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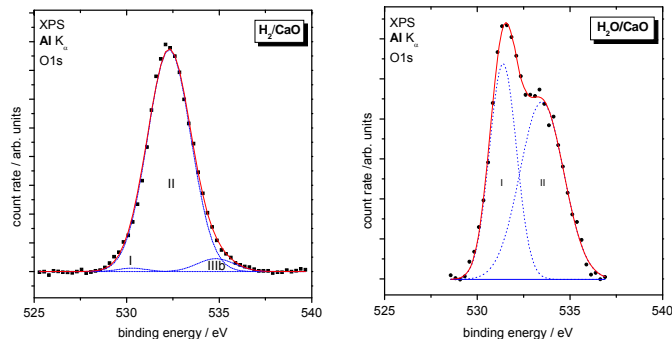
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1. Introduction

The oxide and hydroxide species of calcium and underlying reaction processes are of great technological interest. Even the hydration of burnt limestone is just barely predictable. Our investigations start with the preparation of the calcium oxide and hydroxide species in a clean ultra high vacuum (UHV) environment. During the development of in-vacuo preparation methods of calcium hydroxide, the adsorption of hydrogen and water molecules has been investigated. We have found that hydrogen leads to the formation of hydroxide groups, which appears to be unlikely due to thermodynamics at the first glance. Furthermore, hydrogen apparently acts as catalyst for the hydroxidation of a complete calcium oxide film through water impinging on the surface out of the residual gas. These effects have been studied with Metastable Induced Electron Spectroscopy (MIES), Ultraviolet Photoelectron Spectroscopy (UPS) and X-ray Photoelectron Spectroscopy (XPS).

3. XPS



Stoichiometry:

Species	425 L H ₂ / CaO	140 L H ₂ O / CaO	Assignment
I	0.01	0.43	oxide
II	0.94	0.57	hydroxide
III	0.05	-	-

Film thicknesses (from XPS attenuation):

1.4 nm CaO (before gas dosage)

1.3 nm Ca(OH)₂ (after exposure to H₂)

5. Discussion



The surface of the prepared CaO film most probably contains numerous defects. Therefore, we assume a dissociation of the impinging hydrogen molecules followed by an interstitial diffusion of the H atoms into the film. The UPS peak of a free hydrogen atom should appear at a kinetic energy of $E_{kin} = h\nu - IP$, with the ionisation potential IP. Since we plot the spectra against binding energy via $E_B = h\nu - E_{kin} - \Phi$ we would find the H 1s peak at a binding energy of $E_B = IP - \Phi = 13.6 \text{ eV} - \Phi$ below the Fermi level E_F . [2] After the gas dosage we find a work function of about 3 eV, giving $E_B = 10.6 \text{ eV}$. This fits quite likely to the surplus peak (s) in the MIES spectra taken at the beginning of the hydrogen exposure. Komeda et. al. found similar values for hydrogen terminated Ni(110) surfaces (right fig.; from [3]). Photoelectrons measured by UPS originate from the first few layers, whereas MIES represents the outermost surface states only. Therefore, the shift of the UPS peak relative to MIES might be to lower binding energies because of the lattice deformation by the hydrogen atoms penetrating the CaO bulk.

Another possible origin of the surplus peak in the spectra could be the formation of hydride-like defects by the hydrogen atoms. Nevertheless, the binding energies found for different hydrides are considerably smaller. Rogozia et. al. investigated Cs-H films (left fig.; from [4]) and found values of 6 eV (feature A) and 7.5 eV (feature B). This assumption also would not explain the difference in binding energy between MIES and UPS.

7. Literature

- [1] F. Bebensee, F. Voigts, W. Maus-Friedrichs, Surf. Sci. 602 (2008) 1622
- [2] H. Betho, Z. Phys. 57 (1929) 815
- [3] T. Komeda, Y. Sakisaka et al., Phys. Rev. B 36 (1987) 922
- [4] M. Rogozia, H. Niehus, A. Böttcher, Surf. Sci. 519 (2002) 101
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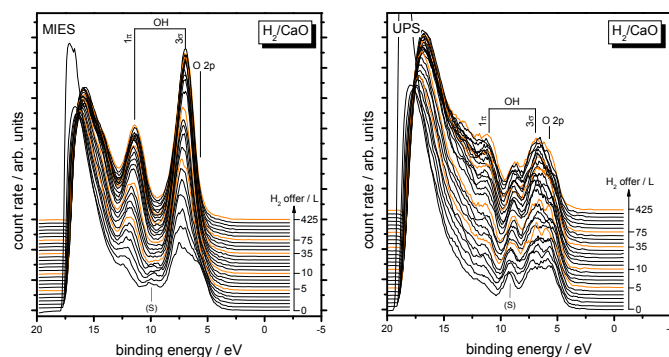
2. Experimental

For probing the surface density of states (SDOS) we applied Metastable Induced Electron Spectroscopy using a hemispherical analyzer (VSW HA100) combined with a source for metastable helium atoms (mainly He²⁺2S_{1/2}) and ultraviolet photons (HeI). Additional information for chemical analysis was obtained by XPS utilizing a commercial non-monochromatic X-ray source (Specs RQ20/38C). All XPS spectra presented are recorded with a resolution of 1.1 eV using Al K_α at a photon energy of 1486.7 eV. Fit curves were gained using OriginPro 7G with the Peak Fitting Module, setting preferences after previously obtained data [1].

The CaO films were prepared on a cleaned Si(100) target using an Omicron EFM3 e-beam evaporator charged with calcium pieces (Sigma-Aldrich, 99%). During the evaporation of Calcium, the substrate was kept at a temperature of 400° C in an oxygen partial pressure of 6.7×10^{-7} mbar. Thus, stoichiometric CaO films were gained.

H₂ (Linde Gas, 99.999%), O₂ (Linde Gas, 99.995%) and H₂O (deionised) were offered via backfilling using a bakeable leak valve, controlled by a quadrupole mass spectrometer (Balzers QMS 112 A).

4. MIES / UPS

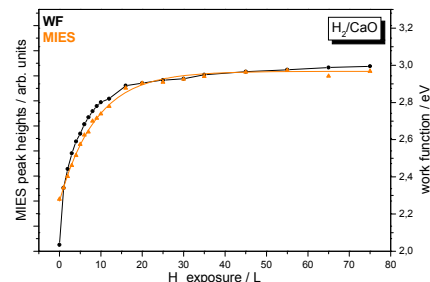


Bottom spectra:
(CaO after preparation)

- mainly O 2p from CaO at $E_B = 5.5 \text{ eV}$
- few OH from residual gas
- surplus peak (s) at $E_B = 10 \text{ eV}$ in MIES and $E_B = 9 \text{ eV}$ in UPS

Top spectra:
(425 L H₂ on CaO)

- mainly OH groups
- few O 2p in UPS
- surplus peak (s) in UPS at $E_B = 9 \text{ eV}$

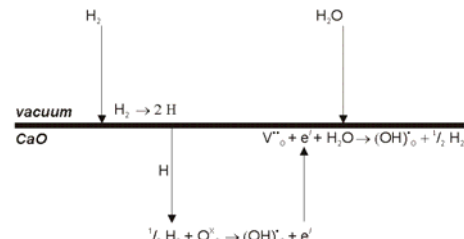


The evolution of work function (black) and MIES OH 1π peak (red) shows an exponentially converging behavior. Thereafter, the numerical fit yields:

$$I(D) \propto 1 - \text{Exp} \left[- \frac{(D + 2.89L)}{8.85L} \right]$$

6. Hydroxation process

The surplus peak in the MIES and UPS spectra taken during the hydrogen gas offer may originate in atomic hydrogen as discussed above. Since the intensity of this peak was markedly larger for UPS than for MIES, the CaO film bulk seemed to be packed with hydrogen atoms. Under such circumstances, the incidental formation of hydroxide groups should become possible throughout the whole film, even at depths not reachable by water molecules from the residual gas. However, the total reaction from Calcium oxide and hydrogen to Calcium hydroxide leaks of oxygen. The stochastic formation of hydroxide groups is a creation of bulk defects and diffusion should be accelerated, though. At the surface, these defects may be restored by water from the residual gas. This creates a chemical gradient and thus induces a diffusion of hydroxide groups into the bulk. Subsuming all proposed steps, the hydrogen seems to be acting as a catalyst, whereas the water content of the residual gas is needed for the actual hydroxation. In our case, the film got exposed to about 21 L water from the residual gas, corresponding to nearly 10L per monolayer. [5]



8. Acknowledgements

We are thankful for the technical assistance of Denise Yvonne Rehwagen.