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Structure and defects of an ordered alumina film on NiAl(110)

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Abstract

Via oxidation a well ordered Al_2O_3 film may be grown on an ordered NiAl(110) surface. Its structure has been studied with SPA-LEED (spot-profile analysis) as well as with scanning tunneling microscopy (STM). The oxide overlayer grows strictly two-dimensional with a thickness of close to 5 Å. Double diffraction spots have been observed but they are very weak, thus not excluding the existence of an interfacial layer between NiAl(110) and the oxide film. STM provides preliminary evidence for such a film and presents first clues to what the structure of the interface may be.

The defect structure of the Al_2O_3 film has been investigated. In addition to boundaries between two rotational domains constituting the Al_2O_3 film, we also identify anti-phase domain boundaries through both the SPA-LEED as well as the STM measurements.

1. Introduction

The transition phases of alumina represent a group of technically important support materials in heterogenous catalysis [1]. In order to provide a more detailed understanding of the adsorption behaviour and the catalytic properties of dispersed metal catalysts as well as the function of the support, several studies on model systems have been performed [2,3]. Serious complications may arise from the polycrystalline or amorpous structure of several aluminium oxide samples [1] or aluminium oxide films grown on aluminium single crystals [4-8]. Obtaining insight on a molecular level into the processes occurring on these complex systems becomes even more difficult, if one has to deal with a highly defective and less well-defined surface structure.

The catalytic properties of dispersed metals supported on various oxides are often modified by the support [1]. Obviously, the interaction between the oxide and the metal plays a major role in determining the chemical behaviour of these systems. Studying these effects is much easier on structurally well-defined and well-ordered surfaces. This is not only due to the simplification concerning the interpretation of experimental data, but also due to the applicability of several structure sensitive experimental methods. For ex-

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ample, AFM and STM have been applied to ordered alumina surfaces and metal deposits [9,11]. Furthermore, as we have shown recently, defects induced by metal deposition onto the ordered $Al_2O_3/NiAl(110)$ can be monitored by LEED spot-profile analysis [12].

In principle, there are two possible ways of preparing well-ordered oxide surfaces: the first is to use oxide single crystals. This method usually has the advantage that surfaces with low defect densities can be obtained [2]. The second way of obtaining well-ordered surfaces is by epitaxial growth of oxide films on metal single crystals [13–17]. Epitaxial oxide films offer various advantages and opportunities, e.g. charging is avoided when using electron spectroscopic methods, the sample can be cooled efficiently, and different surface structures can be prepared, which might not be available on single crystals [16–18].

The ordered Al_2O_3 film grown on NiAl(110) combines the advantages of a thin film with a high degree of order [10,15]. Furthermore, HREEL spectra point to a structure which is comparable to γ -Al₂O₃ [15], one of the transition phases of alumina used as a support in technical catalysis. Clearly, detailed investigations on the structure and chemical properties of such a film are necessary before it may be used as a model support. Thus, we have characterized the geometric and electronic structure of the film by LEED, ISS, ARUPS, XPS and EELS [15,10,11,18]. The adsorption behaviour has been probed by TDS and EELS [19]. The most important features of the structure model, which was proposed on the basis of these investigations, may be summarized as follows [15]: the atomically flat film has a lavered structure with a thickness of about 5 Å, corresponding to about two layers of oxygen and aluminium ions. As shown by ISS, the surface is oxygen-terminated. LEED and band structure measurements point to a distorted hexagonal arrangement of the first layer. As already mentioned, the three phonon losses observed in HREELS indicate a γ -Al₂O₃-like rather than a α -Al₂O₃-like structure.

In this paper the results of recent studies by STM and SPA-LEED (spot-profile analysis) are reported concerning the structure of the substrate-oxide interface, the growth and the defect structure of the oxide film. Also, we have started to investigate the growth, adsorption behaviour and catalytic properties of metals deposited onto such a film. First results have been published elsewhere [12,18,20]. In particular, STM experiments on $Al_2O_3/NiAl(110)$ have shown that indeed stable tunneling conditions can be achieved [20]. The application of STM to a thin insulating surface is therefore useful and will provide information on both its structural and electronic properties.

2. Experimental

The experiments have been performed in two different ultrahigh-vacuum (UHV) systems. One was equipped with a SPA-LEED system (Leybold) [21] with a specified transfer width of more than 800 Å. The NiAl(110) single crystal was mounted between two tantalum wires, which were spotwelded to two tungsten rods. As defective areas near the crystal edges might influence the spot profile, the crystal was placed behind a graphitecoated copper aperture during the measurements. It was possible to cool the sample to temperatures below 100 K by a liquid nitrogen reservoir. The crystal was heated by radiation from a filament mounted behind the crystal or by electron bombardment. The NiAl(110) surface was prepared by several cycles of sputtering and subsequent annealing as reported elsewhere [15]. The cleanliness and composition of the surface was checked by Auger electron spectroscopy (AES) and ion-scattering spectroscopy (ISS). For the LEED spot-profile measurements the fullwidth at half-maximum (FWHM) of the NiAl(110) spots was determined by the mosaic spread of the crystal, which was calculated to be about 0.15° . This effect limits the effective transfer width within an energy range of 60 to 100 eV to a value of approximately 300 to 200 Å.

The preparation of the ordered Al_2O_3 film was performed as reported in the literature [15]. After dosing 1200 L O₂ at elevated temperatures and annealing to 1150–1200 K for five minutes, the well-ordered oxide film forms. As previously reported, it can be checked via CO-TDS (thermal desorption spectroscopy of CO) whether the surface is completely oxidized [18,22]. The method uses the fact that CO does not adsorb at temperatures above 90 K if the Al_2O_3 film covers the whole surface.

The STM images were measured in a second UHV system, which was equipped with additional surface analytical tools for LEED, AES and ISS. Details of the STM instrumentation have been described elsewhere [23]. A second NiAl(110) crystal has been used here. It was mounted on a Ta plate and treated in the same way as described above to grow the epitaxial Al oxide film. The LEED pattern of the oxidized surface qualitatively agreed with that obtained in the SPA-LEED experiments. The STM images were acquired in the form of constant-current topographs (CCTs). The influence of the oxide electronic structure on the results was explored by varying the sample bias voltage U. Since Al_2O_3 is a wide band-gap (8 eV) insulator [24] tunneling into empty or from filled states of the oxide film is only possible by using a sufficiently large sample bias voltage. If we assume the Fermi level $E_{\rm F}$ to be located near the center of the band gap,

direct electronic contributions from the oxide are only expected for $U \le -4$ V or $U \ge 4$ V.

Note that in this work the polarity of U is given with respect to the sample, i.e., negative Uleads to tunneling from the filled states and positive U to tunneling into the empty states of the sample. In principle for -4 V < U < 4 V only contributions to the tunneling current from the metallic substrate electrons are possible. This means that in this range of U an imaging of structural properties of the oxide film is only possible through a local variation of the tunneling barrier as defined by the charge distribution of the oxide film. Since several layers of Al and O ions are contained in this film and the projection of their charge density normal to the surface determines the tunneling barrier, we do not expect atomic resolution due to the oxide structure in this case. On the other hand, if we do see atomic features at low values of U it is more plausible to assign them to the metallic substrate. It is expected that the averaged electronic states of the oxide layer will give rise to additional large-scale modulations in the CCTs. In our previous work [20] we have already demonstrated that electronic contributions from the oxide film



Fig. 1. Dimension of the $Al_2O_3/NiAl(110)$ unit mesh and orientation with respect to the substrate in real space (a) and reciprocal space (b).

are recognized by a measurable height change of the tip upon scanning of an oxide island for large sample bias voltage (U = 4 V) in contrast to small U allowing only tunneling from substrate electrons through the oxide islands where we did not see a height change of the tip.

3. Results and discussion

3.1. Structure

3.1.1. LEED

The LEED pattern of the ordered alumina film, which forms at the preparation conditions given above, has previously been reported by Müller et al. [10]. The unit mesh of the superstructure was determined to be rather small and nearly rectangular. The unit mesh vectors of the superstructure in real space are given by [10]:

Domain A:
$$\begin{pmatrix} \boldsymbol{b}_1 \\ \boldsymbol{b}_2 \end{pmatrix} = \begin{pmatrix} 3.37 & -1 \\ 2.53 & 4 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{a}_1 \\ \boldsymbol{a}_2 \end{pmatrix},$$

Domain B: $\begin{pmatrix} \boldsymbol{b}_1 \\ \boldsymbol{b}_2 \end{pmatrix} = \begin{pmatrix} -3.37 & -1 \\ -2.53 & 4 \end{pmatrix} \cdot \begin{pmatrix} \boldsymbol{a}_1 \\ \boldsymbol{a}_2 \end{pmatrix}.$

Here $\boldsymbol{b}_{1,2}$ are the superstructure unit mesh vectors and $a_{1,2}$ are the unit vectors of the NiAl(110) unit mesh as indicated in Fig. 1a. Due to the substrate mirror planes two superstructure domains exist. According to Fig. 1a, they will be denoted as domain A and B, respectively. Length and orientation of the unit cell vectors in reciprocal space are given in Fig. 1b. Obviously, the oxide superstructure is commensurate with the substrate along the $[1\overline{10}]$ direction of the NiAl, whereas along [001] it is incommensurate. Although superstructure and substrate spots do not coincide along [001], it has been possible to determine the unit mesh vector components with unusual high accuracy [10]. This was due to the large number of sharp superstructure spots, nicely developed up to high diffraction orders. Thus, it was possible to determine the unit mesh by computer simulation of the diffraction pattern and comparison of characteristic spot ensembles with the corresponding areas of the measured LEED pattern.



Fig. 2. LEED pattern of the clean NiAl(110) surface (130 eV) (a) and the well-ordered Al_2O_3 film on NiAl(110) (110 eV) (b). The insets show the I/V-spectra of the NiAl (10)-spot, which does not coincide with the oxide superstructure, before and after oxidation.

It should be noted that even after complete oxidation those substrate spots which do not coincide with the superstructure are still visible. Here it is necessary to check first, whether the surface is completely covered with oxide. Upon incomplete oxidation, large oxide-covered terraces are found next to non-oxidized NiAl terraces [20]. As previously reported, the oxide coverage can be checked by CO-TDS [18,22]. While above 90 K no CO adsorbs on the oxide [19], desorption from non-oxidized NiAl(110) takes place at around 300 K [25].

Fig. 2 shows the LEED pattern of the NiAl(110) before and after preparation of the oxide film. The corresponding I/V spectra of the

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(10)-spot of the NiAl(110) are displayed in the insets. This spot does not coincide with the oxide superstructure spots so that the intensity scattered into this spot exclusively originates from the substrate lattice beneath the oxide. The position of I/V minima and maxima does not change significantly, while the scattered intensity is strongly attenuated, especially at lower energies. After oxidation, relative spot intensities with respect to the clean surface between approximately 8% (70 eV) and 16% (130 eV) are calculated for the observed intensity maxima. In consideration of the scattering geometry this corresponds to an oxide layer thickness of 2.4 λ (70 eV), or 1.8 λ (130 eV), respectively, in terms of the electron mean free path λ . This value is compatible with an oxide thickness of approximately 5 Å roughly corresponding to two layers of oxygen and aluminium ions. But as there are no exact values available for the electron mean free path, the existence of an additional metallic interlayer which is commensurate with the oxide superstructure cannot be excluded.

Because of the incommensurability of the oxide film along [001], double diffraction spots originating from diffraction at both the oxide superstructure and the NiAl substrate are expected to exist. Nevertheless, such additional spots have not been observed in previous studies [10,15]. As a consequence of the high dynamic range of the SPA-LEED instrument, it has now been possible to identify several of those double diffraction spots. Fig. 3 shows a close up of the LEED pattern around the (00)-spot as well as around the NiAl $(0\overline{1})$ -spot. The oxide reciprocal lattice is indicated by dotted lines. Upon close inspection, it becomes evident that several additional spots appear. By comparing the spot positions to a diffraction pattern, calculated on the basis of the oxide unit mesh given above, all those additional spots can by identified as double diffraction spots with respect to first-order NiAl spots.

Because of the missing double diffraction spots, it was proposed that there should exist an additional interlayer with a periodicity closely related to the oxide superstructure [10,15]. This should lead to a strong attenuation of the intensity back-scattered from the substrate beneath. It re-



Fig. 3. Close-up of the surroundings of the (00)-spot (a) and the NiAl (10)-spot (b) (80 eV). Several additional weak spots due to double diffraction appear, which do not coincide with the oxide lattice indicated.

mains a fact that the observed double diffraction spots are rather weak. This observation as well as the degree of attenuation of the substrate spots already mentioned still seems compatible with an interlayer, as long as its thickness does not exceed about one atomic layer. In the following section STM results are presented which, in consideration of the LEED data, indicate the existence of such an interlayer.

3.1.2. STM

We first start with a description of the results which we obtained for large sample bias voltages U on the fully oxidized sample. In Fig. 4 a CCT is reproduced where two systems of straight lines are recognized. They are inclined by approximately 20° against the [001] direction (as determined on a clean substrate surface, see dashed line) and obviously form two domains of the oxide structure. In both domains a pairing of the lines is visible. Since the distance between the pairs of lines is found to be 18 Å which is in very good agreement with the size of the oxide unit cells in this direction (17.9 Å), the line systems directly reflect the structure of the oxide film. Comparing the observed orientation of the lines with Fig. 1, we may assign the lower part to domain A and the upper part at the right top corner to domain B. The oxide unit cells are indicated in the figure by small rectangles. Note that the total inclination between the two domains is measured to be 42°. The difference to the ideal value (48°) as derived from the LEED pattern may be explained by drift effects during the STM measurements and deviations from the



Fig. 4. CCT from oxidized NiAl(110) obtained with U = 4 V, I = 0.5 nA. The area is 300×190 Å². The unit cells of the oxide layer in domains A and B are shown by dashed lines.



Fig. 5. CCT from oxidized NiAl(110) obtained with U = -2 V, I = 0.5 nA. The area is 210×130 Å². The unit cells of the oxide layer in domains A and B are shown by the dashed lines.

ideal geometry of the xyz piezoelectric scanning system. The corrugation perpendicular to the lines is 0.1-0.2 Å.

If we use a negative sample bias voltage (U =-2 V, see Fig. 5), we observe a regular and nearly hexagonal arrangement of slightly elongated units (blobs), instead of a line pattern, which apparently also form two domains as indicated by A and B. If we assume that the elongation of these blobs is reminiscent of the line pattern shown in Fig. 4, the oxide unit cells are located on the surface as indicated in the figure. Their measured size $(10 \times 19 \text{ Å}^2)$ again is in agreement with the expected value. As inclination of the domains we find 45°, consistent with the LEED value of 48°. The blobs apparently form a kind of centered structure. Their distances in the order of 10 Å, however, seem to be too large to be directly compatible with the distances of subunits in the model proposed by Jaeger et al. [15]. We note that all steps which we have found on the oxidized surface (see, for example, near the right bottom corner of Fig. 5) have a height of approximately 2 Å which corresponds to a monatomic step of the NiAl(110) substrate. We have never observed a step which we could assign to the growth of a second oxide layer. The growth of the oxide film under the used conditions is entirely two-dimensional.

Using large sample bias voltages, as we have chosen for the measurements shown in Figs. 4 and 5, produces CCTs where both structural and electronic properties of the oxide film may be derived. However, under these conditions atomically resolved features are generally lacking in the results probably due to an increased sample-tip distance and simultaneous loss of resolution. We have therefore also studied the oxidized surface by using small sample bias voltages U, where the oxide electrons cannot directly contribute to the tunneling current but only indirectly by modulating the local potential barrier between tip and metallic substrate. We indeed found an improved resolution under these conditions. However, the observed patterns always turned out to be rather complicated and obviously showed influences of both the oxide and the substrate structure which could not be differentiated in a simple way. Two of the CCTs obtained in the range of small U will be described and discussed in the following paragraphs.

In Fig. 6 an image acquired with U = 30 mV is shown. The most obvious features of the measurement are small and distinct protrusions (e.g., at \times) which are regularly spaced on the surface. Obviously, their distribution directly reflects the



Fig. 6. CCT from oxidized NiAl(110) obtained with U = 30 mV, I = 4 nA. The area is 180×200 Å². A unit cell of the oxide layer is indicated by the dashed lines.

unit cell mesh (domain A) of the oxide film. One unit cell has been marked on the surface. The dashed line corresponds to [001]. The relative orientation and the size of the unit cell again are consistent with the previous analysis. The origin of the protrusions is possibly related to a particularly large tunneling probability. A second structural element of the CCT is a somewhat diffuse blob which sometimes is seen around the distinct protrusions and on other positions. These blobs essentially show the same nearly hexagonal arrangement as in Fig. 5 and therefore seem to be a genuine structural element of the oxide film.

As a second example for the range of small Uwe have reproduced a measurement obtained at U = -1 V (Fig. 7a). The resolution appears to be rather good and allows imaging of individual protrusions with a typical lateral separation of 3 Å. The entire pattern is very complicated. To understand the essential features of the image more easily we have plotted a pattern which shows the arrangement of the measured protrusions in an idealized form (Fig. 7b). The idea of the scheme is that in the measured CCT rows of atomic features are recognized (see dashed lines) which closely resemble the substrate lattice. This can be seen more clearly if one looks onto the image from the left or the right bottom corner along the [001] and $[1\overline{1}0]$ directions, respectively, which have been determined from a measurement of the clean substrate surface. If we now assume that the CCT reproduced in Fig. 7a results from a substrate layer where a number of atoms are regularly displaced (indicated by the filled circles) from their original position (dashed circles), we are able to describe the essential features of the measurement. In particular, we do see that the filled circles follow lines which are inclined by 20° against the [001] direction. The distance between these lines (19 Å) and their periodic structure again agree with those expected from the presence of the oxide unit cells.

It is tempting to assign the majority of the atomic features to undistorted rows of atoms on ideal NiAl(110) if we assume that only one kind of atomic species (probably Al atoms) is imaged by the tunneling tip. The unit cells of the substrate and the oxide lattice are displayed by parallelograms. Note that deviations from rectangularity may be caused by the above-mentioned experimental imperfections of the system. If we compare our model which describes the essential features of the measurement satisfactorily with the position of the unit cell as expected from the



Fig. 7. CCT from oxidized NiAl(110) (a). U = -1 V, I = 1.5 nA; the area is 90×90 Å². (b) Schematical representation of (a). (c) Oxide unit cell atop of ideal NiAl(110) (dashed lines) and as experimentally found on the CCT (full lines).

LEED analysis, we find an interesting discrepancy. In Fig. 7c we have plotted the oxide unit cell as derived from LEED by the dashed lines and that of the STM experiment by the full lines. While the right lower edge of the "LEED" oxide unit cell is approximately located on a bridge position, the STM measurement suggests to place it in an atop position. This discrepancy can only be explained if we assume that the visible rows of atomic structures seen in Fig. 7a are distinctly compressed as compared to their positions on the uncovered substrate. Moreover, they are not located on a rectangular lattice, see top part of Fig. 7c. Such an assumption may not be unreasonable since a strong interaction between the substrate and the oxide overlayer is certainly present as may be concluded from the two-dimensional nature of the oxide film growth. Anyway, the atomic features seen in this image probably have to be associated with those of the uppermost metallic substrate layer whose positions are distorted by the presence of the oxide film and thereby contain structural elements of the oxide. It has therefore become possible to image the metallic interface layer through the oxide film.

3.2. Growth and defects

3.2.1. LEED

In the previous section it has been shown that the oxide film forms an atomically flat overlayer with a low defect density. In particular, a major part of the large substrate terraces is completely covered with an oxide film of either domain A or domain B. Consequently, the LEED reflex profiles of the oxide superstructure are expected to exhibit a FWHM which is only slightly enlarged with respect to the width of the substrate spots.

A closer inspection of the profiles reveals that this is the case only for a part of the superstructure spots. Fig. 8b shows the profile of the broadened (12)-spot of domain B and the corresponding (11)-spot (Fig. 8a) which shows almost no broadening. This broadening or splitting of certain spots indicates that in addition to the formation of different domains A and B a further defect structure forms during the process of oxide growth: boundaries between anti-phase domains, i.e. domains which are only laterally shifted with respect to each other.



Fig. 8. Spot profiles of oxide superstructure spots of domain B (85 eV): (A) (11)-spot, near in-phase position, 0.12×0.12 Å⁻²; (B) (12)-spot, near out-of-phase condition, 0.14×0.14 Å⁻².



Fig. 9. (a) Schematic representation of the FWHM along $[1\overline{10}]$ of the oxide superstructure spots of domain B at 85 eV. (b) FWHM of the oxide superstructure spots given in (a) plotted as a function of the component of the parallel scattering vector along $[1\overline{10}]$.

Fig. 9a shows a schematic representation of the FWHM of superstructure spots (domain B) along NiAl[110]. The width of the spots in this direction strongly depends on the parallel scattering vector, whereas along NiAl[001] such a strong effect cannot be found. If the FWHM is plotted as a function of the component of the parallel scattering vector along [110], a characteristic oscillation is observed (see Fig. 9b). On the other hand, upon variation of the perpendicular component of the scattering vector, i.e. the electron energy, the profiles remain almost unchanged. Therefore, it is obvious that the domains can only be laterally shifted with respect to each other.

Comparing the profiles of broadened spots (near the out-of-phase position) for different preparations, it is found that the direction of broadening always occurs nearly, but not exactly along the $[1\overline{10}]$ direction of the substrate (see Fig. 8b). This can be understood considering STM

results which are presented in the following section: there are two types of boundaries, one (denoted as type A) running along the [01] direction of the oxide (i.e. the rows visible in Fig. 4) and a second one which encloses an angle of about 40° with respect to the first type (denoted as B). Frequency and distribution of these boundaries determine the exact direction of broadening and the shape of the out-of-phase profile in Fig. 8b. i.e. whether a splitting or only a broadening can be observed. Small differences between different preparations can be explained, if we consider the remaining defect density of the substrate surface before oxidation, i.e. step density and impurities, which can be expected to be an important factor regarding the formation of the domain structure.

With respect to a quantitative description, the LEED profiles contain information concerning the direction of the domain boundaries, the domain length distribution and the displacement distribution between adjacent domains. We have already discussed the first point and will therefore continue with an estimation of the density of domain boundaries. Along the [001] direction of the substrate a higher degree of order exists. The spots show almost no broadening along this direction should be in the range of the effective transfer width (200 to 300 Å) or larger.

The mean domain length along [110] can be determined within the kinematic approximation from the spot profiles in out-of-phase condition. As in our case the variation of the scattering phase is restricted to discrete spot positions, those spots closest to an out-of-phase condition have to be used. Apparently, one of these spots is the $(\overline{12})$ reflex of domain B displayed in Fig. 8b. Integrating this two-dimensional profile along [001] yields a one-dimensional spot profile which corresponds to a one-dimensional pair-correlation along $[1\overline{1}0]$. A profile analysis of the splitted spot can be performed following an evaluation procedure recently proposed by Wollschläger and Henzler [28]. An additional constant broadening mainly due to the mosaic spread has to be taken into account, which is superimposed on all profiles and can be determined from the (00) spot. Finally, average domain lengths along [110] of

approximately 120 ± 20 Å were found for those preparations where a splitting of the out-of-phase profiles was clearly visible.

Fig. 10 shows line scans along the NiAl $(1\overline{10})$ direction for one row of oxide superstructure spots, indicated in the upper plot. Upon variation of the parallel scattering vector along this row a characteristic behaviour is observed: near the out-of-phase condition the spots start to split asymmetrically. In case of macroscopically misoriented surfaces with sharp terrace length distributions this type of spot profiles is frequently observed as a function of energy, i.e. the perpendicular scattering vector [26]. Here, as we are dealing with exclusively lateral displacements, it is found to be a function of the parallel scattering vector. However, this is characteristic for a distribution of displacements between adjacent domains, where there is more or less only one particular displacement dominating.



Fig. 10. Line scans along $[1\overline{10}]$ for a certain row of superstructure spots of domain B indicated above (85 eV).



Fig. 11. Antiphase boundaries of oxide domains belonging to the A type. U = 4 V, I = 0.5 nA; the area is $500 \times 500 \text{ Å}^2$.

Assuming only one particular lateral displacement between adjacent domains the spot profiles were calculated within the kinematic approximation [27,28]. A good agreement was found for a lateral displacement of 3.6 ± 0.3 Å along NiAl[110].

3.2.2. STM

The existence of antiphase boundaries and antiphase domains in both domains A and B has also been confirmed by STM. In Fig. 11 a CCT has been reproduced which reveals the characteristic line structure of oxide unit cells in A domains. As additional features protruding walls are recognized in the image. Some of them (the broader ones) directly run parallel to the line structure of the oxide film (e.g., at X) and others appear to be more irregular and approximately follow the diagonals of the unit cells (e.g., at Y). A more close examination shows that the oxide lines in the various regions are slightly shifted against each other by a fraction of the line separation which is consistent with the value of about 3.6 Å derived from the SPA-LEED analysis.

An overview image on a large terrace (Fig. 12) shows the general distribution of the domains as



Fig. 12. Overview image of a large terrace of oxidized NiAl(110). The protruding lines correspond to the domain boundaries. U = -8 V, I = 0.5 nA; the area is 2500×2500 Å².

may be inferred from the pattern of protruding walls. In this case the individual lines of the oxide layers are no more resolved, however, their orientation can be determined in most cases by the width and the straightness of the protruding walls. The majority of the domains belong to the A type, B domains are also recognized as is representatively indicated by the labels A and B. The average domain size is 120 ± 60 Å for the shorter and 520 ± 290 Å for the longer edges of the domains. They are preferentially elongated into the [001] direction which agrees well with the SPA-LEED analysis where the spot broadening is smaller in this direction.

4. Conclusions

We have investigated the structure of a thin Al_2O_3 film grown via oxidation of a clean NiAl(110) surface. The thickness of the strictly two-dimensional oxide film is close to 5 Å and consists of two aluminium-oxygen double layers. In the present study, weak, but clearly identifiable double diffraction spots have been observed. The low intensity of the double diffraction spots

is compatible with the presence of an interfacial layer between the NiAl(110) substrate and the oxide overlayer. By changing the tunneling voltage from high absolute values, where tunneling between tip and oxide dominates, to low values, where the substrate electrons are involved in the tunneling process, we have been able to preliminary identify such an interfacial layer and in addition present an educated guess about the structure of this interfacial layer.

Also, by a combination of SPA-LEED and STM techniques, we have investigated the defect structure of the Al_2O_3 film. We identify rotational domains and present additional evidence for the existence of antiphase domains in the film. They are deduced from the oscillatory increase and decrease of spot-width as we move through the Brillouin zone as well as by direct imaging with STM.

The findings of the present study will be of importance to the study of metal deposition onto oxide films.

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