Stabilizing CrO by epitaxial growth
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Chapter 1

Introduction

In the last decade, the amount of research efforts in the field of thin film research has increased considerably. One of the motivations is that new materials can be made with new or improved properties. It is more and more recognized that physical and chemical properties of materials in thin film form depend strongly on their environment, especially for highly correlated materials and molecular crystals.

There are many examples in the literature that demonstrate the opportunities provided by thin film research. A nice example from the field of magnetism is the work carried out by the group of Kawai [1], in which they succeeded in realizing a ferromagnetic spin order in thin films of LaFe$_{0.5}$Cr$_{0.5}$O$_3$, a material that normally, i.e. in bulk form, is always a paramagnet. The films become ferromagnetic by making the material as a superlattice of LaFeO$_3$ and LaCrO$_3$ layers alternatingly stacked along the [111] direction such that the dominant magnetic interactions are given by the ferromagnetic $(d^5-d^3)$ Fe-O-Cr superexchange [2–4]. Also spectacular is a claim from the field of high-T$_c$ superconductivity, namely the one in which Locquet et al. [5] stated that the critical temperature of La$_{0.9}$Sr$_{0.1}$CuO$_4$ can be doubled using epitaxial strain, i.e. by growing the material as a thin film epitaxially on a SrLaAlO$_4$ substrate.

There are several approaches possible to modify the properties of materials using thin film technology. An approach often applied for (inter)metallic magnetic systems is to make use of the reduced dimensionality of the ultra-thin film to create quantum well states or interface states, as to alter the magnetic properties of the materials. For oxides, the presence of the substrate can be used to provide a different crystal field near the interface or to induce strain in the thin film, thereby influencing the magnetic anisotropy like in the case of NiO films.
on MgO(100) [6,7], and/or changing the magnitude or even the sign of the various (super)exchange interactions [1–5]. The substrate can also be used to create a modified Madelung potential near the interface or to provide extra polarizability with which the properties of the film can be altered [8–12].

The use of substrates in thin film research is also extremely valuable for the preparation of materials. The substrate, for instance, can act as a template for the overlaying film so that it grows in a particular crystal structure that could be different from the bulk at ambient conditions. In some cases one can even stabilize thin films of materials that otherwise do not exist as bulk material in nature. By using MBE (molecular beam epitaxy) techniques, one can make materials far out of the equilibrium conditions, and thus one has the possibility to find alternative and perhaps also better routes to make high quality materials.

Motivated by the spectacular colossal magnetoresistance (CMR) behavior - which is the magnetoresistance associated with a ferromagnetic to paramagnetic transition - observed in La$_{1-x}$Sr$_x$MnO$_3$ compounds [13], we would like to explore the properties of CrO, a material in which the transition metal ion has the Jahn-Teller 3$d^1$ configuration, the same as that found in LaMnO$_3$. However, not much is actually known about CrO. Worse, to our knowledge there is no indication in the literature that CrO even exists as a bulk material in nature. We therefore first have to find ways to grow this material in an artificial manner, for instance, by making use of the MBE technique as a powerful tool to create single crystal thin films far out of equilibrium conditions. This is in principle a non-trivial task, but the efforts that we may have to put in are perhaps well spent, since it is tantalizing to speculate that CrO may have equally fascinating magnetic and electrical properties as those observed in the manganates. The origin of these phenomena lies in the strong interaction between the orbital and the spin degrees of freedom typical in Jahn-Teller systems, as we now will briefly explain.

Let us consider first a 3d transition metal ion surrounded by six oxygen ions in a simple octahedral symmetry. The transition metal $e_g$ orbitals ($d_{x^2-y^2}$, $d_{z^2}$) point directly at these oxygen ions, while the $b_{2g}$ orbitals ($d_{xy}$, $d_{xz}$, and $d_{yz}$) point in between the oxygen ions. The electrostatic repulsion causes the $e_g$ orbitals to have a higher energy than the $b_{2g}$ [14] [15], and this octahedral crystal field splitting is labelled as $10Dq$. Which of these orbitals will actually be occupied depends very much on the magnitude of the crystal field splitting relative to the on-site Coulomb and exchange interactions between the electrons, of which the Hund’s rule $J_H$ is an important term that favors the occupation of orbitals with a parallel spin alignment.
For most transition metal compounds in which the ions has a $d^1$ occupation, we expect that the high spin state is more stable than the low spin state, since usually the $10Dq$ values are quite modest (e.g. $10Dq$ not larger than about $4J_{HF}$). This is indeed the case for the manganates, and figure 1.1 shows the corresponding energy level diagram.

In this high spin $d^1$ configuration, one electron is occupying a doubly degenerate $e_g$ orbital. The system now can lower its energy, if this degeneracy can be lifted. This lowering of the symmetry can be done, for instance, by lengthening the transition metal - oxygen bonds in the $z$-direction, as shown in figure 1.1. The result is now that the $d_{x^2-y^2}$ orbital will be occupied, while the $d_{x^2-y^2}$ remains unoccupied. This phenomenon is called the Jahn-Teller effect. The occurrence of such local distortions away from octahedral symmetry in a solid state system has important implications, since one now has to consider in detail how these local distortions, and thus local orbital orientations, can or cannot be made commensurate, and in what manner, with the crystal structure. Using the famous Anderson-Goodenough-Kanamori rules for superexchange interactions [2–4], one can easily understand that certain cooperative arrangements of the Jahn-Teller distortions will lead to ferromagnetism, while other arrangements may result in antiferromagnetism [16–18]. The coupling of local orbital orientations with the spin degrees of freedom
will become even more complex (and interesting at the same time), if extra charge carriers are introduced into the system [13].

In laying out a plan to grow CrO in an artificial manner as a single crystal thin film using MBE, it is quite difficult to make an \textit{a priori} justification for the choice of substrates and growth conditions. The crystal structure of CrO is simply not known, and if we look at all the other 3$d$ transition metal monoxides, we see that they have the rocksalt structures [19] with lattice constants in between $4.062\,\text{Å (VO)}$ and $4.4448\,\text{Å (MnO)}$, except CuO, which is monoclinic, probably related to the fact that Cu$^{2+}$ is a Jahn-Teller ion. This seems to suggest that the Jahn-Teller effect in Cr $d^4$ will also play an important role for the growth and the resulting crystal structure. We will therefore use substrates with various lattice constants: $\text{MgO}$, (100) oriented, having a rocksalt crystal structure and a lattice constant $a_{\text{MgO}} = 4.212\,\text{Å}$; $\text{MnO}$, (100) oriented, with rocksalt structure and $a_{\text{MnO}} = 4.4448\,\text{Å}$; and $\text{SrTiO}_3$, (100) oriented, having a perovskite structure and $a_{\text{SrTiO}_3} = 3.905\,\text{Å}$. The underlying idea is that a substrate with a smaller lattice constant may stabilize the occupation of the $d_{3z^2-r^2}$ orbitals of the chromium ions, while a substrate with a larger lattice constant may induce the occupation of the Cr $d_{x^2-y^2}$ orbitals, or a mixture of superstructured $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbitals. Yet, perfect lattice matching may not be possible, and the CrO film may be strained if the film is thin, or relaxed if a certain (still to be determined) critical thickness is exceeded, complicating the growth process and analysis thereof.

Our hope is that at least the MBE method is capable of inducing various chromium oxide phases. In order to see which ones we can expect, in figure 1.2 the chromium - oxygen phase diagram is shown, indicating the stable phases as a function of temperature and oxygen composition [20], [21]. As it can be seen, the most stable oxide phase is $\text{Cr}_2\text{O}_3$; $\text{Cr}_3\text{O}_4$ is thermodynamically stable only above 1600°C, and CrO does not exist.

The corundum structured $\text{Cr}_2\text{O}_3$ is a magnetic insulator [22] and is an important industrial catalyst which is often used in polymerization reactions [23]. It is also used in passivation of stainless steel. There is another stable form of chromium oxide, $\text{CrO}_2$, a conducting ferromagnet used in magnetic recording media because of its resistance to corrosion and its high coercivity. The formation of a cubic spinel $\gamma - \text{Cr}_2\text{O}_3$ has also been reported under certain thin film growth conditions [19].

Until now, most of the work on chromium - oxygen systems focused on the study of oxygen adsorption and oxide formation on $\text{Cr}(100)$, $\text{Cr}(110)$ and $\text{Cr}(111)$ surfaces, and on growing epitaxial thin films of $\text{Cr}_2\text{O}_3$ on Pt(111), $\text{Cr}(110)$ and
Al₂O₃(0001) substrates. However, Maetaki et al. claimed that they obtained one monolayer of CrO, (111) oriented on Cu(100) and Cu(110) substrates by deposition of chromium atoms, exposure to oxygen and heating at 400°C in vacuum [24], [25]. Xu et al. studied the adsorption and reaction of NO and NO₂ on Cr₂O₃(111)/Cr(110), and they found that the Cr atoms located within the oxide surface are in oxidation states different from the bulk, namely Cr²⁺, Cr³⁺ and some metallic Cr [26]. Here also the study done by Schmid et al. can be mentioned who have observed on the Cr(100) surface covered with one monolayer of oxygen a chromium vacancy concentration of about 17% in the first monolayer [27]. They argue that the vacancy formation is energetically favored and not caused by stress but by electronic effects.
For growing the chromium oxides, we used first $NO_2$ as oxidizing gas and this work is described in chapter 3 of this thesis. $NO_2$ proved to be a very efficient oxidizing agent in preparing $NiO$ and $CoO$ thin films on $MgO(100)$ substrate [28] and $MgO$ thin films on $Ag(100)$ substrate [29]. Moreover, it was shown that most of the iron oxide phases can be induced by $NO_2$ assisted MBE [30–32], and as long as the $NO_2$ flux is sufficiently high it will act exclusively as a source of oxygen. A possible disadvantage of using $NO_2$ could be the fact that at low fluxes phases are formed in which oxygen is partly substituted by nitrogen, and the amount of nitrogen in the samples increases nearly linear with decreasing the $NO_2$ flux. For this reason, $O_2$ and $O_3$ were used also as oxidizing agents, and this work is described in chapter 4.
References

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