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STM study of the nanostructures prepared by deposition of NiO on Ag(001)

M Caffio¹, A Atrei^{2,3}, B Cortigiani¹ and G Rovida¹

¹ Dipartimento di Chimica, Università di Firenze, Polo Scientifico di Sesto Fiorentino, 55019 Sesto Fiorentino (FI), Italy

² Dipartimento di Scienze e Tecnologie Chimiche e dei Biosistemi, Università di Siena, 53100 Siena, Italy

E-mail: atrei@unisi.it

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Abstract

Submonolayers of nickel oxide were grown on the Ag(001) surface by evaporation of Ni in the presence of O₂ at a pressure of 1×10^{-6} mbar. In the early stages of deposition, two-dimensional oxide islands with a (2×1) periodicity grow on Ag(001). After annealing at about 500 K, the (2×1) single atomic layer transforms into NiO(001) double layer islands. The 1:1 stoichiometry of the film is not influenced by whether the annealing is carried out in vacuum or in the presence of oxygen. However, the oxide islands exhibit different morphologies depending on the O₂ pressure during the annealing process.

1. Introduction

Epitaxial ultrathin films of NiO deposited on the Ag(001) surface can be used as model systems to investigate how the thickness of the film and the interaction with the substrate influence the structure and properties of the oxide layer [1, 2]. Recently, we studied by means of several surface-sensitive techniques the mechanism of growth and structure of NiO ultrathin films on Ag(001) [3, 4]. Besides the reduced dimensionality of the film and the interaction with the substrate, the morphology at the nanometric scale and the presence of defects (such as step edges and vacancies) are expected to affect the electronic and chemical properties of the oxide layers significantly. For instance, NiO films of thickness a few monolayers on Ag(001) are capable of adsorbing and dissociating H₂O, and this reactivity has been attributed to the defectivity of the film [5]. By controlling the morphology of the epitaxial oxide films it should be possible to influence the adsorption properties and reactivity of these systems. Hence, it is important to investigate the effect of the preparation conditions (deposition rate, temperature of the substrate, thermal treatments, etc) on the morphology at the nanometric level of NiO films grown on Ag(001). In the present work, we studied by means of scanning tunnelling

³ Author to whom any correspondence should be addressed.

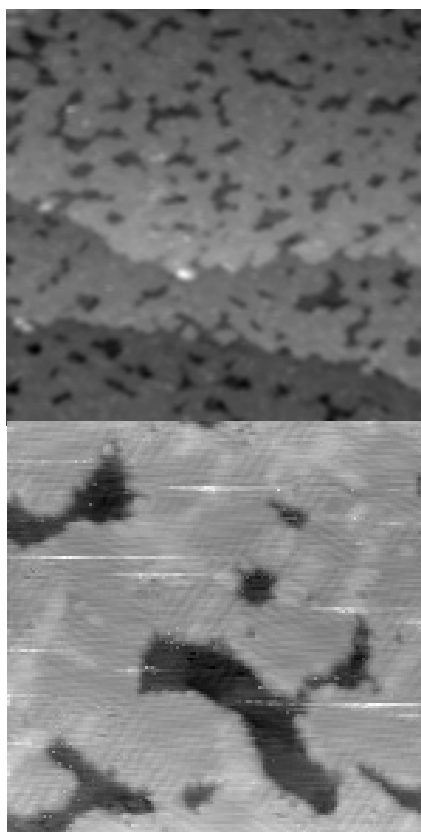


Figure 1. STM images of the (2×1) oxidic phase of NiO deposited on Ag(001). The (2×1) phase was prepared by evaporation of Ni in the presence of O_2 at a pressure of 1×10^{-6} mbar with the sample at 373 K. Top: $100 \text{ nm} \times 100 \text{ nm}$. V: -500 mV , I: 0.2 nA . Bottom: $17 \text{ nm} \times 17 \text{ nm}$. V: -500 mV , I: 0.3 nA . The regions with the rows of bright features running in perpendicular directions correspond to the (2×1) domains rotated by 90° to each other.

microscopy (STM) the effect of the annealing conditions on the morphology of the NiO islands. We found a drastic change in the shape of the islands depending on whether the annealing of submonolayers of nickel oxide is carried out in vacuum or in the presence of oxygen.

2. Experimental details

The experiments were carried out in an ultra-high vacuum (UHV) apparatus equipped with facilities for sample preparation and characterization. X-ray photoelectron spectroscopy (XPS) and low-energy ions scattering (LEIS) spectra were collected by means of a hemispherical electron/ion energy analyser. LEIS spectra were obtained using a focused He beam with an energy of 1 keV. The scattering angle was 135° . The sample could be transferred under UHV in a second vessel housing the STM microscope. STM images were acquired at room temperature in constant current mode using a tungsten tip chemically etched and cleaned *in situ* by Ar ion bombardment. The NiO films were deposited by evaporation of Ni (using an electron beam evaporator) in the presence of O_2 at a pressure of 1×10^{-6} mbar.

3. Results and discussions

After deposition of submonolayers of NiO the film has an ordered structure with a (2×1) periodicity as shown by low-energy electron diffraction (LEED) and STM. The STM images shown in figure 1 were measured after deposition of 0.7 monolayers of NiO. At this coverage,

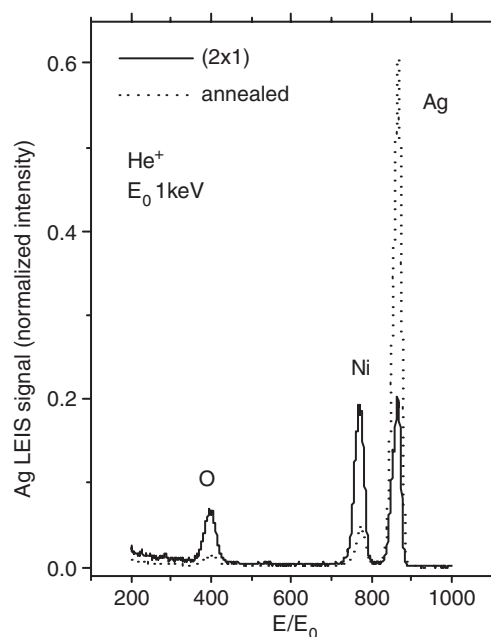


Figure 2. LEIS spectra measured for the (2×1) phase of NiO and after annealing in vacuum at 520 K for 10 min. The LEIS signal of Ag is proportional to the fraction of substrate surface not covered by the oxide film.

a large fraction of the substrate is covered by two-dimensional oxide islands with (2×1) periodicity. Before the (2×1) layer is completed, NiO(001) islands start to grow. The (2×1) regions are characterized by rows of bright features. On different islands the rows run along perpendicular directions, in agreement with the formation of domains rotated by 90° to each other. At all sample biases used in the measurements, the (2×1) islands appear as protrusions with respect to the Ag substrate. At a sample bias of -100 mV they have an apparent height of 1.8 – 2.0 Å. The images are similar to those reported for NiO/Ag(001) by Bertrams and Neddermeyer [6, 7].

The (2×1) oxidic phase was heated in UHV at 520 K for 10 min. After annealing the (2×1) LEED pattern disappears and a (1×1) diffraction diagram is observed. As reported in previous studies, the (2×1) layer transforms into NiO(001) islands upon annealing [4]. Since the lattice mismatch between NiO(001) and the substrate is small (about 2%), NiO(001) can easily assume the in-plane lattice parameter of the Ag(001) substrate, resulting in a film with a (1×1) periodicity. The XPS spectra show a variation of the Ni 2p peak shape associated with the formation of NiO(001). However, the O/Ni atomic ratio for the (2×1) phase which was found to be 1.0 ± 0.1 does not change after annealing in vacuum [4]. LEIS spectra (which are sensitive to the composition of the outermost layer only) measured after annealing indicate a large increase of the fraction of substrate surface not covered by the nickel oxide (figure 2). The increase of the Ag LEIS signal after annealing is consistent with the transformation of the (2×1) oxidic phase into NiO(001) islands having a double layer thickness [4].

The STM images reveal a substantial modification of the surface morphology upon annealing (figure 3). Areas with various levels and lateral extensions can be observed. On the basis of the LEIS results and of the height expected for a monatomic step of Ag(001) (2.04 Å) we can distinguish between regions of clean substrate and regions covered by the oxide. The oxide islands appear with irregular, polygonal shapes. For some of these islands an octagonal perimeter is more evident. This shape is the result of oxide domain edges oriented along the $[100]$ and $[110]$ directions of the substrate.

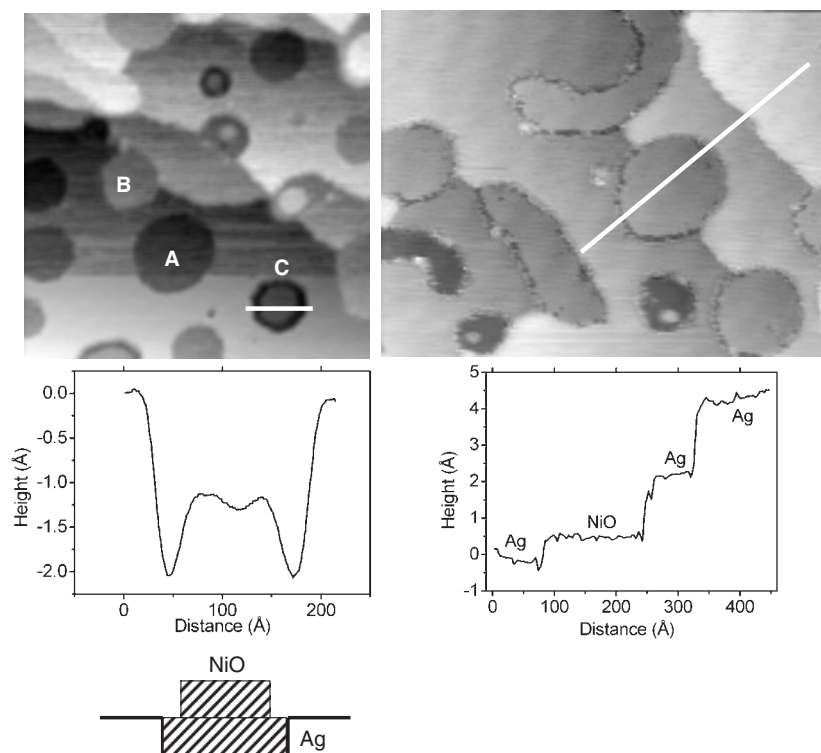


Figure 3. STM images of the surface obtained after annealing the (2×1) oxidic phase in vacuum at 520 K for 10 min. Left: $100 \text{ nm} \times 100 \text{ nm}$. $V: -70 \text{ mV}$, $I: 0.2 \text{ nA}$. Right: $53 \text{ nm} \times 71 \text{ nm}$. $V: -200 \text{ mV}$, $I: 0.2 \text{ nA}$. The insets show the height profiles along the white lines drawn in the images. The height profiles are attributed to oxide islands with a thickness of two atomic layers, embedded in the outermost layer of the surface.

It is well known that the height of ultrathin films of wide band gap oxides on metal surfaces measured by STM strongly depends on the sample bias. In the case of CoO [8] and MgO [9] films on Ag(001) it has been shown that, for sample biases within the band gap of the oxide film, the regions covered by the oxide are imaged as depressions, whereas they appear as protrusions when the sample bias is larger (in absolute value) than the band gap.

In the present case, the observed height profiles can be explained on the basis of the two following hypotheses: (i) double-layer NiO islands appear with a height smaller than that of a substrate monatomic step, at the sample biases used to get stable tunnelling conditions; (ii) NiO islands are embedded in the outermost layer of the substrate. Hence, NiO islands in the middle of terraces (completely surrounded by Ag) appear as depressions with respect to the Ag terrace (see zone A in figure 3, left). On the other hand, NiO regions partially incorporated in upper terraces are imaged as protrusions with respect to the lower terraces (for example zone B in figure 3, left). Some of the oxide islands (marked as C in figure 3) appear to be surrounded by a ‘trench’. This height profile can be explained if the second layer is not completed and a rim one atomic layer thick is seen at a lower level than the centre of the island.

When the annealing of the (2×1) oxidic layer is carried out under the same conditions but in the presence of O_2 at a pressure in the 10^{-6} mbar range, the XPS and LEIS spectra do not change (within the uncertainty of the measurements) compared to those obtained for the surface annealed in vacuum. On the other hand, the morphology of the oxide islands is drastically

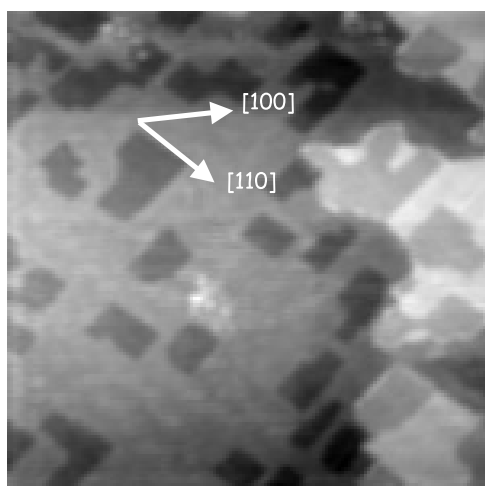


Figure 4. STM image of the surface after annealing the (2×1) oxidic phase at 520 K for 10 min with $p_{\text{O}_2} = 5 \times 10^{-6}$ mbar. $100 \text{ nm} \times 100 \text{ nm}$. V: 2000 mV, I: 0.25 nA. The principal crystallographic directions of the substrate are indicated.

changed when the surface is heated in O_2 . Most of the NiO(001) islands now have a square shape with the borders oriented along the [110] directions of the substrate (figure 4). At the sample bias corresponding to the best imaging conditions the NiO islands appear as depressions with respect to the substrate surface. The orientation of the NiO(001) islands observed in the STM images implies the existence of polar (that is alternating rows containing either Ni or O atoms) edges of the islands (figure 5). The polar orientation of step edges was also observed in previous studies of NiO(001) on Ag(001). In those works, square-like islands were seen after annealing the (2×1) layer at 450 K in vacuum, without exposure to O_2 [6, 7]. On the basis of electrostatic considerations, the most stable edge border should be the non-polar one, containing both oxygen and nickel atoms. If the NiO islands are embedded within the substrate surface, the polar and the non-polar edges of the oxide imply the formation of [110] and [100] step edges of Ag(001), respectively. Since the [110] substrate steps are more stable than the [100] ones, the formation of [110] substrate steps may stabilize the polar edge termination of the oxide islands when these are embedded in the surface. Indeed, recent *ab initio* calculations for MgO(001) on Ag(001) show that the formation of [110] substrate steps reduces the energy cost of polar edges for MgO(001) clusters embedded in the substrate [10, 11].

The formation of extended polar edges of the NiO islands when the (2×1) oxidic phase is heated in the presence of O_2 can be explained in terms of kinetic factors. We can assume that for NiO(001) embedded within the Ag(001) the polar borders in contact with the [110] steps of the substrate are more stable than non-polar borders in contact with the [100] step edges of the substrate. O_2 adsorption could increase (by increasing the atomic mobility) the rate of the processes needed to achieve the most stable orientation of the oxide island edges. Possible reconstructions of the NiO step edges during annealing in O_2 cannot be ruled out. For instance, the presence of O_2 could lead to the formation of borders all terminated by oxygen atoms. This would correspond to the formation of an oxygen-rich NiO film. Unfortunately, XPS cannot provide clear evidence for the existence of such non-stoichiometric oxide since, for the lateral size of the islands observed here, the expected increase of the O/Ni atomic ratio is comparable to (or below) the accuracy of the measurements. Moreover, NiO islands with polar borders have also been observed when the annealing is carried out in vacuum [6, 7]. On the basis of these considerations, the kinetic explanation for the effect of oxygen on the morphology of the NiO appears to be more plausible.

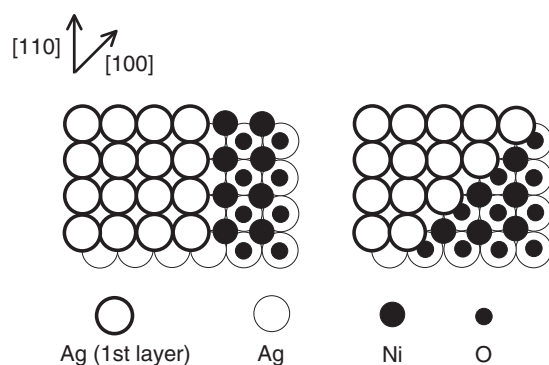


Figure 5. Schematic structure of NiO(001) on Ag(001). NiO has a rock salt structure and a lattice parameter of 4.17 Å. The NiO(001) film has a (1×1) periodicity (i.e. the same in-plane lattice parameter of the substrate). The NiO islands are incorporated in the outermost layer of Ag(001). Only the NiO layer at the Ag-oxide interface is shown. Left: NiO(001) cluster terminated by polar borders in contact with the [110] steps of the substrate. This model corresponds to the ideal structure of NiO(001). Polar steps, all terminating with oxygen, can be obtained adding rows of oxygen atoms (on the bottom and right sides of the NiO cluster). In this case the oxide film would be oxygen rich. Right: NiO(001) cluster with non-polar borders in contact with the [100] steps of the substrate.

4. Conclusions

In conclusion, we have shown that nickel oxide with different atomic structures and morphologies at the nanometric scale can be grown on Ag(001) by reactive evaporation of Ni depending on the preparation conditions. In particular, NiO domains with octagonal or square shapes can be obtained, depending on whether the (2×1) oxidic phase is annealed in vacuum or in the presence of O_2 . Thus, by controlling the morphology of the NiO islands it may be possible to clarify the role of the steps and kinks on the chemical reactivity of these oxide films.

Acknowledgments

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