

The adsorption of oxygen and water on Ca and CaO films studied with MIES, UPS and XPS

F. Bebensee^{a,b}, F. Voigts^b, W. Maus-Friedrichs^{b,*}

^a *Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstrasse 3, 91058 Erlangen, Germany*

^b *Institut für Physik und Physikalische Technologien, Technische Universität Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany*

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Abstract

Metastable induced electron spectroscopy (MIES), Ultraviolet photoelectron spectroscopy (UPS), and X-ray photoelectron spectroscopy (XPS) are employed to study the adsorption of water on Ca and CaO films as well as the adsorption of oxygen on Ca films. Ca films are prepared by evaporation of Ca onto clean Si(100) substrates. CaO films are produced by Ca evaporation in an oxygen atmosphere at a substrate temperature of 400 °C. Gas adsorption on the Ca films at room temperature, both for oxygen and water, is initiated by complete dissociation of the impinging molecules leading to the formation of Ca–O bonds. Exposure to water furthermore leads to the formation of hydroxyl groups via hydrogen abstraction from water forming a complete surface layer. Hydroxyl groups are also formed upon exposure of CaO films to water, but to a significantly smaller amount compared to Ca films exposed to water.

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1. Introduction

The adsorption of molecules on metals is both of fundamental and of technological interest. Dissociation processes are of great interest and have been studied for a lot of technologically important surfaces. Many metals and oxides form various types of surface hydroxyl groups, which play a role in chemical surface properties like the catalytic activity [1].

Interest in the investigation of Ca surfaces and its interaction with various gases including O₂, H₂O, CO, and CO₂ arises for example from the application of alkaline earth titanates as oxygen sensors with strontium titanate (SrTiO₃) being one promising candidate. Alkaline earth titanates show a macroscopic change in electrical conductivity as a function of the ambient oxygen partial pressure facilitating

their use as high temperature oxygen sensors [2]. This prompted the study of the interaction between Sr and the above mentioned gases [3]. As Calcium has been found to enhance the performance of SrTiO₃ sensors [4], similar investigations on Ca films promise relevant information.

Calcium is furthermore used as a promoter in catalytic reactions, for example methane reforming with CO₂ [5]. In this context, a lot of studies show the influence of Ca on various catalysts. To our knowledge, however, only little has been published on the interaction of Ca with various gases including the ones mentioned above, although such studies might contribute to the understanding of the role of Ca as a promoter in catalysis.

Yet another application of Ca is its use as metal electrode in semiconducting polymer diodes [6] owing to the low work function (WF) of Ca. Again, the understanding of the electronic structure and the interaction of calcium with various species may prove helpful to gain more fundamental insights. A first step in elucidating the interaction of Ca with polymers has been done by Zhu et al. who applied

* Corresponding author. Tel.: +49 5323 722310; fax: +49 5323 723600.
E-mail address: w.maus-friedrichs@pe.tu-clausthal.de (W. Maus-Friedrichs).

adsorption microcalorimetry to study the interaction of Ca with polymethyl methacrylate surfaces [7]. It was found in this study that calcium bonded predominantly to subsurface oxygen rendering the processes under investigation similar to one of those studied in the work presented here.

In this paper, we present Metastable Induced Electron Spectroscopy (MIES) and Ultraviolet Photoelectron Spectroscopy (UPS) data complemented by X-Ray Photoelectron Spectroscopy (XPS) for the adsorption of oxygen and water on Ca and CaO films under ultrahigh vacuum (UHV) conditions. In a forthcoming paper, the adsorption of carbon monoxide and carbon dioxide on Ca and CaO, respectively, will be addressed.

In a previous study we investigated the chemisorption of CO₂ and partly O₂ on Ca and CaO surfaces with the same techniques [8]. As mentioned in this earlier paper, possible influences of water on these experiments were not excluded. It is therefore also an aim of this paper to expand our previous investigations concerning possible influences from water.

2. Experimental

An ultrahigh vacuum apparatus with a base pressure of 5×10^{-11} mbar, which has been described in detail previously [9], is used to carry out the spectroscopic measurements. All experiments are performed at room temperature.

Electron spectroscopy is performed using a hemispherical analyzer (VSW HA100) in combination with a source for metastable helium atoms (He*) and ultraviolet photons (HeI line). A commercial non-monochromatic X-ray source (Specs RQ20/38C) is utilized for XPS.

During XPS, X-ray photons hit the surface under an angle of 80° to the surface normal, illuminating a spot of several mm in diameter. For all measurements presented here, the Al K_α line with a photon energy of 1486.7 eV is used. Electrons are recorded by the hemispherical analyzer with an energy resolution of 1.1 eV under an angle of 10° to the surface normal. All XPS spectra are displayed as a function of binding energy with respect to the Fermi level.

For quantitative XPS analysis, photoelectron peak areas are calculated via mathematical fitting with Gauss-type profiles using OriginPro 7G including the PFM fitting module. Photoelectric cross sections as calculated by Scofield [10] and inelastic mean free paths from the NIST database [11] as well as the transmission function of our hemispherical analyzer are taken into account when calculating stoichiometry. Details for the fitting procedure may be found in [9].

MIES and UPS are performed applying a cold cathode gas discharge via a two-stage pumping system. A time-of-flight technique is employed to separate electrons emitted by He* (MIES) from those caused by HeI (UPS) interaction with the surface. The combined He*/HeI beam strikes the sample surface under an angle of 45° to the surface normal and illuminates a spot of approximately 2 mm in

diameter. The spectra are recorded simultaneously by the hemispherical analyzer with an energy resolution of 220 meV under normal emission within 150 s.

MIES is an extremely surface sensitive technique probing solely the outermost layer of the sample, because the He* atoms interact with the surface typically 0.3–0.5 nm in front of it. This may occur via a number of different mechanisms depending on surface electronic structure and WF, as is described in detail elsewhere [12–14]. Only the processes relevant for the spectra presented here shall be discussed shortly:

During Auger Deexcitation (AD) an electron from the sample fills the 1s orbital of the impinging He*. Simultaneously, the He 2s electron carrying the excess energy is emitted. The resulting spectra reflect the surface density of states (SDOS) directly. AD-MIES and UPS can be compared and allow a distinction between surface and bulk effects.

For low WFs below about 2.2 eV, the resonant transfer of an electron from the surface to the 2s orbital of the impinging He* atom becomes sufficiently probable. This results in a He* (1s¹2s²) ion in front of the sample surface which decays via an autodetachment (AU) process into its ground state very quickly [15]. Hereby, one 2s electron undergoes a transition into the 1s level while the other 2s electron is emitted carrying the excess energy. This process produces a sharp structure near a kinetic energy of about 19 eV with a typical full width at half maximum (FWHM) of 0.7 eV.

All MIES and UPS spectra are displayed as a function of the electron binding energy with respect to the Fermi level. The surface WF can be determined from the high binding energy onset of the MIES or the UPS spectra with an accuracy of ±0.1 eV.

Calcium layers were prepared by evaporating calcium (Sigma–Aldrich, 99% pure) with a commercial UHV evaporator (Omicron EFM3) onto a Si(100) target (CrysTec). The Si target is cleaned by heating to approximately 950 °C prior to deposition. Calcium is subsequently offered at a rate of 0.01 nm/s for 360 s at room temperature. This procedure results in calcium layers of about 3.6 nm thickness as estimated from XPS measurements. XPS data of freshly prepared calcium films are generally showing no significant contamination, especially no significant signal arising from the O 1s level can be detected. In MIES and UPS, no signal due to the Si(100) substrate can be detected for layers of this thickness.

CaO layers were prepared by evaporation of Ca at a rate of 0.01 nm/s in an oxygen partial pressure of 6.7×10^{-7} mbar for 360 s at a target temperature of 400 °C. The temperature is subsequently held at 400 °C for several minutes after stop of Ca evaporation.

Oxygen (Linde Gas, 99.995% pure) and water (deionized distilled water) are offered via backfilling the chamber using a bakeable leak valve. The gas line is evacuated and can be heated in order to ensure cleanness. Additionally, a cold-trap is installed to minimize water contamination during

oxygen dosage. A quadrupole mass spectrometer (Balzers QMS 112A) is used to monitor the partial pressure of the reactive gases during experiments simultaneously to MIES and UPS measurements.

Additional adsorption experiments with water were carried out in a high pressure cell attached to the UHV apparatus via a transfer system.

3. Results

3.1. Adsorption of oxygen on Ca

Fig. 1a shows MIES spectra of the Ca film exposed to oxygen in a waterfall manner. All exposures as given on the right hand side of the spectra denote the exposures reached at the end of the respective spectrum. For the clean film (bottom spectrum), a feature with a binding energy of 1.5 eV is visible. This feature is assigned to the emission from the Ca 4s orbital, based on experiments with Ca [8] and Sr [16]. The fact that this is the only feature in the bottom spectrum (before dosage of oxygen) clearly indicates that the Ca film is void of contaminations. A mathematical fit analysis (inset Fig. 1a) reveals that the feature can be decomposed into two peaks: emission originating from the Ca 4s orbital via the AD process and emission caused by the AU process. The latter one manifests itself as a peak with a FWHM of 0.7 eV near the Fermi level. The probability for the AU process to take place requires low work functions and increases drastically with decreasing work function. The work function as estimated from the onset

of secondary electrons decreases with oxygen exposure and thus the intensity attributed to the AU process rises initially. The Ca 4s contribution diminishes with further oxygen exposure and is hardly visible after an oxygen dosage of 12 L.

In both MIES and UPS (Fig. 1b) spectra, a peak evolves at a binding energy of 5.5 eV and grows in intensity with oxygen dosage. As in previous works [8,16], it can be attributed to emission from the O 2p orbital. The continuing growth of this feature in the UPS spectra with oxygen exposure and the similarity of the final spectrum with the one measured for a freshly prepared CaO film (Fig. 7) suggests that the oxygenation of Ca is not confined to the outermost layer.

The features appearing in the MIES spectra at binding energies of 7.6 and 11.8 eV are attributed to OH groups. This attribution is based on earlier results [3] and the experiments with water described later on. Additionally, the composition of the residual gas was monitored using a QMS excluding other contaminations; the amount of water exposure during this experiment is certainly below 1.5 L. In the last UPS spectrum of the series, similar features can be sensed at similar binding energies.

With the exception of the feature attributed to emission from the Ca 4s orbital, the same features have been found in MIES and UPS spectra. The same has been observed for Sr films [3] and is attributed to the small photoionisation cross section of s-like orbitals for UV radiation [17].

The development of the peak heights of the peaks assigned to Ca 4s, O 2p and OH as well as the work function

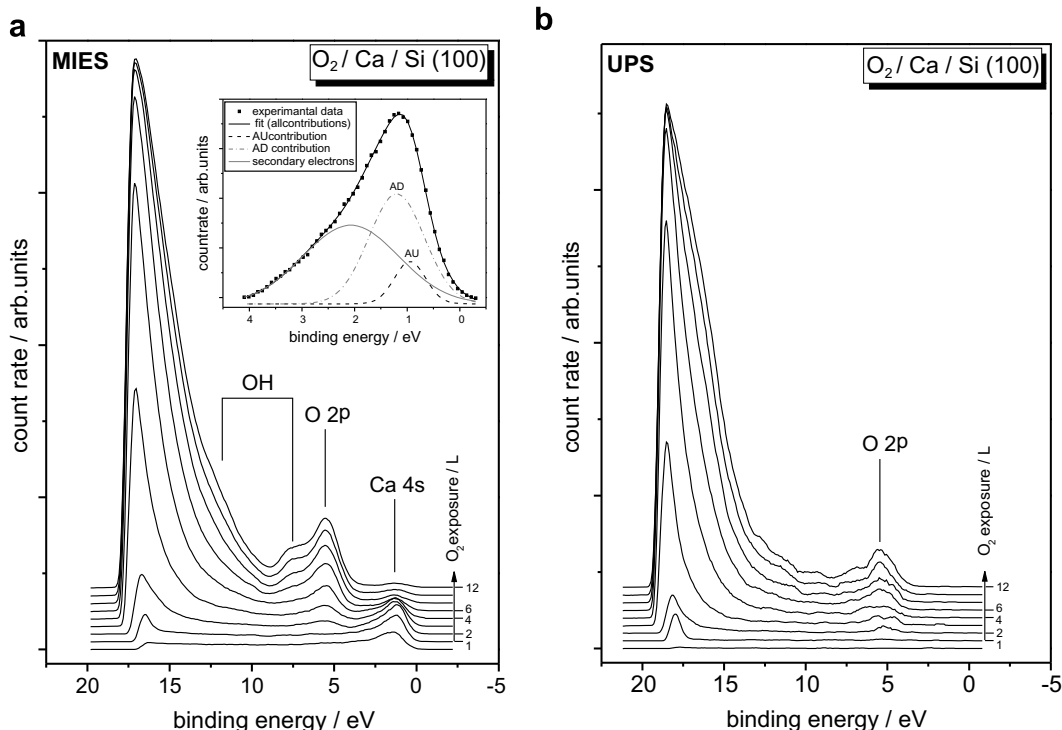


Fig. 1. MIES (a) and UPS (b) spectra of a Ca film recorded during oxygen exposure, the inset in (a) shows a detailed analysis of the Ca 4s peak applying mathematical fitting.

in the MIES spectra as a function of oxygen exposure is shown in Fig. 2. Here, it is noteworthy that the growth of the oxygen induced peak is linear with respect to the oxygen dose. Also, the rapid decrease of the WF from an initial value of 2.9 eV (slightly higher than the value given by Ertl and Küppers [18] of 2.8 eV) to 1.7 eV after 4 L oxygen dosage seems remarkable.

A XPS spectrum of the O 1s region (binding energy range 528–537 eV) recorded immediately after the MIES/UPS experiment is shown in Fig. 3. A good agreement between the original data and the fitted features is only achieved when assuming three contributions, instead of the two features expected from reference [19]. The justification for using the components for this fit along with a suggested assignment of these individual contributions is given in the discussion. Along with all other XPS results, the fitting results for this measurement are summarized in Table 1.

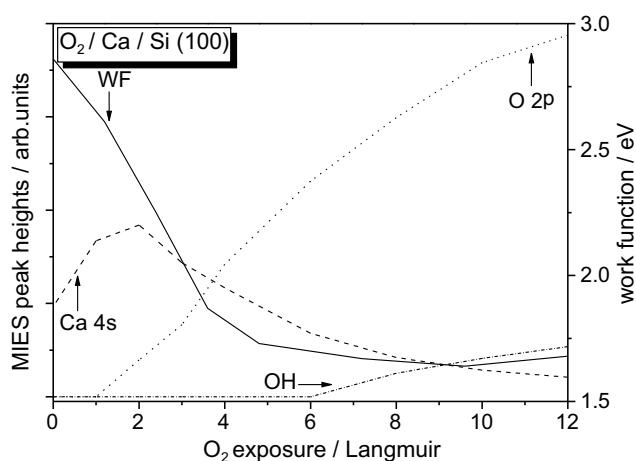


Fig. 2. Peak heights and work function plotted as a function of the oxygen exposure to a Ca film.

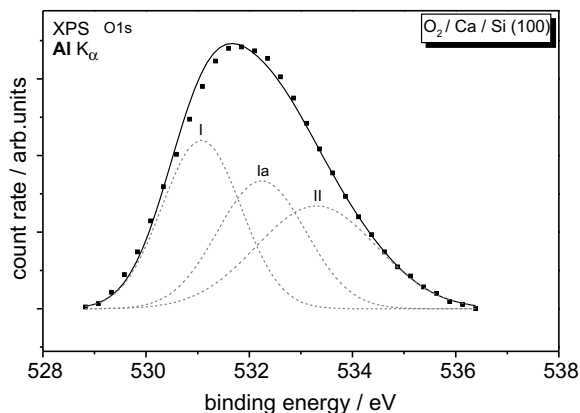


Fig. 3. XPS spectrum of the O 1s region after exposure of a Ca film to 12 L oxygen.

Table 1
Summarized XPS results from the O 1s region

System	Figure	Peak	Binding energy (eV)	FWHM (eV)	Relative intensity
O ₂ /Ca 12 L	3	I	531.1	1.8	0.36
		Ia	532.2	2.0	0.31
		II	533.3	2.75	0.33
H ₂ O/Ca 10 ¹¹ L	6	I	530.9	1.8	0.10
		II	532.9	2.75	0.90
CaO	8	I	531.7	1.8	0.63
		II	533.7	2.75	0.37
H ₂ O/CaO 140 L	10	I	531.4	1.7	0.43
		II	533.5	2.75	0.57

3.2. Adsorption of water on Ca

The spectra recorded during the exposure of a Ca film to water are shown in Fig. 4a (MIES) and b (UPS). Again, the bottommost MIES spectrum indicates that the starting point of the experiment is a clean Ca film not showing any features beside emission from the Ca 4s (only visible in the MIES spectra) and a strong emission of secondary electrons beyond binding energies of 10 eV. Upon exposure to water, emission from the Ca 4s orbital strongly decreases, while a peak at a binding energy of 5.5 eV evolves, in the MIES spectra as well as in the UPS spectra. This feature is attributed to emission from the O 2p orbital, alike in the exposure of a Ca film to oxygen. Continued exposure to water leads to the development of a peak doublet: the binding energies of this doublet are 7.5 eV and 11.8 eV (MIES) and 7.4 eV and 11.8 eV (UPS), respectively. These peaks are assigned to OH groups, which have also been found – as a contamination – during the oxygen exposure of the Ca film. A striking difference between the last MIES and UPS spectra (exposures of more than 6 L) is the size of the feature(s) attributed to OH groups, which is much larger for MIES.

The most important trends in the development of the different peak sizes, as shown in Fig. 5, are: a feature with a binding energy of 5.5 eV is visible in the MIES spectra, before the first traces of a peak attributed to OH groups can be detected at water exposures of about 2 L. The work function decreases drastically from a starting value of 2.7 eV to about 1.4 eV after exposure to 4.25 L water. Additional water exposure leads to an increase in work function, unlike in the case of oxygen adsorption on Ca films.

An additional experiment applying very high water exposures to a Ca film is shown in Fig. 6. It displays a XPS spectrum of the O 1s region after exposure of a Ca film to about 10¹¹ L water in a high pressure cell. In this case, two features exhibiting binding energies of 530.9 eV and 532.9 eV, respectively, are sufficient to reach a good agreement between the experimental data and the fit. These two features are corresponding to two of the three features

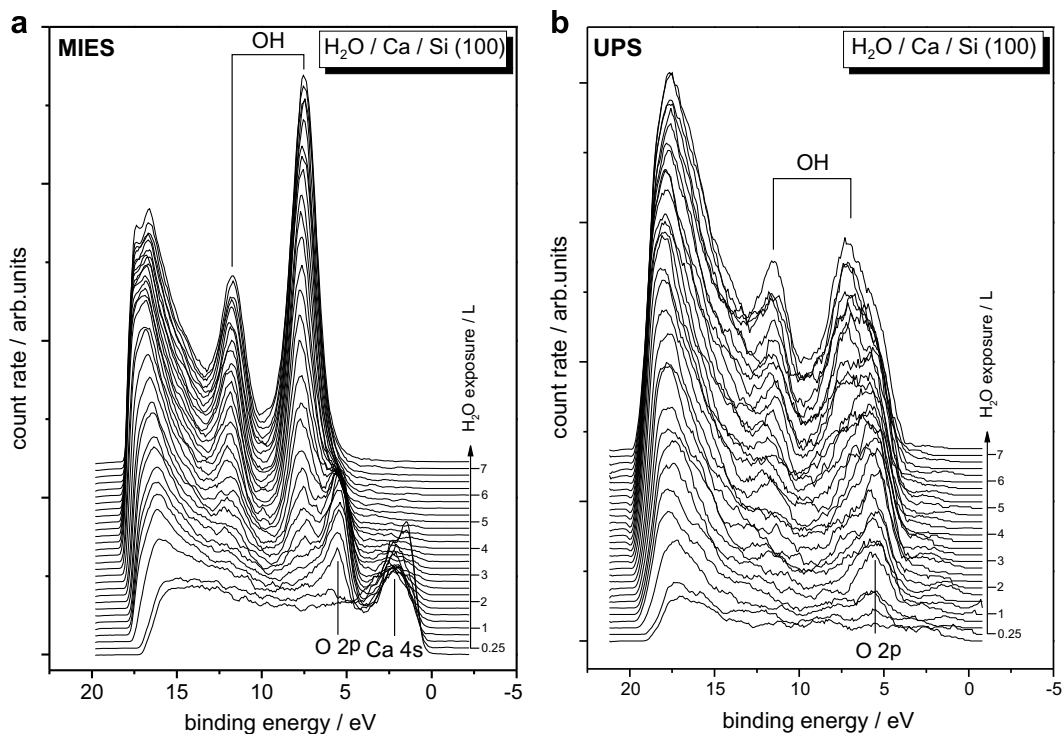


Fig. 4. MIES (a) and UPS (b) spectra of a Ca film recorded during water exposure.

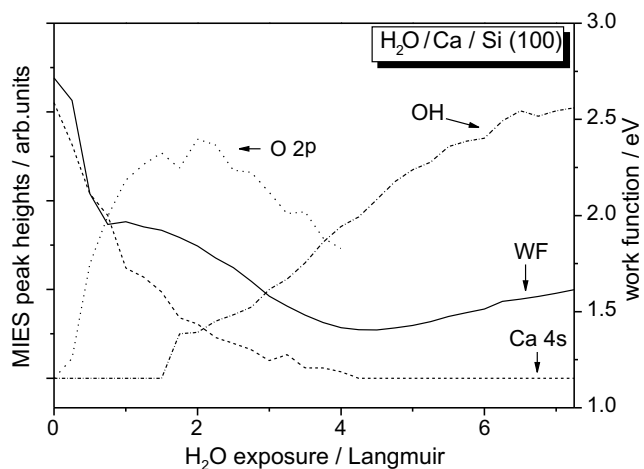


Fig. 5. Peak heights and work function plotted as a function of water exposure to a Ca film.

found in the XPS spectrum of a Ca film exposed to 12 L oxygen.

3.3. Adsorption of water on CaO

The UPS spectrum of a freshly prepared CaO film (Fig. 7, see experimental for preparation details) shows a single feature with a binding energy of 5.2 eV, which we attribute to emission from the O 2p orbital. The corresponding MIES spectrum shows two additional features, matching the peak doublet assigned to OH groups in the experiments described above. The amount of water respon-

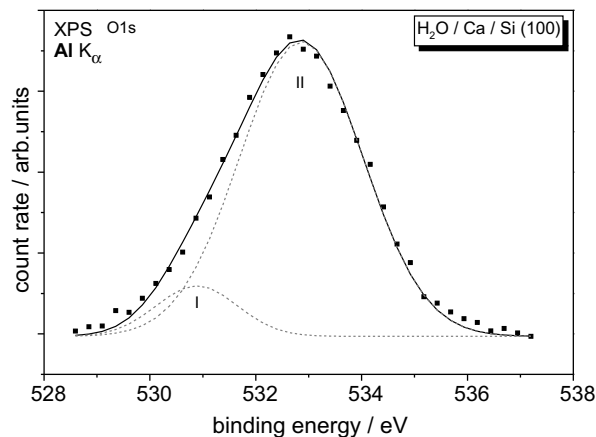


Fig. 6. XPS spectrum of the O 1s region after exposure of a Ca film to about 10^{11} L water.

sible for this contamination, however, is rather small (less than 10 L), as could be estimated using our QMS monitoring data.

The stoichiometry of the CaO film was obtained by analysis of the peak areas of the O 1s (shown in Fig. 8) and the Ca 2p peaks (not shown here): the calculations applying the procedure for quantitative XPS analysis described in the experimental yield a content of 42% Ca and 58% oxygen.

The exposure of the CaO film to water (Fig. 9) shows similar effects in the MIES and UPS spectra as in the exposure of Ca films to water, once the features attributed to emission from the O 2p orbital is visible: the peak doublet

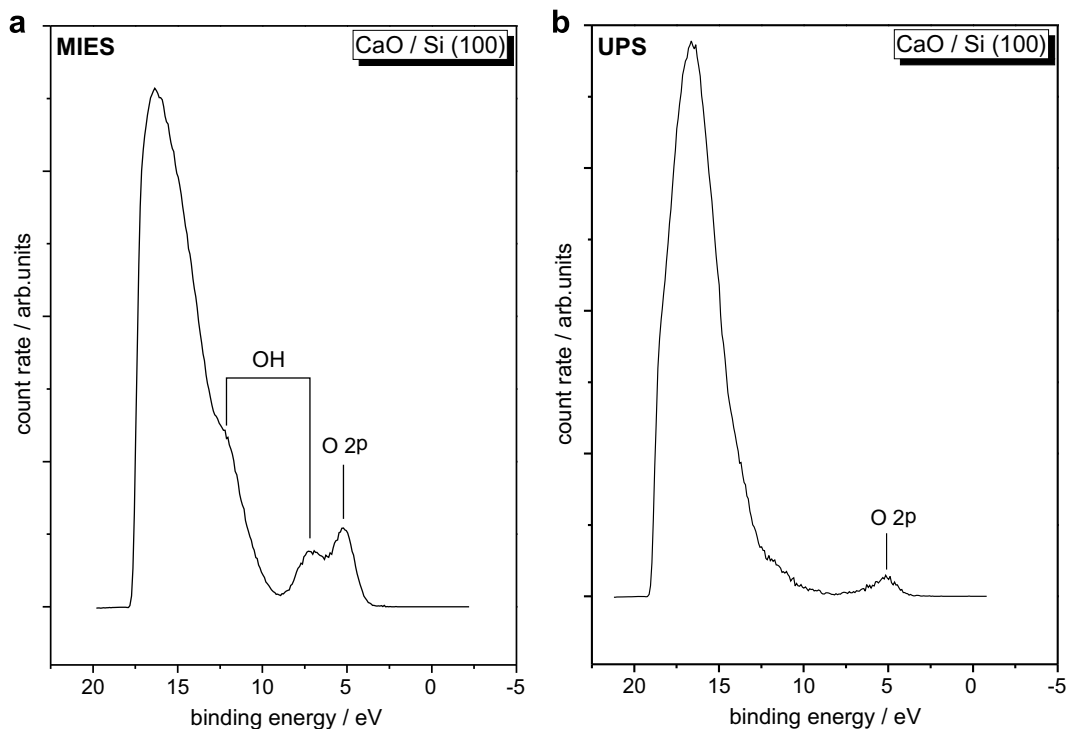


Fig. 7. MIES (a) and UPS (b) spectra of a CaO film directly after preparation.

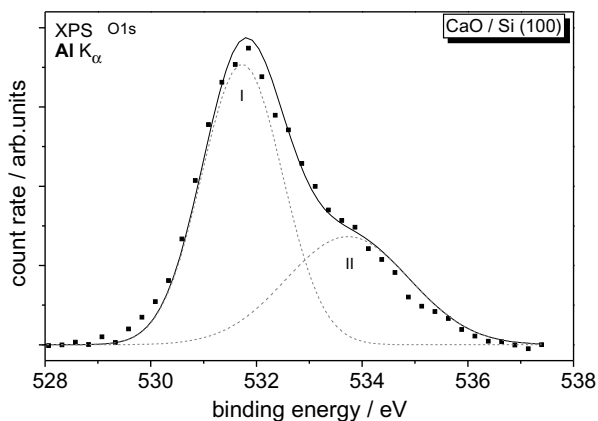


Fig. 8. XPS spectrum of the O 1s region of a CaO film.

assigned to OH groups evolves. In contrast to the exposure of Ca to water, much higher doses of water are necessary before the features become visible and especially in the UPS spectra, the features caused by emission from the O 2p orbital (binding energy: 5.2 eV) and the lower binding energy feature attributed to the OH groups (binding energy: 7.0 eV) form a single broad feature centred around 6 eV binding energy. Also, the higher binding energy feature attributed to OH groups appears more like a shoulder in the secondary electron peak instead of a well resolved peak.

The XPS spectra of the O 1s region of the CaO film exposed to 140 L water shown in Fig. 10 reveals that the same two features used for the fit in Fig. 8 (clean CaO film)

can be successfully used in this case: the only difference being a different ratio of the corresponding peak areas.

The evolution of the peak heights and the WF depicted in Fig. 11 exposes that after 80 L of water exposure, saturation with respect to the formation of OH groups has set in. Furthermore, the course of the WF as a function of water dosage is quite different from the ones observed in the other cases: after a drop from 2.3 eV to 2.2 eV, it increases rapidly to 2.6 eV and finally saturates at 2.7 eV after an exposure of 140 L.

4. Discussion

Our MIES/UPS results for the adsorption of calcium with oxygen suggest the following picture: oxygen is adsorbed dissociatively on calcium and chemisorbs on the surface. The O 2p feature increases almost linearly with exposure while the Ca 4s (AD) diminishes, just like expected for this interpretation. Oxygen atoms incorporated into the topmost layer are generally thought to cause a decrease in the WF which is supported by the experimental results for the studied case. The same behaviour has been reported for strontium films exposed to oxygen [3].

The UPS results imply that the oxygenation of the Ca film is not confined to the topmost layer. It is noteworthy, that the last MIES and UPS spectra resemble the spectra of a CaO film very closely, unfortunately including the slight water contamination, as can be deduced by comparison of the last MIES and UPS spectra with those displayed in Fig. 7.

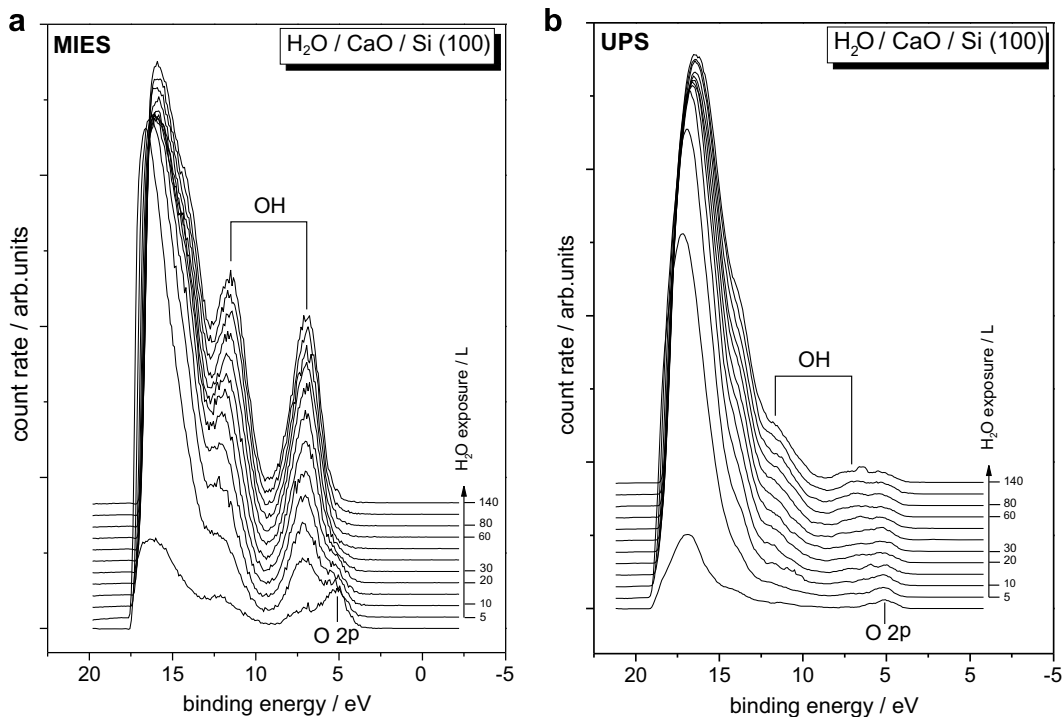


Fig. 9. MIES (a) and UPS (b) spectra of a CaO film recorded during water exposure.

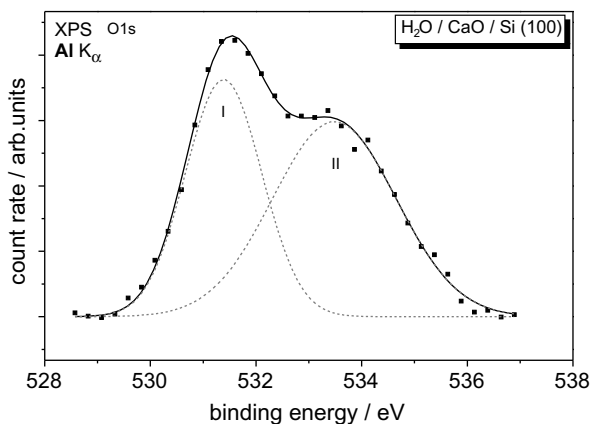


Fig. 10. XPS spectrum of the O 1s region of CaO film exposed to 140 L water.

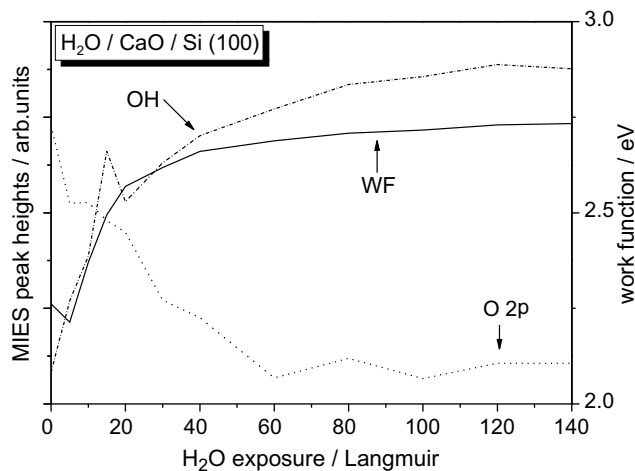


Fig. 11. Peak heights and work function plotted as a function of water exposure to a CaO film.

The peak doublet at 7.6 eV and 11.8 eV in the MIES spectra, which becomes visible after more than 6 L of oxygen exposure, is attributed to OH groups resulting from water contamination, basing on comparable results obtained on strontium surfaces [3] and the calcium exposure to water presented here. This contamination, however, is rather small and only becomes evident after the interaction of oxygen with the Ca as discussed above is already completed sufficiently.

The results for water exposure suggest that the adsorption of water on Ca proceeds in compliance with the model successfully describing the adsorption of water on strontium [3]. At room temperature, water dissociates completely at the bare Ca surface leading to the formation of

Ca–O bonds, which are responsible for the peak at the binding energy of 5.5 eV accompanied by a decrease in the intensity attributed to Ca 4s. This is strongly supported by the observation (see Fig. 5), that OH formation does not start before an exposure of 1.8 L. The water exposure leads to the incorporation of oxygen in the Ca layer and thus to a decrease in the WF, similar to the observations made for oxygen exposure to Ca films. Experience from previous work [20] gives evidence that the dissociation is not caused by our incident He^{*}/HeI beam.

Surface hydroxyl groups cause two features at binding energies of 7.5 eV corresponding to the 1 π molecular orbi-

tal (MO) and 11.8 eV corresponding to the 3σ MO. The findings suggest that two hydroxyl groups are possible via hydrogen abstraction from an impinging water molecule. In this scheme, which was proposed by Thiel and Maday [1], a hydrogen atom is abstracted from an impinging water molecule, which in turn adsorbs as a hydroxyl group. The abstracted hydrogen atom then attaches to a nearby chemisorbed oxygen atom, as well, so that the reaction can be written as



Judging from the relative peak heights of the peaks attributed to chemisorbed oxygen and hydroxyl groups, it appears that Ca–O bonds are readily converted into Ca–OH by the hydrogen abstraction reaction. Again, this is similar to the behaviour of strontium exposed to water [3]. The formation of hydroxyl groups as judged from the peak heights stops soon after the feature originating from metallic calcium is vanished. Obviously, the surface is inert after the loss of its metallic character.

Molecular adsorption of water on the Ca surface can be detected very precisely with our setup, as MIES shows the corresponding MOs $1b_1$, $3a_1$ and $1b_2$ with high accuracy. The corresponding spectral features are clearly distinguishable from the ones caused by 1π and 3σ MOs of surface hydroxyl groups [20]. As we do not detect emission from water MOs, molecular adsorption of water on the Ca surface can be ruled out.

The comparison of MIES and UPS peak intensities of the water saturated Ca clearly shows that the surface is completely covered by one hydroxyl layer. OH incorporation into the subsurface region is not observed. In that case, the relative peak heights of the peaks attributed to OH and O 2p, respectively, in the UPS spectra should be similar to the ones in the MIES spectra. We find that the OH peaks in the UPS spectra are dramatically smaller compared to the O 2p peak than in the MIES spectra and thus conclude that the hydroxylation is confined to the topmost layer.

The XPS results indicate that the CaO films have a fairly good quality, as the stoichiometry (42% Ca, 58% O) determined by the XPS spectra of the Ca 2p and the O 1s region shows. The additional oxygen in comparison to a perfect stoichiometry of 50% calcium and 50% oxygen may be explained by water and oxygen adsorbed onto the CaO films, as the oxygen partial pressure of these two species was significantly high when the evaporation of Ca was stopped. The contamination has to be rather small, as XPS data do not hint at a significant contamination. The MIES and UPS spectra (see Fig. 7) clearly exclude a significant hydroxylation at this point, as the spectra show only small peaks attributed to OH groups. As the XPS signal is strongly dependent on the distance from the surface, the contribution of molecules on top of the films is overestimated when calculating the stoichiometry. In any case, contributions from carbonaceous species can be ruled out, as neither QMS nor XPS data suggest the presence of such species in a relevant quantity.

On CaO only a smaller number of hydroxyl groups can be found at the surface with MIES and UPS even after large exposures to water. The WF reaches a minimum after dosage of 5 L of water before rising fast and approaching asymptotically a final value of 2.7 eV. This behaviour can be explained assuming that the hydroxyl groups are not integrated into the surface but protruding into the vacuum. Here, only defect sites seem to facilitate the hydrogen abstraction reaction, which also accounts for the low number of hydroxyl groups detected on this surface; as soon as these defect sites are saturated, the partial dissociation becomes impossible and consequently no formation of additional hydroxyl groups can be detected. As in the case of water adsorption on calcium, hydroxyl groups are confined to the topmost layer, as long as the water pressure is in the typical range for UHV studies.

All XPS results support the findings gained with MIES/UPS. The peak contribution with the lowest binding energy (I) in the O 1s peak region seems to be visible in all spectra of that kind displayed here, although in varying intensity. As it appears to be higher in intensity for the CaO films, we propose that this is due to bulk CaO (see [19]).

The broader feature at about 2 eV higher binding energy (II) can be observed in all cases, as well. Among the result obtained under UHV conditions, it is especially pronounced on the water treated CaO surface, suggesting that the origin of this features are hydroxyl groups. This interpretation is backed up by the high pressure experiment shown in Fig. 6, where Ca was exposed to about 10^{11} L water. The results seem to indicate a different hydroxylation behaviour of Ca which is not constricted to the first layer, because the feature is much more pronounced here. This difference may be explained by the higher pressure, which was eight orders of magnitude larger compared to the other experiments shown here.

As can be seen from Table 1, the binding energies and FWHMs of these features are consistent for all spectra, confirming the validity of this interpretation.

In Fig. 3, a third feature (Ia) between the two mentioned before is required to obtain a good agreement of the fit with the experimental data. The deconvolution of the peak was performed by using the position and FWHM of the two features (I) and (II), which are consistent with the results obtained by Dupin [19]. As these two features are not sufficient to yield an adequate fit to the experimental data, we allowed the fitting procedure to insert an additional feature while keeping the FWHM and position of features (I) and (II) fixed. The result is the presented fit showing an additional feature, labelled (Ia), which was not strongly dependent on restraints of the other two features and displays a reasonable FWHM. This feature, in our opinion, is due to chemisorbed oxygen not forming an ordered layer. This oxygen phase is not observed on the CaO films because they were produced at temperatures of 400 °C, where it matures into bulk-like calcium oxide. A similar behaviour has been found on aluminium [9] and is in qualitative agreement with the results obtained in a previous XPS study on metal oxides and

hydroxides [19]. It is remarkable that the sum of the relative intensities of peaks I and Ia from Fig. 3 equals the relative intensity of peak I from Fig. 8, thus giving evidence to the ripening process of the oxide at temperatures of 400 °C.

5. Summary

Exposure of Ca films to oxygen leads to the formation of Ca–O bonds via dissociation of oxygen molecules. Incorporation of oxygen into the Ca film is not limited to the topmost layer, as the UPS spectra indicate and UPS and MIES spectra of Ca films exposed to substantial doses of oxygen show a striking similarity to those of CaO films.

The adsorption of water on Ca films is also initiated by the formation of Ca–O bonds originating from complete dissociation of the water molecules. Subsequently, hydroxyl groups, which are confined to the outermost layer, are formed by hydrogen abstraction from water occurring close to a Ca–O bond. Obviously, the complete dissociation of water only takes place in the presence of metallic Ca and is suppressed by the presence of Ca–O complexes.

Exposure of CaO films to water also results in the formation of hydroxyl groups at the surface. Differently from the Ca films exposed to water, the number of hydroxyl groups as judged from the corresponding feature in the MIES spectra appears rather low.

XPS peak fits allow to distinguish between chemisorbed oxygen (Ia), oxide (I) and hydroxyl groups (II).

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