

Summary

This thesis describes the efforts to stabilize chromium monoxide (CrO) as a thin epitaxial film on various substrates.

The most stable and common oxidation phase for chromium is in chromium sesquioxide (Cr_2O_3). CrO does not exist as a bulk material in nature, therefore we have to grow it in an artificial manner as a single crystal film using molecular beam epitaxy (MBE). The motivation behind this project is that in CrO , Cr ion has the same electronic configuration as the manganese ion in the lanthanum manganates ($LaMnO_3$), a material that doped with strontium or calcium ($La_{1-x}Sr_xMnO_3$) is the so-called colossal magneto resistance material. One may expect that CrO has equally fascinating magnetic and electrical properties as the manganates.

Chromium monoxide is a compound build up from two different types of atoms: chromium and oxygen. Stoichiometric phases are those for which the sample chemical composition has one Cr atom to one O atom. The expected crystal structure is rocksalt, since all the transition metal monoxides (except copper monoxide) have this crystal structure arrangement.

The reason that CrO is not stable in the nature and nobody made it so far has to do with the d orbitals occupation of the Cr^{2+} ion which is surrounded by six O^{2-} ions in the rocksalt structure. The orbital represents the shape of the electron cloud in solid. Cr^{2+} ion has four anisotropic-shaped d-orbital electrons and five possibilities for them to arrange. Three of the electrons occupy three of these orbitals (d_{xy} , d_{xz} and d_{yz}) and have about the same energy, but the fourth electron has to choose one of the two left orbitals with higher energy than the previous ones ($d_{x^2-y^2}$ and d_{z^2}), due to a greater Coulomb (electrostatic) interaction of the electron with the oxygen negative ions. This seems to be not an easy choice for the electron and is the so-called Jahn-Teller problem.

In the MBE technique a material is evaporated onto a single crystal substrate under ultra-high vacuum conditions. In certain cases, the deposited material can grow in a nice single-crystal film, with the atoms symmetrically ordered in a lattice. This depends on the crystal structure and orientation of the film as compared with

the surface of the chosen substrate. MBE method is suitable for growing materials under strongly non-equilibrium conditions, for the making of new materials with unexpected atomic and electronic structures. But also in growing yet well-known materials by MBE, the presence of the substrate can be used to provide a different crystal field near the interface or to induce strain in the film, thereby influencing the physical and chemical properties of the material in thin film form.

We don't know what the CrO lattice constant would be, and so three substrates with different lattice constants were used: MgO , (100) oriented, MnO , (100) oriented, both having rocksalt crystal structure, and $SrTiO_3$, (100) oriented, having a perovskite structure. For growing CrO , the Cr metal deposit onto the substrate was oxidized simultaneously by a beam of nitrogen dioxide (NO_2), oxygen (O_2) or ozone (O_3). For obtaining the desired chemical composition of the chromium oxide layers we varied a few growth parameters: substrate temperature, Cr metal deposition rate (flux) and oxidizing gas flux. High-energy electron diffraction upon the growing surface gave patterns characteristic of the surface atomic arrangement and was helpful to control the film thickness within one atomic layer. After growth, different analyzing techniques were further used to investigate the crystal structure and electronic structure of the new material. The principle idea of these techniques is that the material surface is bombarded with electrons, X-rays or ions, and the electrons or ions which are coming out are analyzed.

Chapter 3 and chapter 4 are describing the actual work and the results. In chapter 3, NO_2 gas was used to oxidize the evaporated chromium beam. Surprisingly in the view of the fact that CrO does not exist as a bulk material, a very good crystallinity of the sample was achieved. Nevertheless, the chemical composition of the samples proved to be not of stoichiometric chromium monoxide, but a substantial amount of nitrogen was built-in the films, depending on the NO_2 gas pressure that was used for the growth. The nitrogen is uniformly incorporated in the layers by replacing part of the oxygen ions, leading to a composition of: $Cr_{0.7}N_{0.3}$ for low gas pressures. For high gas pressures a Cr defect structure was found with the composition of $Cr_{0.7}O$.

Our meaning was to grow stoichiometric CrO , so in order to avoid the nitrogen contamination in the samples, O_2 and O_3 gases were used further as oxidizing agents. This work is described in chapter 4. We succeeded on growing CrO at low gas pressures, with a composition which is closed to one Cr atom to one O atom. Nevertheless, the crystal structure this time proved to be rocksalt with a substantial amount of disorder. Another unexpected result is that for high gas pressures the

composition of the grown layers is of $Cr_{0.7}O$, but now defect rocksalt structure shows a superstructure which seems to indicate that the defects are ordered. Apparently the Cr defects and/or build in nitrogen ensures the absence of a Jahn-Teller problem for our grown samples.

The CrO growth study described in this thesis shows the important stabilizing role of the substrate.

