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Hydroxyl driven reconstruction of the polar NiO(111) surface

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Abstract

We have studied the reconstruction of the polar NiO(111) surface predicted recently by D. Wolf with low energy electron diffraction. Thin NiO films (10–20 Å) are used as substrates. As prepared, the films with a p(1 × 1) NiO(111) structure are covered with hydroxyl groups, which may be removed through a simple heat treatment. As the hydroxyl groups are desorbed, the surface reconstructs, exhibiting a diffuse p(2 × 2) structure. Readsorption of water onto the reconstructed surface lifts the reconstruction and again leads to the formation of the p(1 × 1) hydroxyl covered surface.

1. Introduction

Adsorption and reaction of molecules on surfaces of ionic materials have gained increasing interest in recent years [1]. Most of the studies have been restricted to the investigation of the stable, nonpolar cleavage planes of ionic materials. However, there are indications that the polar surfaces are more reactive [2]. The situation for ionic surfaces is somewhat related to the one encountered for semiconductor surfaces, although in this case the covalent part of the bonding is at least as important as the ionic part, e.g. in III–V compounds [3].

In contrast to nonpolar (100) surfaces of rocksalt structured ionic oxides, which are thermodynamically stable, (111) polar surfaces of bulk single crystal oxides are unstable if they remain in the bulk terminated structure due to the diverging surface potential [4–6]. Wolf [5] has recently predicted that the (111) surfaces of NaCl, NiO and related materials reconstruct from the p(1 × 1) bulk terminated structure into a p(2 × 2) structure, which is claimed to have the structure schematically shown Fig. 1. Independent of whether the surface is cation or anion terminated, the reconstruction lowers the surface energy from infinity to 4.67 J m^{-2} [7] (or even 4.27 J m^{-2} [5], if relaxation is taken into account), which is still larger than the surface potential of the NiO(100) surface, i.e. 1.74 J m^{-2} [5].

We have studied the reconstruction on 20–50 Å thick NiO(111) films grown on a Ni(111) single crystal surface [2,8]. The films have been prepared by prolonged oxidation and heating cycles which lead to well ordered NiO(111) surfaces. These surfaces were shown [2] to be covered with hydroxyl groups, which stabilize the (111) surface. The mechanism for stabilization of the surface via hydroxyl groups is obvious: The formation of

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hydroxyl groups which carry a single negative charge leads to a reduction of the surface charge with respect to the double negatively charged lattice oxygens and thus to an electrostatic stabilization of the surface. Heating of the surface to above 600 K leads to removal of the OH-groups and reconstruction of the surface concomitantly. Readsorption of water causes a lifting of the reconstruction. Recently, Neddermeyer and co-workers [9] reported a very nice study of NiO(111) p(2 × 2) reconstruction for a very thin NiO(111) film grown on Au(111). It is not clear that the driving force for the reconstruction within these very thin films (2 double layers) is the same as for the rather thick films reported in the present study, because in the former case the electrostatics are probably less important.

2. Experimental

The experiments have been performed in various different ultrahigh-vacuum chambers employing low energy electron diffraction including spot-profile analysis (SPA-LEED) as well as X-ray photoelectron spectroscopy (XPS) with monochromatized $AlK\alpha$ radiation and electron energy loss spectroscopy (ELS).

The Ni(111) single crystal sample was spotwelded to two tungsten wires which were attached to a liquid nitrogen reservoir. With this arrangement temperatures below $T = 100$ K could be reached. A tungsten filament was mounted behind the sample which could be used for sample heating by electron impact or radiative heating. The Ni samples were cleaned by repeated cycles of etching with Ne ions and annealing. Studies on the oxidation of Ni have been performed rather early [10]. The NiO(111) film has been prepared by oxidation of a Ni(111) single crystal in an oxygen atmosphere. The oxide was grown by cycles of oxidation with 1000 L (1 L = 10^{-6} Torr · s) of O_2 at elevated temperature ($T = 570$ K) followed by annealing at $T = 650$ K. These cycles were repeated until the LEED pattern indicated the formation of an ordered oxide film.
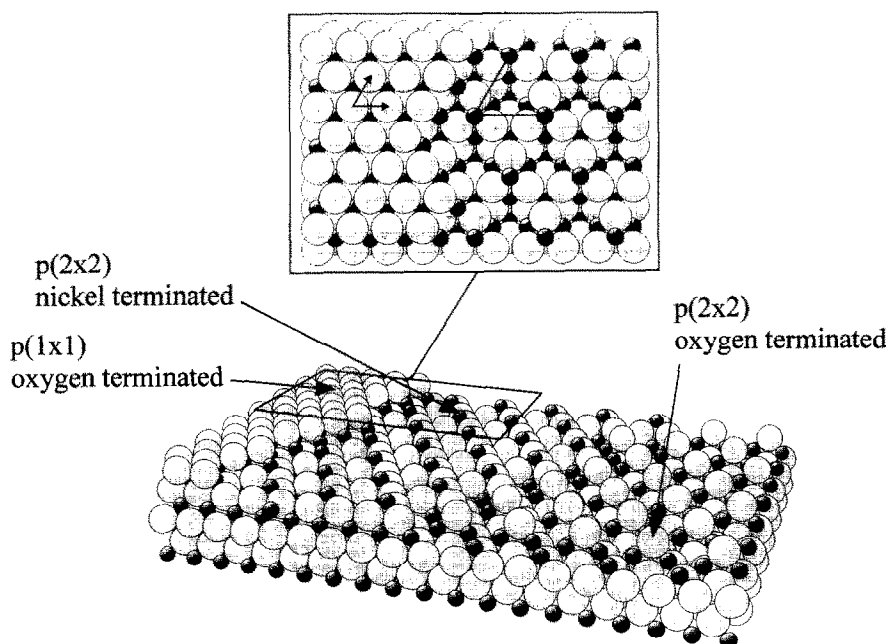

Fig. 1. Schematic representation of the p(1 × 1) NiO(111) as well as the p(2 × 2) NiO(111) surface. The p(2 × 2) octopolar reconstruction involves several layers in the substrate and is shown for two possible surface terminations.

3. Results and discussion

Fig. 2 shows LEED patterns of the Ni(111) surface as it is prepared. Three stages of the preparation are selected. The clean Ni(111) shows sharp spots (Fig. 2a). Then after oxygen adsorption a sharp p(2 × 2) overlayer forms (Fig. 2b). At this stage no ordered oxide film is present on the surface. As the oxide film grows the wider NiO spots are observed together with the p(2 × 2) O adsorbate spots with a smaller unit cell in reciprocal space (Fig. 2c). Finally, on the surface completely covered with oxide (Fig. 2d) the oxide spots are still considerably broader than the metal
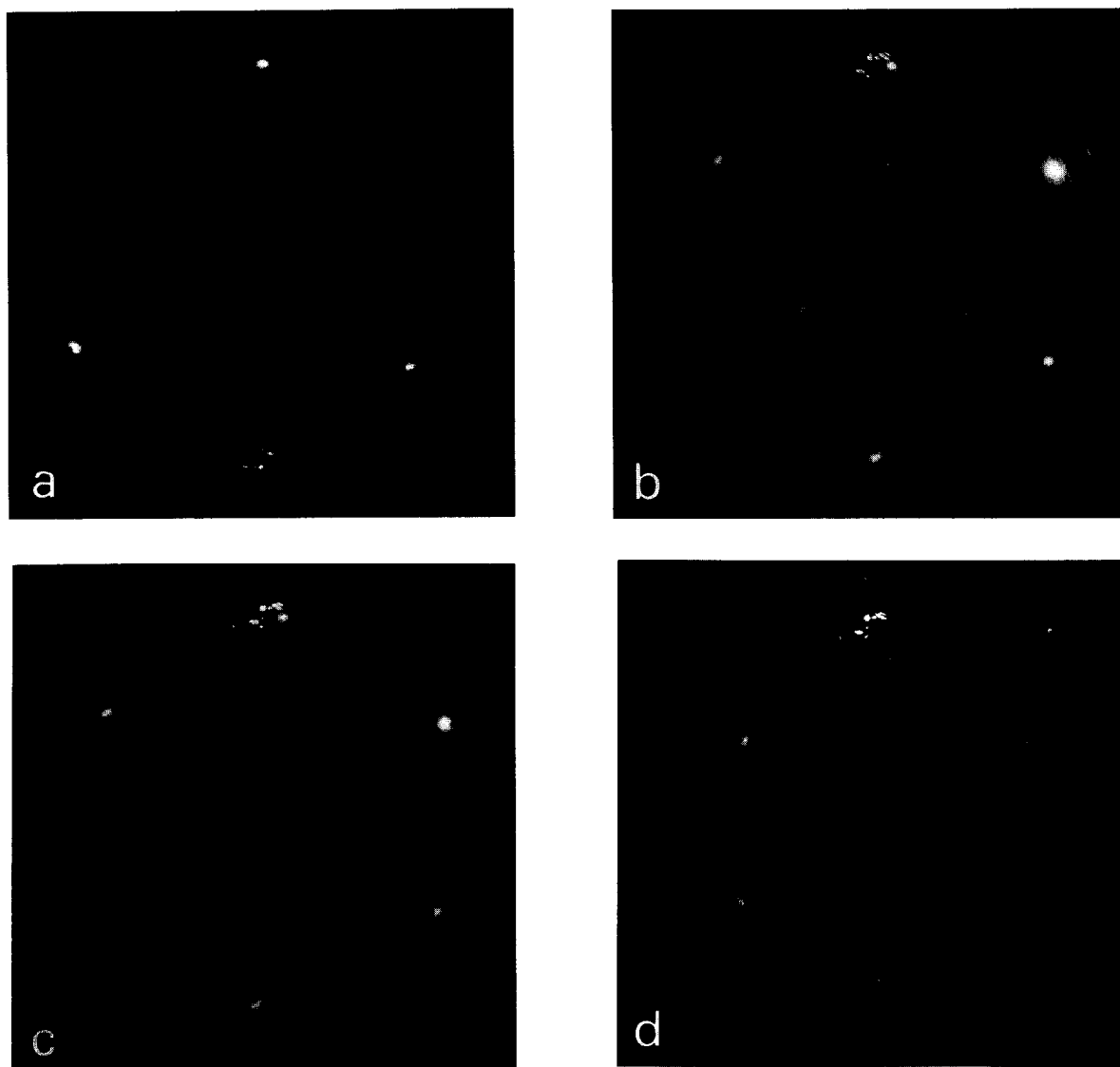

Fig. 2. LEED patterns observed during preparation of the NiO(111) oxide film. (a) Ni(111) (clean), (b) p(2 × 2) O/Ni(111), (c) p(2 × 2) O/Ni(111) and p(1 × 1) NiO(111), (d) p(1 × 1) NiO(111).

reflexes due to the imperfections induced by the large lattice mismatch between metal and metal oxide (18%) [11] but the substrate spots are no longer observed.

The ELS spectra in Fig. 3a indicate the adsorption of considerable amounts of hydroxyl groups by the observation of strong losses at 460 meV. The OH groups may be partially exchanged through exposure of the surface to D_2O, which leads to an isotope shift as seen in Fig. 3. These losses are situated on top of a background of electronic excitations within the NiO band gap as has been previously discussed for the NiO(100) surface by Freitag et al. [12]. A detailed analysis of the NiO(111) ELS data will be published elsewhere [13]. It was shown earlier that the adsorbed hydroxyl groups lead to a pronounced shoulder in the O 1s XP spectra at approximately 1.5 eV higher binding energy [2] as compared with the lattice oxygen feature.

As monitored via ELS and XPS, the hydroxyl groups can be removed to a large extent by a simple heat treatment. Fig. 3b also shows the ELS spectra after removal of the majority of the hydroxyl groups. In conjunction with this change in composition, we observe changes in the LEED patterns. Fig. 4a shows a two-dimensional SPA-LEED pattern of the oxide film taken at an electron energy of 80 eV. This pattern corresponds to the p(1 × 1) NiO pattern in Fig. 2d. The distortion of the symmetry of the pattern is due to the experimental arrangement in the SPA-LEED set up. If the sample is heated to slightly above 600 K, we see changes in the intensity distribution of the LEED pattern. Figs. 4b and 4c show SPA-LEED patterns taken at two different electron energies. It is obvious that there is considerable variation of spot intensity with electron energy. At 65 eV the second order p(2 × 2) spots are intense, while the first order p(2 × 2) and p(1 × 1) spots have very low intensity. At 78 eV, on the other hand, intense p(1 × 1) and first order p(2 × 2) spots are found. Even though the SPA-LEED patterns are distorted, it is clear that the p(2 × 2) NiO spots are not located near the portions of the sharper p(2 × 2) O/Ni(111) spots. Therefore, the p(2 × 2) reconstruction is clearly connected with the NiO lat-
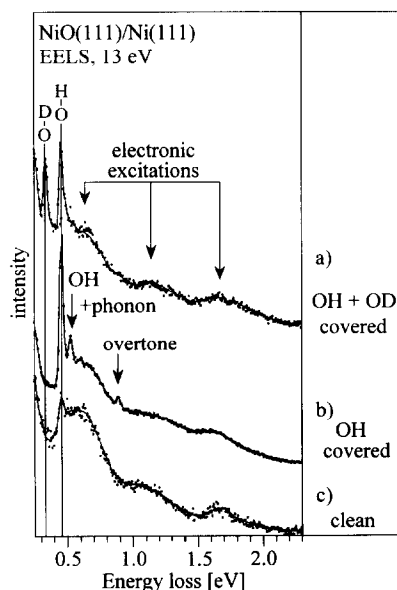

Fig. 3. Electron energy loss spectra of the (a) OH/OD; (b) (OH) covered NiO(111) surface and the (c) OH depleted ("clean") surface.

tice. A detailed structure determination, however, has not been undertaken yet. One reason is the sensitivity of the substrate towards the impinging electron beam in commercial standard LEED-systems. We have set up a channel-plate LEED system [14] which operates with electron currents in the nA regime and with which we shall tackle this problem in the near future. It is very likely that the present p(2 × 2) reconstruction is of the octopolar type predicted earlier and schematically shown in Fig. 1.

A way to follow the formation and lifting of the reconstruction is to record one-dimensional scans containing two neighboring first order NiO spots and the second order p(2 × 2) spot. The measurements were performed at particular electron energies. Fig. 5 shows a one-dimensional scan for 71 eV and a surface temperature of $T = 300$ K at the top. The two p(1 × 1) NiO spots are clearly visible. In comparison, a scan is shown for 65 eV where the p(1 × 1) spots are considerably attenuated. If we heat the sample to temperatures around 600 K, the p(1 × 1) spots decrease in intensity even at 71 eV electron energy, and at 65 eV electron energy there is a broad

peak developing between the p(1 × 1) spots in a position where we expect the second order p(2 × 2) spot. These findings are fully compatible with the two-dimensional patterns in Fig. 4.

The patterns are rather diffuse but various attempts to find optimal preparation conditions to form a well ordered structure failed. The p(2 × 2) spot intensity is sensitive to the background pressure, while the p(1 × 1) structure is rather insensitive. In fact, after several hours the p(2 × 2) spot is strongly attennuated. The same result can be obtained if we expose the p(2 × 2) structure to 0.3 L H_2O. The process is completely reversible and may be cycled. Therefore, it is an experimental fact that the NiO(111) surface reconstructs after the OH covered surface has been heated to 600 K. This reconstruction does not lead to a well ordered surface as indicated by the large spot widths. Nevertheless, the process is perfectly reproducible in every preparation cycle.

The reconstruction can be lifted upon exposure to water, and this process is also reversible.

It is quite probable that the sensitivity of surface structure to the presence of water on the surface has general consequences for the reactivity of the oxide surfaces. We have demonstrated before [2] that the number of adsorbed NO molecules – as monitored via thermal desorption – increases by about a factor of three after desorption of the hydroxyl groups. In addition, high temperature desorption of NO (above 400 K) is observed indicating the reaction of adsorbed NO, tentatively to NO_2 for example. In this sense, water steers the reactivity of the oxide surface as a function of surface temperature where the temperature for OH desorption sets the threshold to activate the sample and in particular the polar surface patches. Whether this observation is relevant to catalytic processes is not clear at present but there are indications that the catalytic activity
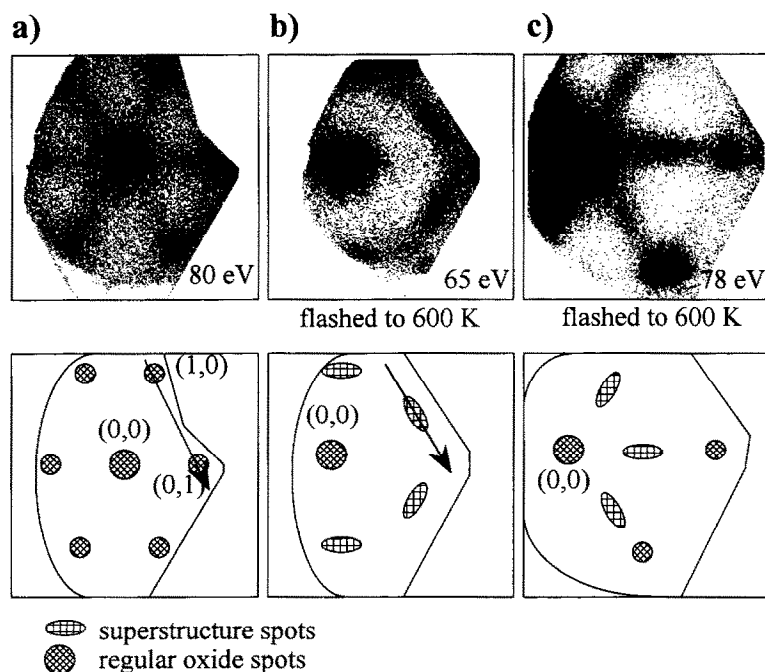

Fig. 4. Two-dimensional SPA-LEED patterns of (a) the p(1 × 1), (b), (c) the p(2 × 2) reconstructed surface at two different electron energies. The arrow refers to Fig. 5.

LEED intensity profile

(1,0)-spot   (0,1)-spot

71 eV

65 eV

65 eV
flashed to
600 K

65 eV
after 24 h

65 eV
0,3 L H$_2$O

intensity (arb. units)

0   20   40   60   80

K$_\parallel$ (% Brillouin zone(Ni))
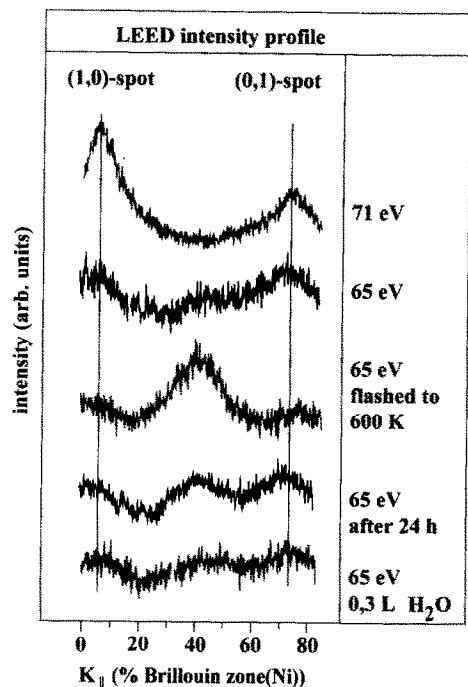
Fig. 5. One-dimensional SPA-LEED scans along a direction as indicated by the arrow in Fig. 4 for the p(1 × 1) surface (two topmost traces) and the reconstructed surface at 65 eV electron energy. The two lowest traces indicate the changes occurring if the sample is exposed to the background pressure for 24 h or to a dose of 0.3 L H$_2$O directly after reconstruction has taken place.

of NiO catalysts prepared through topotactic dehydration of Ni(OH)$_2$, i.e. forming crystallites with (111) orientation [15], is strongly influenced by water in the gas phase and on the sample.

4. Conclusions

We have observed a diffuse p(2 × 2) reconstruction on a thin NiO(111) film which is covered by hydroxyl groups as prepared. OH-termination leads to the stabilization of the surface. Upon heat treatment, the hydroxyl groups are removed and the surface reconstructs. It is very likely that the reconstructuion is of the oc-topolar type as recently predicted by D. Wolf. Readsorption of water onto the reconstructed surface leads to a lifting of the reconstruction yielding again a hydroxyl covered NiO(111) surface.

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