

# Chapter 1

## Insulator films: from basic research to technological applications

Thin films of ionic insulators have gained increasing interest over the last years due to their use in current and possible future technologies. In addition, they offer unique opportunities for studying fundamental questions in physics and chemistry. In this thesis we will concentrate on two choices out of the huge variety of possible materials and applications: wide-gap oxides, notably in the context of heterogeneous catalysis [1–3], and ultrathin sodium chloride films that have recently attracted attention as substrate for single-atom and single-molecule-manipulation experiments [4–6].

Focussing on oxides first, their surfaces and thin films play an important role in various technological applications such as heterogeneous catalysts, corrosion and scratch protection, or electronic devices. The decisive microscopic processes that control their functionality often take place at the atomic scale. For a systematic understanding and improvement of the relevant properties, a detailed atomistic understanding of these materials is therefore highly desired. Let us take heterogeneous catalysts as an example. Many present-day catalysts<sup>1</sup> consist of small metal particles on a ceramic support, which is often based on silica or alumina. A famous example is the catalytic converter in automobiles, in which platinum and rhodium is dispersed on a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support with various additives. The support material, though chemically quite inert, exerts an important influence on the catalytic activity of the noble-metal catalyst. While a particular metal may be highly effective on

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<sup>1</sup>Catalysts for redox reactions often belong to this category, while e.g. isomerisation reactions are catalysed by doped transition metal oxides or zeolites.

one support, it may be inactive on another. The reasons for this behaviour are presently not well understood. One possibility is that the oxide support directly modifies the properties of the metal clusters, another that it takes part in some of the many steps in the catalytic process.

Since real catalysts are very complex systems and not amenable to the full spectrum of the experimental surface science “tool box”, little is known about the microscopic and atomistic mechanisms that determine the catalytic activity under real-life conditions. In the surface science approach (schematically illustrated in Fig. 1.1) to heterogeneous catalysis the full problem is broken down into different aspects that can be addressed with well-defined model catalysts. For this, the ceramic support is replaced by a defined, clean and ideally crystalline oxide surface that can be studied with the different surface science experiments developed over the past decades, most often under ultrahigh vacuum conditions [3, 7, 8]. Although a number of important factors such as the influence of the gas phase (pressure gap, materials gap) or the temperature are neglected, this approach currently provides the best means to learn more about possible mechanisms for the catalytic processes from experiment.

An immediate problem of this approach lies in the insulating nature of the oxide materials. Certain techniques such as photoelectron spectroscopy (PES) or scanning tunnelling microscopy (STM) require electrically conducting samples, limiting their application to metals and semiconductors. The solution for insulating materials has been to grow thin epitaxial films on conducting substrates. The tunnelling current to the substrate is then sufficient to avoid charging problems. This strategy has been successfully applied to wide-gap oxides [1–3], but also to other insulators like NaCl [9, 10]. However, the use of epitaxial films to model the insulator surfaces in model catalysts introduces a further level of approximation as depicted on the right-hand side of Fig. 1.1.

The growth and the characterisation of well-ordered epitaxial insulator films has become an area of active research for this reason. Considerable progress has been made in the last decade for a large variety of oxide materials on various metal substrates [1, 2, 11, 12]. It was found that epitaxial oxide films can exhibit complex and unique structures not known from the bulk materials. Nevertheless, they often show bulk-like features in their vibrational and electronic spectra which has been regarded as an indication that the films represent the bulk materials reasonably well. Recently, however, the detailed atomic structure of several well-ordered oxide films used in this context has been resolved, e.g. silica/Mo(112) [13, 14] and alumina/NiAl(110) [15]. It was found that the films consist of only one or two monolayers of the oxide material, considerably less than previously thought. This raises

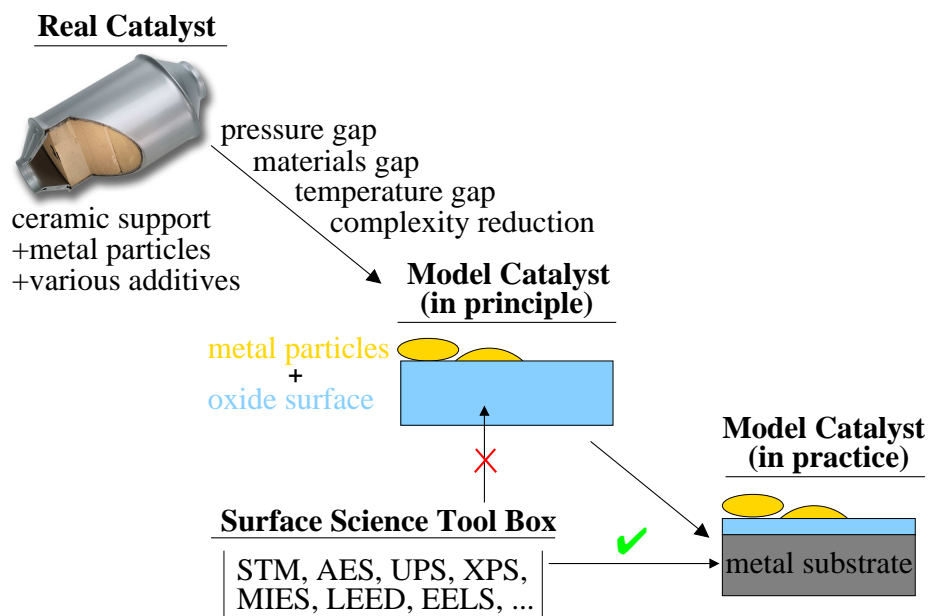


Figure 1.1: Schematic of the surface science approach applied to heterogeneous catalysts.

doubts about whether these films actually resemble the corresponding bulk materials and their surfaces. To study its validity will be a main topic of this thesis.

While earlier studies conducted with different experimental techniques emphasised the similarity of well-ordered thin films with their corresponding bulk materials, recent work has provided evidence for a film-specific behaviour. One example is the valence electron spectrum of thin silica films on Mo(112) which was found to depend on the film thickness [16, 17]. Another example is the adsorption of small linear gold clusters on alumina/NiAl(110) whose orientation was found to be closely matched with the NiAl substrate. Such an orientational preference is unexpected from the film's surface structure, providing strong indication that the substrate modifies the adsorption properties [18].

From a conceptual point of view one would thus like to isolate the influence of the substrate from those of the finite thickness or the thickness dependence, to analyse each contribution separately as depicted schematically in Fig. 1.2. However, experimentally this poses several challenges that cannot be met with currently available techniques. Not only is it not possible to produce a freestanding ultrathin oxide film experimentally, even the thickness dependence cannot be investigated for all crystalline films. While

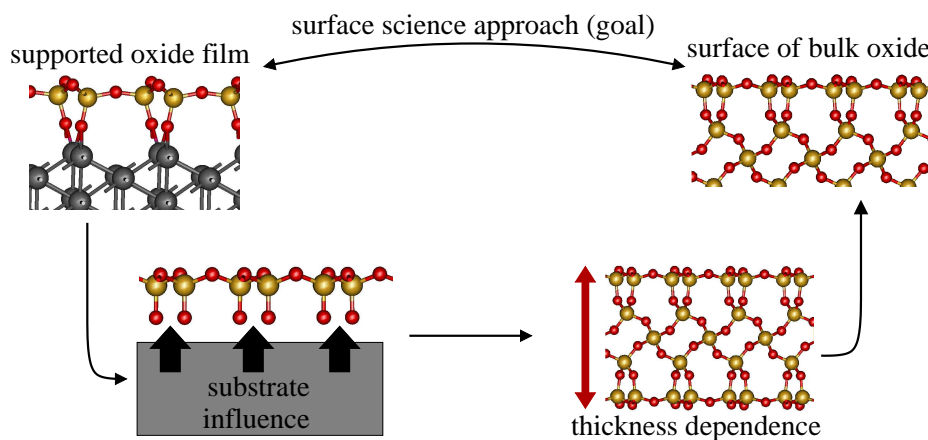


Figure 1.2: Important aspects of the comparison between supported thin films and bulk surfaces.

for some cases such as MgO on Mo(001) [19] or Ag(001) [20, 21] thicker high-quality crystalline films can be grown, most other oxide films become amorphous when the thickness exceeds one or two monolayers.

First principles simulations on the other hand are not bound to these constraints. In our simulations we have atomistic control over the structure and can take the compound system apart in a controlled manner. As shown in Fig. 1.2 for silica, we can then easily transform the  $\text{SiO}_2$  film on Mo(112) into an  $\alpha$ -quartz surface by first stripping away the metal substrate and then increasing the thickness of the free film. Using density-functional theory (DFT) further allows us to compute the equilibrium geometry at every step. In this way, we can not only disentangle the influence of the substrate from the thickness dependence, but moreover answer the question if the surface of an ultrathin silica film behaves like that of  $\alpha$ -quartz or not. We find that the substrate significantly modifies the atomic structure, which then induces noticeable differences in the electronic properties. Likewise, the thickness introduces large variations in the atomic and electronic structure of freestanding films.

The thickness dependence of certain properties is also an important question in microelectronics, where thin oxide films are frequently used. The functionality of integrated circuits for example is based on field-effect transistors (FET), see Fig. 1.3. In a FET, the gate electrode must be electrically insulated from the conducting channel that the gate electrode controls. The properties of this insulating oxide layer (“gate dielectric”) crucially influence the overall performance such as the switching speed or the power consumption [22]. With regard to the on-going miniaturisation in electronic devices,

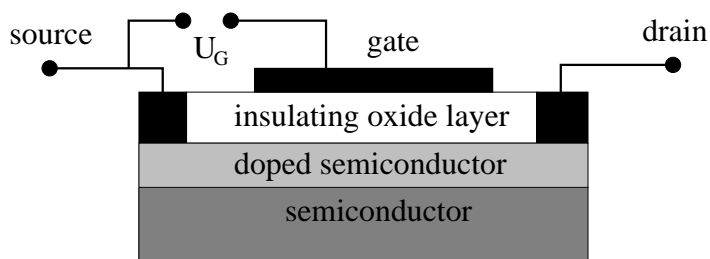


Figure 1.3: Metal-oxide-semiconductor field-effect transistor (MOSFET), schematically. By applying a gate voltage  $U_G$ , the charge carrier density in the doped semiconductor can be varied, which controls the current between source and drain.

the fundamental physical limits for the thickness of these films are of great interest. It is expected that silica, the gate dielectric in current silicon-based devices, will soon have to be replaced by another material with a larger dielectric constant. We have therefore extended our study of the thickness dependence to materials ( $\text{Al}_2\text{O}_3$ ,  $\text{HfO}_2$ ) that have been discussed in this context [22].

We will show in Sec. 4 that oxide films of one or two monolayer thickness are in general not representative for the bulk materials and their surfaces, with considerable differences in the atomic and electronic structure. For NaCl films, on the other hand, we find only negligible variations when we focus on the electronic ground-state effects. When comparing with spectroscopic measurements, however, ground-state DFT offers a slightly warped view, because self-energy effects are not included at this level of theory. The self-energy connects the DFT electronic structure to the quasiparticle spectrum measured in photoemission spectroscopy or other experiments that involve charged excited states. Since this type of spectroscopic tools is routinely employed to characterise epitaxial films, it is important to understand the origin of the experimental features in detail.

We employ the  $G_0W_0$  approximation (GWA), where  $G_0$  is the Green's function and  $W_0$  the screened Coulomb interaction, as a practical way to compute the self-energy corrections. In practice,  $G_0W_0$  not only introduces quasiparticle effects (e.g. the correct value of the gap or finite lifetimes), but also corrects for deficiencies in the underlying DFT starting point such as the self-interaction contained in many approximate density functionals. The GWA has been shown to describe the valence electron spectra in good agreement with experiment for many weakly correlated bulk systems such as the main group semiconductors and simple metals [23]. In order to use existing computer codes based on periodic boundary conditions for systems with bro-

ken periodicity such as films or surfaces, an artificial periodicity is introduced by repeating a slab of material in the direction perpendicular to its surface (repeated-slab approach). However, recent work on e.g. semiconductor slabs or nanowires has demonstrated that long-range polarisation effects require a special treatment for low-dimensional systems [24–27], questioning the reliability of the repeated-slab approach for  $G_0W_0$  calculations. In Sec. 3, we will present a thorough review of polarisation effects in  $G_0W_0$  calculations for the repeated-slab approach. From this, an efficient scheme will be developed to compute accurate quasiparticle band structures that no longer depend on the computational parameters in the numerical calculation.

Using this improved scheme, we have studied self-energy effects for sodium chloride films. NaCl is *the* prototypical ionic insulator, and it is therefore one of the most important toy systems for studying fundamental questions arising in this context. Recently, NaCl films have attracted renewed interest for the manipulation of single atoms [4] or molecules [5] in STM. Since STM experiments require a conducting substrate, the majority of studies is performed for metals or doped semiconductors. When a molecule is adsorbed on their surfaces, the molecular orbitals usually couple strongly to the substrate states or in other words the metallic substrate required for the experiment perturbs the adsorbate’s electronic structure. To study weakly perturbed adsorbates, ultrathin NaCl films of 1–4 monolayers (ML) thickness have been successfully used as insulating spacer layers to decouple the adsorbate levels from the substrate below, in this case Cu(001), Cu(111), or Cu(113) [6]. Repp *et al.* found that the STM then images the unperturbed molecular orbitals of the adsorbate [28]. Using the STM tip as local electrode, it is also possible to switch the charge state of an adsorbate, e.g. a gold atom, reversibly by applying short voltage pulses [4]. The high quantum yields achievable for this process suggest a two-step process in which the additional electron localises on the adsorbate before it tunnels into the substrate [6]. This implies a quasiparticle picture for the primary process, whose energetics is therefore expected to be well described by  $G_0W_0$  calculations.<sup>2</sup>

We have studied NaCl films on Ge(001), which represents a prototypical insulator/semiconductor interface. On this substrate, flat epitaxial NaCl films with a few ML thickness can be grown [9], and STM experiments can be carried out [29]. Since the structure of the NaCl/Ge interface is not known, we will first present a model derived from DFT-LDA calculations in Sec. 5.2.2 that is consistent with the experimental findings. We will then show that the

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<sup>2</sup>DFT calculations qualitatively reproduce the observed STM pictures of the switched states, but failed to locate the energy position of the negative ion resonance responsible for the switching [4].

self-energy for films contains additional contributions beyond those for bulk NaCl. These arise from polarisation effects that become important when a charged state is created in a dielectrically heterogeneous environment. It is well known that image effects are taken into account by the  $G_0W_0$  self-energy [30], but their influence on adsorbate levels was demonstrated only very recently for a benzene molecule on graphite [31]. We have studied these effects also for an adsorbate on the supported NaCl films. As suitable adsorbate, we have chosen carbon monoxide, the “fruit fly” of molecular adsorption experiments in surface science.

These calculations not only demonstrate that a whole range of interesting phenomena can now be approached with *ab initio* methods. We can furthermore use the  $GW$  calculations to tailor a dielectric model for the polarisation effects. This in turn can be applied to the  $\text{SiO}_2/\text{Mo}(112)$  system, for which full  $G_0W_0$  calculations are presently not possible due to computational constraints<sup>3</sup>, to estimate the polarisation effects.

The remainder of this thesis is organised as follows. In Sec. 2, we will present the theoretical framework of the *ab initio* calculations performed in this work, namely density-functional theory in Sec. 2.1 and many-body perturbation theory in Sec. 2.3 as well as their implementation in the computer codes employed, **SFHingX** (DFT) and **gwst** (GWA). We will then discuss the implications of the repeated-slab approach for  $G_0W_0$  calculations in Sec. 3. Our DFT investigations of the structural and electronic properties of oxide films are presented in Sec. 4. The self-energy effects for thin films are discussed in Sec. 5 for the free-standing NaCl films and the NaCl/Ge(001) system, where we also present the atomistic model of the interface. We will then summarise our conclusions in Sec. 6.

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<sup>3</sup>To treat metallic systems reliably in the  $GW$  space-time method, a finite-temperature formalism must be employed, which is currently under development [32].