ULTRATHIN, EPITAXIAL ALUMINUM OXIDE ON NIAL(110)

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ABSTRACT:

The geometric and electronic structure of ultrathin oxide films grown by oxidation of NiAl(110) was studied by LEED (low energy electron diffraction), EELS (electron energy loss spectroscopy), XPS (X-ray photoelectron spectroscopy) and ARUPS (angle resolved ultraviolet photoelectron spectroscopy). Two different ultrathin aluminum oxide films have been observed which are characterized by a hexagonal arrangement of oxygen atoms. The films are approximately 5 Å thick, most likely consisting of two alternating oxygen - aluminum layers and are oxygen terminated. The second oxide phase shows close similarities with the (111) face of $\gamma - Al_2O_3$ and the (0001) face of $\alpha - Al_2O_3$ respectively.

INTRODUCTION:

Oxides are important materials in a vast range of disciplines. They are often used as insulating materials or as supports for dispersed metal catalysts. In this respect the use of Al_2O_3 is especially widespread. On the other hand the understanding of the geometric and electronic structure of oxide surfaces is only in its infancy. This is partly due to severe charging problems that occur when oxide surfaces are investigated with electron spectroscopic techniques. One has thus tried to grow well-ordered oxides on metal surfaces to avoid these problems. In the case of aluminum this was only partly successful since the oxide films were disordered and did not show epitaxy [1-5]. Recently well ordered oxides have been grown on NiAl(110) [6-8] but a more detailed characterisation with respect to the geometric and electronic structure is still missing.

In this paper we present the results of a combined LEED, EELS, XPS and ARUPS study and propose a structure which is basically that of a distorted hexagonal Al_2O_3 surface with a thickness of two oxygen/aluminum layers and oxygen surface termination.

RESULTS:

Experimental details and the sample preparation have already been described elsewhere [9]. The adsorption of oxygen was followed by LEED both at room temperature and at elevated temperatures (550 - 650 K). At 300 K the following scenario is observed: With increasing oxygen coverage the LEED spots of the NiAl(110) surface are becoming more and more diffuse until at saturation (1200 L) LEED spots of the substrate are no longer visible. This does not only point towards a disordered adsorption but also shows that oxygen destroys the long range order within a region that is at least 5 - 7 Å thick. This thickness is supported by Auger spectra for this structure [8,9]. They show a strong shift of the Al LMM transition typical for the formation of Al^{3+} ions and are thus indicative for the formation of an (aluminum) oxide structure. From the damping of the Al KLL transition at 1396 eV a layer thickness of 5 Å has been deduced [8]. Upon subsequent annealing to 600 K a weak ring with an average radius of 2.36 $Å^{-1}$ is observed and the substrate spots reappear (fig 1.a). Further annealing to 1000 K leads to an increased intensity of the substrate reflexes and splits the ring into six different ring fragments. The ring fragments already show a distinct spot structure. These spots sharpen upon further annealing to 1300 K (fig. 1c). This LEED pattern describes a hexagonal or quasihexagonal overlayer that exists in four different orientations relative to

the NiAl(110) substrate (rotational epitaxy). The lattice constant of this superstructure is 3.07 Å as deduced from the ring diameter. Initially these hexagonal oxide layers show a random orientation with respect to the NiAl(110) surface.

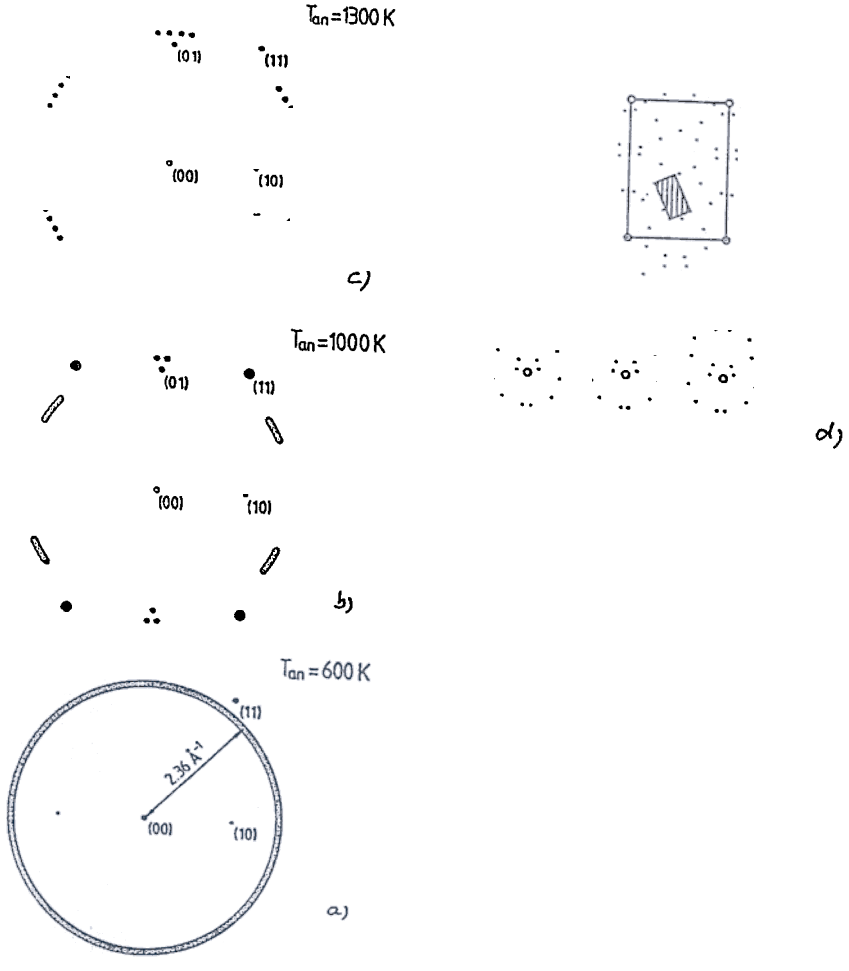

Fig.1: Schematic LEED patterns for oxgen on NiAl(110)
a.) dosed with 1200 L O_2 at 300 K and annealed to T = 600 K
b.) annealed to 1000 K,
c.) annealed to 1300 K,
d.) Leed pattern of Al_2O_3 on NiAl(110) obtained after dosing 1200 L O_2 at T = 550 K and subsequent annealing to 1200 K.

A second LEED pattern (fig. 1.d) is observed after oxygen adsorption of 1200 L O_2 at 550 K and subsequent annealing to 1200 K. This structure is obviously much more complex, i.e. has a much larger unit cell. The LEED reflexes are very sharp indicating that the oxide is well-ordered. The unit cell of this oxide is rather large but the intensity distribution for the superstructure reflexes shows maxima close to the positions of a hexagonal lattice. This indicates that the atomic arrangement within the overlayer is hexagonal or quasihexagonal as for the first oxide film. Please note that the hexagon is now rotated by $\simeq 90°$ as compared with the unit cell of the first oxide. Besides this difference the unit cell of the second oxide structure is much larger as mentioned above. The angle between the two lattice vectors a = 10.55 Å and b = 17.88 Å is 88.7° and the unit cell is rotated by 24° with respect to the substrate mesh. Two different domains can be found due to the C_{3v} symmetry of the substrate. With these two domains all diffraction spots that are visible in fig. 1.d can be explained.

After probing the long range order of the adsorbate film with LEED vibrational properties of the oxide structure were studied with EELS. The same adsorption and annealing sequence that was followed by LEED before was now investigated with EELS. Fig. 2 shows a series of EELS spectra for increasing coverage adsorbed at room temperature. With increasing oxygen coverage the intensity of the elastic peak is decreasing strongly indicating that the surface reflectivity is decreasing. The loss features that are observed after oxygen adsorption are rather broad which points to a disordered adsorption. The frequencies of the different loss peaks show a coverage dependence that is especially pronounced in the initial oxidation stage. Annealing a structure that has been produced by the adsorption of a saturation coverage of oxygen at room temperature leads to an increase in elastic intensity and a sharpening of the loss peaks but the frequencies remain unchanged. This indicates that the surface order is increasing while the local adsorption geometry is uneffected by the annealing procedure.

Interesting enough also the second oxide structure which is produced by oxidation at elevated temperatures shows an almost identical loss spectrum (fig. 2.b). Since the frequency of the oxygen vibrations which we detect in the EELS experiment depends strongly upon bond length and bond angles we can conclude that the local arrangment has to be very similar in both cases. This is in agreement with LEED observations that both oxide structures are characterized by a hexagonal arrangement. An assignment of the observed vibrations should enable us to identify the nature and geometry of the oxide layer. Since almost identical loss spectra have been observed after oxidation of NiAl(111) and Al(111) this supports the identification of the loss spectrum as being due to the formation of a thin aluminum oxide film. Strong and Erskine [4] have compared the spectrum observed for oxygen adsorbed on Al(111) with lattice dynamical calculations and came to the conclusion that the loss at 635 cm^{-1} is due to the perpendicular vibration of surface oxygen bond to the aluminum layer beneath while the loss at 880 cm^{-1} is due to the perpendicular vibration of subsurface oxygen between the first two aluminum layers. This would indicate that the oxide has always an oxygen termination and could also explain why the oxide covered surface is so inert. A more elaborate analysis of the EELS spectra in terms of the electronic state and the geometry of the film appears possible but depends upon the knowledge of a large number of lattice dynamical parameters and is thus beyond the scope of this work.

The electronic state of the oxide film has been investigated by XPS and UPS, too. A comparison between the spectra of the clean surface and a highly oxidized surface shows no evidence for the formation of NiO or $NiAl_2O_4$ whereas the aluminum 2p states are strongly modified due to the formation of aluminum oxide. This shows once more that the film consists of aluminum oxide and does not contain oxidized nickel. This is not surprising since the heat of formation of Al_2O_3 is much higher than the corresponding value for NiO [10].

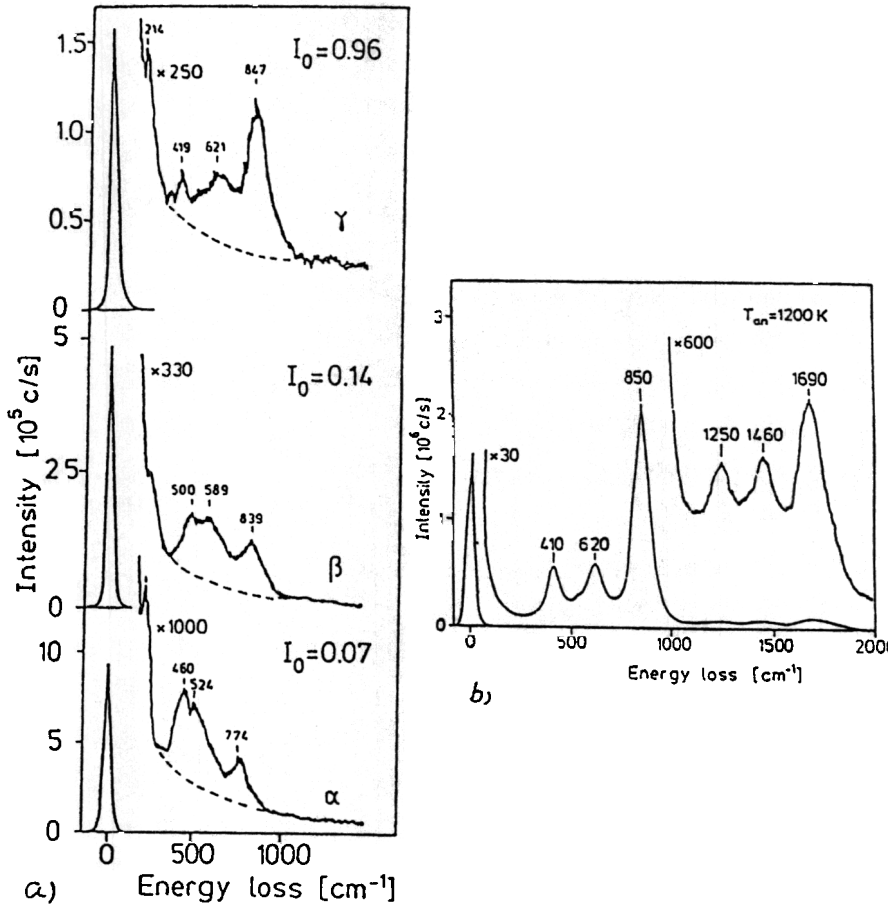

Fig.2 EELS spectra for oxygen on NiAl(110) obtained for different conditions of preparations.
a.) EEL spectra obtained for different exposures at room temperature. The I_0 values are the ratios of the oxygen Auger lines at 512 eV and the Ni Auger lines at 848 eV.
b.) EEL spectrum of the Al_2O_3 film on NiAl(110) with the LEED pattern shown in Fig. 1d.

The next interesting question is whether the oxide film covers the entire substrate. Since the oxidized surface is inert to adsorption of for example CO, contrary to the clean NiAl(110) surface which is rather reactive one can conclude that the whole surface of the NiAl(110) sample is covered by a thin aluminum oxide film. This is supported by the angle resolved photoemission spectra where at glancing incidence the signal from the substrate cannot be distinguished from the noise.

The dispersion of the electronic bands of the thin oxide film was determined from the angle resolved photoemission data. These bands show pronounced dispersions with $k_{\parallel}$ but no dispersions with $k_{\perp}$. This is further support for the assumption that the oxide film is ultrathin

since dispersion with $k_\parallel$ would only show up for bulk-like bands. The band width for $k_\parallel$ closely resembles the value calculated for $\alpha - Al_2O_3$ [11]. Since the band width is mainly determined by the number and distance of nearest and next nearest neighbours we come again to the conclusion that the local arrangment for the oxygen ions in the oxide film closely resembles the oxide structure in $\alpha - Al_2O_3$. On the other hand a hexagonal close-packing of oxygen ions is characteristic for a variety of Al_2O_3 species such as α- and γ- Al_2O_3 and without further band structure calculations we are unable to identify which Al_2O_3 modification is present based upon the measured dispersion.

CONCLUSION: THE STRUCTURAL MODEL

LEED investigations have shown that after adsorption of oxygen on NiAl(110) at different temperatures and subsequent annealing two different well ordered superstructures can be observed. They are due to the formation of an aluminum oxide as shown by EELS and Auger. Even though the sizes of the unit cells are very different for the two oxides they both are characterized by a hexagonal or quasihexagonal arrangement of atoms. A major difference between the two hexagonal oxides is their arrangement on the NiAl(110) substrate. They are rotated by $\simeq 90°$ with respect to each other. The close similarity of the local atomic arrangement is also shown by vibrational spectroscopy. The EELS spectra for the two oxides are almost identical. The vibrational spectrum is typical for a sandwich structure that is composed of alternating aluminum and oxygen layers with an oxygen terminated surface. From the damping of the Al KLL transition at 1396 eV and the angular dependence of the XPS spectra one can conclude that the oxide film is $\simeq 5$ Å thick. This indicates that the oxide film consists of two oxygen and aluminum layers in the sequence oxygen (surface) - aluminum - oxygen - aluminum (interface). The aluminum termination at the interface to the substrate is supported by the absence of any oxygen- nickel interaction as deduced from the UPS spectra. Since a typical Al - O layer distance in different Al_2O_3 species is around 1.1 Å [12] and the distance between the last aluminum layer of the oxide and the first NiAl layer of the substrate should be at least 1.2 Å we obtain a film thickness of $\simeq 4.5$ Å. This is in close agreement with the measured value. After describing the number of layers and their stacking sequence the last question is: How are the atoms arranged within the oxide layers? It was already mentioned that the two different oxide films show a hexagonal arrangment of oxygen atoms.

In the case of the hexagonal structure (phase I) it is not to difficult to obtain a structural model. The oxygen - oxygen distance has been determined to be 3.07 Å from the ring diameter in the LEED pattern. The orientation of the hexagon with respect to the substrate can be determined from the LEED pattern in fig. 1.c. It should be noted that the oxygen-oxygen distance is larger than the average value in most Al_2O_3 modifications which lies between 2.75 and 2.85 Å. In the case of the second phase the situation is slightly more complex since it is difficult to determine the oxygen-oxygen distance from the LEED pattern precisely. On the other hand the size of the unit cell can be determined precisely to 188.7 Å^2. Assuming an oxygen termination of the oxide with a hexagonal arrangement of oxygen atoms we obtain a structure that resembles the (0001) termination of $\alpha - Al_2O_3$ or the (111) termination of $\gamma - Al_2O_3$ respectively. Under these very probable assumptions there is only one possibility to obtain the observed LEED pattern for the second oxide phase by a slight modification of the oxygen-oxygen distance in the oxide film. This leads to an oxygen-oxygen distance of 3.01 Å in close agreement with the value of 3.07 Å observed for the first oxide phase. The corresponding structural model is shown in fig. 3 and closely resembles the oxygen terminated (0001) face of $\alpha - Al_2O_3$ [12]. A similar structure is obtained by an oxygen terminated (111) face of $\gamma - Al_2O_3$. Interesting enough also in this case the oxygen-oxygen distance is enlarged as compared to the average distance in the bulk (2.75 Å) [12]. This indicates that an enlarged oxygen-oxygen distance is a property of both thin oxide films and might rather be a general

feature of ultrathin ionic films since the average Madelung energy in a thin ionic film seems to be reduced as compared to the bulk.

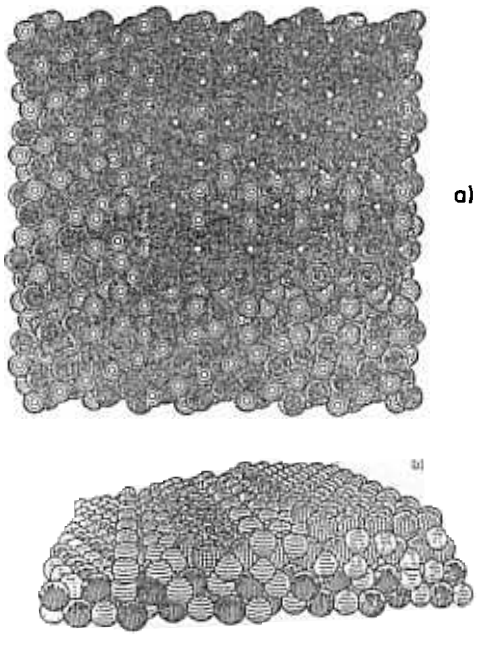

Fig. 3: Structure model for $\alpha - Al_2O_3$ (0001)/NiAl(110)
a) top view and b) side view. Longitudinally and lattitudinally striped and chequered circles denote nickel, aluminum and oxygen atoms respectively. The unit cells of the NiAl(110) surface and the oxide cell are denoted by a small and a large rectangle.

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