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Structural characterization of platinum deposits supported on ordered alumina films

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Platinum on γ-Al_2O_3 represents one of the technically important supported catalysts. In order to
model such a system, we have prepared a well-ordered 5-Å-thick and atomically flat oxide film with
γ-alumina-like structure on NiAl(110). Its defect structure has been subject to a spot-profile
analysis–low-energy electron diffraction (SPA-LEED) investigation. The formation of antiphase
domains leads to a broadening or splitting of certain superstructure spots, which exhibit unusual
intensity up to high diffraction orders. The deposition of small amounts of platinum results in
destruction of the oxide superstructure to a great extent. This behavior allows the investigation of
small platinum coverages ($\theta \approx 0.1$). Island sizes and further information about size distributions were
extracted from a spot-profile analysis of the (00)-LEED reflex, revealing a high dispersion of
platinum with Pt atoms changing the structure of the oxide in their immediate neighborhood.
Thermal desorption spectroscopy results suggest an embedding of Pt in the Al_2O_3 matrix. To a large
extent this process can be suppressed by deposition at low temperature (100 K), whereas heating
higher than 800 K leads to diffusion of Pt through the oxide into the substate followed by a
recovering of the oxide superstructure. Deposition of several monolayers of platinum at 500 K
results in the formation of a polycrystalline film. The crystallites grow in (111)-orientation and show
preferential azimuthal orientations with respect to the substrate.

I. INTRODUCTION

Noble metals supported on oxide surfaces play a major
role in the field of heterogeneous catalysis. Besides stabiliz-
ing highly dispersed metal aggregates against agglomeration,
supports often modify the adsorption behavior and thus the
catalytic properties of the metal.[1]

It has been shown that the development of simple model
catalysts provides a promising way of understanding the el-
ementary processes occuring on these highly complex
systems.[2,3] Concerning the choice of model supports, thin
oxide films grown on metal substrates offer various advan-
tages and opportunities, e.g., efficient cooling of the sample
is possible, charging is avoided, different surface structures
can be prepared,[4–7] and defect structures as well as chemical
properties of the surface can be varied.[8]

Apart from their electronic structure and adsorption be-
havior, detailed information on the geometric structure forms
a basis for the interpretation of catalytic processes carried out
on these systems. Their structure becomes much more easily
accessible, if one succeeds in modeling major properties of
technically important support materials by applying well or-
dered oxide films.

One interesting candidate for such a model system has
been shown to be a thin and highly ordered Al_2O_3 film which
can be epitaxially grown on NiAl(110).[9,6] The clean oxide
film has been investigated by several methods.[6,10] It has been
proposed, that its geometric structure should be comparable
to γ-Al_2O_3, one of the high surface area transition phases of
alumina used as a support.[6]

The next step has to be the characterization of metal ag-
geragates deposited onto this film. The electronic structure of
ultrathin platinum films on Al_2O_3/NiAl(110) and the adsorp-
tion of small molecules, i.e., CO and NO, has been studied
by x-ray photoelectron spectroscopy (XPS), ultraviolet pho-
toelectron spectroscopy (UPS), high-resolution electron
energy-loss spectroscopy (HREELS), and thermal desorption
spectroscopy (TDS).[11–13] Concerning the structure of these
systems the results of a spot-profile analysis–low-energy
electron diffraction (SPA-LEED) study on Pt/Al_2O_3/
NiAl(110) are presented here. The LEED profile analysis can
provide information on the defects existing on the clean ox-
ide layer and it will be shown that one can follow the defects
induced by evaporation of platinum onto the well-ordered
film. It turns out that platinum interacts strongly with the
alumina film even at room temperature resulting in a high
dispersion and an incorporation of platinum atoms into the
oxide. This contrasts the behavior of silver on
Al_2O_3/NiAl(110), which does not wet the surface as shown
recently by scanning tunneling microscopy (STM).[10]

II. EXPERIMENTAL

The experiments have been performed in a ultrahigh
vacuum (UHV) system, which was equipped with a SPA-
LEED system (Leybold)[14] with a specified transfer width of
more than 800 Å. The NiAl(110) single crystal was mounted
between two tantalum wires, which were spot welded to two
tungsten rods. During the SPA-LEED measurements the
sample was placed behind a graphited copper aperture to
avoid an influence of defective areas near the crystal edges
on the spot profiles. The sample was cooled by a liquid-
nitrogen reservoir and heated by radiation from a filament
mounted behind the crystal or by electron bombardment. The
NiAl(110) surface was prepared by repeated cycles of sput-
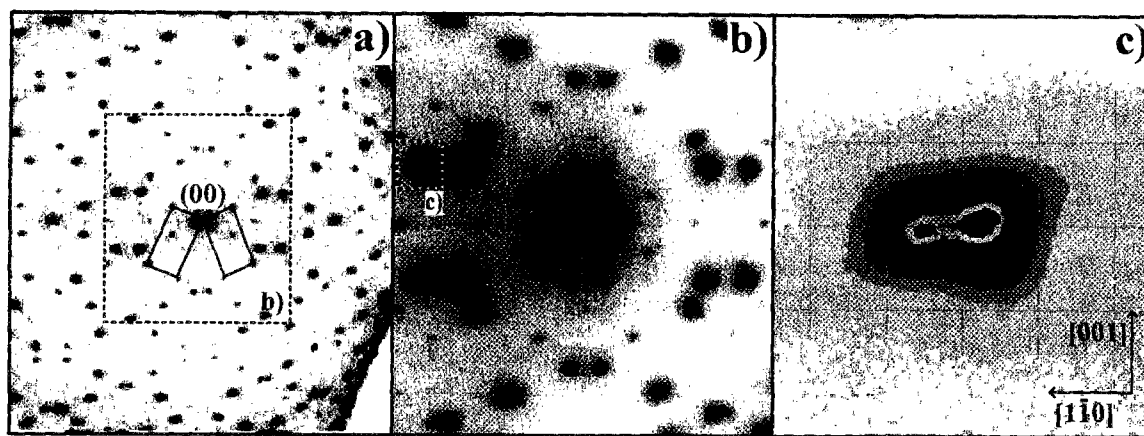tering with Ne ions (500 eV) and subsequent annealing as

FIG. 1. (a) SPA-LEED pattern of Al_2O_3/NiAl(110), an overview (110 eV); (b) enlarged view of the area indicated in a (80 eV); and (c) profile of the spot marked in b (65 eV).

reported in the literature.[6] The cleanliness of the surface was checked by Auger electron spectroscopy (AES).

The full width at half-maximum (FWHM) of the LEED spots of the NiAl(110) surface was governed by the mosaic spread of the crystal which was determined to be about 0.15°. This limits the effective transfer width in the energy range from 50 to 100 eV to a value of 350 to 250 Å. The spot profiles of the NiAl(110) surface revealed no indication for a macroscopic misorientation.

The preparation of the well-ordered oxide has previously been described.[6,9] Upon dosing 1200 L O_2 at 550 K and subsequent annealing to 1150–1200 K for 5 min, the characteristic LEED pattern can be observed. After evaporating platinum onto the film, several cycles of sputtering and annealing were frequently found to be necessary before preparing a new oxide film. Whether the surface is completely oxidized, can be checked by TDS.[11,12] While above 90 K no CO adsorbs on the oxide,[15] desorption from the NiAl(110) takes place at around 300 K.[16]

Platinum was deposited from a filament at a rate of 0.01 Å s^{-1}. The deposition rate was controlled by a quartz balance.

III. RESULTS AND DISCUSSION

A. Al_2O_3/NiAl(110): Structure and defects

The electronic and geometric structure as well as the adsorption behavior of the clean oxide film have already been investigated by LEED, XPS, UPS, HREELS, ion scattering spectroscopy (ISS), TDS, and STM.[6,9,10,15] On the basis of the experimental data, a structure model was proposed.[6] The most important features of this model can be summarized as follows: The well ordered and atomically flat film has a layered structure with a thickness of about 5 Å. This corresponds to about two layers of oxygen and aluminum ions. It is terminated by oxygen in a distorted hexagonal arrangement. Concerning the distribution of aluminum ions, HREEL spectra point to a γ-alumina-like structure rather than a α-alumina-like structure. γ-Al_2O_3 shows a defect spinel

structure with aluminum occupying octahedral as well as tetrahedral sites[17] whereas in α-Al_2O_3 the aluminum ions occupy octahedral sites only.

As shown in Fig. 1(a) the LEED spots are sharp and visible up to high diffraction orders. The real-space unit cell was determined by Müller et al. to be 10.55 Å×17.88 Å and nearly rectangular (α=88.7°).[9] It is rotated by about 24° with respect to the substrate [NiAl(110)-unit mesh: 2.887 Å×4.083 Å, α=90°]. Because of the symmetry of the substrate, two domains are expected to exist. Their unit cells are also indicated in Fig. 1(a). It has been shown that along the [1$\bar{1}$0] direction of the NiAl the film is commensurate with the substrate, whereas along the [001] direction it is incommensurate. Therefore, the substrate spots do not coincide with the oxide superstructure spots along the latter direction. Even after complete oxidation the substrate spots are clearly visible. Because of the incommensurability, double diffraction spots should exist, which, nevertheless, could not be observed in previous studies.[6] Due to the high dynamic range of the SPA-LEED instrument, several double diffraction spots could now be identified. Figure 1(b) shows a close up of the part of the LEED pattern marked in Fig. 1(a). A comparison with the schematic pattern in Fig. 2 reveals that apart from the oxide superstructure spots there are weak additional spots. The reflex positions in Fig. 2 have been calculated on the basis of the oxide mesh given in Ref. 9. Only double diffraction with respect to NiAl spots of first order is taken into account. Obviously, all additional spots observed can be identified in that way.

Previously, the missing double diffraction spots led to the speculation that there could be some sort of interlayer between the oxide and the substrate, which is commensurate with the oxide superstructure.[6,9] Because of their weakness, the observation of the additional spots as well as the degree of attenuation of the substrate spots still seems compatible with an additional oxide-bulk interface, as long as its not thicker than about one atomic layer. At least STM results point to the existence of such an interlayer.[18,19] As a more detailed discussion on the structure and the defects on the clean oxide film will be given elsewhere,[19] only one obser-

● (00)-spot

● Al_2O_3-spots:
Domain A   Domain B

Double diffraction spots with re-
spect to NiAl-spots of first order:
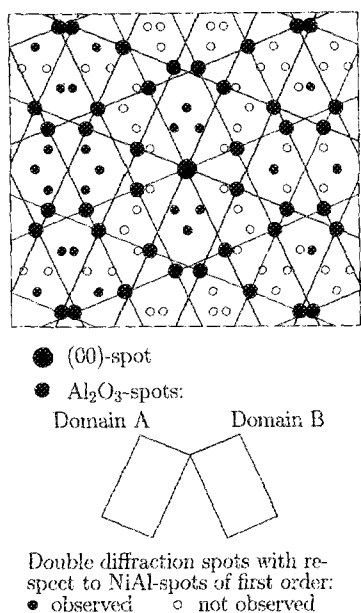● observed   ○ not observed

FIG. 2. Schematic representation of the LEED pattern indicating two oxide domains and double diffraction spots.

vation strongly affecting the spot profiles may be mentioned here; the oxide superstructure shows a characteristic pattern of one-dimensionally broadened spots. Along the [110] direction of the substrate, an oscillating broadening or splitting is observed as illustrated by the two-dimensional profile [Fig. 1(c)] of the spot marked in Fig. 1(b). While there obviously is a pronounced dependence on the parallel component of the scattering vector, the profile of a reflex does not depend on the energy, i.e., the component perpendicular to the surface. Therefore, we can attribute the broadening to a domain structure only laterally shifted (antiphase domains). Although the details of the profile prove to be dependent on preparation, a spot profile analysis (for details of the evaluation procedure
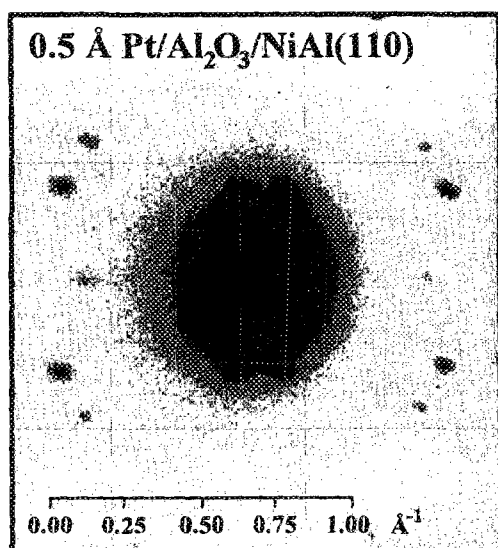

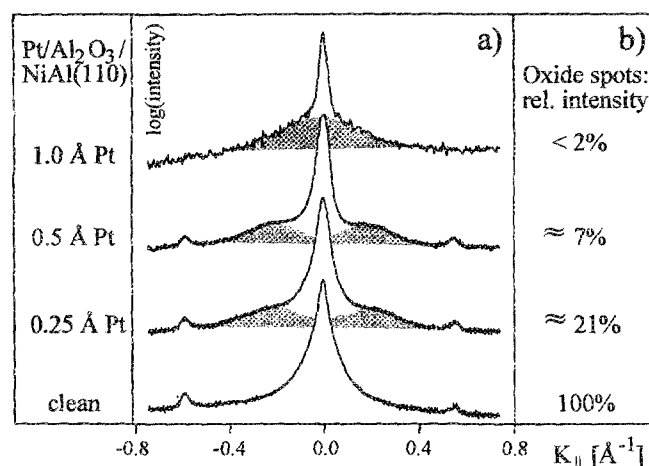FIG. 3. LEED pattern (40 eV) after evaporation of 0.5 Å Pt at 300 K.

FIG. 4. (a) Comparison of (00)-spot profiles (45 eV) upon Pt deposition at 300 K. All profiles were measured along the [110] direction of the NiAl crystal (indicated in Fig. 1). (b) Relative intensity of the oxide spots with respect to the clean oxide.

see Ref. 20) yielded a domain size of about 100 Å for those preparations, where splitted spots where clearly visible.

B. Platinum deposited on Al_2O_3/NiAl(110)

1. Low coverage regime

Deposition of small amounts of platinum onto the alumina film results in a drastic change of the diffraction pattern. Figure 3 shows a two-dimensional scan of an area around the (00) reflex after evaporation of 0.5 Å of platinum (about 0.2 ML) at a substrate temperature of 300 K. The size of the scanned area of the LEED pattern roughly corresponds to Fig. 1(b). In comparison with the spectra of the clean oxide, two things can be seen changing on metal deposition: (1) the intensity of all superstructure spots is strongly reduced; (2) a ring-shaped diffuse shoulder emerges around the (00) spot. This behavior as a function of coverage is more clearly illustrated in Fig. 4. Figure 4(b) shows the relative intensity of the oxide spots with respect to the intensity of the clean oxide as determined from the most intense superstructure spots. Even after deposition of 0.25 Å of platinum (about 0.1 of a monolayer) at 300 K a reduction of 80% of the original value is found. Upon deposition of 1 Å of platinum, the oxide spots completely vanish. Intensity and profile of the diffuse shoulder depend on platinum coverage. At coverages below 0.5 Å Pt the ringlike shape is clearly visible, on deposition of more than about 1 Å Pt even the (00) reflex becomes very weak. The profiles shown in Fig. 4 correspond to an electron energy of 45 eV, where the shoulder shows a maximum intensity. Varying the energy does not change the profile of the diffuse part but its intensity with respect to the central spike. On the other hand, heat treatment has a strong effect on both, the intensity of the oxide spots, which become even more attenuated, and the shape of the shoulder decreasing in width. We will come back to this later.

First a short interpretation of the observations shall be given: The strong effect on the intensity of the oxide spots at low coverages leads to the conclusion that the metal exists in
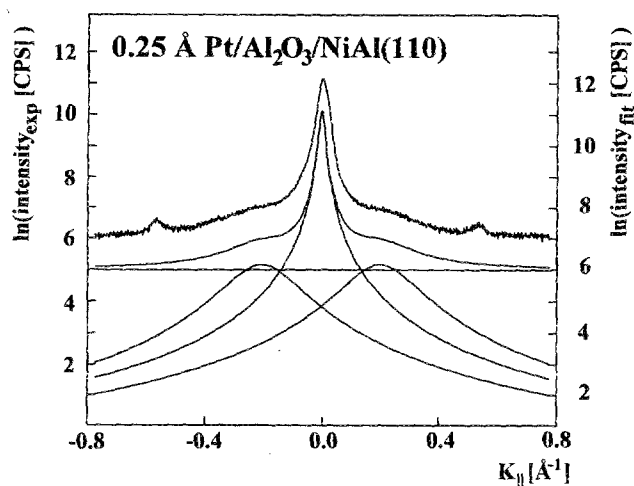
FIG. 5. The spot profiles (here 0.25 Å Pt/Al$_2$O$_3$, 45 eV) can be fitted by a sharp Lorentzian (here FWHM=2.2×10^{-2} Å^{-1}, taken from the profile of the clean oxide) and two broad Lorentzian functions shifted against the central spike (here FWHM=0.25 Å^{-1}, shift=0.2 Å^{-1}). In addition, a constant background has to be taken into account.

a highly disperse form. Even if a two-dimensional growth mode is supposed, the oxide would not be covered in a sufficient degree to explain the attenuation. Thus it seems as if the oxide is structurally modified through the action of the platinum atoms. The appearance of the diffuse shoulder can be attributed to these metal modified areas. Its ring-shaped profile points to a correlation of the distances between the modified areas. This could be due to platinum atoms only affecting the substrate within a rather well-defined area or, on the other hand, only modifying the oxide at particular sites, e.g., where the metal can be incorporated into the film.

From the diffuse profile the size of the areas involved can be estimated. Here, it becomes important that the profile of the diffuse part of the reflex exhibits no dependence on the perpendicular momentum transfer, i.e., on energy. This means that, in a first approach, this highly complex system can be considered as being made up of two distinct structures: the unaffected oxide areas on the one side and metal modified patches on the other. For such a surface consisting of two structures the kinematic approximation yields no dependence on energy for the diffuse profile. On the other hand, the relative intensity of the diffuse part of the reflex may vary with respect to the central spike.[21,22] As shown in Fig. 5, the profile can be fitted by using two broad Lorentzians shifted against the Bragg position for the diffuse shoulder, a constant background and a sharp Lorentzian for the central spike. The latter closely resembles the intensity distribution in case of the clean substrate in those parts of the profile where the shoulder emerges on metal deposition. This might be due to steps or point defects on the oxide film.

For the lowest coverage of 0.25 Å Pt for the diffuse Lorentzians a FWHM of 0.25 Å^{-1} and a shift with respect to the central spike of 0.2 Å^{-1} was found. From this an average distance of the modified areas of approximately 25 Å is calculated according to a simple evaluation procedure for this type of diffuse profiles, which recently has been proposed.[20]

If one further assumes that the modified patches do not contribute to the oxide superstructure spots, as suggested by their uniform attenuation and unchanged energy dependence, their intensity provides a measure for the coverages. In a kinematical approximation, the intensity of the central spikes of the oxide spots are proportional to the square of the oxide coverage.[21,22] Thus one calculates a coverages of approximately 0.5 for the system 0.25 Å Pt/Al$_2$O$_3$ and an average size for modified and nonmodified patches of about 12 Å. It has to be emphasized that, because of the applied one-dimensional kinematical model,[20] these numbers should be considered to be an estimation. Nevertheless, we conclude that the modified areas must be quite small (possibly corresponding roughly to a hexagon of oxygen ions on the surface).

As already mentionend, the width of the diffuse shoulder decreases and the oxide spots usually lose even more intensity upon heat treatment. For low platinum coverages, however, heating to temperatures higher than 800 K results in an increase of intensity. Figure 6 shows this behavior as well as the development of the spot profile upon subsequent annealing. After deposition of 0.25 Å Pt at 100 K, a weak shoulder appears, which increases in intensity if the sample is heated to 300 K. Further annealing leads to a considerable decrease of its width and a loss of the ring-shaped profile. Finally, the diffuse part cannot be separated from the central spike anymore. Simultaneously, the superstructure gains intensity reaching almost its original value after annealing to about 1100 K. Heating to even higher temperatures has been shown to result in a destruction of the oxide film.[6]

Two processes are possible explaining these observations: On the one hand, platinum, possibly as an oxidized species, might be incorporated into the oxide film, leading to a distortion of the oxide superstructure. As with increasing tem-
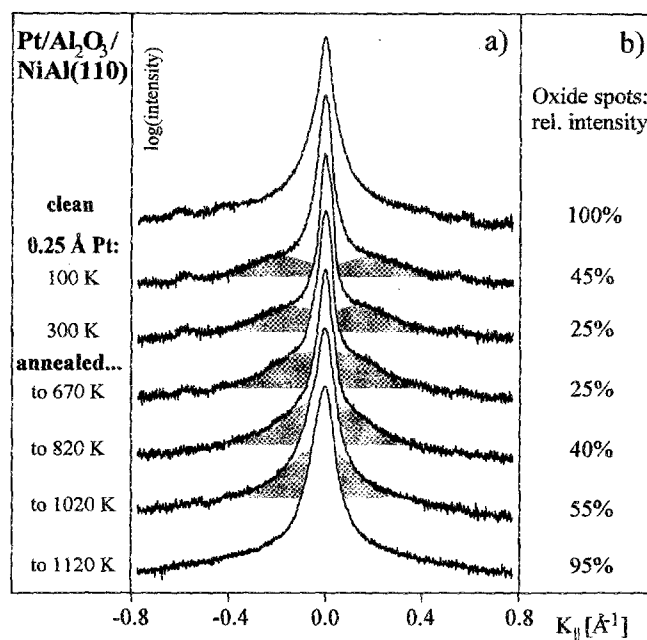

FIG. 6. (a) Variation of the (00)-spot profiles upon heat treatment (65 eV). (b) Relative intensity of the oxide spots with respect to the clean oxide.

perature diffusion becomes faster, the long-range order of the oxide is temporarily destroyed. Moving to higher temperatures, diffusion of platinum through the oxide film into the substrate becomes sufficiently fast. With the platinum being dissolved in the metallic substrate, the superstructure of the clean oxide reappears. On the other hand, a second explanation has to be taken into consideration: The metal may also stay at the surface, forming clusters of increasing size upon heat treatment. This process should lead to larger areas of clean oxide, on which after annealing the superstructure could be formed again.

As no CO adsorption above room temperature can be detected after annealing to 800 K, we favor the first model for the low coverage regime. This interpretation agrees with TD spectra previously reported:[23,13] Besides the CO desorption at a temperature of 350–550 K from metallic platinum, a weakly adsorbed CO species desorbing around 150 K has been found. Since CO desorption from transition metal oxides has been observed in this temperature regime[5,8] this feature has been attributed to Pt species incorporated into the topmost oxide layer.[13] Moreover XPS results suggest the formation of an oxidized Pt species.[11] Therefore, we conclude that diffusion into the oxide is the major process occurring at low coverage. One might speculate that one reason for this behavior might be the defect structure of the oxide providing vacant octahedral sites for embedding Pt ions.

2. High coverage regime

Apart from the very low coverages, where the interaction between the metal and the oxide can be observed, the formation of metal crystallites at higher coverage is of major interest intending to model a supported noble metal catalyst.
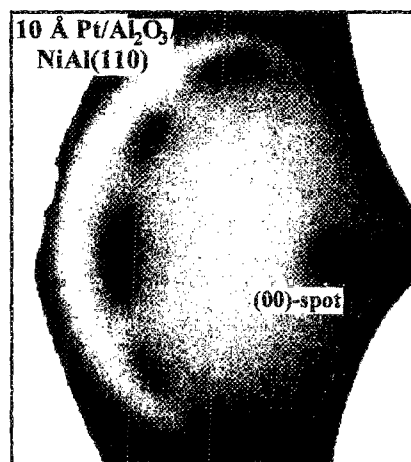
FIG. 8. LEED pattern after deposition of 10 Å Pt at 500 K. Due to the limited scan range of the SPA–LEED instrument in the first diffraction order only a part of the fragmented ring is visible.

As concluded from the attenuation and the broadening of the optical phonons of the substrate observed by HREELS, a two-dimensional growth mode is found at 300 K.[12,13] Nevertheless, upon deposition of several monolayers of platinum at room-temperature LEED revealed no indication for the formation of ordered crystallites so far.[11]

This is different for evaporation of platinum films onto the oxide at elevated temperature. Figure 7(a) shows a comparison of the spot profiles of the (00) reflex for deposition of platinum at 500 K. While in the low coverage regime its intensity rapidly decreases at a coverage of 10 Å Pt an increase is found again. Simultanously, one observes the formation of a diffuse shoulder around the (00) spot which narrows with increasing coverage. After deposition of 10 Å Pt it shows a Lorentzian shape with a FWHM of 0.18 Å^{-1} independent on energy. At the same time a fragmented ring-shaped intensity distribution is observed in the first diffraction order (Fig. 8). The 12 fragments can be interpreted as to be due to the superposition of Pt(111) crystallites, exhibiting two preferential azimuthal orientations. The lattice constant of 2.8 Å calculated from the diffraction pattern perfectly agrees with that of Pt(111) [2.78 Å (Ref. 24)]. Figure 7(b) shows the variation of the relative intensity of the central spike with respect to the integral intensity of the (00) spot as a function of energy. Strictly speaking the relative intensity is plotted against the phase calculated from the step height of a Pt(111) surface (integers correspond to in-phase conditions). The oscillatory behavior points to the existence of monoatomic steps.

These observations are compatible with the formation of small crystallites of platinum growing in (111) orientation with respect to the surface. Their azimuthal orientation is governed by the substrate. As the low coverage experiments reveal, at the same time a metal-oxide interface may be formed by incorporation of metal into the oxide layer.
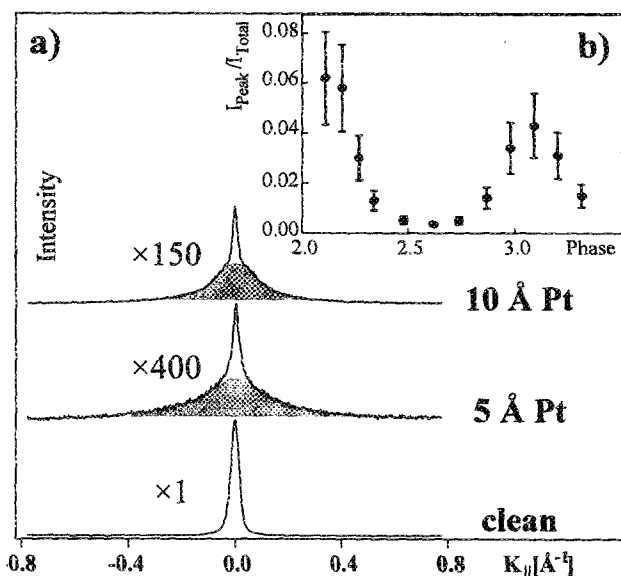

FIG. 7. (a) Development of a diffuse shoulder on deposition of several monolayers of Pt at 500 K (40 eV). (b) Relative intensity of the central spike as a function of the phase calculated for the (00) reflex and monoatomic Pt(111) steps. Integrals correspond to in-phase conditions, i.e., electrons scattered from different height levels interfere constructively.

IV. SUMMARY AND CONCLUSIONS

Platinum was deposited onto a well-ordered alumina film grown on NiAl(110) in order to model a supported noble

metal catalyst. The structural changes induced by the metal can be observed by a LEED spot-profile analysis. At low coverages, the metal exists in a highly disperse state. This results in a destruction of the oxide superstructure with the platinum atoms probably being incorporated into the oxide. At sufficiently high temperatures the metal diffuses through the oxide film into the bulk. Upon deposition of several monolayers of platinum at elevated temperatures, the formation of Pt crystallites with (111) orientation can be observed.

ACKNOWLEDGMENTS

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