In-situ preparation and characterisation of thick films of Calciumhydroxide

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Introduction

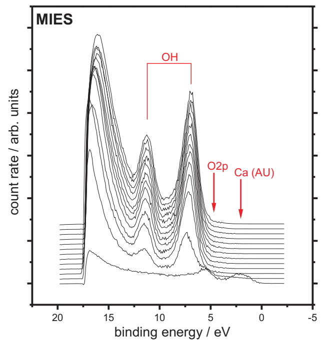
The interaction of Calcium hydroxide with different gases is of technological interest for various applications. For example Calcium hydroxide is used as absorbent and reacting agent for neutralisation and desulphurisation, as well as a plaster. Understanding the behaviour of Calcium hydroxide in different environments is expected to lead to increased environmental protection und energy efficiency. The investigation of the interaction processes starts in a clean environment under controlled conditions. Therefore clean films of Calcium hydroxide have to be prepared.
The preparation of thick films of Calcium hydroxide in an Ultra High Vacuum environment using a metal evaporator in combination with a gas inlet system is presented on this poster. In contrast to Calcium oxide that can be prepared easily, Calcium hydroxide shows effects of reduction via impinging Calcium atoms during the preparation. These effects have been studied with Metastable Induced Electron Spectroscopy (MIES) and Photoelectron Spectroscopy (UPS(HeI) and XPS).

Experimental

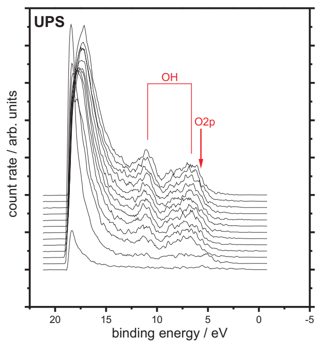
For probing the surface density of states (SDOS) we applied Metastable Induced Electron Spectroscopy using a hemispherical analyzer (VSW HA100) combined with a source for metastable helium atoms (mainly $He^*2^3S_1$) and ultraviolet photons (HeI). Additional information for chemical analysis was obtained 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 [F. Bebensee, Surf. Sci. 602 (2008) 1622].
All Ca films were prepared on a cleaned Si(100) target using an Omicron EFM3 e-beam evaporator charged with calcium pieces (Sigma-Aldrich, 99%).
H_2 (Linde Gas, 99.999%), O_2 (Linde Gas, 99.995%) and H_2O (deionised) were offered via backfilling using a bakeable leak valve, controlled by a quadrupole mass spectrometer (Balzers QMS 112 A).

H_2O / Ca / Si

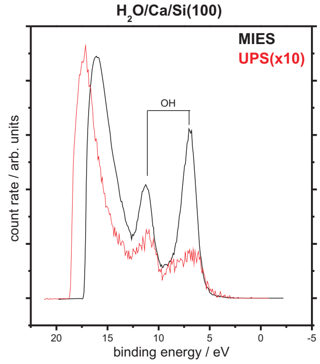
H_2O/Ca/Si(100)



H_2O/Ca/Si(100)

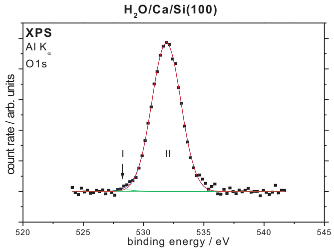


H_2O/Ca/Si(100)



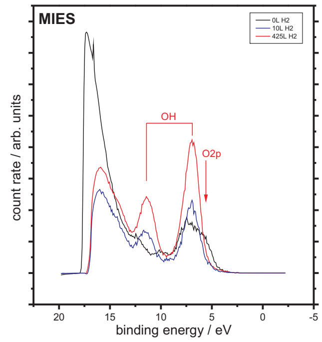
After the preparation of a monoatomic layer of Calcium, a dosage of 14L H_2O was sufficient to lead to a saturated hydroxide. No oxidic structures remain visible in MIES nor UPS. The oxidic part (I) of the O1s feature is assumed to originate from the substrate.

H_2O/Ca/Si(100)

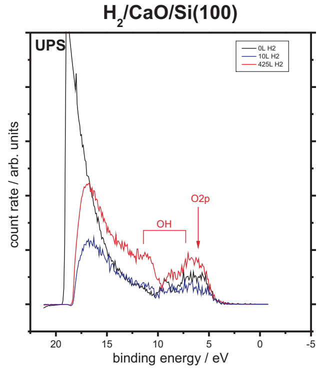


H_2 - adsorption / CaO

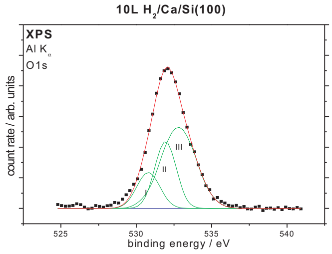
H_2/CaO/Si(100)



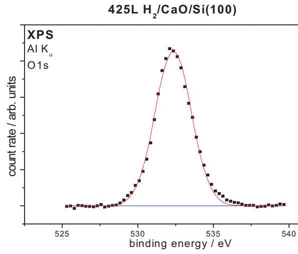
H_2/CaO/Si(100)



10L H_2/Ca/Si(100)



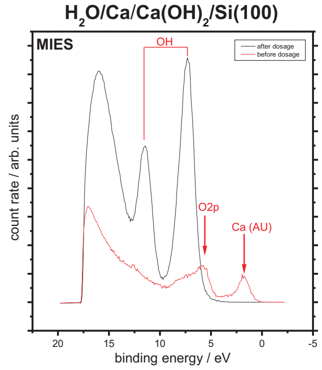
425L H_2/CaO/Si(100)



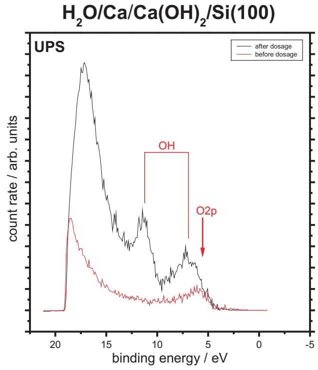
Exposing a freshly prepared Calcium oxide film to H_2 leads to formation of hydroxyl groups due to MIES, UPS and XPS. Spectra show that only 10L are sufficient for saturation in MIES. At that point, XPS results denote a Ca/O ratio of 2,16, whereas three oxide species are visible at the following stoichiometry. Calcium oxide (I) at 7,1%, an intermediate phase of absorbed oxygen (II) at 14,8% and Calcium hydroxide (III) at 78,1%.
To achieve saturation in UPS spectra, more than 400L are required. XPS measurements afterwards suggest a Ca/O ratio of 2,33 where only the hydroxide species is left.

H_2O / Ca / $Ca(OH)_2$ / Si

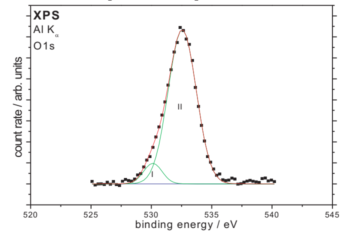
H_2O/Ca/$Ca(OH)_2$/Si(100)



H_2O/Ca/$Ca(OH)_2$/Si(100)



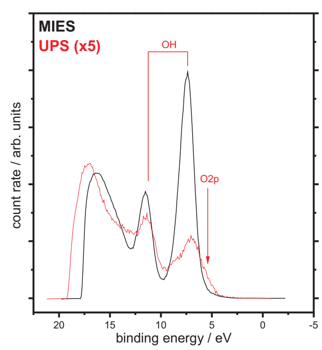
H_2O/Ca/$Ca(OH)_2$/Si(100)



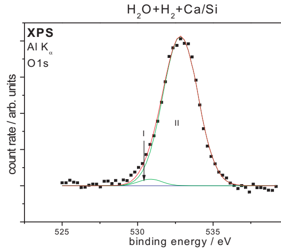
Having prepared another monolayer of Calcium upon the monomolecular film of Calcium hydroxide, spectra of MIES and UPS before and after the evaporation show a significant reduction of the surface according to
$Ca(OH)_2 + Ca \rightarrow 2CaO + H_2$
The remaining intensity of metallic Calcium and Calcium hydroxide are due to probability considerations.
After H_2O was offered until saturation again, the topmost layer consists of pure hydroxide according to the MIES spectrum, whereas an oxidic O2p structure remains in the UPS spectrum. XPS shows an additional peak at the O1s region with a fraction of 8%.

H_2O + H_2 + Ca / Si

H_2O+H_2+Ca/Si



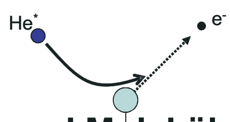
H_2O+H_2+Ca/Si



The evaporation of Calcium in an atmosphere combined of $1\cdot10^{-7}$mbar H_2O and $9\cdot10^{-7}$mbar H_2 leads to a clean film of Calcium hydroxide due to MIES, whereas UPS shows a small amount of oxide intensity. The XPS results point out a fraction of less than 3% oxide (I) besides the hydroxide (II).

Acknowledgements

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



Atom- und Molekülphysik an Oberflächen