Chapter 1

Introduction

Metal oxides, especially transition metal oxides comprise a very diverse and fascinating class of compounds with properties covering almost all aspects of material science and physics [1]. The bonding characteristics may be classified as covalent for one system and highly ionic for the other. For the electrical conductivity, they cover the entire range from metals to semiconductors and insulators. For example, they can be insulators (CoO, NiO, BaTiO$_3$), semiconductors (Fe$_{0.9}$O), metals (CrO$_2$, ReO$_3$) and superconductors (YBa$_2$Cu$_3$O$_7$) [2]. They can be ferromagnetic (CrO$_2$), anti-ferromagnetic (CoO, NiO), ferrimagnetic (Fe$_3$O$_4$, Y$_3$Fe$_5$O$_{12}$) and ferroelectric (BaTiO$_3$). Many oxides have different oxidation stats, e.g. vanadium oxide (VO, VO$_2$, V$_2$O$_3$ and V$_2$O$_5$). For the crystal structure, they can be simple binary monoxides (NiO, CoO) with NaCl structure or ternary oxides (BaTiO$_3$, SrTiO$_3$) with perovskite structure. They also can form complicated structures such as Co$_3$O$_4$ or Fe$_3$O$_4$ with the normal and/or inverse spinel structure [3].

Due to the diverse physical and chemical properties, transition metal oxides find applications in many fields of technical interest, from nonlinear optics to sensors and catalysis. In some cases the bulk properties are important, as for example very often in nonlinear optics. In other cases the surface properties play a major role, as in catalysis [4]. The bulk properties of simple binary oxides are pretty well understood. In contrast, rather little is known about the surfaces of oxides, even the most simple ones. The present knowledge has been comprehensively reviewed by Henrich and Cox in their book *The Surface Science of Metal Oxides* [1].

Applications of Transition Metal Oxides. One of the most important applications of transition metal oxides is heterogeneous catalysis. They are used for synthesizing many organic compounds via selective oxidation, dehydrogenation, isomerization and other chemical processes. Not much is known about atomic scale mechanisms of catalytic reactions on transition metal oxides, and our understanding of basic transition metal oxide surface chemistry greatly lags behind that of semiconductors and metals. This basic understanding, in particular the relationships between the catalytic function of transition oxide materials and their crystallographic structures and chemical compositions in the surface region, is needed for a targeted catalyst development. On pure metal catalysts the delocalized electrons can easily
be transferred resulting in redox chemistry reaction mechanisms. Transition metal oxides are ionic compounds exposing acidic and basic sites, which may control their surface chemical properties. At the same time, the redox chemistry loses in importance, because the electronic states are separated by the bandgap and become less accessible. Metallic and semiconducting oxides with small bandgaps allow a combination of redox and acid base chemistry, whereas highly ionic oxides with large bandgaps become pure acid base catalysts. In this context, a large amount of work has been performed over polycrystalline oxide catalyst samples, resulting, for example, in the important concept of surface coordinatively unsaturated sites. But since electronic surface structures and acid base properties of oxides may vary greatly with the surface orientation, the conclusions to be drawn from studies on polycrystalline samples are limited. Therefore, a direct elucidation of atomic structural elements involved in chemisorption processes and catalytic conversions requires samples exposing one defined surface orientation. This has led to an increasing number of surface science studies on single crystal metal oxide samples within the last decade, accompanied by theoretical work [1, 5].

While transition metal oxides proved to be important in heterogeneous catalysis for decades, their application in the field of magnetic electronic came to be a subject of research only recently. For example, barium titanate (BaTiO$_3$) is a typical representative of ferroelectric materials with the useful properties of high spontaneous electric polarization and permittivity. In non-volatile ferroelectric computer memories both of these properties, the high permittivity and the permanent electrical polarization, are utilized [6]. Owing to the permanent polarization the charge of the capacitor of the memory cell circuit is maintained, even if the power is switched off, which makes the memory a nonvolatile one. Furthermore, the high permittivity helps to reduce the size of the capacitor, which is a rather large circuit element on computer chips. Since the material will be deposited as thin films in these applications, there is an increasing interest in the growth of such films. They have been grown on (100) and (111) oriented substrates using a variety of growing techniques, e.g. r.f.-sputtering [7, 8], pulsed laser deposition/ablation [9, 10], reactive evaporation [11, 12] and metallo-organic chemical vapor deposition [13, 14]. Most of these investigations concentrate on the 'bulk' properties of such films. To an increasing extent, the films however are characterized using surface sensitive methods, such as Low Energy Electron Diffraction (LEED). The scope of interest has mainly been grain size, faceting and surface roughness on the scale of micrometers and nanometers. Structure on an atomic scale is still lacking, though.

Another application of BaTiO$_3$ is the use of polycrystalline n-doped material in thermistors of thermal overload protection circuits, where the specific resistivity of BaTiO$_3$ increases with temperature by several orders of magnitude in the range from 110 to 140 °C. The increase of resistivity with temperature results in a positive temperature coefficient of resistivity (PTCR). The PTCR effect in BaTiO$_3$ is obviously
related to the phase transition of BaTiO$_3$ at the Curie point ($T_c \approx 120^\circ$C), where the ferroelectric tetragonal room temperature phase converts to the paraelectric cubic one [15]. The permittivity undergoes dramatic changes during this phase transition. It has been widely accepted that the PTCR effect can be interpreted by a grain boundary layer model proposed by Heywang [16]. According to his model, the PCTR effect is caused by an increase in the potential height of double Schottky-type barrier layers formed at the grain boundaries associated with the ferroelectric-paraelectric phase transition at $T_c$. The existence of two dimensional surface acceptor states is indispensable to the formation of the barrier layers. He assumed that a rapid decrease of the dielectric constant of the material above $T_c$, according to the Curie-Weiss law, causes an increase in the potential barrier height, consequently, a PTCR anomaly results. The Heywang model was improved by Jonker to account for a low resistance below the Curie point by taking account of the compensation effect of surface acceptor states by the spontaneous polarization [17]. However, the origin of acceptor states has not been firmly identified yet. Supposedly, they are due to segregation of impurities or changes in stoichiometry at the grain boundaries. The low resistivity at lower temperatures is more controversial. The barriers at grain boundaries could either be lowered by the large permittivity or by special ferroelectric domain boundaries. A more recent detailed discussion of this topic can be found in Refs. [18,19].

In spite of these important applications and the progress in structure characterization of the ferroelectric domains by secondary electron microscopy [20], atomic force microscopy [21] and optical microscopy [22], our knowledge on the structure of single crystalline BaTiO$_3$ surfaces is still rather incomplete. While a number of publications exist for the (100) surface of BaTiO$_3$ and the related material SrTiO$_3$, only a few papers on the (111) surface of a perovskite oxide have come to our attention. Regarding the structure determination by LEED analysis, only one paper on the SrTiO$_3$(100) surface has been published [23], no quantitative LEED $I-V$ (Intensity vs Voltage) analysis has been performed on any BaTiO$_3$ surface. Our work has originally started with the BaTiO$_3$ system, where we made attempts to image and to characterize grain boundaries of polycrystalline samples as they may be visualized in the surface plane. It soon became clear during the experiments that a characterization of low index single crystalline surfaces of BaTiO$_3$ was also necessary for our understanding of polycrystalline material.

**Preparation of Thin Oxide Films.** The question of oxide preparation is central to all surface science investigations, and herein lies, what is possibly the greatest difficulty of all [1]. Compared to elemental solids, the preparation of any stoichiometric compound surface, in particular oxides, is extremely difficult, especially if we consider the preparation of different crystallographic orientations of oxide surfaces [1, 24]. In the cases of binary monoxides with NaCl structure (e.g. CoO and NiO), the polar (111) surfaces are more reactive than the non-polar (100) surface [25,26]. Non-polar and polar surfaces of ionic binary oxides exhibit fundamentally different behaviors
as far as cleavage, which is one of the desirable preparation methods. The reason
for this was pointed out long time ago and is intimately connected with the surface
potential [27]. For non-polar surfaces, such as the CoO(100) and NiO(100) surfaces,
the surface potential is finite [28]. Therefore, CoO and NiO can easily be cleaved
along the (100) direction. However, the surface potential per unit charge diverges for
polar surfaces (e.g. the NiO(111) or CoO(111) surfaces) so that cleavage of a rocksalt
structure in this direction is not possible. Thus, if we are interested in preparing
surfaces of different surface orientation, cleavage is not the most favorable method of
preparation for an ionic polar oxide surface.

There are alternative methods of preparation of stable non-polar surfaces. One is
to cut a crystallographic plane mechanically or by spark erosion and then polish the
surface [1]. This technique is similar to procedures known for the preparation of metal
surfaces. Once the sample resides in the vacuum chamber, these surfaces are sputtered
and consecutively annealed in oxygen in order to replace oxygen vacancies induced
via sputtering. This method has been successfully applied to bulk samples. TiO$_2$
is an example, where this method has been frequently used with apparently satisfactory
results. Again, the preparation of polar surfaces is difficult, because these surfaces
have the tendency to facet during the preparation process.

Another, rather different method of preparation is, that oxide films of varying
thickness may be grown on metallic substrates [29]. The geometry of the metallic
substrate then determines the structure of the oxide film to a large extent. It is this
technique that allows preparation of non-polar as well as polar surfaces. Of course, the
structural quality of the film depends very strongly on the epitaxial relation between
the lattice constants of the metallic substrate and the oxide film. In other words, we
can to a certain extent control the defect structure and defect density of the layers
grown by controlling the lattice mismatch. Three techniques have been mainly used
for this purpose. The most simple one makes use of the fact that a metal single crystal
may be oxidized and a more or less well ordered oxide film is formed. In the case of
NiO and CoO, ordered thin oxide films can be grown by oxidation of Ni or Co single
crystal surfaces. The growth of NiO(100) layers on Ni(100) has been described in
ref. [30]. The LEED pattern of oxidized Ni(100) surfaces, however, mostly indicates
the presence of a rather imperfect NiO(100) film on top of Ni(100), which might
result from the large lattice mismatch of nearly 20% between Ni and NiO. Although
the use of highly oriented Ni(100) as substrate leads to considerable improvement of
the LEED pattern from the oxidized surface [25], the large lattice mismatch always
remains a problem, with the possible consequence of defect structures in the oxide
film. An different approach to prepare well ordered NiO(100) films was used by Marre
and Neddermeyer, who evaporated Ni onto a Ag(100) surface in an O$_2$ atmosphere.
LEED and UV photoelectron spectroscopy have shown that a well ordered and smooth
NiO(100) can indeed be obtained in this way [31]. The reason for this more perfect
growth of NiO(100) layers by using a Ag(100) substrate is the smaller lattice mismatch
(only 2%) between NiO and Ag. These results were confirmed by Scanning Tunnelling Microscopy (STM). It has been demonstrated that deposition of Ni onto Ag(100) in an O\textsubscript{2} atmosphere leads to much better NiO(100) films than oxidation of Ni(100), at least regarding surface orientation, which is accessible by standard Laue techniques \cite{32}. The third technique is the oxidation of alloy surfaces. The advantage here is that the physical properties of the alloy may be advantageous for the preparation process. Using this technique, a well ordered Al\textsubscript{2}O\textsubscript{3} film on NiAl(110) \cite{33} and Ni\textsubscript{3}Al(111) \cite{34,35} has been prepared. The Al\textsubscript{2}O\textsubscript{3} film can be heated to above 1000 °C without melting the substrate. This is of crucial importance to order the layer. On Al metal such a heat treatment would lead to melting of the substrate before the oxide layer could order.

It is the purpose of the present work to provide some details on the growth of CoO(100) films on Ag(100) and to compare the results from NiO(100) films with those from CoO/Ag(100) prepared and measured in the same way. The lattice mismatch between CoO(100) and Ag(100) is slightly larger (4.3%) than that of NiO(100)/Ag(100) and it might be interesting to look for defect structures associated with the differences in lattice mismatch. It should be mentioned that Castell \textit{et al.} have observed, at elevated temperatures (nearly 500 K), atomic defect states on the (100) cleavage planes of bulk NiO \cite{36}. Similar defect states had already been detected in our previous study of NiO(100) film, but had not been described explicitly. We have also concentrated on the presence of such defect states in CoO(100) films.

The present work will demonstrate that the growth phenomena and the structural changes of the CoO film, when changing from a precursor structure to a well ordered (100) oxide layer, are very complicated and are also dependent on the layer thickness. Only for thicker films a rather uniform appearance of the surfaces was detected. In the very thin film limit (1-2 ML) the surprising variety of structures and island shapes indicates an unexpectedly large interaction between the growing film and the substrate. As already shown in the example of the NiO films grown on Ag(100) and Au(111), the substrate temperature during evaporation and the O\textsubscript{2} partial pressure are very important to determine the quality of the NiO films \cite{31,32,37}. Heiler \textit{et al.} systematically examined the growth of CoO films on Ag(100) and Au(111) as a function of these two parameters by means of Angle Resolved Ultraviolet Photoelectron Spectroscopy (ARUPS), Auger Electron Spectroscopy (AES), Auger Electron Diffraction (AED), LEED and show similar results \cite{38}. The emphasis of that investigation was to determine the electronic structure of the CoO films. The present investigation is concerted on the geometric structure characterization of thin CoO films, which combines STM and Spot Profile Analysis LEED (SPA-LEED) methods. The emphasis of the investigation is to characterize the surface of the CoO films as a function of the growth parameters on an atomic scale.

The structure of the thesis is organized as follows: Chapter 2 gives an introduction to general properties of transition metal oxides and surfaces. Chapter 3 gives the
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theoretical basis of LEED, both kinematic and dynamic theory are described. Chapter 4 deals with the Ultra High Vacuum (UHV) equipment used in this study and the details of sample preparation, with the data acquirement techniques applied to the LEED. In Chapter 5, the CoO film growth on Ag(100) is analyzed by SPA-LEED, and the results are discussed. The tensor LEED analysis is described in Chapter 6, with results of three systems, the clean Ag(100) surface, the 4 ML CoO/Ag(100) film and the BaTiO$_3$(111)(\(\sqrt{3} \times \sqrt{3}\))R30° reconstruction are presented and discussed. Finally, the conclusions are given in Chapter 7.