Growth and thermal behaviour of NiO nanolayers on Pd(100)

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Abstract

The growth of ultrathin nickel oxide overlayers (nanolayers) on Pd(100) from submonolayer coverages up to 20 monolayer thick films has been investigated by scanning tunneling microscopy (STM), in conjunction with LEED and high-resolution electron energy loss spectroscopy (HREELS). The first nickel oxide monolayer on Pd(100) forms a wetting layer with a c(4 × 2) structure, which has been interpreted in terms of an interface stabilised Ni3O4-type structure. Stoichiometric NiO grows on top of the c(4 × 2) monolayer in a strained lattice with the (100) surface orientation parallel to the substrate. The lattice relaxation of the NiO phase occurs gradually and is completed after ≈10 monolayers, where a bulk-type NiO phase is obtained. The phonon spectra of the c(4 × 2) monolayer and the subsequent NiO layers, as measured by HREELS, are characteristic and of diagnostic value to identify the different oxide phases. The morphology of the nickel oxide nanolayers has been analysed by quantitative evaluation of the STM images in terms of their roughness parameters. The roughness of nickel oxide nanolayers prepared by different kinetic routes has been compared and the optimal preparation conditions for obtaining smooth morphologies are proposed.

Keywords: Epitaxial thin films; Growth; Oxide nanolayer; Nickel oxides; Palladium (100); Scanning tunneling microscopy (STM); High-resolution electron energy loss spectroscopy (HREELS); Phonon

1. Introduction

Thin films of transition metal monoxides such as MnO, CoO, or NiO are attracting increasing attention because of their possible application in modern magnetoelectronic systems, for example in spin transistors, spin valves or spin-dependent tunneling devices [1]. The oxides are used as tunneling barriers in spin-dependent transport systems [2–5], and the magnetic properties of the interfaces between the dielectric oxide layer and
the ferromagnetic electrode materials on both sides of the oxide barrier are crucial for the magnetic tunneling resistance effect, which is a promising process for sensing the magnetisation orientation in both electrodes. There is also interest in the catalytic chemistry of transition metal monoxide surfaces, which are present as catalysts in a large variety of commercially applied processes for the conversion of hydrocarbons [6]. For example, NiO is chemically active as a component in many oxidation catalysts and is able to promote the methanation reaction of CO and the dissociation of N₂O [6–8]. The magnetic properties of NiO are another interesting aspect of this compound, which make it an attractive material for its implementation in high-density magnetic storage technologies. The latter application of thin layers of oxides, viz. in complex nanometric device structures, requires high quality ultrathin films of the materials of thicknesses of only a few nanometers (such films are commonly designated as nanolayers). This necessitates the optimisation of growth parameters and the careful characterisation and control of the physical and chemical properties of ultrathin oxide films, including the growth morphology, the roughness, and the stability of oxide nanolayers under various environments.

Here we report the growth properties, the surface structure, and the thermal stability of NiO nanolayers on a Pd(100) substrate. The Pd(100) surface as a substrate for the growth of NiO has a number of interesting features, which renders it suitable for fundamental growth studies of NiO nanolayers. It is chemically stable under the typical oxidising conditions of the NiO preparation via physical vapour deposition (PVD), is has the right symmetry for mediating the growth of non-polar NiO layers, and it has a reasonably close lattice match to the NiO lattice (7.3% lattice mismatch between Pd(100) and NiO(100)), which is necessary for the growth of epitaxial layers. Moreover, the Pd–NiO system is of fundamental interest, because Pd appears to show ferromagnetic behaviour in the proximity of NiO, as reported recently for NiO/Pd multilayer systems [9].

The growth of NiO films on Pd(100) has been investigated recently by Orzali et al. [10] using mainly low energy electron diffraction (LEED) and photoelectron spectroscopy (XPS) techniques. They reported two-dimensional growth of the first NiO monolayer and nucleation of three-dimensional islands at higher coverages. Photoelectron diffraction (XPD) results indicated the formation of a strained NiO(100) structure for very thin layers, with strain relaxation occurring gradually as a function of film thickness.

The present paper gives a full account of a detailed study of the growth and the thermal properties of NiO nanolayers on Pd(100) as viewed by scanning tunneling microscopy (STM). We report the surface structure and morphology of the NiO layers as prepared by different kinetic routes and the evolution of the film morphology under oxidising and reducing thermal treatments. Moreover, we present the phonon spectra of the NiO nanolayers during the various growth stages as measured by high-resolution electron energy loss spectroscopy (HREELS). The phonon spectra give very distinct fingerprints of the different oxide phases present at the surface and thus help identifying the oxide structures seen in STM. A couple of STM data obtained in this study have been included recently in a preliminary report [11].

At the monolayer stage of nickel oxide growth on Pd(100) a \(c(4 \times 2)\) wetting layer of an interfacial oxide is observed, onto which a (100) oriented stoichiometric NiO phase grows in a 3D island fashion. The morphology of the NiO phase depends strongly on the kinetic parameters during growth and on the post-deposition annealing conditions. The roughness of the NiO surfaces, which is an important parameter for the use of oxide nanolayers in device oriented applications, has been analysed from the STM images and is shown to depend on the film thickness and the annealing temperature. The thermal stability of NiO nanolayers is a function of the layer thickness.

2. Experimental

The experiments have been performed in two different ultrahigh vacuum (UHV) systems in Graz, custom-designed for STM and HREELS. The STM system contains a variable-temperature STM (Oxford Instruments), a LEED optics, a
CMA Auger electron spectrometer, and facilities for crystal cleaning and PVD [12]. The STM images were recorded in a constant current mode at room temperature, with electrochemically etched W tips, which have been cleaned in situ by electron bombardment. Typical tunneling conditions employed for imaging the NiO structures were ±1–1.5 V sample bias, 0.1 nA tunneling current, for overlayers up to 3 monolayers, ±2–4 V, 1–50 pA, for films 3–20 monolayers.

The HREELS measurements were performed with an ErEELS 31 spectrometer, as described in Ref. [13]. The HREELS spectra were taken at room temperature with a primary energy of 6.5 eV in a specular reflection geometry, with a typical resolution of 4–5 meV as measured at the FWHM of the elastically reflected primary peak.

Clean Pd(100) surfaces were prepared by cycles of 2 keV Ar⁺ ion sputtering, followed by a short 0.5 keV Ar⁺ bombardment, and by subsequent annealing at 750 °C. The cleanliness and order of the Pd(100) surfaces were checked by AES or HREELS in combination with LEED. LEED was also used to control the preparation of the respective oxide phases in the two different experimental chambers. Nickel oxide overlayers were prepared by two different PVD procedures: reactive evaporation of Ni metal in 2·10⁻⁶ mbar O₂ with the Pd substrate held at room temperature, and reactive evaporation under the same conditions with the substrate at 250 °C. In the latter case, the sample was cooled down to room temperature in oxygen. Typical evaporation rates were 0.5–1 MLE/min (1 monolayer equivalent (MLE) is referred to the atom density of the Pd(100) surface and corresponds to 1.3·10¹⁵ Ni atoms/cm²) as measured with a quartz microbalance. The Ni-oxide films have been subjected to various post-deposition treatments such as annealing in UHV or in oxygen atmosphere.

3. Results and their discussion

3.1. Ni-oxide growth at room temperature (RT)

Fig. 1 gives a series of STM images showing the evolution of the Ni-oxide overlayer as a function of coverage (layer thickness), thus illustrating the growth morphology. For low coverage (0.25 MLE, Fig. 1a) the Pd surface is covered randomly by small oxide islands with random shapes,
whose internal structure cannot be resolved in the STM. Their mean size is about 100 Å² and their apparent height is about 1.5 Å, which corresponds thus to one monolayer. With increasing coverage the islands grow and percolate into an irregular network with fractal-type boundary lines (0.5 MLE, Fig. 1b). On some parts of the oxide surface a weak corrugation with a c(4×2) periodicity can be resolved (see insert of image b). After deposition of 0.8 MLE Ni-oxide, small clusters appear on top of the c(4×2) structure, the latter covering the Pd surface almost entirely at this coverage (Fig. 1c). The c(4×2) layer is continuous with only a few holes in it, but the c(4×2) domains are small (of the order of 50×50 Å²) and are separated by regions of local disorder. After deposition of 1.25 MLE Ni-oxide, the second oxide layer becomes apparent in the form of small islands and elongated structures on the flat c(4×2) monolayer (Fig. 1d), and these islands grow with increasing oxide coverage into flat second layer structures (Fig. 1e for 1.75 MLE). For coverages >2 MLE 3D island growth sets in, see for example Fig. 1f after deposition of 3 MLE, where 3D oxide islands with ill-defined shapes and different height levels are recognised. The Ni-oxide overlayer becomes increasingly rougher with increasing layer thickness (see Fig. 1g for 6 MLE), and after 20 MLE deposition a rough, poorly ordered Ni-oxide film with large, randomly shaped grains has formed (Fig. 1h).

The growth pattern of Ni-oxide on Pd(100) at room temperature can thus be summarised as follows. At low coverages, random growth of monolayer islands takes place without preferential nucleation sites; the monolayer islands percolate and form a uniform wetting monolayer with a local c(4×2) periodicity. The second layer of Ni-oxide grows initially in form of flat islands, but 3D island growth sets in before the completion of the second oxide layer. Further growth is dominated by the formation of poorly ordered, randomly shaped 3D islands yielding rough film morphologies.

3.2. Annealing of RT deposited Ni-oxide layers

Post-deposition annealing of RT grown Ni-oxide nanolayers leads to significant modifications of the film morphologies and to greatly improved ordering of the overlayers. This allowed us to image the oxide structures in the STM with high resolution, so that atomic details can be revealed. The STM images of Figs. 2 and 3 illustrate the effects of annealing at 300 °C in 5×10⁻⁷ mbar O₂, the respective annealing time was 2 min each. Fig. 2(a) shows the 0.25 MLE Ni-oxide/Pd(100) surface after annealing in oxygen: the originally small Ni-oxide islands have undergone coalescence.
and the Pd surface is now covered by regular rectangular islands of the c(4 × 2) phase, with domains of p(2 × 2) chemisorbed oxygen and (\sqrt{5} \times \sqrt{5})R26.9° PdO reconstructions in between (see insert of Fig. 2a). Substantial Pd mass transport has taken place, since the morphology of the step edges has changed from fuzzy straight (Fig. 1a) to zig-zag with well-ordered straight segments. The lower step edges are decorated partly by the c(4 × 2) layer, but c(4 × 2) islands are also distributed over the terrace areas. Some dark depressions are visible in the STM image, some of which have a very large aspect ratio (see rectangle marked in the figure). They are due to vacancy islands formed by displaced Pd atoms and are aligned along the Pd(011) directions; STM indicates that the vacancies mostly contain embedded oxide islands of the c(4 × 2) structure. Statistical analysis of the oxide coverage before and after annealing demonstrates that the oxide coverage is essentially stable, less than 5% diffusion of Ni into the Pd occurs at this annealing temperature.

At 0.5 MLE the percolated Ni-oxide network has become more regular after annealing (see Figs. 2b vs. 1b) and on the annealed 0.8 MLE Ni-oxide surface (Fig. 2c) the c(4 × 2) overlayer covers large parts of the Pd surface. The vacancy islands, however, have also grown in size at this stage. A magnified part of this surface in Fig. 2(d) shows that the c(4 × 2) structure decorates the lower step edge perfectly at the atomic level, whereas at the upper step edge the c(4 × 2) covering is less complete (see Fig. 3. (a–c) STM images of 1.75 MLE Ni-oxide on Pd(100), deposited at room temperature and annealed at 300 °C in oxygen. (a) (1000 × 1000) Å²; (b) (250 × 250) Å²; (c) (26 × 26) Å². The insert of (c) shows a line scan along the [011] direction, the axis units are in Å. Panel (d) displays a LEED picture of the annealed 2.5 MLE Ni-oxide/Pd(100) surface (primary energy 100 eV). For further details see text.
arrow). The c(4 × 2) structure on a Pd(100) surface forms two equivalent domains, which can be identified in this image. The Pd step edges have an enhanced contrast in the STM (which is also apparent in Fig. 2a), but the steps cannot be atomically resolved. The vacancy island marked A on Fig. 2d allows one to distinguish the c(4 × 2) structure therein. The annealed 1.25 MLE Ni-oxide/Pd surface (Fig. 2e) is covered completely by the c(4 × 2) wetting layer, the vacancy islands have healed out. The atom-resolved image of Fig. 2f shows a perfectly ordered lattice with c(4 × 2) periodicity (primitive rhombic and c(4 × 2) unit cells are indicated) with very few defects. Note that the centred c(4 × 2) unit cell vectors are aligned along the (011) substrate directions.

STM images of the 1.75 MLE Ni-oxide/Pd(100) surface annealed at 300 °C in 5 × 10⁻⁷ mbar O₂ are displayed in Fig. 3. As compared to the RT deposited Ni-oxide surface (Fig. 1e), the surface is smoother after annealing and the oxide islands have rounded-off boundaries. The higher resolution image 3(b) shows part of a larger oxide island structure surrounded by the well-ordered c(4 × 2) monolayer: it appears that the Ni-oxide island is grown on top of the c(4 × 2) layer. The image also indicates that the oxide islands at this coverage consist actually of second and third layer regions (marked 2nd and 3rd in the image). The high resolution STM image from a second layer area in Fig. 3c displays a square lattice with a unit cell of 2.90 ± 0.05 Å, oriented parallel to the (110) Pd(100) directions; the corrugation in STM of the second layer is very small, ≤0.04 Å, as indicated by the line scan in the insert of Fig. 3c. The square unit cell suggests that the second layer oxide consists of stoichiometric NiO, oriented with the (100) plane parallel to the (001) substrate and rotationally aligned with it. The measured lattice constant of 2.9 Å gives evidence that the NiO lattice of the second layer is neither strictly pseudomorphic to Pd(100) nor in its bulk form, but that it is strained due to the interaction with the substrate (it is pointed out, however, that the c(4 × 2) monolayer is commensurate with the Pd(100) surface). Fig. 3d shows a LEED picture of a ~2.5 MLE annealed NiO/Pd(100) surface, which has a similar morphology with a comparable STM fingerprint as the 1.75 MLE surface displayed in Fig. 3(a)–(c). Sharp c(4 × 2) reflections are visible together with the Pd(100)1 × 1, p(2 × 2)-O, and the NiO (100) spots (marked in the figure). This sharp LEED pattern is indicative of the good long range order of the coexisting phases at this stage of the growth process.

The boundaries between the second layer and the third layer regions of the oxide islands often do not appear with a sharp contrast in the STM images as expected for monoatomic steps, but show a gradually changing contrast (see dashed arrows in Fig. 3b). This is suggestive of small angle mosaic defect structures on the island surfaces, which may be the result of a strain relieving process [14]. The strain release and the orientation of mosaic defects of NiO on Pd(100) as a function of film thickness has been investigated in detail with high resolution spot profile analysis LEED (SPA-LEED) and will be the subject of a forthcoming publication [15].

Fig. 4 compares STM images of Pd(100) covered with 3 MLE and 6 MLE NiO, after deposition at RT and annealing in 5 × 10⁻⁷ mbar oxygen at various temperatures. As compared to the RT deposited 3 MLE surface (Fig. 4a) annealing to 300 °C leads to a contraction of the oxide overlayer with the formation of flat terraces on different height levels and large holes in between (Fig. 4b). Higher magnification STM images (not shown here) reveal that the bottom of the holes reaches down to the c(4 × 2) structure on the Pd surface. Further annealing to 400 °C leads to the partial decomposition of the NiO layer and major parts of the surface expose the Pd surface as recognised by the appearance of small dark vacancy islands (Fig. 4c). The remaining Ni-oxide is left in smaller islands, the Pd surface is covered by various chemisorption phases of oxygen, and the Ni atoms after oxide decomposition have presumably diffused into the Pd bulk. Annealing of the 6 MLE NiO/Pd(100) to 400 °C also reduces the roughness of the overlayer and forms a rather flat surface (cf. Fig. 4d and e). On the resulting flat NiO overlayer a characteristic pattern is recognised in the STM contrast of image Fig. 4e, which is due to a Moiré pattern. This Moiré pattern is interpreted in terms of the formation of an ordered...
dislocation network across the NiO layer as a strain relieving process, as discussed elsewhere [15]. The annealing temperature of 550 °C marks the onset of decomposition of the 6 MLE NiO layer: Fig. 4f shows a part of the surface of the latter, where several rectangular Pd ad-islands are visible amidst the NiO phase. The Pd ad-islands are covered by p(2×2) and (5×5) chemisorption phases of oxygen as recognised in the insert of Fig. 4f.

Fig. 5 shows the effects of annealing in UHV of 6 MLE and 20 MLE NiO layers, by comparing STM images of the RT deposited surfaces (Fig. 5a and d) with those of the annealed surfaces. Annealing to 400–450 °C leads generally to smoother surfaces with flatter morphologies and larger grain sizes (Fig. 5b and e), as discussed below in the context of the roughness analysis. However, the annealing in UHV has a less positive effect on improving the structural order than annealing in oxygen (cf. Fig. 5b with Fig. 4e for the 6 MLE surface). Annealing to higher temperature induces decomposition of the oxide nanolayers, in the case of the 6 MLE layer heating to 600 °C produced rectangular areas of 2–4 mono-layer high oxide islands separated by bare Pd patches (as indicated in Fig. 5c). We note that the mass transport of Pd under UHV conditions appears to be less pronounced than under oxygen atmosphere (cf. Fig. 5c with 4f). For the 20 MLE NiO film annealing to 650 °C generated large islands with flat top surfaces and some bare Pd areas appeared in between (Fig. 5f). The LEED pattern after heat treatment at 650 °C showing the reappearance of the Pd(100)1×1 reflections confirmed the partial decomposition of the nickel oxide.

Summarising thus briefly, annealing of Ni-oxide nanolayers on Pd(100) in O2 or UHV leads both to improved structural order and smoother film morphologies with larger island sizes and flat top facet surfaces. Annealing in oxygen is, however, more effective in inducing good structural order. The onset of decomposition of the NiO sets an
upper limit to the applicable annealing temperature and is dependent on the thickness of the overlayer, commencing at $400^\circ C$ for 3 MLE films and $650^\circ C$ for 20 MLE thick films. The low thermal stability of NiO nanolayers on Pd(100) is driven by the interdiffusion and alloying tendency of Ni and Pd.

3.3. HREELS of Ni-oxide on Pd(100)

The HREELS experiments have been performed on Ni-oxide/Pd(100) surfaces annealed in oxygen ($300^\circ C$, $1 \times 10^{-6}$ mbar $O_2$), since good quality HREELS spectra require flat and well ordered surfaces. In Fig. 6 the HREELS spectra of different chemisorption phases of oxygen and surface oxide on Pd(100) are compared to a spectrum of the c(4×2) Ni-oxide monolayer. The p(2×2)-O and c(2×2)-O chemisorption phases are characterised by a single vibrational loss peak at 44 meV and 45 meV, respectively, correspond-

![Fig. 5. Comparison of STM images of 6 MLE (a–c) and 20 MLE (d–f) Ni-oxide/Pd(100) surfaces in their RT as-evaporated (a, d) and vacuum annealed states. 6 MLE: (a) as-evaporated surface ($500 \times 500$ Å$^2$); (b) annealed to $450^\circ C$ ($500 \times 500$ Å$^2$); (c) annealed to $600^\circ C$ ($750 \times 750$ Å$^2$). 20 MLE: (d) as-evaporated surface ($500 \times 500$ Å$^2$); (e) annealed to $400^\circ C$ ($500 \times 500$ Å$^2$); (f) annealed to $650^\circ C$ ($1000 \times 1000$ Å$^2$).

![Fig. 6. HREELS spectra of Pd(100) covered with p(2×2)-O and c(2×2)-O chemisorbed oxygen, (√5×√5)R26.6° PdO, and c(4×2) Ni-oxide phases. The insert shows the LEED pattern of the c(4×2) Ni-oxide surface (primary energy 100 eV).]

Fig. 6. HREELS spectra of Pd(100) covered with p(2×2)-O and c(2×2)-O chemisorbed oxygen, (√5×√5)R26.6° PdO, and c(4×2) Ni-oxide phases. The insert shows the LEED pattern of the c(4×2) Ni-oxide surface (primary energy 100 eV).
\(\sqrt{5}R26.6°\) PdO structure gives rise to two loss peaks at 43 meV and 54 meV, which have also been observed by Simmons et al. [16]. In the light of the recently proposed model of the \((\sqrt{5} × \sqrt{5})R26.6°\) structure in terms of a strained PdO (10 1) surface oxide layer [17] the two vibrations are consistent with the two inequivalent oxygen atoms in this structure. The HREELS spectrum of the well-ordered \(c(4×2)\) Ni-oxide structure (see the sharp LEED pattern in the insert of Fig. 6) displays a single sharp loss peak at 46 meV.

The observation of a single dipole allowed phonon peak (note that the HREELS experiment has been performed in specular reflection geometry) of the \(c(4×2)\) Ni-oxide phase, which is similar in frequency to those of chemisorbed oxygen, may be understood along the following lines. The surface structure of the \(c(4×2)\) layer has been determined recently in a quantitative LEED study by Agnoli et al. [18]. According to their model the \(c(4×2)\) structure consists of an almost planar, somewhat distorted NiO (100) layer with Ni vacancies in an ordered \(c(4×2)\) array, yielding an overall stoichiometry of Ni\(_3\)O\(_4\). The oxygen atoms sit on-top of Pd surface atoms and are surrounded each by three (almost coplanar) Ni atoms. We suggest that the HREELS active dipole allowed phonon mode at 46 meV is mainly due to the displacements of the oxygen atoms perpendicular to the surface. This is similar to the particular case of a single-layer vanadium surface oxide (surface-V\(_2\)O\(_3\)) on Pd(11 1), where a single loss feature has also been found in HREELS [19]. Density functional theory calculations have identified this latter loss as the only dipole allowed phonon mode of this two-dimensional oxide layer, resulting from oxygen vibrations perpendicular to the plane of the V atoms and to the surface [12]. The similarity in frequency of the \(c(4×2)\) 46 meV vibration to those of chemisorbed oxygen suggests that the shape of the overall potential of the oxygen atoms in the \(c(4×2)\) layer (i.e. on top of Pd surface atoms and surrounded by 3 Ni atoms) is similar to the one of chemisorbed oxygen atoms in the fourfold hollow sites of the Pd(100) surface.

Fig. 7 gives a collection of HREELS spectra recorded on Pd(100) as a function of Ni-oxide layer thickness, from 0.75 MLE, corresponding to the full monolayer of the \(c(4×2)\) structure (bottom curve), to 13 MLE. The spectrum of 1 MLE Ni-oxide (second curve from bottom) is dominated by the 46 meV \(c(4×2)\) phonon peak, but a weaker loss structure becomes visible at 64 meV. The latter loss grows in intensity on the 1.2 MLE surface and shifts slightly to 66 meV. At 1.8 MLE, the 66 meV peak shifts further to 68 meV and becomes the most prominent feature in the loss spectrum. No further shift with layer thickness is observed in the 68 meV structure, but the 46 meV loss looses further intensity and eventually shifts to 42 meV at the 3.5 MLE surface, before disappearing altogether for thicker Ni-oxide films. On the 3.5 MLE surface a weak shoulder at 52 meV appears first. The HREELS spectra of the thicker Ni-oxide films (\(\geq 5\) MLE) show a
strong loss feature at 68 meV and a weak shoulder at 52 meV, the loss structure at 136 meV is the double loss of the strong 68 meV loss feature.

The HREELS spectra of the Ni-oxide films \( \geq 5 \text{ MLE} \) confirm unambiguously that the oxide phase is NiO. The 68 meV loss peak is identified as the well-known Fuchs–Kliewer surface phonon of NiO, which has been observed on NiO bulk crystal surfaces by Cox and Williams at 69.5 meV [20]. This single active surface mode is related to a bulk mode involving ionic displacements normal to the (100) surface. The presence of a weak lower energy shoulder at 55 meV in addition to the Fuchs–Kliewer phonon peak has also been reported in HREELS spectra of NiO films on Ni(100) and (111) surfaces [21,22]. Although no definitive explanation of this feature has been given, it has been suggested that it could originate from low-coordinated atoms at the surface [22] or—we might add—at the boundaries of the NiO islands in the films.

The advent of the 64 meV phonon in the 1 MLE spectrum coincides with the appearance of the first second-layer oxide islands in the corresponding STM images (see Fig. 3). The 64 meV phonon is thus associated with the formation of the first NiO layer on top of the c(4 \( \times \) 2) monolayer and is likely to be due mainly to similar atom displacements perpendicular to the surface as in the Fuchs–Kliewer phonon case. The lower energy of the 64 meV phonon as compared to the 68 meV Fuchs–Kliewer phonon of NiO bulk samples can be explained by a dimensionality effect (monolayer vs. multilayer) and by the lattice strain in the monolayer film. The shift to higher energy with increasing oxide layer thickness is then due to the 2D to 3D transition of the NiO islands (plus their size increase) and to the strain relaxation in the growing NiO film. The HREELS spectra of the NiO films converge to those of NiO bulk samples for film thicknesses \( \geq 5 \text{ MLE} \), although full lattice relaxation of the NiO overlayers on Pd(100) is observed only for \( \geq 10 \text{ MLE} \) thick films [15]. These observations correlate well with the XPS Ni 2p lineshape analysis reported in a previous study of NiO growth on Pd (100) [10], which showed that the bulk-like NiO lineshape is reached at 5 MLE.

The HREELS spectra presented above provide a specific vibrational fingerprint of the c(4 \( \times \) 2) Ni-oxide monolayer phase, which may be an experimental check point for the theoretical modelling of this structure. They also confirm the NiO identity of the oxide phase growing in the second and subsequent layers on the c(4 \( \times \) 2) monolayer. The disappearance of the characteristic c(4 \( \times \) 2) phonon after deposition of \(~4 \text{ MLE NiO} \) indicates that the c(4 \( \times \) 2) “substrate” surface is fully covered at this coverage by NiO and that the NiO overlayer has become continuous.

### 3.4. Ni-oxide growth at elevated temperature

Reactive evaporation of Ni (\( \rho_{O_2} = 2 \times 10^{-6} \text{ mbar} \)) onto Pd(100) at 250 °C yields surfaces with quite different topographical features as compared to those of RT oxide deposition; this is illustrated in Fig. 8. Fig. 8a shows an STM image of the Pd(100) surface after deposition of 0.25 MLE Ni-oxide. A mixed oxide surface has been formed, consisting of rectangular islands of the c(4 \( \times \) 2) Ni-oxide structure aligned along the Pd \( h011 \) directions (marked 1) and regions of the \((p5\cdot p5)\) PdO structure (marked 2 in the figure). In addition, vacancy islands in the form of rectangular troughs with a large aspect ratio (marked with the rectangle in the image) contain the c(4 \( \times \) 2) structure embedded in the first Pd layer, and Pd ad-islands covered with oxygen (marked 3 in the figure) can be recognised as well. For an oxide coverage of 0.5 MLE (see Fig. 8b and c for a higher resolution image) the surface adopts a fascinating topography at the nanometer scale, with flat terraces on different levels, narrow troughs, ad-islands and line elements of coexisting c(4 \( \times \) 2) Ni-oxide, p(2 \( \times \) 2)-O chemisorbed oxygen, and \((\sqrt{5}\times\sqrt{5})R26.6^o\) PdO structures. Straight lines dominate the phase boundaries and the images are somewhat reminiscent of a bird's view of a modern city outline. Overall, the images give evidence of a large Pd mass transport, which takes place during the reactive evaporation conditions at elevated temperature.

After deposition of 1.8 MLE the STM image displays flat islands of the \((1\times1)\) phase of NiO(100) with rectangular or quadratic shapes.
grown on the c(4×2) monolayer surface (Fig. 8d). The island edges are aligned along the (011) substrate directions (Fig. 8e), which suggests within the epitaxial relationship that they have polar boundaries. After evaporation of 6 MLE Ni-oxide at 250 °C the surface is covered by islands with flat top facets, but the boundary lines are no longer predominantly straight, but rounded. In comparison with the surface obtained after RT deposition (Fig. 1g) the morphology after 250 °C deposition is quite different with much larger NiO islands, which are terminated by flat terraces of (100) orientation. The more quantitative aspects of morphology in terms of a roughness analysis of the deposits after the different preparation conditions will be discussed in the following section.

4. General discussion

The growth of nickel oxide on Pd(100) is characterised by a wetting monolayer phase followed by 3D island growth, it thus follows formally the Stranski–Krastanov growth pattern. However, the c(4×2) monolayer has a different chemical identity than the Ni oxide overlayer growing on top of it, and has been identified as an interface stabilised Ni$_3$O$_4$-type phase [18]. More detailed experimental aspects and ab initio DFT calculations of the electronic and energetic properties of this c(4×2) phase have been reported recently in a different publication [23]. From the viewpoint of growth the c(4×2) structure may be regarded as a precursor phase to NiO growth creating an interlayer, which provides a graded interface for the subsequent growth of cubic NiO with (100) orientation. The NiO (100) unit cells are aligned with the c(4×2) unit cells and the Pd(100) substrate, but although not strictly pseudomorphic they grow initially with a compressed lattice parameter of ~2.9 Å for the first NiO layer. Strain relaxation occurs gradually from layer to layer until the bulk lattice value of 2.95 Å is reached after 10–12 monolayers thick films [15]. These results are in agreement with a photoelectron diffraction investigation of the same system as reported previously [10]. The formation of a precursor oxide phase at the initial stages of oxide growth has also been observed by Sebastian et al. [24] for NiO and CoO on Ag (100), but the structural details of the precursor phases could not be resolved by the latter authors.

The roughness of thin oxide films is an important parameter for their use in advanced electronic device technology. We have evaluated the roughness of the NiO films grown on Pd(100) by analysing STM images that cover a total area of 5000×5000 Å$^2$. The average terrace size on the film surface may be taken as a measure of the lateral roughness parallel to the surface, whereas the vertical roughness may be defined by the root mean square roughness (Rms) as given by [25]
\[
\text{Rms} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (h(x_i) - \bar{h})^2},
\]

where \(\bar{h} = \frac{1}{n} \sum_{i=1}^{n} h(x_i)\) is the average height level; \(h(x_i)\) and \(n\) denote the relative height level and the system size, i.e., the number of probing points, respectively. To give a feeling for the Rms, consider a NiO(100) surface with a single monoatomic step (2.08 Å), which divides the surface into two terraces of equal size: the corresponding Rms is 1.04 Å.

The results of the roughness analysis are listed in Tables 1 and 2. Table 1, upper panel, contains the Rms data as a function of oxide coverage (film thickness) for reactive evaporation of nickel oxide in \(p_{O_2} = 2 \times 10^{-6} \text{ mbar}\) at room temperature. The data show clearly that the vertical roughness increases as a function of film thickness, from <1 Å at submonolayer coverages to ~4 Å on 20 MLE thick films. This confirms the qualitative impression one gets from the inspection of the STM images of Fig. 1. The lower panel of Table 1 displays the roughness values of the 20 MLE annealed surfaces. As pointed out before, annealing improves generally the morphology of the films by decreasing their roughness.

Table 2 compares the roughness values for different oxide overlayer preparation procedures. For the 6 MLE films reactive evaporation at 250 °C (recipe II) yields smoother films than at RT (recipe I), as indicated by both the lower Rms and the larger mean terrace size, but recipe I followed by annealing in \(O_2\) at 500 °C gives a similar result as recipe II. Interestingly, for low oxide coverages (0.5 MLE in Table 2, two bottom lines) recipe II, i.e., the reactive evaporation at elevated temperature, gives somewhat rougher films than recipe I. This is due to the large Pd mass transport, which takes place under the elevated temperature evaporation conditions (see Fig. 8). The Pd–oxygen phase forming under oxygen exposure at elevated temperature is the \((\sqrt{5} \times \sqrt{5})R26.9\) reconstruction, which has been ascribed to a PdO(101) trilayer [17], where a layer of Pd atoms is sandwiched between two oxygen planes. The reactive interaction with deposited Ni atoms disrupts the Pd–O structure and leads to the observed mass transport with the concomitant formation of vacancy islands and Pd ad-islands, which increases the roughness of the surface. For thicker NiO overlayers this substrate roughening becomes less important and is overwhelmed by the intrinsic roughness of the growing film.

The present analysis of the roughness of NiO films on Pd(100) thus suggests the following procedure for the fabrication of high-quality smooth NiO film surfaces: reactive evaporation at room temperature followed by annealing in oxygen to temperatures just below the onset of NiO decomposition. Alternatively, reactive evaporation at elevated temperature is also possible, but leads to substrate roughening which is significant for the case of very thin films.
5. Summary

The growth morphology of nickel oxide nanolayers on Pd(100) has been investigated by scanning tunneling microscopy complemented by LEED inspection and high-resolution electron energy loss spectroscopy to probe the phonon spectra of the oxide phases. The nickel oxide forms a wetting monolayer on Pd(100) exhibiting a c(4×2) surface structure, which has been identified recently by Agnoli et al. [18] using LEED (I–V) analysis as a Ni$_3$O$_4$ layer. It consists of a slightly buckled contracted NiO(100) layer with a c(4×2) array of Ni vacancies [18]. Stoichiometric NiO in (100) orientation grows on top of the c(4×2) monolayer in an island growth mode with a strained lattice, which is gradually relaxed in subsequent layers until the bulk lattice is reached after 10–12 monolayers. The HREELS phonon spectra of the c(4×2) structure and the subsequent NiO layers have been measured and are distinctly different, which allowed us to identify the second layer of nickel oxide on top of the c(4×2) monolayer as a strained NiO structure. The phonons of the NiO films converge to the reported Fuchs–Kliewer phonons of bulk NiO samples after about 5 monolayers film thickness. The morphology of the NiO nanolayers as a function of deposition parameters and post-deposition treatment has been analysed quantitatively from the STM images in terms of their roughness. We have used the mean square roughness to express the vertical roughness perpendicular to the surface and have introduced the mean terrace size as a measure of the lateral roughness parallel to the surface. On the basis of our analysis we propose preparation procedures to fabricate NiO overlayers with optimal smooth morphologies.

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