Stabilizing CrO by epitaxial growth
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Chapter 3

$NO_2$ assisted chromium oxides growth

3.1 Introduction

In a first attempt to prepare chromium monoxide, $NO_2$ assisted MBE is used and this chapter discusses the preparation and characterization of the grown thin films.

$NO_2$ is a strong oxidizing agent with the same capabilities as $O_3$ or oxygen plasma, as known from studies of the growth of high $T_c$ superconducting oxide films [1–3]. $NO_2$ proved to be a very efficient oxidizing agent in preparing $NiO$ and $CoO$ thin films on $MgO(100)$ substrate [4], $MgO$ thin films on $Ag(100)$ substrate [5], and iron oxide on $MgO(100)$ or $Al_2O_3(0001)$ substrates [6] [7] [8]. Moreover, $NO_2$ has the practical advantage that is directly ready to use from a bottle, no plasma nor ozone generators are needed.

In the figure 3.1 we show one of our first attempts to grow $CrO$ on a $MgO(100)$ substrate. It can be clearly seen that we were able to find quickly the proper conditions to obtain a layer by layer growth using $NO_2$ as oxidizing agent, as demonstrated by the pronounced and continuing RHEED oscillations. Moreover, we were also able to grow a $MgO$ cap layer epitaxially on top of this chromium oxide film.

In this chapter we discuss the $NO_2$ assisted MBE growth of chromium oxides using $MgO(100)$ and $SrTiO_3(100)$ substrates. A sapphire substrate is used for growing a reference $Cr_2O_3$ sample. The characterization of the grown samples is done by RHEED, LEED and XPS in situ, followed by RBS, XRD and XAS ex situ. We will study in particular the issue of stoichiometry and nitrogen uptake.

In the iron oxide studies it was shown that all the iron oxide phases can be induced by $NO_2$ assisted MBE, but with the complication that at low $NO_2$ fluxes phases are formed in which oxygen is partly substituted by nitrogen. The amount
of nitrogen in the samples increases nearly linear with decreasing $NO_2$ flux. A speculative model for the nitrogen uptake during growth was proposed in which it is assumed that $NO_2$ molecules dissociate at the growing surface into atomic oxygen and molecular $NO$. The iron reacts first with all the available atomic oxygen and then it starts to consume the $NO$. Only in the low flux cases a rocksalt-like structure is obtained for the films grown on $MgO(100)$, as one would expect for the wustite phase ($Fe_{1-x}O$), and the composition of the layers is found to be $Fe_{1-x}O_{1-y}N_y$.

### 3.2 Sample preparation and experimental

The stoichiometric phase of chromium monoxide is that for which Cr and O atoms have equal concentrations, and will be denoted by $CrO$ in this thesis. Substoichiometric phases, labelled $Cr_xO$ where $x < 1$, contain vacancies in the chromium sublattice. We will assume that the oxygen lattice is complete. The reference sam-
3.2 Sample preparation and experimental

samples used to determine the stoichiometry of the grown films are \( Cr_2O_3 \) grown on \( Al_2O_3(0001) \) and \( Cr_2O_3 \) single crystal cleaved \textit{in situ}.

The stoichiometry of the chromium monoxide is expected to be a function of three parameters: the oxidizing agent flux, the metal flux and the substrate temperature. In the case of \( NO_2 \) - assisted growth, for \( MgO(100) \) substrates, the metal deposition rate was set at about 1.3\( \text{Å/min} \) and the substrate temperatures used were: 300\( ^\circ \)C and 400\( ^\circ \)C, values which we found to be the best for the sample deposition. The \( NO_2 \) flux, which is proportional to the buffer volume pressure \( (P_{\text{buf}}) \), was varied systematically.

We list in the following table the \( P_{\text{buf}} \) used and the corresponding background pressures in the growth chamber \( (P_{\text{chamber}}) \). Note that the base pressure in the growth chamber was \( 1 - 2 \times 10^{-10} \) mbar.

<table>
<thead>
<tr>
<th>( P_{\text{buf}} ) (mbar)</th>
<th>( P_{\text{chamber}} ) when staring the growth (mbar)</th>
<th>( P_{\text{chamber}} ) after 25 min. of growth (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75 \times 10^{-1}</td>
<td>3 \times 10^{-9}</td>
<td>1.1 \times 10^{-8}</td>
</tr>
<tr>
<td>1 \times 10^{-1}</td>
<td>6 \times 10^{-9}</td>
<td>2 \times 10^{-8}</td>
</tr>
<tr>
<td>1.25 \times 10^{-1}</td>
<td>8.8 \times 10^{-9}</td>
<td>3.5 \times 10^{-8}</td>
</tr>
<tr>
<td>1.5 \times 10^{-1}</td>
<td>9 \times 10^{-9}</td>
<td>3.9 \times 10^{-8}</td>
</tr>
<tr>
<td>2 \times 10^{-1}</td>
<td>1.4 \times 10^{-8}</td>
<td>8.5 \times 10^{-8}</td>
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<tr>
<td>3 \times 10^{-1}</td>
<td>2.8 \times 10^{-8}</td>
<td>1.7 \times 10^{-7}</td>
</tr>
<tr>
<td>4 \times 10^{-1}</td>
<td>3.5 \times 10^{-8}</td>
<td>2.7 \times 10^{-7}</td>
</tr>
</tbody>
</table>

The "\( P_{\text{chamber}} \) when starting the growth" was read before opening the Cr K-cell shutter, just after the \( P_{\text{buf}} \) of \( NO_2 \) gas was set to the desired value, and "\( P_{\text{chamber}} \) after 25 min. of growth" was read before the growth was stopped. There is a big discrepancy between the two pressure values due to the fact that the very aggressive \( NO_2 \) molecules react in the first instance with the metal deposited on the chamber walls which act like a sublimation pump, and then not much gas is detected by the ion gauge. We waited at least 2 minutes before opening the Cr K-cell and starting the deposition. After the sample growth is started, \( P_{\text{chamber}} \) is rising gradually.

During the growth we used RHEED to study the crystal structure. Upon completion of the growth, we carried out XPS measurements \textit{in situ} to determine the
chemical composition and the electronic structure, as well as further structural analysis using LEED.

To prevent any change in the oxidation state of chromium when the samples were brought into air for ex situ measurements, they were capped with about 20 ML of MgO. This cap layer was grown at room temperature (after in situ XPS measurements were done on the as-grown chromium oxide films) with a rate of about 120 sec/ML using a magnesium metal flux of 1.2 Å/min and 1 × 10⁻⁴ mbar \( P_{buf} \) of \( NO_2 \). The MgO cap layer grows epitaxially on the chromium oxide film, as seen from RHEED. The calibration for this growth was done also by checking the stoichiometry of the MgO films with XPS, using as reference sample an MgO(100) single crystal cleaned in situ by annealing in oxygen. For this purpose we compared for each sample the ratio of the O1s to Mg2p core levels peak areas after background subtraction, with that of the reference sample.

The growth on a different substrate was also made, namely on SrTiO\(_3\), using 1.3 Å/min for the Cr metal flux, 1 × 10⁻⁴ mbar \( NO_2 \) buffer volume pressure and two different substrate temperatures: room temperature and 400°C.

### 3.3 In situ structural analysis

#### 3.3.1 RHEED

A first indication of the crystal quality of the grown chromium oxide samples was gained from the RHEED patterns and from the RHEED intensity oscillations of the specularly reflected beam.

Figure 3.2 shows the RHEED patterns of (a) a clean MgO(100) substrate and six of the grown samples on MgO(100) substrates under various \( NO_2 \) buffer volume pressures: (b) 0.75 × 10⁻⁴ mbar, (c) 1 × 10⁻⁴ mbar, (d) 1.25 × 10⁻⁴ mbar, (e) 1.5 × 10⁻⁴ mbar, (f) 2 × 10⁻⁴ mbar, (g) 3 × 10⁻⁴ mbar. For \( P_{buf} = 4 \times 10⁻⁴ \) mbar no RHEED data was recorded. The deposition time for all these samples was 30 minutes and the RHEED images presented are recorded with an electron beam energy of 15 keV and with the incident beam along a [100] direction.
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**Figure 3.2.** RHEED patterns of (a) MgO(100) substrate and chromium oxide films grown after 30 minutes on MgO(100) at 400°C, NO₂ assisted with buffer volume pressures: (b) 0.75 × 10⁻¹ mbar, (c) 1 × 10⁻¹ mbar, (d) 1.25 × 10⁻¹ mbar, (e) 1.5 × 10⁻¹ mbar, (f) 2 × 10⁻¹ mbar, (g) 3 × 10⁻¹ mbar
The \( MgO \) pattern was taken before the growth of one of the chromium oxide samples. In this pattern (Fig. 3.2a) sharp streaks corresponding to the \((\bar{2}, 0), (0, 0)\) and \((2, 0)\) reciprocal lattice rods (characteristic for a rock-salt diffraction pattern) are clearly visible, together with intense Kikuchi lines. The very intense spot on the \((0, 0)\) rod is due to the specular reflected electrons for which the position is close to the first Bragg position in the geometry of this picture.

Except for \( P_{buf} = 0.75 \times 10^{-4} \) mbar (Fig. 3.2b), all the RHEED patterns show that the film surfaces had the same crystallographic symmetry as the substrate: the streaks have positions corresponding approximately to those of the substrate pattern and no extra satellite features are observed. The streakiness, checked at different angles of the incidence beam, suggests that the patterns are dominated by reflection rather than transmission indicating reasonably smooth film surfaces for \( 1 \times 10^{-4} \) mbar \( \leq P_{buf} \leq 2 \times 10^{-4} \) mbar (Fig. 3.2 c,d,e,f). The Kikuchi lines are still visible for these samples, suggesting also a long range ordering. These Kikuchi lines are three dimensional features which originate from electrons which have suffered inelastic collisions in the bulk before they are finally Bragg diffracted by a lattice plane. For the samples grown at \( P_{buf} 3 \times 10^{-4} \) mbar and \( 4 \times 10^{-4} \) mbar transmission patterns develop, but the streaked character of the diffused transmission patterns indicate that the surfaces are still relatively smooth. The film thickness of the samples presented in Fig. 3.2 was in between \( 61\AA \) and \( 84\AA \) as determined from the RHEED intensity oscillations and the \textit{ex-situ} XRD and RBS measurements.

For thicker films \((150\sim 250\AA)\) the RHEED patterns are dominated by transmission due to island growth, especially for the high buffer volume pressure cases, the lines are diffuse and the background has a high intensity. This fact together with the damping out of the RHEED intensity oscillations indicate that the surface is getting quite rough. At thicknesses over \( 300\AA \) even additional spots appear in between the rock-salt lines indicating that the crystal structure begins to deteriorate.

On the other hand, \( P_{buf} = 0.75 \times 10^{-4} \) mbar seems not to be sufficient for growing crystalline chromium oxide. Directly after starting the growth, a pattern of transmission spots appears indicating a rough surface. As the growth continues, polycrystalline features appear (circles centered on the direct beam) and become more intense with the film thickness. There seems to be also additional spots, evident in the figure 3.2 (b), probably due to some unoxidized chromium.

In our case, RHEED was used for a qualitative evaluation of the sample structures including surface topography and crystallography. In order to make a more
definite interpretation of the RHEED diffraction experiments, a quantitative study is needed, and this could be quite complex: see, for instance, reference [9] and for investigation of polycrystalline samples see for example reference [10] and [11].

Also the quantitative analysis of the RHEED intensity oscillatory behavior is very complex and it has been a subject of considerable study [12] [13]. But it is generally accepted that RHEED intensity oscillations necessarily indicate a 2D layer-by-layer or Frank van der Merwe growth mode [13] [14], and the number of oscillations correspond to the number of monolayers grown. We now will use the oscillation time period to determine the relative Cr to O stoichiometry in our studies, where we keep the Cr evaporation rate constant, while varying systematically the NO$_2$ pressure.

In Figure 3.3 the intensity oscillations in the specularly reflected RHEED beam are presented as a function of the deposition time for the samples grown on MgO substrates with the following NO$_2$ buffer volume pressures: (a) $1 \times 10^{-4}$ mbar, (b) $1.25 \times 10^{-4}$ mbar, (c) $1.5 \times 10^{-4}$ mbar, (d) $2 \times 10^{-4}$ mbar, (e) $3 \times 10^{-4}$ mbar. The intensity was normalized for each sample. The flat intensity region at the beginning of the graphs corresponds to the reflected electron beam on the bare MgO(100) substrate before starting the growth, and the deep minima are recorded with the RHEED beam shuttered for a couple of seconds, in order to have the ”true” minimum for the intensity. The maximum intensity is very close usually to the saturation point of the CCD camera. All the oscillations have been recorded with an incident electron beam angle correspondent to the first anti-Bragg position of MgO(100) and with an electron beam energy of 15 keV. At this angle there will be destructive interference between electrons scattered from terraces separated in height by $(n + 1)$ ML. Upon start of deposition (time = 0 sec), the intensity first decreases followed by strong evenly spaced oscillations. The recording of the RHEED intensity oscillations was stopped always before the sample deposition was stopped, in order to assure a as-quick-as-possible sample transportation to the XPS chamber after growth.

The small damping in the oscillatory behavior at $1 \times 10^{-4}$mbar $\leq P_{buf} \leq 2 \times 10^{-4}$mbar in Fig. 3.3 a,b,c,d (for $P_{buf} = 1.5 \times 10^{-4}$mbar see also Fig. 3.1) indicate, as do the corresponding RHEED patterns, a layer-by-layer growth at this thicknesses. For $P_{buf} = 3 \times 10^{-4}$mbar the average specular beam intensity and the oscillation amplitude are damped much faster, but pronounced oscillations are seen in the early stages of growth (Fig. 3.3e), suggesting in this case an increased surface roughening as compared with the lower buffer volume pressures cases.
Chapter 3  \( NO_2 \) assisted chromium oxides growth

Figure 3.3. Oscillations in the intensity of the specularly reflected RHEED beam, as a function of the deposition time on \( MgO(100) \) substrates at \( NO_2 P_{nu} \) of: (a) \( 1 \times 10^{-4} \) mbar, (b) \( 1.25 \times 10^{-4} \) mbar, (c) \( 1.5 \times 10^{-4} \) mbar, (d) \( 2 \times 10^{-4} \) mbar, (e) \( 3 \times 10^{-4} \) mbar.

The oscillation period was relatively constant for all the samples, but it was different from one sample to another, raising a first supposition that we are growing different stoichiometries of chromium oxide, \( Cr_xO \). This is because the oscillation period of the different \( Cr_xO \) samples is proportional to the relative chromium content of a monolayer [15].
If we assume that the $P_{buf} = 1 \times 10^{-4}$ mbar sample with the 60 sec $/ML$ period corresponds to $CrO$, then the $P_{buf} = 1.25, 1.5$ and $2 \times 10^{-4}$ mbar samples with the 47 sec $/ML$ period should correspond to $Cr_xO$ with $x = 0.75$; and the $P_{buf} = 3 \times 10^{-4}$ mbar sample with the 43 sec $/ML$ period to an oxide with $x = 0.7$. These stoichiometry assignments will be more firmly substantiated in the section below, in which we describe the XPS and XAS results as well as the RHEED experiments on the growth of $Cr_2O_3$ on $Al_2O_3$ as reference sample.

At this moment we may conclude that we are able to make chromium oxide with a cubic structure, but one in which vacancies are built in. The oxygen sublattice has probably a rocksalt arrangement, while the chromium vacancies are likely not to be ordered since the RHEED shows no superstructures.

A distinct case from the point of view of RHEED oscillations is the sample grown at $P_{buf} = 0.75 \times 10^{-4}$ mbar. As expected from the transmission RHEED pattern developed right from the beginning of the growth, no oscillations were obtained supporting the conclusion that we are dealing with a polycrystalline growth in this case.

The $NO_2$ assisted chromium oxide growth was also successful on the $SrTiO_3$ substrate. Figure 3.4a is a RHEED pattern of this substrate before growth and we can see the streaks corresponding to the $(\overline{2}, 0)$, $(\overline{1}, 0)$, $(0, 0)$, $(1, 0)$ and $(2, 0)$ reciprocal lattice rods, characteristic for a perovskite structure. The Kikuchi lines are also visible. Figure 3.4b presents a plot of the intensity distribution measured along a cross section perpendicular to the RHEED streaks (a horizontal line scan in the box in fig. 3.4a). The peaks in this figure are indexed with the corresponding reciprocal lattice rods. Fig. 3.4 c and e show the RHEED patterns of the samples grown on $SrTiO_3(100)$ substrate with $P_{buf} = 1 \times 10^{-4}$ mbar, at room temperature (RT) and $400^\circ C$ respectively. The sample deposition time was 30 minutes and the images c and e are recorded at the end of each growth. In the first 3-4 minutes of the film deposition the RHEED lines of the substrate disappear and instead a characteristic rocksalt pattern develops. This is proven also by the horizontal line scans presented in fig. 3.4d (in the box drawn in fig. 3.4c) and in fig. 3.4f (for the corresponding box in fig. 3.4e). It catches the eye that the growth is better at $400^\circ C$ than at RT: see the long, sharp RHEED streaks indicating a smooth surface at $400^\circ C$, as compared with the transmission spots and a tendency to become polycrystalline at RT.
Figure 3.4. (a) RHEED pattern of a $SrTiO_3(100)$ substrate, (b) horizontal line scan in a box indicated in (a), (c) RHEED pattern of a sample grown on $SrTiO_3(100)$ at room temperature with $1 \times 10^{-4}$ mbar $NO_2$ buffer volume pressure, (d) horizontal line scan in a box indicated in (c), (e) RHEED pattern of a sample grown on $SrTiO_3(100)$ at room temperature with $1 \times 10^{-4}$ mbar $NO_2$ buffer volume pressure, (f) horizontal line scan in a box indicated in (e), (g) RHEED intensity oscillations for the sample grown at RT, (h) RHEED intensity oscillations for the sample grown at 400$^\circ$C.
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Another indication of the two different qualities of these samples come from the RHEED intensity oscillations in the specularly reflected beam: fig. 3.4g at RT, fig 3.4h at 400°C. The few oscillations obtained at RT suggest a strong roughening and probably increased disorder in the crystalline structure. On the other hand, at 400°C oscillations go on until the end of the growth suggesting a relatively flat film surface. The oscillation period is comparable for the two samples: about 60 sec/ML. It is actually quite remarkable that chromium oxide can be grown so well on both the SrTiO$_3$ as well as the MgO substrates, in view of their large lattice constant discrepancy of 7.3%.

3.3.2 LEED

The normal incidence geometry makes LEED complementary to RHEED with the same degree of surface sensitivity. During the sample growth studies, LEED patterns of the films were checked, but no good data were recorded due to some surface roughness of the films, even in the cases of low buffer volume pressure growths.

![Figure 3.5](image)

**Figure 3.5.** (a) LEED patterns of MgO(100) substrate, (b) LEED patterns of a chromium oxide film grown on MgO(100) substrate at 300°C, N$_2$O$_2$ assisted with $P_{buf} = 1.5 \times 10^{-4}$ mbar.

In Figure 3.5 two LEED patterns are compared: (a) one of a clean MgO(100) substrate taken at an electron beam energy of 222 eV and (b) the other one of a chromium oxide film grown on MgO(100) substrate at 300°C and $P_{buf} =$
3.4 Reference sample

Before discussing the chemical composition of the films as determined from the XPS measurements, it is useful to describe the results of the reference samples that we used for these measurements, namely the most stable phase of chromium oxide, $Cr_2O_3$.

Chromium sesquioxide has a corundum crystal structure with approximately a hexagonal closed-packed array of oxygen atoms in which the $Cr^{3+}$ ions occupy two-thirds of the octahedral holes [16]. It contains 3 d-electrons per cation and in the bulk form is an antiferromagnetic insulator below the Neel temperature of $307^\circ K$, like $\alpha - Fe_2O_3$, with a band gap of 3.4 eV. The color of the crystal is green due to the d-d transitions in the $Cr^{3+}$ ions [17]. The dimensions of the corresponding trigonal cell using hexagonal axes are: $a_0 = 4.954\,\text{Å}$ and $c_0 = 13.584\,\text{Å}$ [18].

For our purpose we used two types of sample: one is a $Cr_2O_3$ single crystal which was cleaved in-situ, and the other one is an $\alpha - Cr_2O_3$ sample grown by MBE on polished sapphire $Al_2O_3(0001)$ substrates. Sapphire has also a corundum structure with the unit cell of the dimensions: $a_0 = 4.763\,\text{Å}$ and $c_0 = 13.003\,\text{Å}$ leading to a mismatch with $Cr_2O_3$ of 3.9%. 

1.5 $\times 10^{-4}$ mbar, taken at an electron beam energy of 211 eV. The thickness of the film was approximately 91Å. Due to strong charging effects and consequently a blurred LEED pattern at lower beam energies than $\approx 200$ eV, data collection at these energies was impossible. The clean $MgO(100)$ substrate was charging at energies lower than $\approx 70$ eV. The two pictures were taken at slightly different electron beam energies because not all the $MgO(100)$ diffraction spots were visible with similar intensities at 211 eV, an energy which was carefully chosen for a relatively good LEED pattern of the film.

It is easy to see that the chromium oxide film pattern have weak, diffuse spots and a high background intensity indicating that there is some disorder in the crystalline structure. But still it can be observed that both the $MgO(100)$ substrate and the film have the same crystallographic symmetry, with no surface reconstruction for the film.

The same chromium oxide sample was used also for ex-situ XRD and RBS measurements, revealing a good crystal structure, as will be discussed in section 3.6 of this chapter.
3.4 Reference sample

In the literature $\alpha - Cr_2O_3$ growth on various substrates is reported: on $Pt (111)$ $Cr_2O_3$ has a $(\sqrt{3} \times \sqrt{3}) R 30^\circ$ symmetry structure [19] [20], on a $Cr (110)$ substrate and on a $Al_2O_3 (0001)$ substrate orthorhombic $Cr_2O_3$ layer in (0001) orientation is formed [21] [22] [23]. We preferred to use a sapphire substrate because it shares the corundum structure with $\alpha - Cr_2O_3$, it is easy to clean and it is cheaper than the other substrates.

The cleaning procedure of the $Al_2O_3$ substrates was similar to the one applied in the case of $MgO$ and $MnO$ substrates: annealing for about 3 hours at 650°C in an oxygen atmosphere pressure of $1 \times 10^{-8}$ mbar, with the gas nozzle positioned at $\approx 5$ cm from the sample. After annealing the substrates exhibited good (1 x 1) LEED patterns (see Fig. 3.6a) with the fundamental three fold symmetry of $\alpha - Al_2O_3 (0001)$ [24], and no carbon contamination could be detected with XPS. For the $Cr_2O_3$ sample growth, the Cr metal flux was set again to about 1.3Å/ min as in the case of the other samples grown on $MgO (100)$, the substrate temperatures used were 300°C and 500°C and this time the oxidizing agent was oxygen, with a buffer volume pressure of $12.5 \times 10^{-4}$ mbar leading to a background pressure in the growth chamber of $\approx 1 \times 10^{-6}$ mbar. This pressure has proven to be sufficiently high to grow $\alpha - Fe_2O_3$ by $O_2$ - assisted MBE [25] [26].

RHEED and LEED data showed that good, epitaxial crystals of $Cr_2O_3$ can be grown, with the same crystallographic symmetry as the sapphire substrate. At thicknesses varying between 150Å and 540Å the films had an almost unchanged RHEED pattern as compared with the substrate, indicating smooth and ordered surfaces of the films. The film thicknesses were determined from the RHEED intensity oscillations, taking into account that a unit cell of $Cr_2O_3$ includes six monolayers, and a monolayer consists of one oxygen and two chromium layers.

In the following we will refer to the sample grown at 500°C which was used in the XPS measurement as "the reference chromium oxide" sample. The sample deposition time was one hour and the growth rate determined from the RHEED intensity oscillations (Fig. 3.6c) was 55 sec / ML resulting in a sample thickness of about 150Å. A LEED pattern of this film, taken with an electron beam energy of 227 eV (Fig. 3.6b) is compared with a LEED pattern of the $Al_2O_3 (0001)$ substrate (Fig. 3.6a), taken with a similar electron beam energy (of 235 eV), and the crystal symmetry proves to be the same for the film and for the substrate. Again charging effects did not allow us to work with smaller electron beam energies.

The oscillation period was again used for a check of the sample stoichiometry, by comparing it with the oscillation periods found for the $NO_2$ assisted samples
grown on $MgO(100)$ substrates. In comparing chromium oxides with different crystal structures (cubic vs hexagonal) we must take into account the density of the cations in a monolayer (the number of chromium atoms per area unit), because the oscillation period of the different chromium oxides is proportional to the chromium content of a monolayer.

The cubic chromium oxides described in the section 3.3 had three different
oscillation periods: 60, 47 and 43 sec/ML and they correspond to CrO, Cr$_{0.75}$O and Cr$_{0.7}$O, respectively, if we assume that the 60 sec/ML sample is CrO. Using now the Cr$_2$O$_3$ on Al$_2$O$_3$ data and the formula:

$$\rho_{\text{cub}} = \rho_{\text{hex}} \times \frac{t_{\text{cub}}}{t_{\text{hex}}} ,$$

where $t_{\text{hex}}$ is the time to grow 1 ML of Cr$_2$O$_3$ on Al$_2$O$_3$(0001), $t_{\text{cub}}$ is the experimental time obtained for growing 1 ML of one of the cubic chromium oxides grown on MgO(100), and $\rho_{\text{hex}}$ and $\rho_{\text{cub}}$ are the corresponding cation densities in a monolayer of hexagonal and respectively cubic chromium oxide, then we find that the 60 sec/ML sample on MgO corresponds to Cr$_{0.91}$O, the 47 sec/ML sample to Cr$_{0.71}$O, and the 43 sec/ML sample to Cr$_{0.66}$O, indicating that the assumptions made earlier were not too bad.

### 3.5 XPS results

#### 3.5.1 Sample chemical composition

The RHEED results suggest that Cr$_x$O with a good crystallinity can be achieved for a wide range of $x$, even for $x$ close to one. This is quite surprising in view of the fact that bulk CrO does not exist. A further study using XPS revealed probably the key to this. We notice that, as in the case of iron oxide films grown by NO$_2$-assisted MBE [27], there is a substantial amount of nitrogen built in the chromium oxide films, depending on the NO$_2$ gas pressure that is being used for the growth.

The nitrogen content relative to the total anion content (oxygen and nitrogen) in the sample was determined by comparing the $N 1s$ and $O 1s$ core level peak areas after background subtraction and after correcting for the difference in the photoionization cross-sections of the two peaks [28]. With the photoionization cross-sections of $N 1s$ being 0.024 and of $O 1s$ 0.040 [29], the nitrogen content ($y$) was determined by using the formula:

$$y = \frac{N 1s \times \frac{40}{21}}{O 1s + N 1s \times \frac{40}{21}} .$$

In figure 3.7 the results are plotted as a function of the NO$_2$ buffer volume pressure. The data points are for the samples presented in section 3.3.1 of this chapter and for a couple of other samples grown at different times on MgO(100) substrates at 400$^\circ$C, in similar growth conditions as for the ones already presented.
For $P_{buf} = 4 \times 10^{-4}$ mbar no nitrogen could be detected in the sample. The nitrogen start to appear at $3 \times 10^{-4}$ mbar and increases strongly with decreasing $NO_2$ flux, up to a concentration of 30% at $P_{buf} = 1 \times 10^{-4}$ mbar. At $P_{buf} = 0.75 \times 10^{-4}$ mbar, the nitrogen content seems to decrease slightly. This last sample is associated with a non-epitaxial, polycrystalline growth, as could be seen from the RHEED data. There also seems to be a difference between the two samples grown on SrTiO$_3$(100) substrates: the RT sample has a lower nitrogen content than the sample grown at 400°C substrate temperature, while the $y$ value of the last one overlaps with the data points obtained for the films grown on MgO(100) substrates at 400°C. These facts suggest that the crystallinity of the samples may be related to the nitrogen content in the samples, i.e. that nitrogen may help to stabilize the crystalline compounds. Later ex-situ RBS and XAS measurements confirm that the nitrogen is uniformly incorporated in the layers and that it is not just a surface peak seen by XPS.

The chemical composition $x$ of the $Cr_xO_{1-y}N_y$ samples was obtained from...
the ratio of $Cr 2p$ peak area over the sum of $O 1s$ and $N 1s$ core levels peak areas, after background subtraction for each of these core levels peaks. The XPS measurements were started immediately after the growth with a quick broad scan, then the $Cr 2p$ and $O 1s$ core level peaks were measured in the same scan, and the $N 1s$ was measured in the following scan. The reference samples: $Cr_2O_3$ single crystal cleaved in-situ and $Cr_2O_3/Al_2O_3 (0001)$, described in the previous section of this chapter, gave for the ratio of $Cr 2p$ versus $O 1s$ two different values: 2.63 and 2.92 respectively. We decided to use as a reference for the chemical composition determination the sample grown in our system on sapphire, with the ratio of 2.92, because the surface quality of the fractured single crystal may be very different from those of $Cr_3O$ epitaxially grown on epi-polished $MgO$ or $SrTiO_3$, while the surface quality of the $Cr_2O_3$ grown on epi-polished $Al_2O_3$ is likely to be more similar to those of the $Cr_3O$ films. Then for $CrO$ the corresponding ratio should be $2.92 \times \frac{3}{2}$. For the chemical composition determination this expected value was
compared with the experimental values obtained for each grown sample, where in
the denominator instead of the $O1s$ peak area, the total $1s$ anion peak area is taken
into account, as it was explained above. The results are plotted in the Figure 3.8
as a function of the buffer volume pressure. For the samples used, no Mg nor Al
signals coming from the substrates could be detected, i.e. all the oxygen $1s$ signal
is coming from the chromium oxide overlayer.

Looking at these data it can be seen that we can grow samples which have
the chemical composition close to one chromium atom to one anion atom and this
is possible on MgO substrates, for $NO_2$ buffer volume pressures of $1 \times 10^{-4}$
mbar for our growth conditions. In the following table are given the approximative
chemical formulas for the different $NO_2$ buffer volume pressure growths on MgO
substrates, as a conclusion from both chemical composition and nitrogen content
plots.

<table>
<thead>
<tr>
<th>$P_{buf}$ (mbar)</th>
<th>Approximative chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.75 \times 10^{-4}$</td>
<td>$Cr_{1.05}O_{0.73}N_{0.27}$</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>$Cr_{0.9}O_{0.7}N_{0.3}$</td>
</tr>
<tr>
<td>$1.25 \times 10^{-4}$</td>
<td>$Cr_{0.75}O_{0.75}N_{0.25}$</td>
</tr>
<tr>
<td>$1.5 \times 10^{-4}$</td>
<td>$Cr_{0.75}O_{0.75}N_{0.25}$</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>$Cr_{0.71}O_{0.86}N_{0.14}$</td>
</tr>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>$Cr_{0.68}O_{0.95}N_{0.05}$</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>$Cr_{0.65}O$</td>
</tr>
</tbody>
</table>

It is important to mention that the life time of the grown chromium oxide films
turned out to be limited, especially for the low $P_{buf}$ growth cases, despite the fact
that the pressure in the spectrometer chamber was as good as $1 \times 10^{-10}$ mbar during
the XPS measurements. By remeasuring the $Cr2p - O1s$ scan after four hours, the
$O1s$ peak area relatively to the one of $Cr2p$, was higher by as much as 10% from
that measured immediately after the growth. And still, from the moment when the
growth was stopped it took us about 30 minutes until the $Cr2p - O1s$ scan was
started, due to sample transportation and alignment for the XPS measurement. The
measuring time of this scan was 32 minutes. In conclusion, it is very likely that
the chemical composition $x$ is higher by $\approx 3\%$ for the samples grown at low $P_{buf}$. 
Likewise the nitrogen content is maybe higher for this samples with \( \approx 3\% \).

In principle, other core level peaks can be used also for determining the sample chemical composition like: \( \text{Cr}3p \) versus (vs) the \( 2s \) of \( O \) and \( N \) or \( \text{Cr}3s \) vs the \( 2s \) of \( O \) and \( N \). A scan including all these peaks and the valence band region (\( \text{Cr}3d \) and \( O2p \)) was measured after the \( N1s \) scan and it took about 2 hours for good enough statistics. This is a first problem for a reliable determination of \( x \), since the samples made at low \( P_{\text{air}} \) tend to oxidize further on their surface as was discussed above. Another problem for the accuracy in this case is the determination of the \( N2s \) peak area which has a weak intensity even for the highly contaminated samples, and it is very close to the \( O2s \) peak so no proper background subtraction can be made for these two peaks. Nevertheless, we tried to determine the \( N2s \) peak area in three ways: (a) using the \( N1s \) peak area corrected for the difference with \( N2s \) in the photoionization cross-section; (b) \( N2s \) was found by using the \( O2s \), determined by a gaussian fit of the line, and the nitrogen contamination \( y \) known from the \( N1s \) and \( O1s \) area scans; (c) just fitting the intensities of \( O2s \) and \( N2s \) peaks with gaussians. The results were very different for the three cases: (b) gave a \( N2s \) peak area more than two times higher than in case (a), and for (c) the \( N2s \) peak area was more than three times higher than for (a). In conclusion, we decided that the most reliable way to determine the chemical composition was by using the intense, well separated \( \text{Cr}2p, O1s \) and \( N1s \) peaks.

Besides the chemical composition, XPS can give information on the valence of \( \text{Cr} \) in the grown samples, by comparing the ratio of \( \text{Cr}3d \) vs \( O2s \) (measured in the same scan) peak areas for each sample, with the same ratio for the reference \( \text{Cr}_{2}O_{3}/\text{Al}_{2}O_{3}(0001) \). The expected value of this ratio for \( \text{Cr}O \) and \( \text{Cr}_{0.75}O \) is determined from the experimental value for \( \text{Cr}_{2}O_{3} \) by taking into account the number of \( \text{Cr} d \) electrons per oxygen atom for each chromium oxide phase:

- for \( \text{Cr}_{0.67}O \):

\[
\frac{2 \times d^3Cr}{3 \times O} = 2 \times \frac{\text{Cr} \text{ d - electrons}}{O} ;
\]

- for \( \text{Cr}O \):

\[
\frac{1 \times d^4Cr}{1 \times O} = 4 \times \frac{\text{Cr} \text{ d - electrons}}{O} ;
\]

- for \( \text{Cr}_{0.75}O \):

\[
\frac{1 \times d^4Cr + 2 \times d^3Cr}{4 \times O} = 2.5 \times \frac{\text{Cr} \text{ d - electrons}}{O} .
\]
For the nitrogen contaminated samples the charge of the chromium ions (i.e. the number of 3d electrons) is not easy to determine due to the fact that the N 2s needs to be added to the O 2s peak area. As it was explained above, no easy determination can be done for these peak areas, and yet another problem arises in this case: for the chromium oxide samples the Cr 3d peaks overlap with O 2p. In consequence we need to subtract the O 2p spectral weight from the total (Cr 3d + O 2p) spectral weight measured. O 2p can be deduced from the O 2s peak area using the corrections in the photoionization cross-sections of the two peaks: \( \frac{O_{2s}}{O_{2p}} = 2.64 \) [29]. This ratio was also checked for an MgO(100) clean substrate, for which O 2s and O 2p are clear and well separated peaks, and we found \( \frac{O_{2s}}{O_{2p}} = 2.86 \), value bigger with 8% than what it was found using the cross-section table. This value is also considerably different from the value found by Sawatzky for Al₂O₃ (1.754) [30], and the one found by Scofield for \( O^2^- \) (4.167) [31]. We decided to use the ratio determined experimentally for MgO(100), since we believe that it was more accurate for our set-up. Then, in figure 3.9 the Cr 3d vs (O 2s + N 2s) spectral weights for a couple of samples grown on MgO substrate is plotted, as a function of the NO₂ buffer volume pressure used during the samples growth. Cr 3d vs O 2s ratio for Cr₂O₃ single crystal is 0.62 and for Cr₂O₃ grown on Al₂O₃ is 0.66. The O 2s and N 2s peak areas were determined by gaussian fits and they were added after N 2s was corrected for the difference in the photoionization cross section with O 2s.

It can be seen that none of the films has the Cr 3d vs anions 2s spectral weights ratio as high as two times the same ratio for Cr₂O₃, as we would expect for CrO, not even the sample grown at \( P_{buf} = 0.75 \times 10^{-1} \) mbar. We believe that this is partly due to the measurement error and partly to the fact that, this ratio may be lower for the nitrogen contaminated samples than for a purely CrO sample. Moreover, the photoionization cross-section per electron could be different for a \( Cr^{3+} \) ion than a \( Cr^{2+} \) ion which has bigger orbitals, and then we may not expect double intensity of the Cr 3d vs O 2s ratio, even in the case of CrO compared with Cr₂O₃.

An extra complication to the problem arises if we try to add also the N 2p spectral weight to the one of O 2p; we don’t even know how many p electrons the nitrogen has. However, for making the previous plot we subtracted from the total (Cr 3d + anions 2p) area the anions 2p = total anions \( \frac{2s}{2.86} \) where 2.86 is the \( \frac{O_{2s}}{O_{2p}} \) value of found for the annealed MgO.

An eventual phase separation of chromium monoxide into \( CrO = Cr \) +
3.5 XPS results

Figure 3.9. Cr 3d vs (O 2s + N 2s) spectral weights for $Cr_xO_{1-y}N_y$ samples grown on MgO substrate, as a function of the NO$_2$ buffer volume pressure, as determined from XPS spectra.

$Cr_2O_3$ cannot be distinguished from a stoichiometric $CrO$: using the cross-sections table to calculate the Cr 3d vs O 2s ratio in the two cases we found just a 5% difference, which is within the error of its experimental determination.

3.5.2 Electronic structure

Chemical shifts in the core level binding energies are largely utilized in investigations of the charge transfer in transition-metal oxides, carbides and nitrides. The binding energy (BE) of the core electrons can be very sensitive to the charge of the ion. However, sometimes the BE due to the ionic shift can be cancelled by the Madelung potential, as for example in the NaCl case [32]. Therefore it may be difficult to extract the oxidation state from binding energy data. See for example the little change in the BE of the V 2p$_{3/2}$ electrons in various vanadium oxides [30]. We made an attempt to determine the chromium oxidation state also by looking at the chemical shifts in the Cr 2p photoemission spectrum of various samples.
The Cr 2p core level photoemission spectrum contains two relatively intense lines, \(2p_{1/2}\) and \(2p_{3/2}\), where the separation of the two lines (\(\Delta E\)) is given by the atomic spin-orbit interaction. After removing one electron from the 2p shell, the remaining core hole will have a spin \(\pm \frac{1}{2}\) or \(-\frac{1}{2}\) which will couple parallel or antiparallel with the orbit angular momenta. The \(2p_{3/2}\) line has a lower binding energy, i.e. it costs less energy to remove the antiparallel spin electron than the parallel spin electron. The intensity ratio of the two lines as estimated by the occupation numbers of the emitting orbitals, should be:

\[
\frac{2P_{3/2}+1}{2P_{1/2}+1} = \frac{2\frac{3}{2}+1}{2\frac{1}{2}+1} = \frac{4}{2} = 2.
\]

This prediction is approximately born out by the experimental findings [34]. Each of the two spin-orbit split components is accompanied by a satellite peak at higher binding energy, due to charge-transfer (CT) screening [35]. In the configuration interaction theory the ground state wave function of chromium oxide is a linear combination of \(3d^n\) and \(3d^{n+1}L\) states. \(3d^n\) is the configuration of the Cr ion and \(L\) indicates one hole in the highest occupied ligand shell, which is 2p for \(\Theta^2-\), after one electron is transferred from the ligand shell L into the d shell, leading to a \(3d^{n+1}\) configuration for the Cr ion. The energy separation in between these two states is given by \(\Delta\), the charge-transfer energy, and the state \(3d^n\) is the lowest in energy. The photoexcitation on the Cr site leads to two final states: \(2p^73d^n\) and \(2p^53d^{n+1}L\). The 2p core hole on the Cr ion lowers the energy of the \(d^{n+1}\) configuration with respect to the \(d^n\) configuration and this lowering is described by the Coulomb interaction between the 2p core hole and a 3d electron (\(U_{cd}\)). Depending on the relative magnitude of \(U_{cd}\) and \(\Delta\), either the \(2p^73d^{n+1}L\) is the lowest in the final state (\(U_{cd} > \Delta\)) or the \(2p^53d^n\) configuration is the lowest (\(\Delta > U_{cd}\)) [34].

For a detailed description of the Cr 2p spectral line shape, one should also include the multiplet structure due to the interactions of the 2p core hole with the holes in the 3d band, and the possible interactions between Cr neighboring ions [36], [37].

Figure 3.10 shows the Cr 2p core level spectra for the grown chromium oxides samples described in in the section 3.3.1 of this chapter, with the corresponding \(P_{ba,f}\) indicated on the right side of each line. The reference samples are: the \(C_2\)O\(_3\) single crystal cleaved \textit{in situ} and \(Cr_2O_3/Al_2O_3\) (top), and Cr metal deposited on polycrystalline tantalum (bottom line). In the oxides spectra the CT satellite of Cr \(2p_{1/2}\) can be seen around 597 eV, while the CT satellite of Cr \(2p_{3/2}\) overlaps with the \(2p_{1/2}\) line. All the intensities are normalized.
Figure 3.10. XPS Al $K_x$ of the $Cr^{2}p$ levels, as a function of the $NO_2$ buffer volume pressure $P_{buf}$ during deposition. $P_{buf}$ (in mbar) is indicated on each spectrum for the grown $Cr_xO_yN_{1-y}$ samples. The lowest spectrum is for the Cr metal deposited on polycrystalline tantalum substrate. On the top there are two spectra for $Cr_2O_3$: one for a cleaved in situ single crystal sample, one for a grown film on $Al_2O_3(0001)$ substrate at $P_{buf} = 12.5 \times 10^{-4}$ mbar of $O_2$. The spin-orbit energy splitting ($\Delta E$) of the $Cr^{2}p$ is indicated on each spectrum.
Due to the insulating substrates used for growing the oxides and an insulating $Cr_2O_3$ single crystal, a positive charging tended to make peaks appear at higher binding energy, whereas excessive compensation using the flood gun made the peaks shift to lower binding energy. To correct for the charge we used the following steps:

1). The oxides were aligned having for the O 1$s$ peak position the same BE, by taking the same energy interval from the O 1$s$ peak of each spectrum: with 35 eV minimum and 75 eV maximum, interval which included all the Cr 2$p$ features. (About the same interval was used also for determining the Cr 2$p$ spectral weight in the previous section.)

2). For Cr metal we made use of the high reactivity of chromium with oxygen in the XPS chamber. A small O 1$s$ peak arose in the $Cr\,2p - O\,1s$ scan, measured in the similar conditions as for the oxides, giving a $Cr\,2p$ vs $O\,1s$ spectral weights ratio of 45. The O 1$s$ peak was good enough to find the peak position (530.14 eV) and to use the same energy interval from this peak (35 eV min. and 75 eV max.) for the Cr 2$p$ lines, as done in the oxides case.

3). Having the spectrum so aligned, we compared the Cr 2$p_{3/2}$ peak position for Cr metal (574.02 eV) and the corrected value for $Cr_2O_3/Al_2O_3$ (576.32 eV) resulting in a BE difference of 2.3 eV for the two peaks. This value is lower by 0.2 eV than the same difference calculated from ref. [38], with 0.5 eV than the one obtained by comparing $Cr_2O_3(111)/Cr(110)$ with Cr metal [39], and with 0.9 eV than for $Cr_2O_3/NaAl_2O_4$ compared with Cr metal [40]. The Cr 2$p_{3/2}$ for $Cr^{3+}$ ion has a peak position of 576.9 eV in ref. [38], 577 eV in ref. [39] and 577.2 eV in ref. [40]. In order to get a similar value for the $Cr_2O_3/Al_2O_3$, all the oxide spectra were shifted with 0.7 eV to higher binding energy, while the Cr metal spectrum was not shifted. The O 1$s$ peak position for the chromium oxides became then 530.84 eV, comparable with 531 eV given by ref. [38] for the $Cr_2O_3$ O 1$s$ peak.

The resulting Cr 2$p_{3/2}$ binding energies for the grown samples at different $NO_2$ buffer volume pressures are listed in the following table, together with the shifts in the BE as compared with the Cr 2$p_{3/2}$ peak position of Cr metal, 574.02 eV. For comparison, the reference samples are included in the bottom lines. The BE of Cr 2$p_{3/2}$ in Cr metal is 574.2 eV in ref. [39], and 574.0 eV in ref. [40].
It can be seen that the BE shifts observed for the grown samples indicate that chromium has a 2+ valency state for the growth done at $P_{bu} = 1 \times 10^{-4}$ mbar; $P_{bu} = 1.25, 1.5$ and $2 \times 10^{-4}$ mbar growths look like a combination of $Cr^{2+}$ and $Cr^{3+}$ as in $Cr_{0.75}O$; and finally the growths done at $P_{bu} = 3$ and $4 \times 10^{-4}$ mbar look like pure $Cr^{3+}$, as in $Cr_2O_3$. Moreover, the spin-orbit splitting energy $\Delta E$ indicated on the left side of each spectrum in Fig. 3.10, confirms also the fact that different valence states are obtained for chromium in the different samples. We obtained for $\Delta E$: 9.3 eV in the case of Cr metal, $\approx 9.5$ eV for $P_{bu} = 1 \times 10^{-4}$ mbar, and $\approx 9.8$ eV for $P_{bu} = 4 \times 10^{-4}$ mbar. These observed values for $\Delta E$ are compatible with observed spin-orbit splitting of chromium ions in chemical environments equivalent to $Cr^{2+}$ in $CrF_2$ and to $Cr^{3+}$ in $CrF_3$ [43]. In the latter studies $\Delta E$ was found to be 9.3 eV for Cr metal, 9.6 eV for $Cr^{2+}$ and 9.9 eV for $Cr^{3+}$. In reference [38] $\Delta E = 9.2$ eV for Cr metal and 9.8 eV for $Cr_2O_3$.

In Figure 3.10 it can also be seen that the sample grown at $P_{bu} = 0.75 \times 10^{-4}$ mbar has broad and asymmetric Cr 2p lines, which probably indicate a polycrystalline mixture of $Cr_2O_{1-x}N_y$ and unoxidized Cr phases.

Also the 2p lines of the sample grown at $P_{bu} = 1 \times 10^{-4}$ mbar look broad and consequently the CT satellite of Cr 2p$_{1/2}$ has a low intensity, smeared-out structure,
as compared with the samples grown at higher \( P_{buf} \). But yet, we cannot conclude from this fact that oxidized and unoxidized chromium phases are involved in this sample, since the crystal structure proved to be excellent in this case. For example, a material will always look like (without being) a mixed valence material if the Coulomb interaction between the core hole and the valence electrons is larger than the valence electron band width [32]. In addition, non local screening effects in the photoemission final states may lead to the formation of extra satellites; see for instance the 2p XPS spectra of single crystal \( NiO \) [33].

The spectra of the 1s level of nitrogen for all the nitrogen contaminated samples consists of a single line, and the peak positions - obtained by considering the O 1s peak BE of 530.84 eV - are listed in the following table for the different \( P_{buf} \) growths. The error made to the determination of these values is about 0.1 eV.

<table>
<thead>
<tr>
<th>( P_{buf} ) (mbar)</th>
<th>N 1s BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75 ( \times ) ( 10^{-1} )</td>
<td>396.87</td>
</tr>
<tr>
<td>( 1 \times ) ( 10^{-1} )</td>
<td>396.87</td>
</tr>
<tr>
<td>1.25 ( \times ) ( 10^{-1} )</td>
<td>396.72</td>
</tr>
<tr>
<td>1.5 ( \times ) ( 10^{-4} )</td>
<td>396.92</td>
</tr>
<tr>
<td>2 ( \times ) ( 10^{-1} )</td>
<td>396.92</td>
</tr>
<tr>
<td>3 ( \times ) ( 10^{-1} )</td>
<td>397.02</td>
</tr>
</tbody>
</table>

It can be seen that the BE values are close to 397 eV; a value typical for the N 1s BE in mononitrides of d-metals [44]. In the latter studies, an analysis of the X-ray photoelectron spectra of nitrides has shown that in the metallic nitrides (\( TiN \), \( VN \), \( NbN \), \( MoN \)) the N 1s BE is \( \approx 397, 2 - 398.1 \) eV, and it is \( \approx 397, 6 - 398.4 \) eV for the covalent nitrides (\( AlN \), \( GaN \), \( Si_3N_4 \), \( BN \)). The ionic component of the metal-nitrogen bond in metallic nitrides is higher than in covalent ones, but it decreases for the metallic nitrides with an increase in the number of d electrons in the metal atom. The BE of 1s electrons of nitrogen in nitrate \((NO_3)^{-1}\), nitrite \((NO_2)^{-1}\) ions, etc, is much higher then what we found for our samples (403-408 eV) [45], so the presence of these compounds in the grown layers could be excluded. Now looking back to the Cr \( 2p_{3/2} \) line shape of the sample grown at \( P_{buf} = 1 \times \) \( 10^{-4} \) mbar we speculate that the broadening of this line at low BE toward the metallic
state could be due to a not pure ionic bonding of chromium with the incorporated nitrogen, as one would expect for the chromium-oxygen bonding.

Sometimes, the peak position of the CT satellite is also used to determine the metal oxidation state [46], [47], [48], because these satellite lines have intensities and separations from the parent photoelectron line that are unique to each chemical state. In a study done by Wallbank [49], [50] it was found that the Cr 2p satellite separation from the main line is different for $\text{Cr}^{3+}$ and $\text{Cr}^{2+}$ ions: $\approx 11$ eV and $13$ eV respectively. If we consider the separation energy of Cr 2p$_{1/2}$ BE of $\text{Cr}^{3+}$ and $\text{Cr}^{2+}$, 1 eV, as listed in the precedent table, and if we take into account the $\Delta E$ separation obtained for 2p$_{3/2}$ and 2p$_{1/2}$ in "CrO" ($P_{bu} = 1 \times 10^{-4}$ mbar) and $\text{Cr}_2\text{O}_3$, then a separation energy will result of $\approx 0.7$ eV for the 2p$_{1/2}$ CT satellites of $\text{Cr}^{3+}$ and $\text{Cr}^{2+}$, with the last one at higher binding energy. The CT satellites of 2p$_{3/2}$ and 2p$_{1/2}$ have the same separation energy from the main lines, and this separation is given by the difference between $U_{cd}$ and $\Delta$, where $U_{cd}$ is the Coulomb interaction between the 2p core hole and a 3d electron, and $\Delta$ is the anion-cation charge transfer energy [5].

In our case it was difficult to determine accurately the CT satellite positions since they are broad and have a low intensity, even for $\text{Cr}_2\text{O}_3$ calibration samples. For the samples in which Cr has a valency as in $\text{Cr}_2\text{O}_4$, a superposition of the satellites corresponding to $\text{Cr}^{3+}$ and $\text{Cr}^{2+}$ is expected, which would lead to even more broadening of the satellites structures than in the $\text{Cr}_2\text{O}_3$ case. This can be seen in Fig. 3.10 especially for the samples grown at $P_{bu} = 1.25$ and $1.5 \times 10^{-4}$ mbar.

As discussed for the chemical composition determination, we consider that the chemical shifts method for determining the Cr oxidation state is the most accurate in our case by using the first measured Cr 2p spectra, so the method will not be applied for the other chromium core level peaks. Nevertheless, in Figure 3.11 the Cr 3p (with the main line around 44 eV) and Cr 3s (around 76 eV) are presented, in order to get a rough idea about the different spectral shapes of these lines on going from chromium metal (bottom line) to $\text{Cr}_2\text{O}_3$ (top lines). The spectra correspond to the same samples used in Fig. 3.10. The background was subtracted, the intensity was normalized and the charge correction was done by using the same method as for the Cr 2p lines, since chemical shifts are very uniform among the photoelectron lines of an element. The buffer volume pressure is indicated in each graph for the grown samples. From the Cr 3p line shapes of the samples grown at $P_{bu} = 0.75 \times 10^{-4}$ mbar (polycrystalline) and $P_{bu} = 1 \times 10^{-4}$ mbar (rocksalt) it is now
Figure 3.11. XPS Al Kα of the Cr 3p and Cr 3s levels, as a function of the NO₂ buffer volume pressure $P_{buf}$ during deposition. $P_{buf}$ (in mbar) is indicated on each spectrum for the grown $Cr_2O_3/Al_2O_3$ samples. The lowest spectrum is for the Cr metal deposited on tantalum substrate. On the top there are two spectra for $Cr_2O_3$: one for a cleaved in situ single crystal sample, and the other one for a grown film on $Al_2O_3(0001)$ substrate at $P_{buf} = 12.5 \times 10^{-4}$ mbar of $O_2$. 
more evident than from the 2p spectra, that the broadening of these lines as compared with the lines of the other samples, is accompanied by shoulder-like structures. For the $P_{buf} = 1 \times 10^{-4}$ mbar sample we cannot conclude from this fact that oxidized and unoxidized phases are involved since the rocksalt crystal structure is clearly observed. The shoulder could be indicative of the occupation of an $e_g$ orbital in the ground state as expected for a $3d^8$ configuration of CrO.

On occasion, the core level lines multiplet splitting can also be helpful in obtaining information about the spin of an ion. Emission of an electron from the 3s core level of chromium can create a vacancy in two ways, due to the parallel or antiparallel coupling of the new unpaired electron left after photoemission with the other unpaired electrons in the Cr d shell. This results in an asymmetrically split Cr 3s line into two components, and the splitting is characteristic of each oxidation state. For the Cr$^{3+}$ ion in CrF$_3$ and Cr$_2$O$_3$ this exchange splitting was found to be $\approx 4.2$ eV [51] [52], and $\approx 5$ eV for the Cr$^{2+}$ ion in CrF$_2$ [53] [54]. For our samples, almost no difference could be noticed in the exchange splitting of the Cr 3s lines presented in Figure 3.11. Only the spectral weight ratio of the two peaks seemed to vary. The spectral weights and the two peak positions were determined by fitting each Cr 3s spectra with two Lorentzian peaks, after the background was subtracted. This method is far from being accurate since the Cr 3s peaks are broad. Nevertheless, the results are summarized in the following table for the grown samples as a function of $P_{buf}$, and for the Cr$_2$O$_3$/Al$_2$O$_3$ and Cr$_2$O$_3$ single crystal reference samples in the bottom lines.

<table>
<thead>
<tr>
<th>$P_{buf}$ (mbar)</th>
<th>Exchange splitting energy (eV)</th>
<th>Cr 3s weights ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75 $\times 10^{-4}$</td>
<td>3.98</td>
<td>1</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>3.97</td>
<td>1.65</td>
</tr>
<tr>
<td>$1.25 \times 10^{-4}$</td>
<td>3.98</td>
<td>2.03</td>
</tr>
<tr>
<td>$1.5 \times 10^{-4}$</td>
<td>4.1</td>
<td>1.96</td>
</tr>
<tr>
<td>$2 \times 10^{-4}$</td>
<td>4.04</td>
<td>2.08</td>
</tr>
<tr>
<td>$3 \times 10^{-4}$</td>
<td>4.03</td>
<td>2.57</td>
</tr>
<tr>
<td>$4 \times 10^{-4}$</td>
<td>4.03</td>
<td>2.8</td>
</tr>
<tr>
<td>Cr$_2$O$_3$/Al$_2$O$_3$</td>
<td>4.1</td>
<td>2.01</td>
</tr>
<tr>
<td>Cr$_2$O$_3$ single crystal</td>
<td>4.1</td>
<td>2.18</td>
</tr>
</tbody>
</table>
Figure 3.12. XPS Al $K_\alpha$ of the VB and O2s levels, as a function of the $NO_2$ buffer volume pressure $P_{buf}$ during deposition. $P_{buf}$ (in mbar) is indicated on each spectrum for the grown $Cr\text{O}_yNi_{1-y}$ samples. The lowest spectrum is for the $MgO$ annealed substrate, then follow the Cr metal deposited on tantalum substrate spectrum. On the top there are two spectra for $Cr\text{O}_3$: one for a cleaved in situ single crystal sample, and the other one for a grown film on Al$_2$$O_3$(0001) substrate at $P_{buf} = 12.5 \times 10^{-4}$ mbar of $O_2$. 

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Chapter 3  
$NO_2$ assisted chromium oxides growth
Finally, in figure 3.12 are shown the valence band spectra, together with the O 2s, N 2s and O 2p and N 2p peaks, for the same samples used in figures 3.10 and 3.11. In the bottom was added an extra MgO annealed substrate spectrum for comparison. The background was subtracted for each line and the intensities were normalized. The charge correction was done by using the same method as for the Cr 2p lines, resulting for the O 1s the same binding energy for all the oxide samples. Also here one can observe the development of a low energy shoulder in the Cr 3d spectrum closest to the Fermi level, when lowering the NO₂ buffer pressure from $4 \times 10^{-4}$ mbar to $0.75 \times 10^{-4}$ mbar. This low energy shoulder suggests the presence of a Cr 3d $e_g$ occupation which one would expect for a CrO like system, i.e. with the $e_g^3$ configuration.

3.6  *Ex situ* structural analysis

3.6.1  RBS/channeling

The study of the crystal structure quality and epitaxy of the grown samples can be done in a more quantitative way by using RBS analysis\(^1\). This kind of analysis also gives information on the composition of the layers.

The sample which was characterized with RBS was grown in similar conditions as the sample presented in Fig. 3.1: on MgO(100) substrate, at 300°C substrate temperature and $1.5 \times 10^{-4}$ mbar NO₂ buffer volume pressure, having a thickness of $\approx 46$ ML as determined from the RHEED intensity oscillations. The chemical composition of this sample was found by XPS measurements - before the MgO cap layer was deposited - to be $Cr_{0.75}O_{0.8}N_{0.2}$.

In Figure 3.13 two RBS spectra are presented: the circles represents the yield of backscattered $He^+$ particles measured in random incidence geometry, and the filled area represents the yield measured with the incident beam aligned along the [001] crystal axis of the MgO substrate, both as a function of the energy of the backscattered particles. The chromium, magnesium, oxygen and nitrogen edges are indicated on the random spectrum. The magnesium intensity peak in the channeling direction spectrum originates from the surface of the MgO cap layer.

By comparing the two spectra the minimum yield for the chromium peak of $Cr_{0.75}O_{0.8}N_{0.2}$ (at about 765 keV) was found to be 7.5% proving a very high crystal quality of the film. The channeling along the [001] crystallographic direction of

\(^1\)These RBS measurements have been performed by P.J.M. Smulders.
the chromium oxide approximately coincides with that of \(MgO\), indicating that the film was grown epitaxial on the substrate, with \((100) \parallel (100)\) and \([100] \parallel [100]\) epitaxial relationships. The oxygen and magnesium intensity peaks in the channelling direction spectrum come from the surface of the \(MgO\) cap layer.

![Figure 3.13. RBS spectra for random direction (circles) and [001] aligned orientation (filled area) for the sample. The minimum yield is 7.5%.

From the fit of the random spectrum we found the chromium oxide layer thickness to be about 90Å and a nitrogen contamination of 20% with respect to the total anion concentration in the sample. This confirms the XPS result and also proves that the nitrogen is incorporated in the layers by replacing part of the oxygen ions. 

By RBS also the [011] axis channelling angle for this sample was measured and in Figure 3.14 the normalized intensity as a function of the ion beam angle of incidence with the [001] surface normal is presented. The continuous line represents the \(MgO\) signal buried below the film, the dashed line is the spectrum for \(MgO\) uncovered substrate which was protected during sample growth by a stainless-steel strip, and finally the circles represent the \(C_{0.75}O_{0.8}N_{0.2}\) signal. These spectra were recorded by scanning the ion beam in the (100) crystal plane of \(MgO\), from
3.6 Ex situ structural analysis

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Figure 3.14. [011] channelling dips in: Cr for \(Cr_{0.75}O_{0.8}N_{0.2}\) layer (circles), Mg for \(MgO\) uncovered substrate (dash line), and Mg for \(MgO\) substrate buried below the film (continuous line).

The [001] surface normal to the [011] axis, until the channelling minima were found.

As expected for a crystal with cubic symmetry, the angle between the [001] and [011] of the \(MgO\) substrate was found to be exactly \(45^\circ\). For the chromium oxide film it can be seen that the channelling dip deviates from \(45^\circ\) by \(1.1(2)^\circ\), indicating that the film has not a cubic, but tetragonal structure. This could be just a distortion due to the fact that the film is not relaxed to its own lattice constant, but is lattice matched at the interface with the substrate and has an expanded in-plane lattice constant. It could also be that the unit cell of this compound is not cubic at all, but is tetragonal due to some Jahn-Teller preferential occupations of the 3d orbitals in the \(Cr^{2+}\) ions. In any case, if we assume complete lattice matching between the substrate and the film as also the minimum yield from Fig. 3.13 would suggest, then the out-of-plane lattice constant of the \(Cr_{0.75}O_{0.8}N_{0.2}\) would be 4.05Å as compared to the in-plane value of 4.212Å.

The scan of the chromium yield has an asymmetric shape around the minimum because the scan was measured in the (100) plane of \(MgO\) which can differ from
the one of the film, due to the fact that the film does not have a perfect cubic structure.

3.6.2 XRD

The structural studies of the same $Cr_{0.75}O_{0.8}N_{0.2}$ sample were completed by XRD measurements\(^{(2)}\).

From a first specular reflectivity scan (Figure 3.15) the thickness of the film appears to be about 91Å and has a rms (root mean square) roughness of about 6Å. The $MgO$ cap layer is about 75Å thick and appears to be very rough. The thickness of the chromium oxide layer is consistent with that calculated from the number of

\(^{(2)}\) These XRD measurements have been performed by M.A. James.

![Figure 3.15](image-url) 

**Figure 3.15.** X-ray specular reflectivity for $Cr_{0.75}O_{0.8}N_{0.2}/MgO(100)$. The measured data is shown by filled circles, the best fit by the solid line. $\theta$ is the angle made by the incident beam of wave length: $\lambda = 0.15418$ nm with the surface plane.
RHEED oscillations observed during growth (92Å), if we consider the out-of-plane lattice constant of the film 4.05Å as found by RBS measurements. The chromium oxide layer could easily be fitted with a simple layer of uniform density, however, the MgO cap layer proved to be more problematic, and to achieve a good fit it was considered to be composed of two separate MgO layers of different densities: a layer of 54Å in thickness with bulk MgO electron density (1.1Å⁻³), on top of which is a layer of 20Å in thickness with a reduced electron density (0.68Å⁻³). This makes sense in view of the fact that the MgO cap layer is rough, so at the surface it is not so dense. This produced the fit shown in Figure 3.15 (solid line).

Further along the specular direction we find the (0, 0, 2) and (0, 0, 4) bulk Bragg diffraction peaks from the MgO substrate. Figure 3.16 shows the MgO(0, 0, 2) reflection. Apart from the main peaks at 2θ is 42.9° and 43° due to Cu Kα1 and Kα2 radiation (1.5406 and 1.5444Å in wavelength respectively), a number of spurious peaks are present in the spectrum. These peaks appear because the flat graphite

![Graph showing MgO(0,0,2) Bragg peak for Cr₀.75O₀.8N₀.2/MgO(100). Also shows CrO(0,0,2) peak at 2θ = 44.7°.](image-url)
monochromator does not fully monochromate the X-ray beam. For example, the
peaks at $41^\circ$ and $41.4^\circ$ arise from W $L_\alpha$ radiation and the peak at $42.7^\circ$ is probably
due to Ta $L_\alpha$, all such peaks being due to impurities in the X-ray source. The use
of a Ni filter in the pre-optics significantly reduces the intensity of the $K_\beta$ radiation
and most of the source impurity lines.

A broad peak is observed at $2\theta \approx 44.7^\circ$ which arises from the $Cr_{0.75}O_{0.8}N_{0.2}$
overlayer, i.e. $Cr_{0.75}O_{0.8}N_{0.2}(0,0,2)$, if a rocksalt structure is assumed. This peak
has a full width at half maximum (FWHM) of $1.3^\circ$ due to the finite thickness of the
film, and a position that corresponds to a structure with a lattice constant of 4.05Å
perpendicular to the (001) surface. The chromium oxide film layer spacing in a
direction perpendicular to the substrate is thus 2.025Å.

To check whether the chromium oxide layer has a rocksalt structure and is
lattice-matched to the $MgO$ surface unit mesh, we can search for off-specular
Bragg reflections arising purely from the $Cr_{0.75}O_{0.8}N_{0.2}$ overlayer. This is most
conveniently done with reciprocal space maps [55]. In Figure 3.17 a reciprocal
space map around the $MgO(2,2,4)$ peak is shown, where the experimentally mea-
sured scans have been converted into scans of perpendicular ($k_\perp$) versus parallel
($k_\parallel$) momentum transfer. The intensity scale in the figure is logarithmic. At the
center of the scan is the $MgO(2,2,4)$ peak. Note that two peaks are visible due
to the presence of Cu $K_{\alpha1}$ and Cu $K_{\alpha2}$ radiation. Also two stripes of scattering
profile perpendicular to each other around the $MgO(2,2,4)$ peak are visible, one
is due to mosaicity of the substrate, and the other one is an inherent instrumental
effect caused by white radiation in spite of the presence graphite monochroma-
tor. At higher perpendicular momentum transfer an additional peak is observed
which arises from the chromium oxide layer. This $Cr_{0.75}O_{0.8}N_{0.2}(2,2,4)$ peak
has the same parallel momentum transfer as the substrate peak, indicating that the
film overlayer has the same in-plane lattice constant as that of the $MgO$ substrate,
i.e. the chromium oxide film is lattice matched to the $MgO$ substrate. No other
reflections than those characteristic for the rocksalt structure were found and in the
real space the lattice constants are: 4.212Å in-plane and 4.05Å out-of-plane, which
confirms the RBS results. The FWHM of the peak is $2.5^\circ$, again due to the finite
thickness of the film.

Finally, Figure 3.18 is a schematic representation of the $Cr_{0.75}O_{0.8}N_{0.2}$ film
structure on top of $MgO$ substrate, with the as-found lattice constants.

XRD measurements done on thicker chromium oxide samples ($\approx 300Å$) grown
at $P_{bu}=1 \times 10^{-4}$ mbar indicated that the films tend to relax to a cubic crystal
Figure 3.17. XRD reciprocal space map around the non-specular (2,2,4) reflection of the Cr$_{0.75}$O$_{0.8}$N$_{0.2}$ sample. Plotted is the log(diffracted intensity) as a function of the in-plane $k_\parallel$ and out-of-plane $k_\perp$ reciprocal wave vectors. The x and y axis are in the units of $2\pi/\lambda$ with $\lambda = 0.15418$ nm.

structure at this thickness having a lattice constant of $\approx 4.13\text{Å}$. For the samples grown at $P_{\text{nuj}} = 3 \times 10^{-4}$ mbar, 500Å thick, all the reflections coming from the chromium oxide except (0,0,1) are hardly visible, indicating a not so good quality of the crystal structure for this type of sample. The in-plane lattice constant was determined from the (0,0,2) Bragg peak position of the film to be $\approx 4.02\text{Å}$. 
3.7 XAS results

The best technique which helps to make a distinction between the $d^8$ and $d^4$ configurations of the chromium ion is XAS and in Figure 3.19 we present the $Cr L_{23}$ TEY X-ray absorption spectra for three samples: one grown on an $MgO(100)$ substrate at $400^\circ C$ and $1 \times 10^{-4}$ mbar $NO_2$ buffer volume pressure (bottom line), another one grown on $MgO$ substrate at $400^\circ C$ and $3 \times 10^{-4}$ mbar $NO_2$ (middle line) and finally the top most curve is the reference spectrum of a $Cr_2O_3$ single crystal sample cleaved in situ. The intensities are normalized for each spectrum. For the grown samples spectra of normal incidence (the incident X-ray beam is perpendicular to the sample, represented with a continuous line) and grazing incidence (the incident beam is parallel with the sample, represented with dotted line) are shown.

The chemical composition of the samples (indicated on each spectra) as found

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(3) All XAS experiments in this thesis have been performed by H.L. Tjeng.
with XPS is: for $P_{buf} = 1 \times 10^{-4}$ mbar $x \approx 0.9$ and 30% nitrogen contaminations, and for $P_{buf} = 3 \times 10^{-4}$ mbar growth $x = 0.7$ and almost no nitrogen is present.

It can be seen that the spectrum looks very similar to the $Cr_2O_3$ single crystal spectrum for the $P_{buf} = 3 \times 10^{-4}$ mbar sample, indicating that the Cr ion is in a $d^3$ state. For the sample grown at $P_{buf} = 1 \times 10^{-4}$ mbar, the spectrum is quite different from that of $Cr_2O_3$ indicating that the Cr is in a different oxidation state. Whether this spectrum is representative for a Cr $3d^4$ configuration is not clear at the moment. It is certainly different from the published $CrF_2$ spectrum [56], which is supposed to be that of an ionic Cr $3d^4$, although there are several features.
in the \( \text{CrF}_2 \) spectrum that cannot be explained by theory, indicating perhaps the presence of impurities or degradation. More detailed calculations will be needed in order to establish the role of nitrogen and defects for the valence and crystal fields of the Cr ion in our \( P_{\text{buf}} = 1 \times 10^{-4} \) mbar sample. For the sample grown at \( P_{\text{buf}} = 1 \times 10^{-4} \) mbar there is also no difference in between the normal and grazing incidence spectra, as one would expect from the theoretical calculations for polarization dependence in the case of a \( d^8 \) ordered Jahn-Teller distorted system. This means that even if some \( \text{Cr}^{2+} \) valence state ions would be present in this sample, as the Cr 2p XPS measurements would suggest, the tetragonally distortion of the crystal structure is due to the stress induced in the film by the \( \text{MgO} \) substrate, and not to a Jahn-Teller preferential occupation of the 3d orbitals in the \( \text{Cr}^{2+} \).

Measurements of the nitrogen K edge absorption spectra showed the high nitrogen contamination for the \( P_{\text{buf}} = 1 \times 10^{-4} \) mbar sample.
3.8 Conclusions

Chromium oxide samples can be grown on MgO and SrTiO₃ substrates using various fluxes of NO₂ oxidizing agent. The RHEED patterns show that the films grow in the rocksalt structure. For the NO₂ buffer volume pressures in between $1 \times 10^{-4}$ and $2 \times 10^{-4}$ mbar, the strong oscillatory behavior in the intensity of the specularly reflected RHEED spot indicates that the films are growing in a layer-by-layer mode. The very good crystalline quality of the films is confirmed by RBS and XRD for a sample grown on MgO(100) with a thickness below 100Å, and the lattice constant is found to be 4.212Å in-plane and 4.05Å out-of-plane. In other words, the chromium oxide film follows in-plane the lattice constant of MgO substrate.

It is quite surprising that such a good crystallinity can be achieved for the grown samples, in view of the fact that bulk CrO does not exist. The spectroscopic investigations using XPS and XAS revealed probably the key issue to this. We found that there is a substantial amount of N built in the chromium oxide films, depending on the NO₂ gas pressure that is being used for the growth. The nitrogen incorporation in the samples increases almost linear with decreasing the NO₂ flux for the crystalline samples, similar as in the case of NO₂ assisted MBE of iron oxides [8]. The XPS, RBS and XAS data suggest that the nitrogen is uniformly incorporated in the layers by replacing part of the oxygen ions.

For low gas pressures the film has a Cr$_{1-x}$O$_{0.7}$N$_{0.3}$ like composition, while for high gas pressures it has the Cr$_{0.7}$O composition. The XPS measurements give some indications that Cr$^{2+}$ ions are present in the Cr$_{1-x}$O$_{0.7}$N$_{0.3}$ samples: the Cr $2p_{3/2}$ chemical shifts and the spin-orbit splitting of the Cr 2p lines. The XAS results indicate that in Cr$_{0.7}$O the Cr ion is in a 3+ valence state, while in Cr$_{1-x}$O$_{0.7}$N$_{0.3}$ part of the Cr ions may be in a 2+ valence state or in a strongly covalent bond with the nitrogen. Nevertheless, the crystal structure of the films is in all cases rocksalt fcc and not corundum nor spinel. This seems to indicate that built-in nitrogen or cation vacancies reduce the number of Cr$^{2+}$ and they also create the space for the Cr$^{2+}$ ions to have the Jahn-Teller distortions directed towards them, and that together with the substrate surface, they can stabilize the rocksalt structure of the oxygen sublattice.
References

References

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