Early Stages of NiO Growth on Ag(001): A Study by LEIS, XPS, and LEED

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Ultrathin nickel oxide films were grown on the Ag(001) surface by evaporation of Ni in an O_2 atmosphere. The growth mechanism, composition, and structure of the NiO layers formed in the early stages of deposition have been investigated by LEIS, XPS, XPD, and LEED. We found that at O_2 pressures in the $10^{-7} - 10^{-6}$ mbar range and sample temperatures between room temperature and 373 K, a nickel oxide layer forms showing a (2×1) LEED pattern. This is a phase of monatomic thickness which gradually covers the substrate surface upon increasing the surface coverage. LEIS and XPS data show that before the (2×1) layer is completed NiO(001) islands start to nucleate. The substrate surface is completely covered by NiO(001) for coverages higher than 2 ML. When NiO is deposited with the sample held at 453 K, we found that in the early stages of deposition metallic Ni is present in the subsurface region of the substrate. Upon further NiO deposition the oxide becomes the prevalent species on the surface. Under these conditions, the (2×1) phase is not observed. We found that the (2×1) phase is not stable upon annealing at 473–600 K and transforms into NiO(001). LEIS and XPD results indicate the formation of NiO islands 2 ML thick upon annealing. The structure of the (2×1) phase has been investigated by LEED intensity analysis (tensor LEED method). The best agreement with the experimental data is obtained for a structural model similar to the (111) surface of NiO. The effects of surface temperature and O_2 pressure on nickel oxide growth are discussed in terms of the low sticking probability of O_2 on Ag(001) and of the interaction between nickel and silver.

1. Introduction

The geometric structure, electronic properties, and reactivity of oxide films a few atomic layers thick deposited on metal surfaces are expected to be different from those of the surfaces of bulk oxides due to the nanometric thickness of the films and the interaction with the substrate.^{1,2} In addition to that, the morphology of the films, the presence of defects, may be important in determining the physical and chemical properties of these systems. The study of relatively simple oxides (such as NiO and MgO) grown on metal surfaces is relevant in order to understand fundamental aspects concerning the structure and properties of ultrathin oxide layers on metal substrates. Wellordered, epitaxial nickel oxide films can be prepared by evaporation of metallic nickel in an O2 atmosphere on substrates having the appropriate lattice parameter. The Ag(001) surface appears to be an ideal substrate for the epitaxial growth of NiO films oriented along the (001) direction due to the small lattice mismatch (2.3%) and the scarce reactivity of silver toward O_2 . Indeed, several studies performed by means of various surface science methods show that well-ordered NiO(001) films grow on Ag(001) (in a wide range of sample temperatures, oxygen pressures, and evaporation rates) for coverages higher than 2 monolayer (ML).3-8 It was found that nickel oxide films completely cover the substrate at a coverage of 2 monolayers (ML), and above this thickness a layer-by-layer growth was observed.3 The NiO(001) is pseudomorphic (that is with the

same in-plane parameter of the substrate) for a thickness ranging from 5 to 10 ML, depending on the preparation conditions.^{3,7,8} For higher coverages, the strain is released by the formation of misfit dislocations³ and NiO assumes its bulk lattice parameter.⁵ The structure of a NiO film 2 ML thick has been determined by low-energy electron diffraction (LEED) intensity analysis.⁴ This study confirmed the formation of a pseudomorphic NiO(001) film and showed that O atoms are on top of Ag atoms at the oxide-substrate interface. The results of these studies are in good agreement with recent ab initio calculations performed for this system.9 The situation is not so well-defined for submonolayer coverages of nickel oxide. In the very early stages of deposition, an oxidic phase exhibiting a (2×1) periodicity is observed.^{3,10,11} Upon increasing the NiO coverage the (2×1) LEED pattern disappears and the (1×1) diffraction diagram, corresponding to pseudomorphic NiO(001), is observed.³ Recently, the effect of the deposition conditions (in particular the O₂ flux during Ni evaporation) on the formation of the (2×1) phase has been studied by Giovanardi et al.¹² The (2×1) phase of NiO has been mainly investigated by means of scanning tunneling microscopy (STM), and on the basis of the STM images a structural model was proposed.^{10,11} However, a detailed spectroscopic characterization and a determination of the composition for the (2×1) phase are missing.

In the present work we investigated by means of X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering (LEIS) the composition and the growth mechanism of the phases formed in the early stages of nickel oxide deposition on Ag(001). X-ray photoelectron diffraction (XPD) and LEED were used for the structural characterization of the nickel oxide films. An analysis of the LEED intensities (using the tensor LEED

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method) was carried out to determine the crystallographic structure of the (2×1) precursor phase. The effect of substrate temperature and O₂ pressure on the composition and structure of the NiO layers was investigated with the aim of understanding the driving force leading to the formation of the precursor (2×1) phase.

2. Experimental Details

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure in the low 10^{-10} mbar range. The chamber was equipped with an ion gun, X-ray source, hemispherical electron/ion energy analyzer, LEED optics, and quadrupole mass spectrometer. Nonmonochromatized Al Ka radiation was used for XPS and XPD measurements. The angle between the analyzer axis and the X-ray source was 55°, and the semicone angle of acceptance of the analyzer was 4°. The XPS spectra were measured with a fixed pass energy of 44 eV. The binding energy (BE) scale was calibrated setting the Ag3d_{5/2} peak to 368.3 eV.¹³ The inelastic background in the spectra was subtracted by means of the Shirley method.¹⁴ For LEIS we used a He ion beam with an energy of 1 keV impinging on the surface at an angle of 45°, along the [100] direction. The scattering angle was 135°. The sample was mounted on a manipulator which permits polar rotation (around the manipulator axis) and azimuthal rotation (around the normal to the sample surface). The XPD curves were acquired by monitoring the intensity of the Ni2p_{3/2} and Ag3d_{5/2} peaks as a function of the polar emission angle in nonequivalent azimuthal directions. The background was estimated by measuring simultaneously the intensity at a given peak maximum and the intensity at kinetic energies 5-10 eV higher than the peak.

The LEED measurements were performed by means of threegrid rear view LEED optics. The intensities versus accelerating voltage (I-V) curves of the diffracted beams were collected by means of a video LEED system. The LEED I-V curves were measured at normal incidence of the electron beam in the energy range of 30–250 eV. The I-V curves of symmetric beams were averaged to compensate for minor differences due to small deviations from normal incidence. The I-V curves were background subtracted and normalized to constant incident electron current. The LEED intensities were collected at room temperature.

The sample was a disk with a diameter of ca. 10 mm cut and polished along the (001) surface with an accuracy of $\pm 0.1^{\circ}$. The temperature was measured by means of a chromel-alumel thermocouple placed near the sample. The surface was prepared by cycles of argon ion sputtering (600 eV) and annealing (700 K for 30 min) until no contamination was detectable by means of XPS and LEIS and a sharp (1 \times 1) LEED was visible.

Nickel (99.999% purity) was evaporated using an electron beam evaporator at O₂ pressures in the $10^{-7}-10^{-6}$ mbar range. For the evaporation rate calibration, Ni was evaporated under conditions leading to the formation of a NiO(001) film. The thickness of the layer was determined (assuming a film of uniform thickness which completely covers the substrate surface) from the Ni 2p and Ag 3d XPS peak areas.¹⁴ The attenuation lengths of Ni2p and Ag 3d photoelectrons in nickel oxide and in silver needed for the thickness calculation were calculated using the Tanuma, Powell, and Penn method.¹⁵ The signals from NiO(001) and Ag(001) crystals of semi-infinite thickness were evaluated using the Ni2p and Ag3d photoionization cross sections reported in ref 16 taking into account the effect of the analyzer transmission function on the intensity (assumed to be proportional to $1/E_{\text{Kin}}$ where E_{Kin} is the kinetic energy of the



Figure 1. Ni2p XPS spectra measured for increasing amounts of nickel oxide deposited on Ag(001). The films were prepared by evaporating Ni in an oxygen atmosphere (pO₂ 3×10^{-6} mbar) with the sample held at 373 K. For comparison the spectrum measured for 1 ML of Ni deposited in vacuum is shown. For the NiO coverage of 0.8 ML, a (2 × 1) LEED pattern is observed. The intensity of each spectrum is normalized to its maximum, and an offset has been added for a better reading.

photoelectrons). Essentially the same thickness was obtained using the Ag3d intensity measured for the clean Ag(001) surface and the Ni2p intensity measured for a NiO film thick enough that the Ag3d signal was barely visible. The thickness of the film is expressed in ML, considering that 1 ML of NiO(001) has a thickness of 2.1 Å. For a pseudomorphic NiO(001) film this corresponds to a density of 0.12 Ni atoms/ Å². The evaporation rate, estimated on the basis of the XPS data, was of the order of 0.1 ML of NiO per min. With such an evaporation rate the flux of oxygen molecules arriving at the surface is much larger than the flux of nickel atoms, the former being nearly 2 orders of magnitude higher than the latter at the lowest oxygen pressure.

3. Results

3.1. XPS and LEIS Results. The XPS spectra measured for increasing amounts of NiO deposited are shown in Figure 1. The spectra shown in the figure are for NiO films prepared by evaporating nickel at an oxygen pressure of 3×10^{-6} mbar on the substrate held at 373 K. Similar results were obtained with the same oxygen pressure but the sample at room temperature and with an oxygen pressure 5×10^{-7} mbar and the sample held at 373 K. Under these conditions, in the early steps of growth, a (2×1) LEED is observed. Significant changes in the Ni2p peak shape and position are observed between 1 and 2 ML of NiO. In this range of coverages the transformation from a (2×1) to a (1×1) LEED pattern is observed.⁴ For NiO coverages below 1 ML (when the (2×1) LEED pattern is observed), the Ni2 $p_{3/2}$ peak is located at a BE of 853.4 eV. The Ni2p_{3/2} BE is intermediate between the values measured for NiO and metallic Ni. The satellite features at 6-7 eV higher BEs with respect to the main Ni2p_{3/2} and Ni2p_{1/2} peaks



Figure 2. O1s XPS spectra measured for amounts of NiO corresponding to the Ni2p spectra shown in Figure 1. The spectrum of the O1s region for the clean Ag(001) surface is reported to show the presence of the Ag $2p_{1/2}$ peak (BE of 603 eV) excited by the K β radiation of the Al X-ray source. The intensity of each spectrum is normalized to its maximum, and an offset has been added. The spectrum of the clean surface has been normalized to the maximum of the O1s spectrum measured for 0.8 ML of NiO.

characteristic of thick NiO layers are barely visible in the XPS spectrum of the (2×1) phase. These features are interpreted as the unscreened 2p hole of the Ni²⁺ ion in NiO.¹⁷⁻¹⁹ The lack of the satellites indicates that the screening of the Ni2p core hole for the (2×1) oxidic phase is more efficient than for the thicker NiO(001). This effect can be due to the different electronic structures of the (2×1) and the NiO(001) films or (more likely) to the valence electrons of the substrate which efficiently screen the Ni2p hole for nickel oxide films of submonolayer thickness. When the Ni is evaporated with an O_2 pressure of 5 × 10⁻⁷ mbar and the sample held at 373 K, after deposition of 0.1-0.2 ML of NiO, the Ni2p_{3/2} BE is lower than that measured for the (2×1) phase and basically coincident with the BE of metallic nickel. Upon increasing the NiO coverages, a Ni2p XPS spectrum characteristic of the (2×1) phase is obtained.

In the spectra measured for NiO films with a thickness above 2 ML, the Ni2p_{3/2} BE is 854.8 eV. This BE is in agreement with the Ni2p3/2 BE values reported in the literature for NiO.^{13,18,20} After 2 ML, only minor changes of the Ni2p peak shape are observed. The most relevant one is the appearance (for thicknesses larger than 4-5 ML) of a shoulder on the high-BE side of the main Ni2p_{3/2} line. This feature, which is interpreted in terms of nonlocal screening of the 2p hole in NiO, is highly sensitive to the long range structure of the film.^{18,19} The corresponding O1s spectra are shown in Figure 2. For the (2×1) phase and the 2 ML NiO film, the O1s BE is 529.7 eV and shifts to 530.2 eV for the thickest NiO film. The O1s peak at low NiO coverages presents a tail on the high-BE side, whereas it is symmetric for the thickest film. Such a tail is due mainly to the Ag $2p_{1/2}$ peak (BE of 603 eV) excited by the K β radiation of the Al X-ray source as we can see from the spectrum of the O1s region measured for the clean surface (see Figure 2). However, the presence of a minor contribution to the O1s peak from hydroxyl contamination (which would fall in this BE region¹³), coming from water dissociation on the NiO film, cannot be ruled out.

The stoichiometry of the deposited films was estimated using the ratio of the O1s and Ni2p peak areas measured for the thickest NiO layer (ca. 20 ML) grown on Ag(001). In order to reduce as much as possible diffraction effects which may affect O1s and Ni2p intensities in a different way, the XPS spectra were measured at a polar angle of 10° and an azimuthal angle of 22°. This emission angle is off the closed-packed directions of Ag(001) and NiO(001) along which intensity enhancement due to forward scattering of photoelectron occurs.²¹ The O1s/ Ni2p peak area ratio was corrected to take into account the different depth probed by the O1s and Ni2p photoelectrons using the following equation:

$$\frac{I_{\rm O}}{I_{\rm Ni}} = \left(\frac{I_{\rm O}}{I_{\rm Ni}}\right)_{\infty} \frac{\left[1 - \exp\left(-\frac{d}{\lambda_{\rm O}}\right)\right]}{\left[1 - \exp\left(-\frac{d}{\lambda_{\rm Ni}}\right)\right]}$$

where I_0/I_{Ni} and $(I_0/I_{Ni})_{\infty}$ are the O1s and Ni2p peak area ratios for a NiO film with thickness *d* and a film with a thickness much larger than the attenuation lengths, respectively. λ_0 and λ_{Ni} are the attenuation lengths of the O1s (17 Å) and Ni2p (13 Å) photoelectrons in NiO calculated using the Tanuma, Powell, and Penn method.¹⁵

The analysis of the XPS intensity shows that the O/Ni atomic ratio for the (2×1) phase is the same as that obtained for thicker NiO films, within an uncertainty of $\pm 10\%$ due to the difficulties in determining the O1s peak intensity at low coverage and residual diffraction effects. The NiO films were studied also by means of LEIS in order shed light onto the growth mode of the oxide layer. Since LEIS is virtually sensitive to the composition of the topmost layer only, the plot of the substrate LEIS signal versus the film coverage provides direct information about the mechanism of growth of the layer.^{22,23} The Ag LEIS signal as a function of the amount of deposited NiO is shown in Figure 3. The Ag LEIS signal is proportional to the fraction of substrate surface not covered by the NiO oxide layer. In the early stages of growth, the linear decrease of the Ag LEIS signal with NiO coverage indicates the formation of a layer of uniform thickness. Extrapolating the linear decrease, we see that the Ag LEIS signal goes to 0 at a coverage close to 1 ML. Hence, the phase formed in the initial stages is a 2-dimensional phase, with monolayer thickness. The substrate surface is completely covered by NiO for coverages above 2 ML. These results are in agreement with previous findings indicating that the Ag(001)surface is entirely covered for NiO coverages higher than 2 ML which corresponds to the onset of a layer-by-layer growth.^{3,4} A similar behavior of the substrate LEIS signal versus the NiO coverages is observed for O₂ pressures and sample temperatures for which the (2×1) phase can be observed (see Figure 3).

The Ag LEIS signal versus NiO coverage curves can be correlated with the changes observed by LEED and XPS. The initial linear decrease of the Ag LEIS signal corresponds to the growth of the (2×1) phase which forms 2-D islands. The extraspots of this structure reach the maximum intensity in the range of coverages at which the deviation from linearity sets in. Upon increasing the film thickness, the reflexes of the (2×1) phase disappear and a sharp (1×1) LEED pattern is observed.⁴ The deviation from linearity of the Ag LEIS signal versus NiO



Figure 3. LEIS signal of the substrate as a function of the NiO coverage (in monolayers). The thickness was estimated on the basis of the XPS data (see text). The LEIS intensity is normalized to the value of the clean surface. The solid line corresponds to the decrease of the Ag LEIS signal with NiO coverage expected for the growth of islands of monolayer thickness which spread on the surface. Under the conditions of temperature and oxygen pressure reported here a (2×1) LEED pattern is observed for submonolayer coverages of NiO.

coverage above 0.7-0.8 ML corresponds to the growth of NiO(001)(1 × 1) islands, probably in the form of bilayers. This interpretation is confirmed by the LEED results.⁴

The XPS and LEIS results obtained evaporating Ni with the O₂ pressures reported above but with the sample at 453 K are presented in Figures 4 and 5. When the NiO is deposited at 453 K, the XPS spectra show that metallic Ni is the main component when nominal submonolayers of NiO are deposited. The Ni2p XPS spectrum obtained after deposition of 0.7 ML of NiO with an oxygen pressure of 5×10^{-7} mbar of oxygen is shown in Figure 4, bottom curve. The Ni2p peak shape is similar to that observed for the (2×1) phase. However, the Ni2p_{3/2} BE (852.8 eV) is closer to that of metallic nickel and the features characteristic of NiO are present in the spectrum shown in Figure 4. Upon further deposition of NiO, the NiO oxide components are more evident and those of metallic Ni appear as a shoulder (Figure 4, top curve). These results clearly indicate that on the surface both metallic nickel and nickel oxide are present when NiO is deposited at 453 K. Indeed, a rather good fit of the Ni2p peak can be obtained by mixing the spectrum measured for metallic nickel deposited on Ag(001) with that measured for a nickel oxide film 2 ML thick. The fitting procedure allowed us to estimate the relative amount of metallic and oxidized Ni. The results of the fitting indicate that after a nominal deposition of 0.7 ML of NiO, on the surface there is 60% of metallic Ni, the remaining fraction being nickel oxide. Upon deposition of 1.5 ML, nickel oxide is the prevalent component (60%). When higher nominal amounts of NiO are deposited, only the NiO components are detectable in the XPS spectra. The analysis of the XPS spectra obtained evaporating Ni with an O₂ pressure of 3×10^{-6} mbar at the same temperature leads to similar results. The only difference is that, with the same nominal amount of NiO, a larger fraction of nickel oxide is present on the surface. For the NiO films prepared under these conditions, a (1×1) LEED pattern was observed.

The Ag LEIS signal versus NiO coverage curves measured for NiO films deposited with the sample at 453 K are shown in Figure 5. The Ag LEIS signals decrease much slower with NiO



Figure 4. Ni2p XPS spectra measured for NiO films deposited by evaporation of nickel with an oxygen pressure of 5×10^{-7} mbar and the sample held at 453 K. The NiO coverage is nominal, estimated from the evaporation rate and the deposition time. For each spectrum (dots), the best-fit curve (solid line) obtained by mixing the spectrum measured for one monolayer of nickel deposited in vacuum (dotted line) with that measured for a NiO oxide film 2 ML thick (dashed line) is shown.



Figure 5. LEIS signal of the substrate as a function of the nominal NiO coverage for nickel evaporation on the Ag(001) sample held at 453 K at O₂ pressures of 5×10^{-7} mbar and 3×10^{-6} mbar. The solid line represents the Ag LEIS signal expected for the growth of a monolayer of NiO.

coverage than expected for the growth of a film with monolayer thickness which gradually covers the substrate surface. This can be explained taking into account the presence on metallic Ni. The deposition of metallic Ni on the Ag(001) was studied in detail by means of LEIS.²⁴ Here we report the LEIS spectrum of the clean Ag(001) surface and that measured after evaporation in vacuum of 1 ML of nickel at room temperature. The Ag LEIS signal basically does not decrease upon deposition of 1



Figure 6. LEIS spectra measured for the clean Ag(001) surface and the surface after deposition of 1 ML of nickel in vacuum at room temperature. The magnified region (\times 10) of the Ni peak is shown.

ML of metallic Ni, and the Ni signal is barely detectable (Figure 6). This is a clear indication that already at room temperature metallic Ni is buried under silver in the subsurface region of the substrate in agreement with the results of previous studies.^{25,26} When Ni is evaporated in an oxygen atmosphere with the substrate at high temperature the incorporation of Ni in the subsurface region of the substrate is faster than the reaction with oxygen. In other words, nickel atoms have a higher probability of being incorporated in the substrate subsurface region than of being hit by oxygen molecules impinging on the surface. Hence, in the earlier stages of deposition, Ni is mainly in the metallic state covered by (at least) one layer of Ag atoms and only in part reacts with oxygen forming NiO. When the amount of Ni in the subsurface region increases the incorporation rate slows down so that Ni can be oxidized. The disappearance of the metallic component of Ni in the XPS upon increasing the evaporation time of Ni in oxygen atmosphere might be interpreted considering that buried nickel can react with oxygen and form NiO on the surface. When nickel oxide is the main species on the surface, the slow decrease of the Ag LEIS signal with NiO coverage is an indication that at this temperature NiO grows forming 3-D islands.

3.1.1. Effect of Annealing of the (2×1) Phase. Changes in the XPS and LEIS spectra are observed after annealing the (2×1) oxidic phase in vacuum at temperatures ranging from 470 to 620 K. The satellites characteristic of NiO appear in the Ni2p XPS spectrum after annealing times of the order of 10-15min at ca. 470 K (Figure 7). For longer annealing times (or higher temperatures) the Ni2p XPS spectrum gradually becomes that typical of NiO. These changes are associated with the disappearance of the (2×1) extraspots in the LEED pattern. The transformation from the (2×1) oxidic phase to NiO is complete upon annealing at 620 K for 15 min (see Figure 7, top curve). At this stage a sharp (1×1) LEED pattern is observed. It is interesting to note that the O/Ni atomic ratio determined from the XPS data does not change (within an accuracy better than 10%) during the transformation of the



Figure 7. Ni2p XPS spectra measured for the (2×1) phase prepared upon deposition of 0.8 ML of NiO (pO₂ 5 × 10⁻⁷ mbar, 373 K) (bottom curve), after annealing the (2×1) phase to 520 K for 30 min (middle curve) and after a further 15 min of annealing at 620 K (top curve). An offset has been added to the intensities of the spectra.



Figure 8. LEIS spectra measured for the clean surface (solid line), for the as-prepared (2×1) phase (dashed line), and after annealing at 620 K for 15 min (small circles). The intensities are normalized to the maximum of the clean surface.

 (2×1) layer into NiO. This is a further evidence that the stoichiometry of the (2×1) oxidic phase is NiO.

The LEIS spectra reveal an increase of the fraction of substrate surface not covered by the oxide upon annealing. The fraction of free substrate surface which is 0.25 when only the (2×1) phase is present increases to 0.62 upon annealing at 620 K for 15 min when NiO forms (Figure 8). This result can be explained taking into account the formation of NiO islands with a thickness of two layers. This interpretation is consistent



Figure 9. Ni $2p_{3/2}$ polar XPD curves measured for the as-prepared (2×1) phase, after annealing at 520 K for 30 min and for a NiO film 20 ML thick. The polar angle is measured with respect to the normal to the surface. For each curve the maximum of the modulation amplitude (defined as $((I_{max} - I_{min})/I_{max})\%$, where I_{max} and I_{min} are the maximum and minimum of the highest peak, respectively) is reported. A schematic model of the NiO(001) structure along the [100] and [110] azimuthal direction is shown with Ni-scatterer directions corresponding to the observed forward scattering peaks. Small circles are nickel atoms, large circles are oxygen atoms.

with the results of the STM study reported in refs 10 and 11. Because the determination by STM of the NiO island's height with respect to the substrate surface is influenced by electronic effects, the formation of double-layer NiO(001) islands was inferred from the halving of the surface area covered by the oxide film upon annealing of the (2×1) phase.^{10,11}

3.2. XPD Results. The polar Ni2p_{3/2} XPD curves measured for the (2×1) phase along the [100] and [110] azimuth are shown in Figure 9. These curves do not show any significant intensity modulation as a function of the polar angle besides the increase of intensity toward higher polar angles characteristic of a phase with a thickness much lower than the photoelectron attenuation length.²⁷ Since the most intense intensity modulations in the XPD curves correspond, for photoelectrons having relatively high kinetic energies, to forward scattering along emitter—scatterer directions, the nearly featureless XPD curves indicate that the (2×1) phase has a monatomic thickness.²¹

Intensity modulations versus polar angle appear upon annealing the (2×1) phase (Figure 9). Besides the peak along the normal to the surface, the main features are located at $\theta =$ 45° in the [100] azimuth and $\theta = 35^{\circ}$ and 55° (considering the centroid of the broad peak at the highest polar angle) in the [110] azimuth. The XPD curves acquired after annealing the (2×1) phase are very similar to those measured for a thick (20 ML) NiO(001) film with changes in the relative intensities of the main features due to the different thicknesses of the films. The XPD curves for the thick NiO film are in good agreement with those reported in the literature for NiO(001) single crystals and thick NiO(001) film epitaxially grown on Ag(001).^{28,29} Since the forward scattering peaks are quite broad, the small shift of these peaks upon increasing the film thickness found with other experimental techniques is not detectable in the present case.^{5,8} The presence of the peak at $\theta = 35^{\circ}$ in the [110] azimuth shows that there is a fraction of NiO islands with a thickness of three layers. The XPD data are consistent with the present LEIS results and with the previous STM studies of the annealing of the (2×1) phase.^{10,11}

3.3. LEED Intensity Analysis. The XPD analysis of the (2×1) film tells us that the precursor phase has a monatomic

thickness, but the absence of significant intensity modulations (at least in the range of polar angles accessible in our experiment setup) prevents a further analysis involving the simulation of the experimental data on the basis of structural models. Hence, we carried out a LEED intensity analysis of the (2×1) phase which is a more suitable method for the structural determination of two-dimensional systems. The fraction order spots of the (2×1) phase are rather weak and have a measurable intensity above the background (at least at room temperature) only in a limited energy range. Moreover, as has been shown above, before the (2×1) oxidic film covers the whole substrate surface islands of NiO start to form. This prevents the use of integral order spots in the analysis since they receive contributions from the clean Ag(001) surface and from the NiO(001) (for coverage around 1 ML).⁴ For these reasons a reduced data set had to be used in the analysis. Therefore, the LEED intensity analysis allows us only to rule out possible models for the (2×1) structure and to determine the main features of the structural model.

The intensity analysis was performed by means of the tensor LEED (TLEED) method. The TLEED method consists of a first step in which a full dynamical calculation is performed for a chosen reference structure to produce the elements of the tensor. With this tensor, the I-V curves for various values of the structural parameters in the neighborhood of the reference structure can be quickly calculated, using a perturbation method.³⁰ The TLEED calculations were performed by means of the Barbieri-Van Hove symmetrized automated tensor LEED package (SATLEED).³¹ The Barbieri-Van Hove program package was used for the calculation of the phase shifts.³¹ Ten phase shifts $(l_{\text{max}} = 9)$ were used in the LEED calculations. The phase shifts for silver and NiO were calculated from the muffin-tin potentials of Ag and NiO. The LEED calculations were performed between 30 and 300 eV. The imaginary part of inner potential was set to 5 eV, whereas the real part was set to 10 eV and optimized in the search procedure. The Debye temperatures were set to 215, 300, and 500 K for Ag, Ni, and O, respectively. These parameters are the same as those used in a previous LEED analysis of a NiO(001) film 2 ML thick deposited on Ag(001).⁴ In the automated search of the structural parameters giving the best agreement with the experimental I-Vcurves, three nonequivalent beams were used for a total energy range of 390 eV. The Pendry reliability factor (R_p) was used in the analysis to judge the agreement between the experimental and calculated I-V curves.³²

First of all we performed the TLEED calculations for the model proposed by Bertrams and Neddermeyer on the basis of the STM results.¹⁰ In this model there are rows of Ni atoms occupying on-top and bridge positions on the Ag(001) surface, whereas O atoms occupy the quasi-3-fold sites on the nickel layer (Figure 10, model A). In the calculations we also considered the same model but with a different registry, namely, with the Ni atoms in 4-fold hollow sites and in bridge sites (Figure 10, model B). These models were used as reference structures and the coordinates of the atoms optimized in the TLEED analysis in order to get the best fit with the experimental I-V curves. The I-V curves calculated for both these models give a very poor agreement with the experimental data, as shown by the visual comparison and the R_p values of 0.7 and 0.5 for model A and model B, respectively. We tested a different structural model with Ni atoms occupying 4-fold hollow and bridge sites and oxygen atoms sitting in bridge sites over the Ni layer (model C). The I-V curves calculated for this structure also gave a high R factor. The best agreement with the



Figure 10. Top view of the schematic models for the reference structures used in the TLEED analysis. Light gray circles: Ag atoms. Gray circles: Ni Atoms. Dark circles: O atoms. For the structure shown in D, the cross section along the a-a' direction is shown in Figure 11. See text for details.

experimental I-V curves is obtained for a model having the same structure of the nickel atoms in models and B and C but a different geometry of the oxygen atoms (Figure 10, model D). This structure is similar to that of NiO(111) although the atoms are displaced from the arrangement in NiO(111) to produce the (2×1) periodicity. Moreover, the NiO(111) structure consists of alternating layers of nickel and oxygen atoms (NiO(111) is a polar surface), whereas here Ni and O atoms are almost coplanar. After optimization of the structural parameters a minimum R_p of 0.35 was obtained. The coordinates of the atoms for the best-fit structure are reported in Figure 11 with the comparison of the experimental and calculated I-Vcurves. The error bars on the derived structural parameters (± 0.1 Å for the interlayer spacings and ± 0.2 Å for the in-plane coordinates) are rather large because of the limited data set. It is assumed that a structural model is correct and the structural parameters reliable when R_p values around 0.3 (or below) are obtained. Hence, the model proposed here can be considered essentially correct although some of the structural parameters may not be fully optimized. The relatively low intensity of the diffraction spots of the (2×1) phase (which makes the I-Vmore sensitive to the background subtraction procedure) could be responsible for the moderate level of agreement between the experimental and calculated data.

4. Discussion and Conclusions

Despite the good structural matching with the substrate, the evaporation of nickel in an oxygen atmosphere does not lead to the formation of NiO(001) for submonolayer coverages. Instead, in a wide range of conditions, a two-dimensional oxidic phase with a (2×1) periodicity grows on the surface up to a coverage close to 1 ML. It is interesting to compare this behavior with the growth mechanism on Ag(001) of other oxides having the same structure as NiO (rocksalt structure, lattice parameter: 4.18 Å) and similar lattice parameters, such as MgO (4.21 Å) and CoO (4.26 Å). For MgO, pseudomorphic islands of MgO(001) are present since the earlier stages of deposition.^{3,33–35} MgO(001) deposited on Ag(001) forms islands one atomic layer thick below 1 ML and grows with a nearly layer-by-layer mode.3,35 On the contrary, a monolayer of NiO(001) on Ag(001) seems to be unstable and tends to form islands with a thickness of two (or more) layers as indicated by the results concerning the deposition at higher temperature and



Figure 11. Top part: Comparison of the experimental and calculated I-V curves for model D shown in Figure 10. For each beam the value of R_p is reported. Bottom part: cross section along the a-a' direction indicated in Figure 10D. The structural parameters corresponding to the optimized models are reported. Large circles: Ag atoms. Gray circles: Ni atoms. Dark circles: O atoms.

the thermal treatment of the (2×1) phase. The different behavior cannot be explained in terms of surface and interface energies. The surface energies of MgO(001) (1.16 J/m²)³⁶ and NiO (1.23 J/m²)³⁷ are very close (and close to that of Ag(001), 1.25 J/m²).³⁸ The ab initio calculations reported in ref 9 indicate that the interface energy is comparable for one monolayer of MgO(001) and NiO(001) on Ag(001). Since the pseudomorphic MgO film is more strained than NiO, the higher cost in energy for increasing the thickness of the pseudomorphic film may stabilize the monolayer of MgO(001)(1 × 1).

The situation for cobalt oxide on Ag(001) is less clear, and a detailed study concerning the growth mechanism is missing. However, for submonolayers of CoO, STM studies have shown that a CoO precursor phase and CoO(001) islands grow depending on the substrate temperature during deposition and subsequent annealing.^{11,39} In a more recent study by STM, a hexagonal lattice was observed for the CoO precursor phase by STM.⁴⁰ This precursor phase of CoO may be equivalent to the (2 × 1) structure of NiO on Ag(001).

The model for the (2×1) phase proposed on the basis of the LEED analysis consists of a nickel layer and an oxygen layer with a distorted hexagonal structure. Besides the distortion of the hexagonal unit cell and the buckling of the Ni and the O layer, this structure is similar to that of NiO(111). With alternating layers of Ni²⁺ and O²⁻ the (111) surface is not a stable termination of NiO, and indeed the NiO(111) surface is reconstructed.⁴¹ The electrostatic interaction of the oxide film with metal substrate may stabilize this structure of the (2 × 1) phase. However, this structure is metastable as indicated by the transformation of the (2 × 1) phase into NiO(001) upon heating at temperatures ranging from 400 to 500 K.

Two important aspects are relevant in order to understand the reactive deposition of NiO on Ag(001): the low sticking probability of O_2 on Ag(001) and the high mobility of Ag atoms. The sticking probability of O_2 on Ag(001) is very low at room temperature, and relatively high pressures are needed to form chemisorbed oxygen phases on this surface.⁴² Thus, nickel atoms evaporated in an oxygen atmosphere (at the pressures used in this work) land basically on a clean substrate surface. This implies that the oxidation process takes place among Ni atoms that are adsorbed and O_2 molecules that arrive at them from the gas phase instead of being a reaction between Ni and O atoms adsorbed on the substrate surface. The mobility of Ag atoms is relatively high (even at room temperature)⁴³ so that nickel atoms are readily buried by Ag atoms as shown by the LEIS data (see Figure 6). The driving force for such a process is the much lower surface energy of Ag compared to Ni.³⁸ Since nickel and silver do not form solid solutions, Ni atoms are expected to be present as clusters embedded in the subsurface region. Indeed, STM images of Ni evaporated on Ag(001) show the formation of clusters.^{10,24} Small clusters of nickel atoms on Ag(001) can either adsorb dissociatively O_2 molecules arriving from the gas phase to form NiO or they can be covered by Ag atoms. For a given evaporation rate of nickel atoms, depending on the O₂ pressure and the sample temperature, the speed of one of the processes described above is higher than the other. The XPS and LEIS data reported here show that between room temperature and ca. 400 K with O_2 pressures in the $10^{-7}-10^{-6}$ mbar range, the formation of nickel oxide is faster than the diffusion of Ag atoms onto Ni clusters. At higher temperatures (ca. 450 K) the diffusion rate of Ag onto nickel clusters is higher than the reaction of Ni with oxygen, and the formation of metallic Ni is observed. Buried metallic Ni can react slowly with oxygen to produce NiO during deposition. In the former case a 2-D oxidic phase with a (2×1) periodicity grows in the earlier stages, whereas in the latter case, in addition to metallic Ni, 3-D islands of NiO(001) are present on the surface. The (2×1) phase can be considered as the product under kinetic control of the growth of nickel oxide on Ag(001). In other words, pseudomorphic NiO(001) would be the stable structure of the oxide film but the (2×1) layer forms faster in the earlier stages of deposition. At higher temperatures the formation of NiO(001) (i.e., the product under thermodynamic control) should occur: Indeed, this is what we observed depositing NiO at 453 K. However, because of the competing diffusion of Ag atoms over the Ni islands, with the limited maximum oxygen pressure we could use in our experimental setup, in addition to NiO metallic Ni is also present in the surface region.

The substrate may play an important role in determining a faster rate of nucleation and growth of the (2×1) phase compared to NiO(001). Indeed, the STM results reported in the literature show that a substantial rearrangement of the step structure of the substrate takes place when the (2×1) phase is transformed into NiO(001) upon annealing.¹¹ A study by STM aimed at investigating in detail this point of the NiO/Ag(001) system is in progress.²⁴

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