Strain relaxation and surface morphology of nickel oxide nanolayers

J. Schoiswohl [a], W. Zheng [a], S. Surnev [a], M.G. Ramsey [a],
G. Granozzi [b], S. Agnoli [b], F.P. Netzer [a],*

[a] *Institute of Physics, Surface and Interface Physics, Karl-Franzens University Graz, A-8010 Graz, Austria*
[b] *Dipartimento di Szienze Chimique and INFM Research Unit, Universita di Padua, I-35131 Padova, Italy*

Abstract

The surface morphology and the lattice constants of NiO overlayers in the thickness range of 1–20 monolayers (NiO nanolayers) on Pd(100) have been investigated by high-resolution spot profile low-energy electron diffraction (SPA-LEED) and scanning tunneling microscopy (STM). NiO islands grow epitaxially on Pd(100) on top of a $c(4 \times 2)$ Ni_3O_4 monolayer with a compressed strained lattice, which relaxes gradually attaining the bulk lattice constant at 10–12 monolayers. The strain relaxation is accompanied by the formation of small angle mosaic defect regions at the surface, which have been characterised quantitatively by following the behaviour of the satellites to the main Bragg diffraction rods. The analysis of the diffuse scattering intensity around the (00) diffraction spot reveals anisotropic NiO island shapes, whose orientation depends on the growth conditions. An incommensurate superlattice in LEED and STM at intermediate NiO coverages (∼2–6 monolayers) is observed and its origin is discussed.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

The epitaxial growth of oxide layers by vapour phase deposition is a preferred method for the fabrication of ordered thin films of oxides with well-defined structural and electronic properties, as required for application in diverse areas of high-level technologies, including nano-electronic devices, spintronics, nanoscale sensors or advanced heterogeneous catalysis [1–4]. Epitaxy is the ordered growth of one crystalline layer upon a pre-existing crystalline surface, and the close lattice matching of overlayer and substrate is an important parameter to support epitaxial growth. In heteroepitaxy, i.e. the growth of one type of material on a different substrate material, perfect lattice matching is rarely encountered. The resulting lattice mismatch at the interface leads to strain in the overlayer [5] and/or defects

in form of misfit dislocations to reduce this strain. Lattice strain influences the electronic structure of the material [6] and its chemical reactivity [7], whereas dislocations cause the loss of coherence of the lattice reducing the mobility of charge carriers and thus are detrimental to the electrical transport properties. In ultrathin films of a few nanometer scale dimensions (nanolayers), the dislocations at the interface may reach the surface of the film causing surface defects and particular surface morphologies such as elastic bending in the growing film. Strained lattices are in a non-equilibrium situation and tend to relax to the stable bulk lattice configuration at a critical distance from the interface. The relaxation process in turn may be accompanied by the creation of defect structures. In this paper we address the lattice relaxation in nickel oxide nanolayers on a Pd(100) substrate and the effects that the lattice relaxation has on the surface morphology of the NiO films. The NiO(100) bulk lattice and the Pd(100) substrate have a lattice misfit of 7.8%. We have used high-resolution low

---

energy electron diffraction applied to spot profile analysis (SPA-LEED) of the diffraction reflexes and their satellites to obtain insight into the defect structures and the surface morphology of the NiO films.

The overall growth behaviour of nickel oxide nanolayers on Pd(100) as studied by scanning tunneling microscopy (STM), high-resolution electron energy loss spectroscopy (HREELS), and LEED has been reported recently [8,10]. Atomically resolved STM images and LEED have revealed that a wetting monolayer forms with a $c(4 \times 2)$ structure, which has been identified by Agnoli et al. [9] in a LEED I–V study as a Ni_3O_4-type oxide phase. Second and subsequent oxide layers grow as stoichiometric NiO islands on top of the $c(4 \times 2)$ monolayer, as indicated by the phonon spectra in HREELS and the STM images. Here we report and analyse SPA-LEED experiments of the nickel oxide overlayers on Pd(100) in the thickness range from one monolayer (ML) to ~20 ML; the SPA-LEED measurements have been complemented by STM observations. The distances between integer order LEED spots have been used for the accurate determination of the lattice constant of the growing NiO layers to probe the lattice relaxation process. The anisotropy of the specular (00) reflex and the additional satellite peaks observed close to the fundamental Bragg peaks have been recorded to obtain information on the shapes and orientation of the oxide islands and on mosaic structures introduced by the strain relaxation process.

We find that the NiO overlayers on Pd(100) relax to the bulk lattice constant after 10–12 ML film thickness. The lattice relaxation process leads to special growth features such as small angle mosaic regions at the surface, which form with decreasing tilt angles as the overlayer thickness increases. In addition, satellite spots of an incommensurate superlattice have been detected, in particular after annealing of the NiO nanolayers, and this superstructure is also observed in the corresponding STM images.

2. Experimental

The SPA-LEED experiments have been performed in an ultrahigh vacuum (UHV) system with a base pressure of 5×10^{-11} mbar equipped with a high-resolution LEED instrument (Omicron), an Auger electron spectrometer for cleanliness and oxide stoichiometry monitoring, a quadrupole mass spectrometer for residual gas analysis, an electron-beam heated evaporator, a quartz crystal microbalance for film thickness measurements, and the usual provisions for surface cleaning. The transfer width of the SPA-LEED instrument is $\geqslant 1000$ Å as determined with a Si(111) sample. The range of electron energies employed include 60–200 eV with sample currents of ~1 nA. The SPA-LEED intensities in the corresponding diagrams have been plotted on a logarithmic scale. The STM measurements were carried out with a variable-temperature STM instrument as reported previously [8]. The STM images presented here were recorded in a constant current

mode at room temperature using W tips, which have been cleaned in situ by electron bombardment.

The Pd(100) surface was cleaned by cycles of 500 eV Ar^+ ion sputtering at 500 °C followed by short annealings to 1100 °C. The nickel oxide films have been prepared by reactive evaporation of nickel metal in 1×10^{-6} mbar oxygen atmosphere onto the cleaned Pd(100) surface at room temperature (RT) or at 300 °C. The RT deposited films have been annealed in UHV at various temperatures. The Ni deposition rate was monitored by the quartz crystal microbalance, which is calibrated in terms of frequency change per weight change, and was typically 0.5 equivalent monolayer/min (one equivalent monolayer (MLE) is defined by the number of Ni atoms corresponding to the density of surface atoms of Pd(100) (1.3×10^{15} atoms/cm²)). The monolayer equivalent (MLE) quantity of the microbalance reading is calculated according to the number of atoms in 1 MLE and the known molar weight of Ni. Note that for the NiO stoichiometry, 1 MLE corresponds roughly to one single layer of NiO(100).

3. Results and discussion

3.1. NiO growth at RT

Fig. 1 shows two-dimensional scans of the LEED pattern after deposition of nickel oxide at RT as a function of film thickness from 4 MLE to 20 MLE. The patterns were recorded with an electron energy E of 124 eV, which corresponds to a scattering phase of $S = 3.8$ for bulk NiO. The scattering phase S is defined by the interlayer distance d, the angle of incidence θ with respect to the surface normal of the electron beam, and the value of E.

$S = 2d\cos\theta\sqrt{[E(\text{eV})/150.4]}$. At this scattering phase the (00), (10), and (11) spots are visible, and the specular beam displays a large intensity. The diffraction patterns demonstrate that the nickel oxide grows with a $p(1 \times 1)$ structure, which is compatible with the NiO(100) orientation of the overlayer. The diffraction around the specular (00) rod is anisotropic with a specific broadening depending on the oxide coverage. Up to a coverage of 6 MLE, increased intensity towards the $\langle 001 \rangle$ directions is observed giving the impression of a square symmetry, which is highlighted by the dashed lines in Fig. 1(a) and (b). For thicker films the anisotropy changes orientation with increased intensity towards the $\langle 011 \rangle$ directions (Fig. 1(d) and (e)). This anisotropy of the diffraction around the (00) rod reflects the anisotropic morphology of the oxide islands and their boundary orientations. The results of Fig. 1(a)–(d) indicate that the NiO islands on average change their anisotropic shape and their preferred boundary alignment during growth. In addition, the anisotropic (00) beam intensity is caused by specific satellites, as apparent from Fig. 1(e).

Fig. 1(e) displays one-dimensional (1D) linescans through the (00) spot along the [011] direction for 4–20 MLE NiO films, as a plot of intensity versus % of the surface Brillouin zone of the Pd(100) substrate. The central