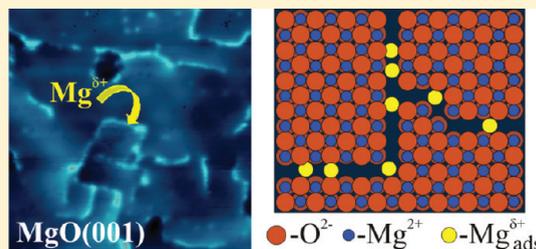


## Spontaneous Oxidation of Mg Atoms at Defect Sites in an MgO Surface

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**ABSTRACT:** Scanning tunnelling microscopy and X-ray photoelectron spectroscopy have been used to study the adsorption of Mg on 12 ML thick MgO films grown either on Ag(001) or Mo(001) supports. The initially arriving Mg atoms spontaneously oxidize on the MgO surface, whereas metallic aggregates only form at higher exposure. The total amount of cationic Mg is considerably larger on the Mo- compared to the Ag-supported oxide films. The charge transfer is suggested to be induced by Mg attachment to MgO line defects with high electron-trapping potential. The density of those defect lines and hence the oxidation power of the film is governed by the lattice mismatch with the underlying metal support.



Charge transfer processes at metal–oxide interfaces have recently moved into the focus of surface science and catalysis research.<sup>1</sup> They have been related to a number of unusual phenomena on thin film as well as bulk oxides, such as the self-organization of adatoms,<sup>2</sup> the bistability of molecules,<sup>3</sup> the development of 1D and 2D metal islands,<sup>4,5</sup> and a strongly enhanced catalytic activity.<sup>6</sup> Two fundamental routes may lead to an electron exchange between the oxide surface and adsorbed entities. In the case of ultrathin films grown on bulk metals, the transfer is triggered by the different chemical potentials of the metal–oxide system and the adsorbed species and occurs via electron tunneling through the oxide film.<sup>7</sup> Hereby, low work-function ( $\phi$ ) systems in conjunction with electronegative ad-species give rise to a negative charging, whereas cationic adsorbates are primarily formed on systems with high  $\phi$ . In contrast, the direct interaction between surface defects and adsorbates is responsible for an electron transfer on bulklike oxides.<sup>8,9</sup> In this case, the direction of the charge flow depends on the nature of the defects being an electron donor or acceptor.

Gold is one of the commonly used materials to study charge transfer processes on oxide supports, both from the experimental and the theoretical side.<sup>1</sup> Because of its high electronegativity, it has a strong tendency to charge up negatively on low  $\phi$  oxide films, such as MgO,<sup>5,10</sup> Li-doped silica,<sup>11</sup> or alumina.<sup>4</sup> Positive charging of ad-species is observed less frequently<sup>12</sup> but occurs for instance on FeO/Pt(111) due to the high work function and polar nature of this oxide layer.<sup>2</sup> The formation of cationic species has also been reported in conjunction with certain acceptor-type oxide defects, for example positively charged color centers, or hydroxyls being present on the oxide surface.<sup>13,14</sup>

In our experiment, we demonstrate that a substantial amount of Mg becomes positively charged upon deposition onto an MgO thin film. This result is somewhat unexpected, as Mg only weakly

interacts with the ideal oxide surface and has a high ionization potential of 7.6 eV (similar to Ag for example).<sup>15</sup> We will show that misfit-induced line defects in the oxide surface are responsible for the charge transfer, which also explains why the metal support below the MgO film has a strong influence on the Mg oxidation behavior.

Two metal single crystals, Ag(001)<sup>16</sup> and Mo(001),<sup>17</sup> have been used for the preparation of the MgO(001) films. In both cases, nominally 12 ML Mg were deposited in  $5 \times 10^{-7}$  mbar O<sub>2</sub> onto the sputtered and annealed metal surfaces. Whereas the MgO/Ag preparation was performed at 550 K, the MgO/Mo was grown at room temperature and postannealed to 1100 K. Both films are stoichiometric according to XPS with an Mg to O ratio of 52 and 49% for the Ag and Mo supported oxide layers, respectively. A comparison between both systems is instructive because the different lattice match between oxide and support leads to a deviating MgO defect structure. On the Ag(001), MgO grows pseudomorphically up to a critical thickness of 5 ML due to the small lattice mismatch (3%) and the high elasticity of the Ag.<sup>18,19</sup> In contrast, a  $\langle 110 \rangle$ -oriented network of misfit dislocations forms already in the very first oxide layer on Mo(001) (5% mismatch).<sup>17</sup> At larger thickness,  $\langle 100 \rangle$ -directed edge dislocations develop in both films to compensate the residual misfit strain (Figure 1). Those dislocations give rise to a faceting of the oxide surface, as deduced from the appearance of crosslike reflexes in LEED (inserts in Figure 1). In addition, grain boundaries are present in the two films that arise from the coalescence of MgO islands with an out-of-phase registry.

In a final preparation step, Mg was deposited from a Mo crucible onto the oxide surface at 300 K. The chamber pressure

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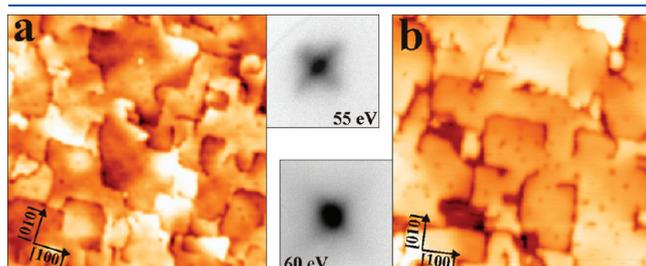
was kept in the  $10^{-10}$  mbar regime to avoid oxidation of the Mg via the rest gas. The metal–oxide system was then explored with scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) using a nonmonochromatic Al K $\alpha$  source.

Figure 2 shows two STM image series of the Mg growth on 12 ML thick MgO/Mo and MgO/Ag films. Surprisingly, almost no aggregates are observed after deposition of 1 ML Mg onto the Mo-supported films, whereas tiny aggregates emerge on MgO/Ag(001). For similar systems, for example Au on MgO/Mo, already dosages as low as 0.1 ML give rise to the formation of aggregates that are discernible in the STM.<sup>20</sup> The absence of particles after low Mg exposure therefore suggests an incorporation of the initially arriving atoms into the oxide film without leaving topographic traces in the STM images. This effect seems to be more pronounced for the Mo- than the Ag-supported films. Mg aggregation sets in only at higher coverage, whereby mainly the MgO dislocation lines serve as nucleation sites. The deposits develop large height-to-diameter ratios and distinct rectangular shapes with edges running along the MgO(110) direction. Their shape is governed by the formation of Mg(11 $\bar{2}$ 0) interface planes that enable a pseudomorphic relationship with the oxygen sublattice of the surface.<sup>21</sup> The pronounced 3D growth of Mg results from two competing effects. Whereas the interaction between Mg atoms in the deposits and O ions in the oxide surface is substantial, the required lattice distortion to realize a commensurate Mg–MgO

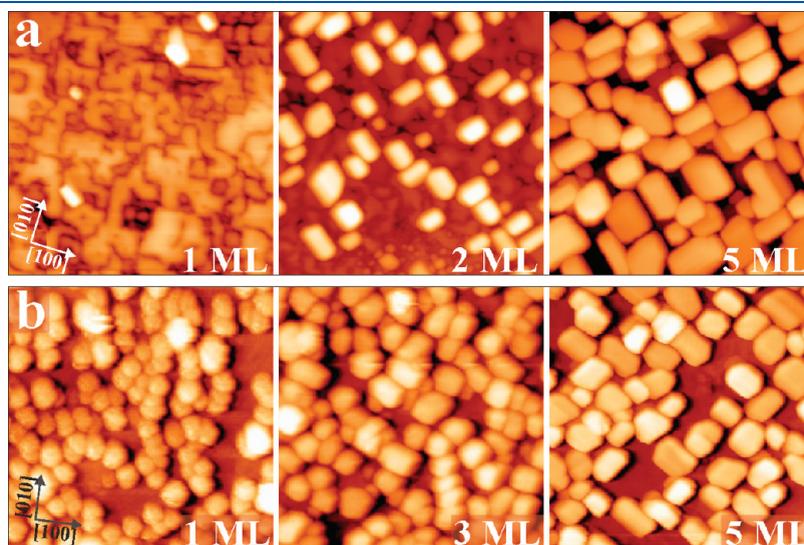
interface largely compensates this attractive contribution and leads to a small net adhesion.

To trace the history of the Mg atoms arriving on the MgO surface, we have measured the Mg KLL Auger line as a function of coverage (part a of Figure 3). This particular transition enables a clear distinction between metallic Mg<sup>0</sup> and ionic Mg<sup>2+</sup> species, as the corresponding bands are shifted by 5.0 eV against each other. As expected, the Mg<sup>0</sup> peak grows in intensity with Mg exposure, manifesting the formation of metallic Mg particles on the oxide film. The peak can be removed again by annealing the sample to 450 K, when the particles evaporate from the surface (part b of Figure 3). A careful analysis of the XPS data reveals however that also the Mg<sup>2+</sup> peak related to the oxide changes upon Mg deposition. To obtain quantitative information, the Mg<sup>2+</sup> intensity was normalized with respect to the Mo 3d peaks and the intensity ratio was evaluated with an exponential attenuation model. Part c of Figure 3 displays the resulting evolution of the MgO layer thickness during Mg exposure. Apparently, the oxide signal strongly increases in the initial deposition regime, indicating spontaneous oxidation of a substantial fraction of the incoming Mg atoms. The slope decreases after dosing 3 ML onto MgO/Ag (5 ML onto MgO/Mo) and finally levels out above 12 ML exposure. Surprisingly, the total amount of oxidized Mg is 50% smaller for MgO/Ag (0.4 ML) with respect to MgO/Mo (0.8 ML), suggesting a higher tendency for charge transfer processes in the latter case. This finding is compatible with the absence of Mg particles in the STM images after depositing 1 ML Mg onto the MgO/Mo films.

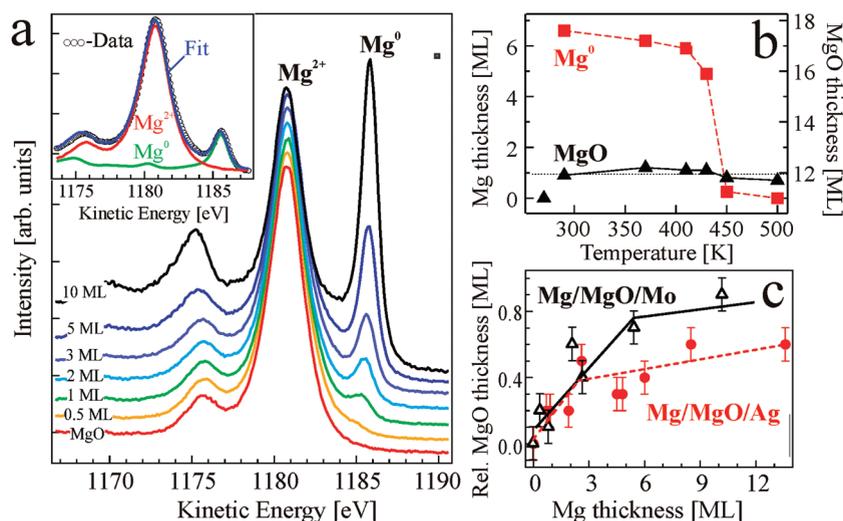
Several scenarios are conceivable to explain the spontaneous oxidation of substantial Mg quantities upon deposition onto the MgO surface. First of all, both films exhibit a small high-energy shoulder next to the O 1s peak in the XPS that is assigned to hydroxyl groups on the oxide surface. The peak intensity is larger for the MgO/Ag (equivalent of 0.2–0.3 ML OH) than for the MgO/Mo film (0.1–0.2 ML), as the latter can be thermally treated after preparation. The presence of hydroxyls and possible traces of water will promote the formation of cationic Mg,<sup>14,22</sup> however, the magnitude of the observed oxidation effect clearly exceeds the amount of surface OH. Based on a rough estimation,



**Figure 1.** STM images of 12 ML thick MgO films grown on (a) Mo(001) and (b) Ag(001) ( $70 \times 70 \text{ nm}^2$ ). LEED patterns of both surfaces are shown in the inserts.



**Figure 2.** STM image series showing the growth of Mg on a 12 ML thick MgO film grown on (a) Mo(001) and (b) Ag(001) ( $100 \times 100 \text{ nm}^2$ ). Bias and current were set to  $\sim 5 \text{ V}$  and  $50 \text{ pA}$ , respectively. Note the absence of aggregates on MgO/Mo at low Mg exposure, where only the dislocation network is revealed on the oxide surface.

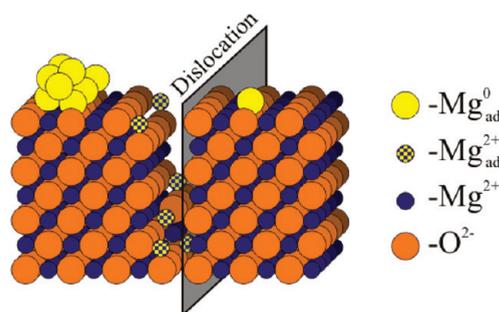


**Figure 3.** (a) XP-spectra taken in the range of the Mg Auger KLL transition for increasing Mg dosages onto 12 ML MgO/Mo(001) films. The insert shows the assignment of the multiplet structure to neutral and ionic Mg species. (b) Evolution of the  $\text{Mg}^{2+}$  and  $\text{Mg}^0$  quantity with temperature. Above 450 K, metallic Mg desorbs from the surface, while the oxide remains unaffected. (c) Change of the oxide thickness during  $\text{Mg}^0$  exposure as deduced from the  $\text{Mg}^{2+}$  intensity. The signal strongly increases at low dosage, indicating spontaneous oxidation of Mg but levels out at higher exposure.

preadsorbed oxidants may account for up to 65% of extra  $\text{Mg}^{2+}$  in the MgO/Ag case but only for 25% on MgO/Mo. In contrast, Mg oxidation via the rest gas can be excluded, as neither the O 1s nor the  $\text{Mg}^{2+}$  intensity was found to increase on the time scale of the measurements, once the Mg has been deposited.

The rise in the  $\text{Mg}^{2+}$  signal after correcting for the influence of surface oxidants thus indicates an interface effect between the incoming Mg and the oxide film. We hereby exclude the possibility that Mg oxidation occurs at the regular MgO surface, for example via electron transfer into the metal substrate below, as the amount of oxidized material neither scales with the contact area nor the perimeter length of the clusters.<sup>23</sup> In fact, less Mg becomes cationic on MgO/Ag films although the cluster density and hence the interface area is larger than that on MgO/Mo. Furthermore, DFT calculations demonstrated that Mg binds mainly via polarization interactions to the defect-free MgO and no charge transfer occurs.<sup>15</sup> The most plausible explanation is therefore a defect-mediated electron exchange between Mg atoms and the MgO surface. As point defects have only a small concentration on well-prepared films, the various line defects observed in LEED and STM are possible candidates to trigger the oxidation. This assumption is supported by the fact that Mg particles preferentially nucleate along the MgO dislocation lines.

We therefore propose the following scenario for a defect-mediated Mg–MgO charge transfer. Neutral Mg atoms attach to distinct sites along the line defects, for example oxygen-rich kinks and inverse corners, and donate their valence electrons to the unsaturated anions or suited electron traps in the direct vicinity (Figure 4). A similar process has recently been proposed in an electron paramagnetic resonance (EPR) study of the Mg/MgO system.<sup>24</sup> Also DFT calculations found an oxidative binding scheme of Mg to be favorable, yielding an adsorption-energy of 1.25 eV for MgO step edges compared to 0.5 eV for terrace sites.<sup>15</sup> However, once an Mg atom has penetrated the dislocation line, even the oxide Madelung potential alone might be sufficient to detach the Mg valence electrons from the ion core. The abstracted electrons are stabilized in trap states along the line defect,<sup>25</sup> a process that is equivalent to the formation of an  $\text{F}^0$  center. The feasibility of such



**Figure 4.** Structure model of a dislocation line in an MgO thin film, displaying potential binding sites for neutral and charged Mg species.

defect-mediated ionization has recently been demonstrated for atomic hydrogen dosed onto MgO/Mo films.<sup>26</sup> Using EPR and STM spectroscopy, the filling of the trap states with the hydrogen electrons was observed, whereby up to five electrons could be captured per nanometer dislocation line. In a similar way, the Mg atoms might be oxidized inside the MgO line defects, a process that is even easier due to the low Mg ionization potential with respect to hydrogen. A defect-mediated charge transfer also explains the different oxidation potential of the two MgO/metal systems. Because of the larger lattice mismatch, misfit dislocations are more abundant in the MgO/Mo films and consequently more binding sites are available for charge transfer processes (Figure 1). In addition, the MgO/Mo system has a comparatively low work function, which leads to a down-shift of the oxide bands with respect to the metal Fermi level and renders MgO defect states better accessible for Mg electrons.<sup>12</sup>

The absolute Mg quantities that become oxidized on the MgO surface shall be commented in the last section of the article. After correcting for the effect of OH and  $\text{H}_2\text{O}$  ad-species, roughly  $8 \times 10^{13}$  and  $3 \times 10^{14}$  Mg atoms per  $\text{cm}^2$  become cationic on the MgO/Ag and MgO/Mo films, respectively. Those numbers compare to  $5 \times 10^{13}$  and  $1 \times 10^{14}$  surface atoms per  $\text{cm}^2$  located in direct vicinity to a line defects, an estimation that has been obtained from STM topographies of both systems. As not

every surface defect will be able to trap and oxidize an Mg atom, the vertical extension of the line defects needs to be considered to explain the observed quantities. At least for the MgO/Mo system, it has been shown that misfit dislocations develop directly at the metal–oxide interface and permeate all oxide layers up to the surface.<sup>17</sup> Apparently, neutral or ionic Mg species are able to penetrate those troughs and populate sites even if they are well below the oxide surface (Figure 4).

In conclusion, considerable quantities of Mg become oxidized upon room-temperature deposition onto an MgO surface. The effect is partly ascribed to an electron transfer from the Mg adatoms to electron traps located inside the MgO line defects. The formation of metallic aggregates only sets in if all ionic binding sites are saturated. Although demonstrated for Mg in this study, we expect a similar behavior for other atomic or molecular adsorbates on MgO films. Our results therefore emphasize the importance of line defects for the physics and chemistry of oxide surfaces.

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