

Adsorption, thermal and photochemical reactions of NO on clean and oxygen precovered Ni(100) surfaces

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We have studied the adsorption, thermal and photochemical reactions of NO adsorbed on clean Ni(100), epitaxially grown NiO, and Ni(100) precovered with chemisorbed oxygen. The electronic and geometric structure of the substrate surfaces and the adsorbed NO molecules were investigated by electron spectroscopic techniques, i.e. HREELS, NEXAFS and LEED, whereas the thermal and photochemical properties of the adsorbate layer were probed using TPD and laser induced desorption, respectively.

Introduction

The aim of our present work is to investigate the adsorption and reaction of small molecules (in this case NO) on epitaxially grown metal oxide single crystal surfaces (here NiO-Ni(100)). A general overview of data for oxide surfaces may for instance be found in ref 1. Epitaxially grown oxide surfaces are experimentally easier to handle than surfaces of oxide single crystals since charging problems hindering the application of electron spectroscopic techniques do not exist if the oxide layer is thin. Here we present data taken by various electron spectroscopic techniques (HREELS, NEXAFS and LEED), TPD and laser induced desorption. In order to obtain information about the influence of the electronic and geometric substrate surface structure on the adsorption behaviour of the NO molecules we varied the quality of the oxide layer by variation of the preparation parameters. For comparison we also present data for NO adsorption on clean Ni(100) and Ni(100) containing chemisorbed oxygen.

Experimental

The data were taken in three different uhv chambers. All of the chambers contained facilities for LEED, AES and residual gas analysis with a quadrupole mass spectrometer. NEXAFS data were taken by a CLAM 100 electron analyser (VG Instruments) with light from the HETGM2 monochromator at the storage ring BESSY 1 in Berlin. For the HREELS investigations we used an ELS22 spectrometer (Leybold AG). The resolution was typically 10 meV. The third system was equipped with facilities for XPS, TPD and laser induced desorption (ArF, $\lambda = 193$ nm). Crystal preparation has been described elsewhere².

Results and discussion

The adsorption of oxygen on Ni(100) leads, depending on the preparation parameters, to different layers of chemisorbed oxy-

gen and oxides, respectively. Figure 1 shows a set of LEED patterns observed during the preparation of a NiO(100) film. Panel (a) shows the clean Ni(100) LEED pattern. After dosing the surface with 10 L O₂ at room temperature and annealing to 450 K a p(2 × 2)O superstructure is observed (not shown here) which continuously converts into a c(2 × 2) pattern at higher oxygen doses (panel b). Repeated cycles of oxygen dosing (1000 L, $P = 10^{-5}$ mbar) at $T = 570$ K and subsequent annealing to $T = 670$ K initially produced a LEED pattern consisting of a mixture of c(2 × 2)O and NiO(100) spots (panel c) and finally pure NiO(100) (Panel d). From the broad NiO spots in panels (c) and (d) we conclude that the epitaxially grown NiO(100) always contains defects, so that adsorption on defects might play an important role in the adsorption behaviour of these surfaces. Another sort of epitaxially grown NiO can be obtained by exposing the Ni(100) surface to 500 L O₂ at room temperature. Upon this treatment a hexagonal LEED pattern is observed which is interpreted to result from a NiO(111) layer². As judged by the rather high background intensity in the LEED pattern this oxide also contains many defects.

Figure 2 displays a set of HREEL spectra for NO adsorption on a Ni(100) surface with differently prepared oxygen adlayers. The NO doses used were in all cases 12 L leading to a saturated NO layer at the temperatures achieved during our experiments (90 and 115 K, respectively). For NO adsorbed on clean Ni(100) (panel (a) of Figure 2) three losses are observed in the region around 1700 cm⁻¹. By comparison with ir data for metal nitrosyl complexes³ these can be attributed to NO molecules adsorbed in different geometries (i.e. linear and bent). On the basis of these data we assign the losses at 1660 and 1515 cm⁻¹ to NO molecules adsorbed on top of the Ni atoms, and in two-fold hollow sites, respectively. By comparison with the spectrum for NO adsorbed on a p(2 × 2)O adlayer (panel b) we tentatively attribute the shoulder at 1830 cm⁻¹ to NO adsorbed in the vicinity of

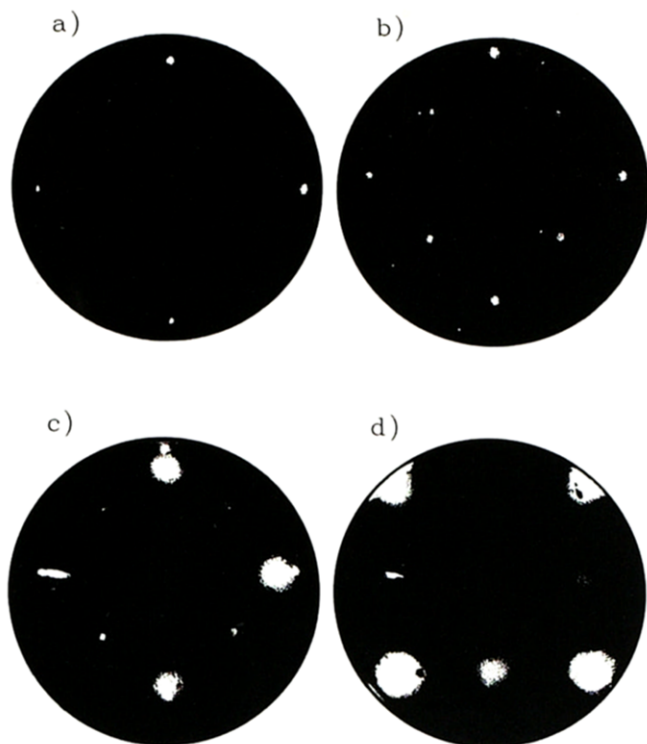


Figure 1. LEED patterns observed during the preparation of an epitaxially grown NiO(100) oxide layer on Ni(100): (a) Ni(100), clean surface, $E = 75$ eV, (b) $c(2 \times 2)$ O-Ni(100), $E = 68$ eV, (c) NiO(100)-Ni(100) with residual $c(2 \times 2)$ O and Ni(100) spots, $E = 68$ eV, (d) NiO(100)-Ni(100), $E = 85$ eV.

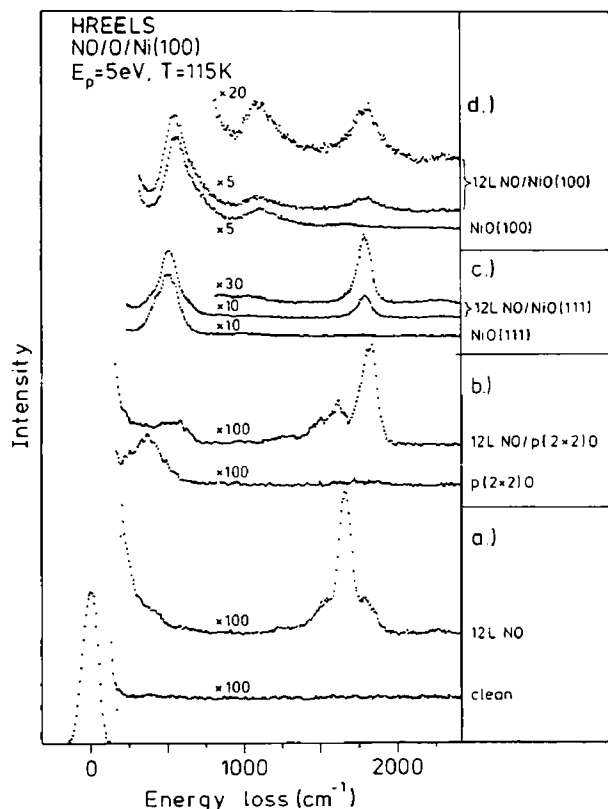


Figure 2. Series of HREEL spectra obtained from NO adsorbed on clean and on oxygen precovered Ni(100).

traces of oxygen impurities which lead to the weak loss at 390 cm^{-1} in the spectrum of the substrate before NO adsorption⁴.

Panel (b) shows the HREELS results for NO adsorption on a Ni(100) surface containing chemisorbed oxygen. For the substrate a $p(2 \times 2)$ LEED pattern was observed. According to ref 5 the pure $p(2 \times 2)$ O layer ($\Theta = 0.25$) exhibits a vibrational loss at 415 cm^{-1} whereas for the $c(2 \times 2)$ O layer ($\Theta = 0.5$) a loss is observed at 320 cm^{-1} . From the observed loss energy of 390 cm^{-1} we conclude that the oxygen coverage is somewhat intermediate between intermediate between $\Theta = 0.25$ and 0.5 , being nearer to $\Theta = 0.25$ ($p(2 \times 2)$ O). Upon NO adsorption this loss peak changes to a broad feature with a maximum at 590 cm^{-1} . The N-O stretching frequency of the terminally bound NO molecules is now found at 1830 cm^{-1} , shifted by 170 cm^{-1} as compared to the stretching frequency of NO molecules adsorbed on clean Ni(100) (a similar effect has been observed in ref 6). The reason for this shift may be the competition of the oxygen atoms and the NO molecules for the nickel valence electrons leading to an increased N-O bonding strength and thus to an increased force constant for the N-O stretching vibration. In this context, and since the cross-section for the ON-Ni vibration is rather weak (panel b), we very tentatively assign the loss at 590 cm^{-1} to the a shifted O-Ni vibration.

In panel (c) the HREELS results for NO adsorption on the NiO(111) layer are shown. It is characterized by a O-Ni loss at 510 cm^{-1} . The N-O stretch is now observed at 1800 cm^{-1} . The upper panel, (d), displays HREEL spectra obtained from epitaxially grown NiO(100). Characteristic for this oxide is the intense loss at 550 cm^{-1} corresponding to the Fuchs-Kliwiler phonon mode of NiO, and overtones of this loss at higher energies². Adsorption of NO on this oxide leads to a single loss at 1800 cm^{-1} without any measurable influence on the losses of the NiO(100) film. The loss energy falls into the range of singly coordinated linear metal nitrosyl complexes. However, we have to consider the effect of the oxygen atoms surrounding the Ni atoms in the oxide. We expect that they shift the NO stretching frequency similar to the effect of the co-adsorbed oxygen on the NO stretch in the case of the NO- $p(2 \times 2)$ O-Ni(100) adsorbate, where an upward shift of 170 cm^{-1} was observed. Therefore the observed frequency is also consistent with a shifted NO stretching frequency of a bent terminal NO co-ordination (1520 – 1680 cm^{-1} ³). The finding of a single frequency is in line with the TPD data (Figure 3) where only a single desorption maximum is found for NO adsorbed on the oxide surfaces.

The vibrational NO stretching frequency for NO-NiO(100) equals the stretching frequency for NO adsorbed on NiO(111). This supports the conclusion that the adsorption sites are similar in both cases.

Information concerning the adsorption geometry is supplied by NEXAF spectra taken as a function of the light incidence angle (Figure 4). Here the intensity of the σ and the π resonance of the N_{1s} excitation was investigated. Since the $N_{1s} \rightarrow \pi$ and the $N_{1s} \rightarrow \sigma$ transitions can only be excited by light polarized perpendicular or parallel, respectively, to the molecular axis, the intensities of these transitions are functions of the molecular orientation and the polarization of the light. The molecular orientation can then be determined by a fit of the relative intensity I_{σ}/I_{π} as a function of the light incidence angle using Fresnel's formulae, as shown in the right part of Figure 4. For NO adsorbed on Ni(100) we obtain the result that the molecular axes are oriented more or less perpendicular to the surface normal⁷ whereas for

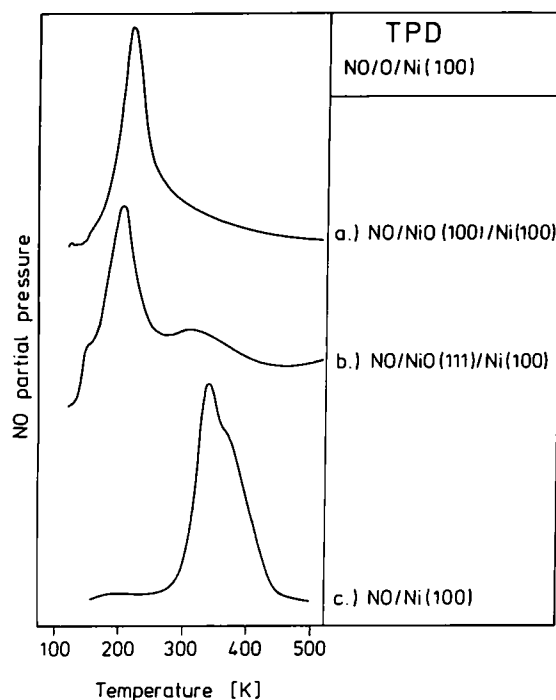


Figure 3. Series of TPD spectra obtained from NO adsorbed on clean Ni(100) (from ref 8, Budde *et al*) and NO adsorbed on epitaxially grown NiO(111) and NiO(100) layers.

NO-NiO(100) the molecules are tilted by $45^\circ \pm 15^\circ$. Additionally it has to be considered that the NiO surface contains a lot of defects. It is therefore not clear whether the inclined adsorption geometry of the NO molecules results from adsorption on defect sites or if it is an intrinsic property of NO adsorption on regular NiO adsorption sites.

Upon ArF laser irradiation we observed desorption and decomposition of NO molecules adsorbed on NiO(111) whereas for NO adsorbed on clean Ni(100) and $c(2 \times 2)O$ -Ni(100) no such effects could be observed. This different behaviour is due to differences in the specific energy dissipation processes. The absorption of a photon results in a electronic excitation of the adsorbate complex. In contrast to adsorption on non-metallic surfaces the electronic excitation energy of adsorbate complexes on metallic substrates can easily be dissipated into the solid by electron-hole pair creation in the solid. Thus the photolytic fission of the adsorbate complex is more likely to occur on non-conducting or semiconducting substrates as compared to metallic substrates. Whether the substrate-adsorbate bond is broken or the adsorbate molecules are decomposed depends on the specific excitation and on the properties of the adsorbate complex. This picture is consistent with data obtained by laser-induced desorption⁸.

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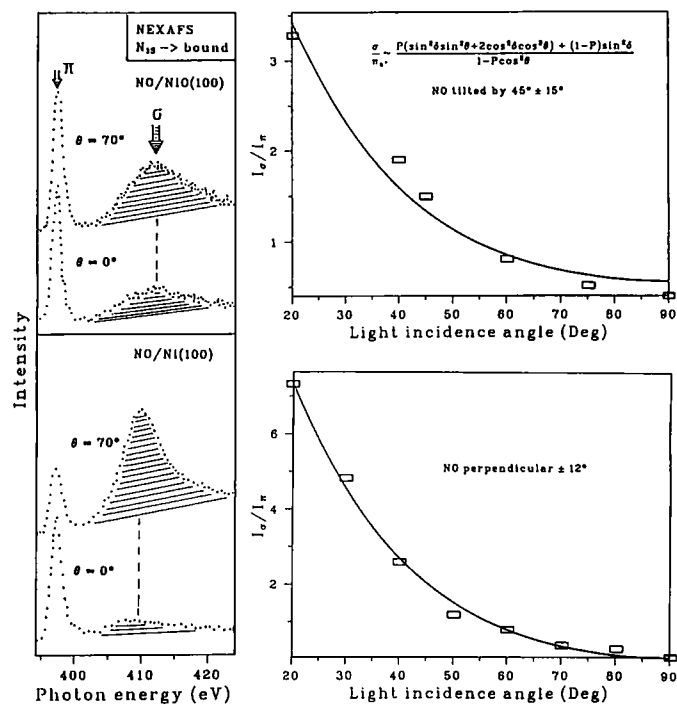


Figure 4. N_{1s} NEXAFS spectra of NO adsorbed on epitaxially grown NiO(100) and on Ni(100) for two different polarizations of the incident light. In the right panel the intensity of the σ resonance normalized to the intensity of the π resonance is plotted vs the angle of light incidence.

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