, has been chemically and morphologically studied by means of XPS and atomic force microscopy (AFM). The XPS results reveal that cobalt oxide grows as CoO (Co^{2+}) for coverages up to some tens of equivalent monolayers on all substrates. For larger coverages, the formation of the spinel oxide Co_3O_4 has been observed. AFM and XPS quantification allowed us to determine the way of growth of CoO on all substrates, being of Volmer–Weber (i.e. islands) mode for SiO_2, whereas for Al_2O_3 and MgO, the growth follows the Frank-van der Merwe (i.e. layer-by-layer) mode. The results are discussed in terms of the mismatch of the lattice parameters of the CoO adsorbates with the substrates. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: oxide growth; oxide/oxide interface; oxide thin films; X-ray photoemission; AFM

Introduction

The main motivation of this paper is the study of the early stages of growth of Cobalt oxides thin films on a series of oxide substrates, namely SiO_2, Al_2O_3, and MgO. The growth mechanism of a thin film on any material can be strongly affected by the chemical nature, electronic structure, and morphology of the support. The interaction of the adsorbates with the surface atoms of the support can be affected by many effects like surface diffusion, surface and interface chemical reactivity, aggregation, etc., which can play an important role for the final properties of the film.[1–3] These effects are particularly observable at the early stages of the film growth, where the growing material is in direct contact with the support. To this end, we have selected a series of metal oxides substrates with different electronic structure such as SiO_2, Al_2O_3, and MgO, being SiO_2 strongly covalent and MgO strongly ionic with Al_2O_3 in between. Besides, the physical and chemical properties of these oxides give them an important role in many industrial applications. Indeed, the most stable Co oxides i.e. CoO (Co^{2+}) and Co_3O_4 ($Co^{2+,3+}$) have recently attracted a lot of interest in materials research due to their technological applications.[4–7]

The study of oxide/oxide interfaces up to date is very scarce. However, it has recently become a hot topic mainly due to their unique properties such as interface superconductivity, magnetoelectric coupling, and quantum Hall effect in oxide heterostructures.[8] The difficulty in their characterization mainly comes due to the insulating character of most of the oxides, which leads to charging effects, which complicates their efficient characterization. In spite of this, works dealing with oxide/oxide interfaces studied by electron spectroscopies can be found elsewhere.[9] In particular, the growth of cobalt oxides thin films on SiO_2[10] and Al_2O_3[11] has already been reported. On the SiO_2 substrate, reactive oxidation with molecular oxygen gas produced CoO (Co^{2+}) species, whereas using an oxygen plasma Co_3O_4 ($Co^{2+,3+}$) species have been obtained. For the alumina substrate, XPS has revealed the transition from an interfacial cobalt oxide (Co^{2+}) layer toward (111) oriented Co_3O_4.[11] Also, the formation of M-O-Si (M = Metal) cross linking bonds has been observed in the growth of different transition metal oxides on SiO_2,[12–15] Al_2O_3,[16,17] and MgO.[18]

Atomic force microscopy (AFM) and x-ray photoemission spectroscopy (XPS) have been used for the characterization of the growth of Co oxides on oxide substrates. In this work, we first present the XPS chemical analysis of the Co species formed during the growth process. Then, a quantitative analysis has been performed using the XPS intensities of both overlayer and substrate, allowing us to estimate the rate of growth and the coverage in equivalent monolayers (Eq-ML). With the information contained in the AFM images for different stages of growth on all substrates, together with the XPS peak shape analysis method[19,20] implemented in the QUASES software,[21] a detailed description of the way of growth of Co oxides on the different oxide substrates has been obtained.

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Experimental details

Cobalt oxides were grown by thermal evaporation of metallic cobalt in a reactive oxygen atmosphere at 2×10^{-5} mbar. Single crystals from MTI Corporation, with nominal roughness ≤ 5 Å, were used as substrates. The single crystals were SiO_2 (11–20), Al_2O_3 (0001), and MgO (100). The substrates were previously heated at 400 °C in UHV for 60 min to desorb possible contamination and then exposed to oxygen atmosphere at 3×10^{-3} mbar to prevent oxygen losses. The substrates were maintained at room temperature during growth. The evaporation rate was maintained constant and very low (see in the succeeding text), to allow the study of coverages below 1 Eq-ML. Successive evaporations were performed, and after each step, the surface was analyzed by XPS.

The XPS measurements were performed with a CLAM-4 MCD hemispherical analyzer from Thermo Fisher Scientific using a twin-anode source. The spectra were measured using the Al anode to avoid overlap of the Auger peaks with the Co 2p energy region. The pass energy of the analyzer was set to 20 eV, giving a resolution of about 1.0 eV. To correct from charging effects, the energy scale was calibrated by adjusting the Si 2p XPS peak for SiO_2 at 103.0 eV, the Al 2p for Al_2O_3 at 74.5 eV, and the Mg 2p for the MgO at 50.0 eV. AFM images of some stages of growth were obtained *ex-situ* with a Nanotec AFM microscope in noncontact dynamic (tapping) mode. The images were processed and analyzed with the WSxM software.[22]

Results and discussion

XPS Chemical analysis

The Co $2p_{3/2}$ XPS spectra of the deposits on all substrates are shown in Fig. 1. The spectra have been labeled with their corresponding coverage as obtained from the inelastic peak shape analysis (see in the succeeding text). In general, all the spectra have a similar lineshape, showing a main peak located at a binding energy around 782.0 eV and a satellite around 787.0 eV, although for the Al_2O_3 substrate, the spectra appear slightly shifted toward lower binding energies. This difference could be due to a charge transfer of around 1 eV from the Al_2O_3 substrate to the CoO overlayer as calculated by density functional theory elsewhere.[23] These spectra correspond to CoO (Co^{2+}) species as reported in the literature.[24] The spectra for very low coverages (<1 Eq-ML) on the SiO_2 substrate show a shoulder at lower binding energies. This shoulder is assigned to some metallic Co, which remains unoxidized, in agreement with other published data.[25] One reason why metallic Co grows only on the SiO_2 substrate could be due to the different coordination of the SiO_2 lattice (tetrahedral) with respect to that of Al_2O_3, MgO, and CoO (octahedral). Except for the MgO substrate, the spectra for high coverages show that the satellite splits into two weak peaks at 786 and 790 eV binding energies. These spectra agree with those published elsewhere for the Co_3O_4 spinel oxide.[24]

Based on the aforementioned chemical analysis, we can conclude that cobalt oxide grows as CoO (Co^{2+}) on all the oxide substrates studied here in the early stages of growth. In turn, for large coverages, the formation of the Co_3O_4 oxide is favored. This is clearly seen in the case of SiO_2 and Al_2O_3 substrates, where for intermediate coverages a progressive shift of the main peak is observed. Once the Co_3O_4 layer has grown up to a thickness larger than the XPS mean probing depth, the spectrum is dominated by the peak corresponding to Co_3O_4. In the case of the MgO substrate, although the spectra still resemble that of CoO, a shift toward

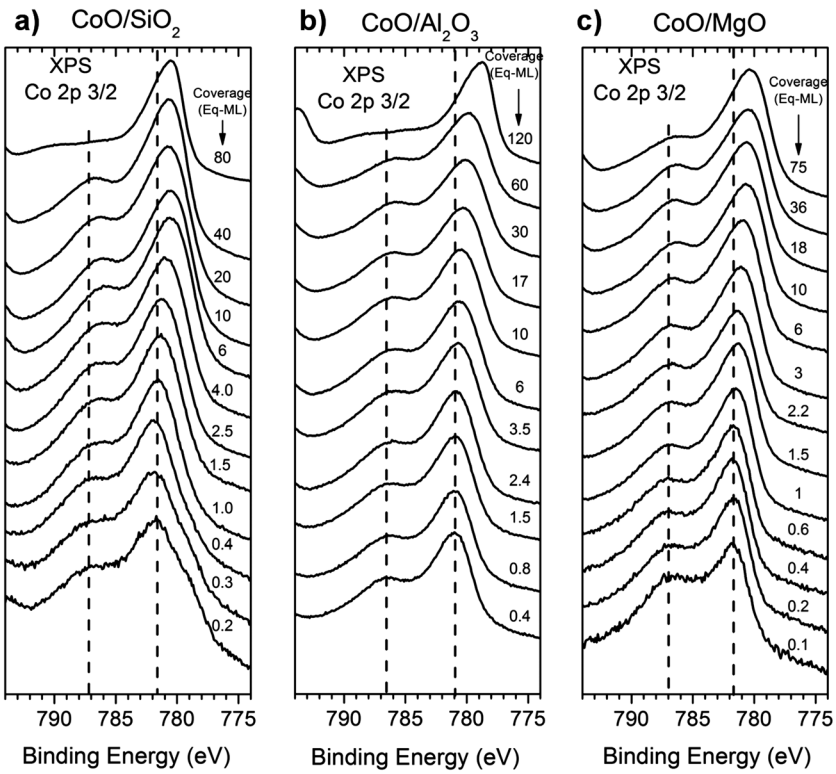

Figure 1. Co $2p_{3/2}$ XPS spectra corresponding to the Co oxides deposits on a) SiO_2, b) Al_2O_3, and c) MgO as a function of the coverage.

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lower binding energies and a relative decrease of the satellite intensity are also observed. This suggests that also a very thin layer of Co_3O_4 spinel oxide has been formed for large coverages on the MgO substrate.

Quantitative analysis

XPS intensities

For quantitative analysis of the XPS intensities, we have fitted the experimental data with exponential growth model of the form $(1\text{-}exp(-d/\lambda))$ for the overlayer peak and $exp(-d/\lambda)$ for the substrate peak.[26] The intensities of the Co 2p XPS peak of the overlayers as well as those of the substrates (Si 2p, Al 2s, and Mg KLL) are represented in Fig. 2. As expected, the intensity of the Co 2p peak increases exponentially as the Co oxide grows, whereas the intensity of the substrate peak decreases correspondingly. It is worth noting that the intensity of the Co 2p peak for large coverages does not fit well to the exponential curve. This is due to the fact that at these stages, the films correspond mainly to Co_3O_4 whose atomic Co concentration is lower than that for CoO. Assuming a constant evaporation rate, the XPS peak intensity as a function of evaporation time given by these models allows estimating the growth rate of the CoO deposits from both overlayer and substrate, being similar in both cases. The values found with this procedure were 0.23, 0.25, and 0.20 Eq-ML/min for SiO_2, Al_2O_3, and MgO, respectively.

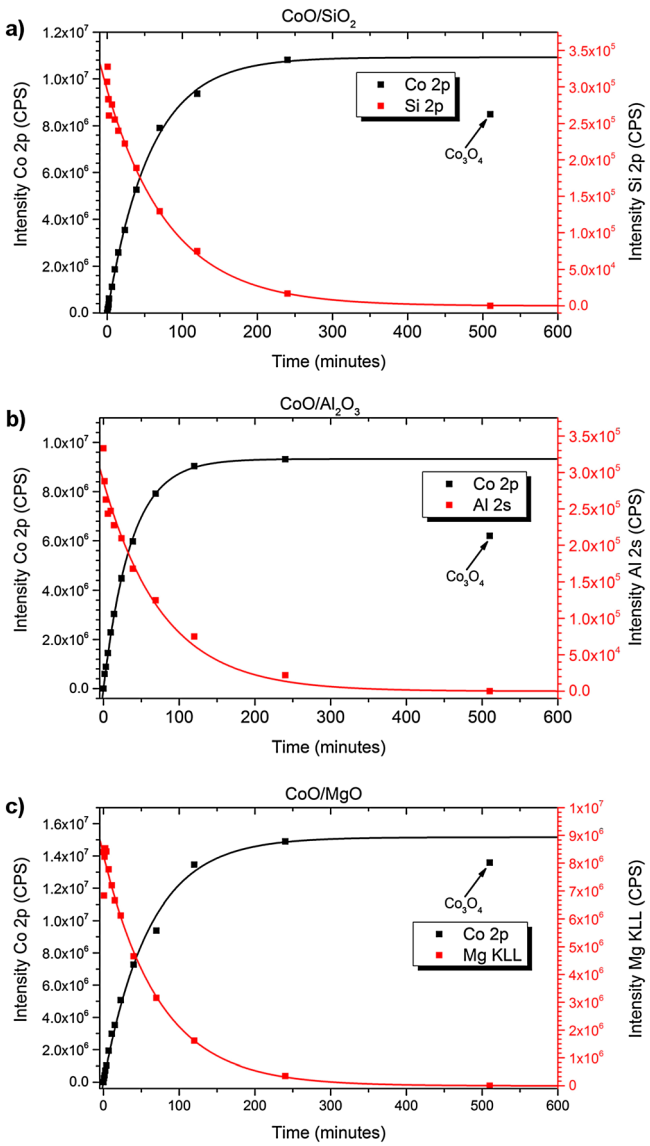

Figure 2. X-ray photoemission spectroscopy (XPS) intensities of the Co 2p peak and the corresponding peak for each oxide substrate (Si 2p, Al 2s, and Mg KLL), as a function of the evaporation time for a) CoO/SiO_2, b) CoO/Al_2O_3, and c) CoO/MgO.

AFM

AFM images taken for different coverages of Co oxides on the oxide substrates are shown in Fig. 3. For the SiO_2 substrate, the image of the clean substrate shows a very flat surface giving an experimental roughness of about 1.8 Å. For larger coverages, small CoO islands of about 8 Å in height (two CoO unit cells) are formed. The substrate appears almost fully covered at coverages about 2.8 Eq-ML, with islands of 4 Å, 8 Å, and 12 Å thick. These sets of islands start growing completing this layer at about 5 Eq-ML. Larger coverages produce a smoothing of the surface giving a flat CoO thin film whose mean roughness decreases. These images show that CoO grows following a Volmer–Weber (i.e. islands formation) mode, which is expected when adatom–adatom interaction is stronger than the adatom–surface interaction. The AFM images of Co oxides on Al_2O_3 show a series of uniform lines corresponding to successive steps and terraces on the Al_2O_3 single crystal surface, as has already been observed.[27] The experimental roughness for the clean single crystal gives values of around 1.3 Å. However, the most important feature is that even with 10 Eq-ML of CoO covering the surface, the terraces and steps are clearly observed, and the roughness of the surfaces remains of the order of the substrate. This suggests the formation of an epitaxial CoO thin film on the Al_2O_3 substrate following a Frank-van der Merwe way of growth, i.e. layer-by-layer mode. Usually this growth mode occurs when adatoms attach preferentially to surface sites leading to an atomically smooth and two dimensional thin films. For the MgO substrate, the AFM images look very similar to that of the clean substrate up to coverages of 10 Eq-ML. In fact, the image of the clean substrate appears similar to that of the SiO_2 substrate with a roughness of 1.5 Å and showing no presence of terraces and steps. The images for coverages of 2 and 10 Eq-ML show the same appearance as the clean substrate, with a similar roughness and showing no islands formation. This also suggests that CoO is also growing on MgO in a layer-by-layer mode as in the case of the Al_2O_3 substrate.

Inelastic XPS peak shape analysis (QUASES)

In order to confirm the way of growth suggested by the AFM images, we have performed an inelastic peak shape analysis[19,20] using the QUASES software.[21] For SiO_2, we have performed such analysis using a model taking into account

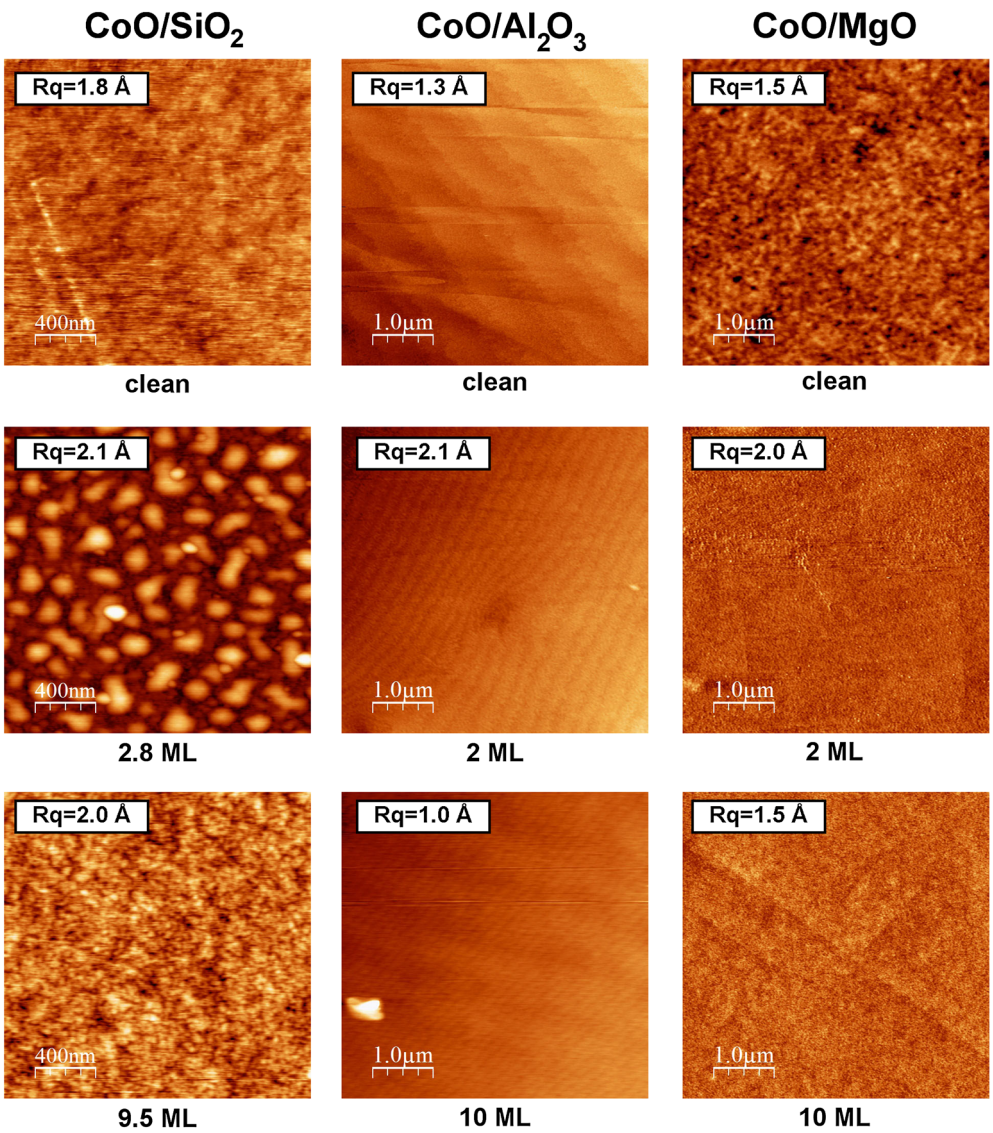

Figure 3. Atomic force microscopy (AFM) images of three stages of growth of Co oxides on SiO_2, Al_2O_3, and MgO. Image sizes as indicated in the inset. The mean square roughness (Rq) for each image is given in Å.

two sets of islands with different heights. The peak chosen for the analysis was the Co 2p of the growing CoO overlayer, for which the inelastic mean free path of the photoelectrons is $\lambda = 13.96$ Å. The results are shown in Fig. 4a. Indeed, the results given by QUASES using this model agree with those observed by AFM, obtaining two sets of islands of about 10 Å and 4 Å height, respectively. Therefore, the AFM images confirm the model prediction. In the case of the Al_2O_3 substrate (Fig. 4b), we have analyzed the Co 2p peak using an overlayer model i.e., assuming the growth of a continuous layer with a definite thickness. Although in this case AFM cannot determine the thickness of the overlayer, the agreement of the model with the layer-by-layer growth mode is clear. For the MgO substrate (Fig. 4c), we have used a buried layer model by analyzing the Mg KLL Auger peak ($\lambda = 24.58$ Å) of the MgO substrate. Using Al K_α as excitation energy, this peak is located at a kinetic energy region where no other contributions to the background are present, making its analysis more accurate. Again, the model predicts the formation of successive epitaxial CoO overlayers on the MgO substrate. Once the total coverage as a function of the evaporation time is obtained with this procedure, the growth rate can also be calculated. The values obtained in this case are 0.18, 0.23, and 0.15 Eq-ML/min for SiO_2, Al_2O_3, and MgO, respectively, showing a good agreement with those calculated from the XPS peak intensities. As stated before, all spectra shown in Fig. 1 have been labeled with this method assuming a CoO Eq-ML as half of the lattice parameter given by Wyckoff,[28] i.e. 2.1 Å.

According to the results obtained earlier, CoO grows on SiO_2 following an island growth mode, whereas on Al_2O_3 and MgO, CoO grows epitaxialy (layer-by-layer mode). This indicates that the CoO adsorbates have stronger interaction with Al_2O_3 and MgO than with SiO_2 surfaces and suggests that the lattice parameter matching of the substrates ($a = 4.914$ Å for SiO_2, $a = 4.758$ Å for Al_2O_3, and $a = 4.216$ Å for MgO)[28] with respect to that of CoO ($a = 4.260$ Å) is playing an important role in the way of growth of CoO on the studied oxides.

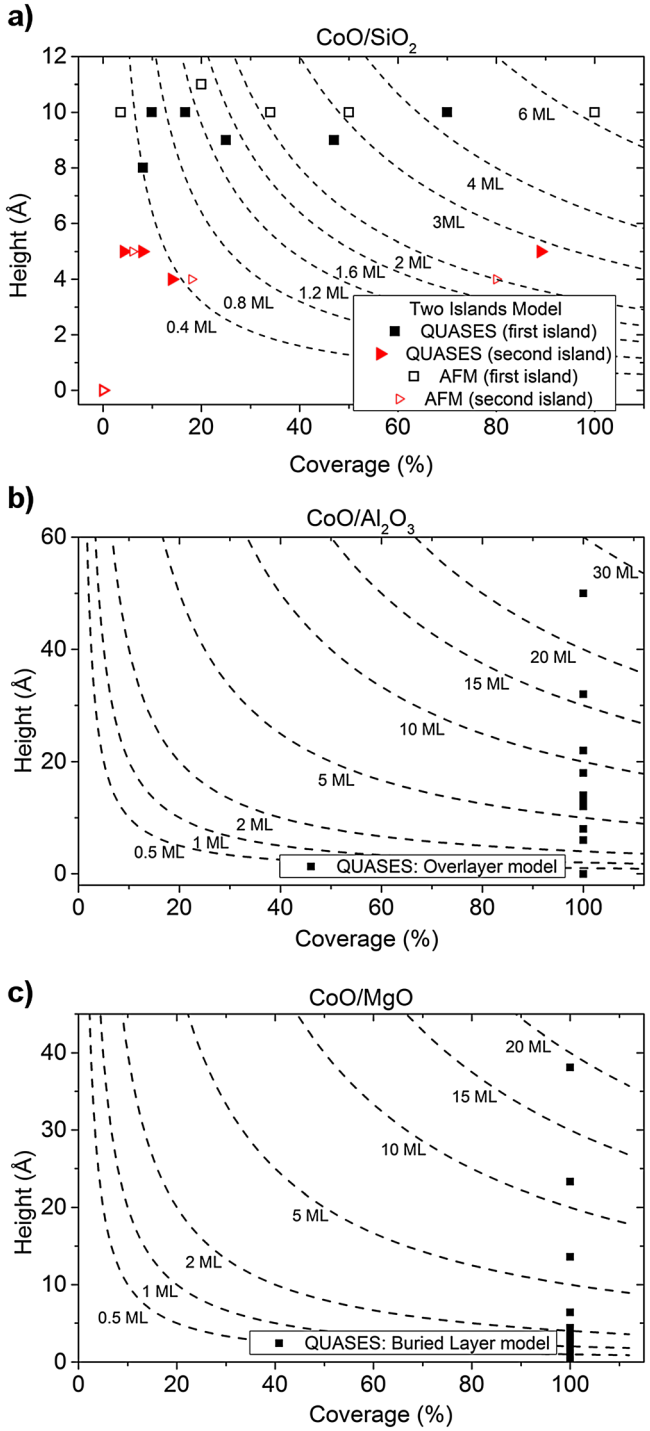

Figure 4. Results of the inelastic X-ray photoemission spectroscopy (XPS) peak shape analysis performed with the QUASES software for a) CoO/SiO_2: calculated by two islands model. The results are compared with those given by AFM b) CoO/Al_2O_3: calculated by overlayer model, and c) CoO/MgO: calculated by buried layer model.

Conclusions

The chemical and morphological analysis of the way of growth of cobalt oxides on different metal oxides SiO_2, Al_2O_3, and MgO have been characterized by XPS and AFM. XPS chemical analysis reveals that, on all substrates, the material starts growing as CoO (Co^{2+}) up to coverages of some tens of Eq-ML, depending on the substrate. In contrast, larger coverages give rise to the formation of the spinel Co_3O_4 oxide ($Co^{2+,3+}$) on all substrates. Combining XPS and AFM, we have quantitatively studied the growth of Co oxides on the aforementioned substrates. For the SiO_2 substrate, the material follows a Volmer–Weber (i.e. islands formation) growth mode, whereas for Al_2O_3 and MgO the growth is of a Frank-van der Merwe (i.e. layer-by-layer) mode. From this, it is concluded that CoO adatoms have stronger interaction with Al_2O_3 and MgO surfaces than with SiO_2. The mismatch of the lattice parameter between the CoO deposits and those of the substrate seems to be playing a significant role in the growth of the CoO layer on the oxide surface studied here.

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