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Interaction of small molecules with Mg and MgO surfaces studied with MIES and UPS(HeI)

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Abstract

Metastable Impact Electron Spectroscopy (MIES) in combination with UPS(HeI) was used to study the interaction of molecular (CO_2 , CO, N_2O) adsorbates with magnesium and magnesia (MgO) surfaces at room temperature (RT). Spectra obtained for Mg on Si(100) surfaces and for MgO surfaces are discussed. CO does not chemisorb on magnesium at RT. Dosing the Mg surface with N_2O leads to the dissociation of the N_2O molecule in N_2 and O and to the subsequent oxidation of the surface.

Mg surfaces exposed to CO_2 show the formation of CO_3^{2-} . From the comparison of MIES and UPS spectra the following reaction mechanism is suggested: (i) dissociation of CO_2 in front of Mg; (ii) formation of a Mg–O bond; and (iii) CO_2 chemisorption at low-coordinated oxygen ion sites of the surface.

Spectra for MgO exposed to CO_2 show only weak CO_3^{2-} features. This can be explained by CO_3^{2-} formation at defect sites only. Dosing MgO with CO or N_2O leads to no new features in the MgO spectrum. © 1998 Elsevier Science B.V.

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1. Introduction

The reaction of molecules with oxide surfaces is of great interest for the development of new gas sensors and devices in heterogeneous catalysis. Nevertheless, a fundamental understanding of chemisorption and catalysis is still limited in these cases. So far, the most popular oxide surfaces for gas sensor applications are ZnO and SnO_2 [1].

On the other hand, MgO is a wide band gap insulator, which is of great importance in the ceramics industry. In this article we characterize Mg and MgO surfaces exposed to small molecules, such as CO, N_2O , O_2 and CO_2 , utilizing Metastable Impact

Electron Spectroscopy (MIES) and photoelectron spectroscopy UPS(HeI).

2. Experimental

The apparatus used in this study has been described in detail previously [2,3]. Briefly, it is equipped with a cold-cathode gas discharge source for the production of metastable $\text{He}^*(2^3\text{S}/2^1\text{S})$ ($E^* = 19.8/20.6$ eV) atoms with thermal kinetic energies and HeI photons ($E^* = 21.2$ eV) as a source for UPS. The triplet to singlet ratio has been measured by He^* –Ar impact as 7:1. Metastable and photon contributions within the beam are separated by means of a time-of-flight technique combined with a double counter system allowing for the measurement of MIES and UPS

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simultaneously. The angle of incidence of the probe beam is 45° ; electrons emitted in the direction normal to the surface are analyzed. The simultaneous collection of a MIES/UPS spectrum requires about 2 min. MIES and UPS measurements are performed using a hemispherical analyzer (VSW HA100) with an energy resolution of 250 meV. The low-energy onset of the electron spectra directly reflects the surface work function; therefore its variation with exposure gives directly the exposure dependence of the work function. Additionally, the apparatus is equipped with the standard XPS, LEED and AES tools.

The interaction of metastable He^* atoms with the surface can occur via the following processes [4]: (1) Auger capture (AC) takes place for metals and semiconductors with work functions larger than about 3.5 eV. In the first step of this process the He 2s electron is transferred into an unoccupied surface state by resonance transfer (RT), producing a He^+ in front of the surface. In the second step, a surface electron fills the He 1s hole while a second surface electron is emitted, carrying the excess energy. (2) Auger de-excitation (AD) of the metastable He takes place when no unoccupied surface states are in resonance with the He 2s state. This is usually the case for metals with work functions below 3 eV and, in general, for insulators. A surface electron fills the He 1s hole while the He 2s electron is emitted, carrying the excess energy. (3) For work functions below 2.2 eV, the resonant transfer of a surface electron to He^* 2s can take place, producing a negative excited He ion in front of the surface prior to de-excitation. This ion decays by a fast intra-atomic Auger process called autodetachment (AU), where one of the He 2s electrons fills the He 1s hole while the second is emitted [5].

Mg layers are produced by evaporating Mg from a commercial Knudsen cell on the Si(100) surfaces. O_2 , CO_2 , N_2O and CO are offered through an UHV valve. MgO(100) crystals are cleaned by sputtering with Ar^+ ions (4 keV with $5 \mu\text{A}/\text{cm}^2$) for 2–3 h with subsequent annealing to 1300 K for 3 min. The surface cleanliness was monitored with MIES and XPS. MgO films are produced by oxygen exposure of magnesium films at room temperature followed by annealing to 800 K; details can be found in Ref. [2].

The base pressure of the apparatus amounts to 7×10^{-11} Torr; during the evaporation of Mg the pressure amounts to 3×10^{-10} Torr. All measurements are

performed at room temperature. MgO(100) bulk crystals charge up during MIES and UPS. To compensate this surface charge, a simple electron source was introduced near the target. A tungsten filament was heated and a potential difference between filament and target of +2 V was applied. Using this simple equipment no shift in the electron energy during the analysis was observed.

MIES and UPS experiments on non-insulating surfaces were performed biasing the target by 50 eV, which has been shown to have almost no influence on the spectral features. Below about 10 eV both the UPS and the MIES spectra appear to be influenced by secondary electrons; this part of the spectra will not be discussed in the following. All spectra are displayed as functions of the binding energy (E_B) where $E_B = 0$ eV corresponds to electrons emitted from the Fermi level E_F of the substrate. This is strictly correct only for AD and AU spectra. Nevertheless, we use the same display for the AC spectra because no features of the AC spectra are discussed.

3. Results and discussion

3.1. Mg exposed to CO_2 , CO, N_2O

Figs. 1 and 2 show the MIES and UPS(HeI) results obtained during the CO_2 exposure of a Mg film (> 20 nm thick) on Si(100). For a detailed review on the surface chemistry of CO_2 see Ref. [6], [10]. A detailed discussion of the spectra from the clean Mg (film and single crystal) can be found elsewhere [2]. The identification of the structure labeled O(2p) seen in UPS follows from our previous study on MgO: the same structure was seen on MgO(100) single crystals and after exposing Mg films to O_2 [2]. In these cases it is due to emission from MgO valence band states having predominantly O(2p) character. Thus, in the present case the structure must also arise from the ionization of (Mg–O) bonds.

Upon exposure to CO_2 two peaks appear at $E_B = 7.6$ eV; 12.2 eV in the MIES spectra. They are also seen with UPS where they are superimposed on the oxide feature O(2p). UPS, but not MIES, shows additional intensity at $E_B = 3$ eV (labeled 'C') which may be due to the formation of a carbide [7] below the surface (and possibly results from a

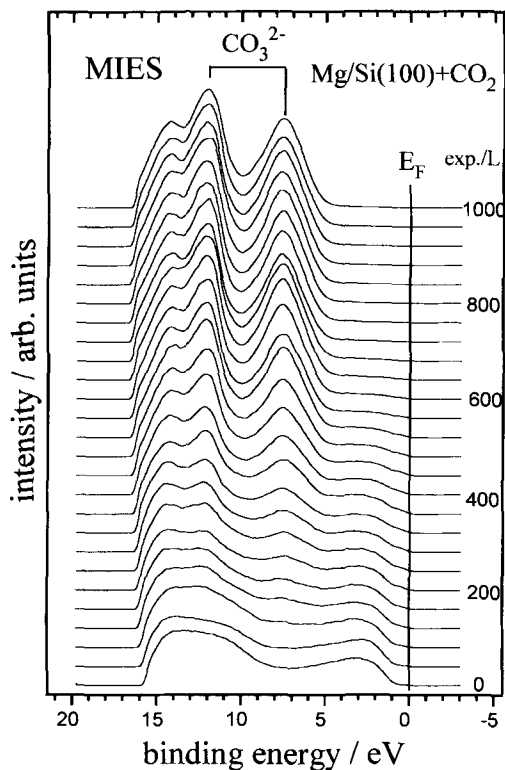


Fig. 1. MIES spectra of Mg film (thickness > 20 nm) on Si(100) as a function of CO₂ exposure.

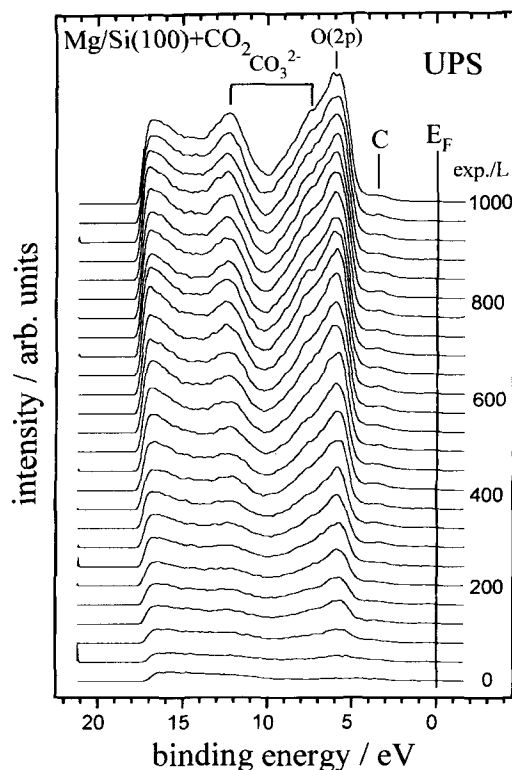


Fig. 2. UPS spectra of Mg film (thickness > 20 nm) on Si(100) as a function of CO₂ exposure.

partial decomposition of the carbonate species at room temperature).

The comparison with photoelectron spectroscopy results for CaCO₃ bulk samples suggests that the features are due to the ionization of a carbonate (CO₃²⁻) species [8]. Both the O(2p) and CO₃²⁻ emission display a linear dependence on the CO₂ exposure up to about 700 L. This behaviour is compatible with the oxidation of the Mg surface followed by the formation of a CO₃²⁻ surface layer by the following mechanism first proposed in Ref. [9] on the basis of XPS and HR-EELS results: (1) the CO₂ dissociates on the surface and (Mg–O) bonds are formed; and (2) CO₂ reacts with surface oxygen atoms which leads to the formation of CO₃²⁻ on the surface.

Fig. 3 displays the MIES spectra of Mg exposed to N₂O. The first spectrum is again for clean Mg. When N₂O is offered (exposure rate of 40 L per spectrum), the peak at $E_B = 6$ eV (well known from MgO surfaces) develops. This peak is caused by the ionization of the O2p orbital in the AD process. Because MIES

displays only the features from oxidation of the Mg surface, resulting in spectra similar to the UPS spectra for Mg + O₂, we suppose that N₂O dissociates in front of the surface; the oxygen bonds to the Mg while N₂ leaves the surface. This results in the formation of a MgO layer on the surface. UPS measurements (not shown here) support this picture. They show only the development of the well known structure from O2p ionization and no additional features.

Already in the early exposure stage the intensity at E_F increases considerably in the MIES spectra: a shoulder develops which becomes a peak close to E_F around 220 L. When the band gap, typical for a MgO surface, appears (around 350 L), the peak intensity rapidly decreases again. We offer the following explanation of this behaviour: upon exposure to CO₂ the surface work function decreases (see the variation of the low-energy onset of the spectra) up to about 300 L. This behaviour may be due to the embedding of oxygen underneath the surface at this stage. Up to about 300 L the surface does still display metallic

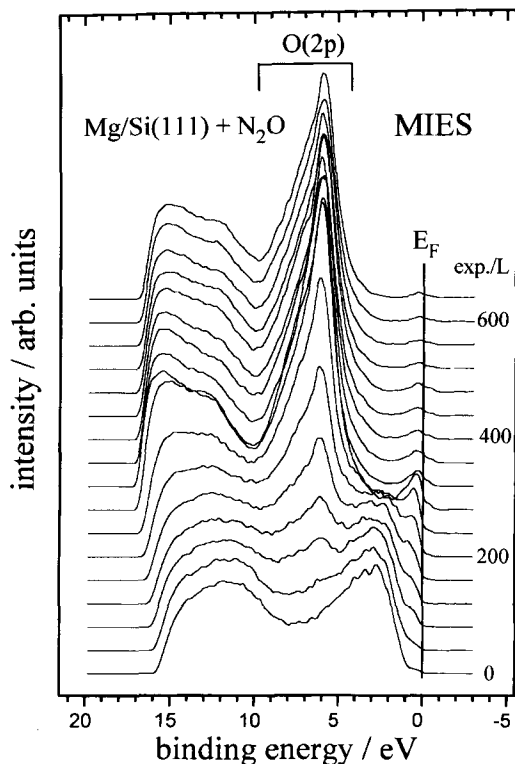


Fig. 3. MIES spectra of Mg film (thickness > 20 nm) on Si(100) as a function of N_2O exposure.

character. However, because of the lowered work function, the interaction of the He^* probe atoms now takes place also by AD, in contrast to the clean Mg surface where the interaction is predominately via the AC process. Thus, the shoulder at E_F is due to AD of He^* at metallic regions of the surface. Above about 240 L the transfer of an additional electron to the He^* may take place, resulting in the formation of a He^{*-} temporary negative ion. The decay by autodetachment to the He ground state produces a peak located close to E_F [5]. When the bandgap develops, the density of states at E_F decreases markedly. Consequently, the formation of He^{*-} from He^* by the transfer of a surface electron to the projectile becomes less probable. It is worth mentioning that UPS(HeI) does not see any significant intensity at E_F , i.e. it remains insensitive to the s-charge density of the states in the near-surface-region.

The MIES spectrum of Mg exposed to CO shows, even after an exposure rate of 400 L, essentially the structure of the clean Mg surface. There is only some

additional emission in the tail of the spectrum. This can be caused by the residual gas in the UHV. Obviously CO does not form (Mg–O) bonds with Mg at RT; therefore, we conclude that CO does not dissociate at RT at the Mg surfaces.

3.2. MgO exposed to CO_2 , CO, N_2O

Fig. 4 shows the MIES results for CO_2 exposure of MgO films on Si(100). The film thickness is about 10 nm [2]. The ‘as prepared’ MgO surface shows the O(2p) valence band structure (Fig. 4(a)); a detailed discussion of results for clean MgO surfaces, together with a comparison of the results obtained for MgO(100) bulk crystals, can be found in Ref. [2]. The spectrum is dominated by a strong peak at a binding energy of about 5.6 eV arising mainly from ionization of O(2p) orbitals.

As a result of the CO_2 exposure the same features as discussed in Section 3.1 appear in MIES ($E_B = 7.6$ eV; 12.2 eV). The intensity of the features is of

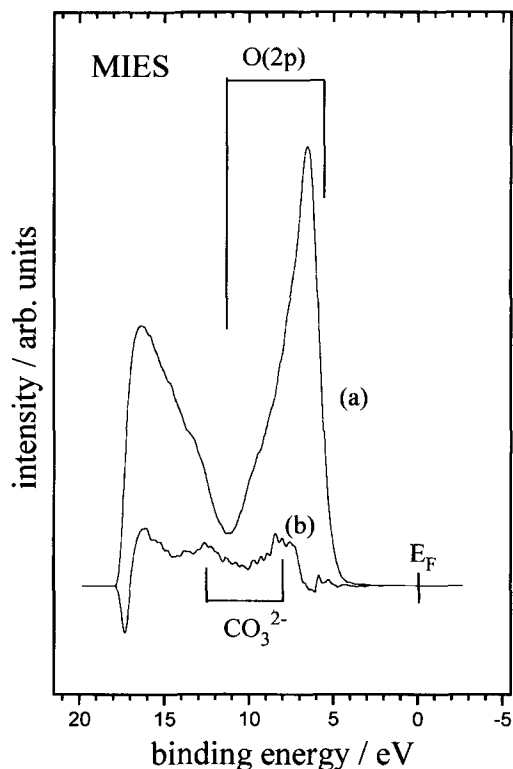


Fig. 4. MIES spectra of a clean MgO/Si(100) surface (a), and difference spectra of clean and exposed (360 L CO_2) surface (b).

the order of 1% of those obtained during the exposure of a Mg film to CO₂, indicating that CO₂ chemisorbs (as CO₃²⁻) at defects only. The spectral features are seen more clearly in the difference of the spectra for 360 L exposure and the 'as prepared' MgO surface shown in Fig. 4(b). No other additional features appear upon CO₂ exposure; in particular no signature can be seen for an O₂²⁻ species originating from an eventual CO₂ dissociation [11]. UPS spectra (not shown here) show no additional features from CO₃²⁻ adsorption; only the band structure of clean MgO is seen; this demonstrates the high sensitivity of MIES for surface adsorbates.

Our results are compatible with theoretical predictions [12,13] where it is found that at room temperature CO₂ chemisorbs (as CO₃²⁻) at defects only. The formation of CO₃²⁻ (and not CO₃^{δ-}) indicates that these defect sites are low-coordinated surface oxygen O²⁻ ions. The comparison with theory [12,13] suggests furthermore that a monodentate carbonate species is formed.

It was suggested in Ref. [2] that O₂²⁻ complexes may be formed during the oxygenation of Mg surfaces. This should produce split-off states above and below the valence band [11]. The numerical results of Ref. [11] do not exclude the possibility that such complexes may be present at MgO surfaces. We would then expect that CO₃²⁻ formation would also occur via the reaction O₂²⁻ + CO → CO₃²⁻. As a test we have offered CO. The exposure of the MgO films to CO does not lead to carbonate formation via O₂²⁻ + CO → CO₃²⁻. This finding suggests that O₂²⁻ complexes (if at all present at the surface of MgO films) may not be important for the formation of carbonate species. The carbonate features at the MgO surface and at the Mg film are very similar, both in their energetic position and in their relative intensities. Because we are fairly sure that a monodentate CO₃²⁻ species is present at the MgO surface [13], this suggests that the same is true for the Mg film, i.e. the CO₂ molecules bond to atomic oxygen, resulting from CO₂ dissociation, coordinated to Mg.

Exposure of MgO to N₂O and CO does not produce any change in the MgO spectrum. Therefore, we conclude that N₂O and CO dosing does not lead to dissociative chemisorption on MgO at room temperature.

4. Summary

The electronic structure of Mg and MgO exposed to CO₂, N₂O and CO at room temperature was studied with the electron spectroscopic techniques MIES and UPS(HeI). MIES spectra of Mg exposed to CO₂ show the development of two new features which arise from the ionization of the carbonate molecule ion (CO₃²⁻). UPS also shows these two features, but weaker. In addition, a structure appears which can be assigned to O2p ionization. The results support the following process sequence for the interaction of CO₂ with Mg: (1) the CO₂ dissociates on the surface and (Mg–O) bonds are formed; (2) CO₂ reacts with surface oxygen which leads to CO₂ chemisorption in the form of CO₃²⁻.

Dosing Mg with N₂O shows the development of the structure which is due to O(2p) ionization. Therefore, we conclude that N₂O exposure leads to molecular dissociation and subsequent oxidation of the Mg surface.

CO exposure leads to no new features in the spectrum. This suggests that there is no CO dissociation at room temperature.

The MIES spectrum of MgO exposed to CO₂ shows the same two features as the exposed Mg surface, but with much less intensity. This supports the picture that CO₂ is adsorbed at defects only. MgO exposure to N₂O and CO has no effect on the MIES and UPS spectra. There is no strong interaction of these molecules with MgO at room temperature.

Acknowledgements

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