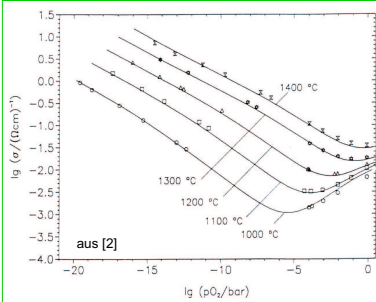


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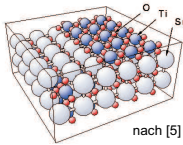
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## Introduction

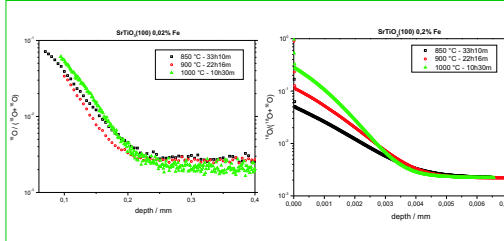


Donor doped Strontium Titanate is well known for its capability as resistive high temperature oxygen sensor. An interesting application of this sensor would be the analysis of automobile exhaust, as it would allow the optimisation of fuel injection and of catalytic oxidation of toxic exhaust, thus reducing fuel consumption and pollution of the environment. Before this application can be implemented, preliminary studies aiming at the interaction of SrTiO<sub>3</sub> with reactive gases must demonstrate the stability of the material in this environment. Also, an interpretation of the sensor's signal in such an environment will only be possible with the understanding of the cross-sensitivity of the strontium titanate for other present gases like water or carbon dioxide.

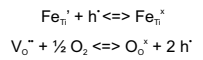
We use Metastable Impact Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy to analyse the valence band structure of SrTiO<sub>3</sub> and its adsorbates. X-ray Photoelectron Spectroscopy is used to check the stoichiometry of the samples. Diffusion and incorporation processes are studied by oxygen tracer diffusion experiments using a Secondary Ions Mass Spectroscopy technique. Fe-doped SrTiO<sub>3</sub>(100) is used as substrate. The TiO terminated surface is shown on the right.



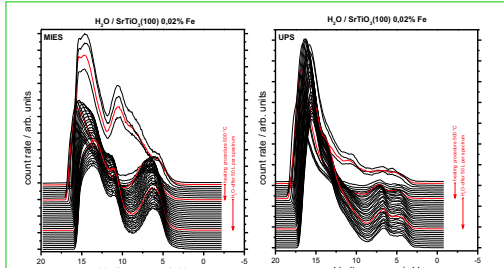
## Oxygen



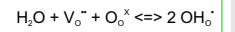
Oxygen tracer diffusion profiles using <sup>18</sup>O<sub>2</sub> as oxygen source show a strong dependency of the diffusion length of <sup>18</sup>O atoms on the dopant concentration due to a different amount of oxygen vacancies.



## Water



Water is interacting with the (100) surface of SrTiO<sub>3</sub>. It is dissociated at least partly and forms surface hydroxyl groups as can be detected with MIES. The same experiments show however, that the coverage is quite low. A strong, irreversible alteration of the surface, especially its chemical properties, is not observed. Consequently, diffusion experiments using D<sub>2</sub><sup>18</sup>O show a diffusion of <sup>18</sup>O into the bulk. Literature proposes the diffusion of hydroxyl groups

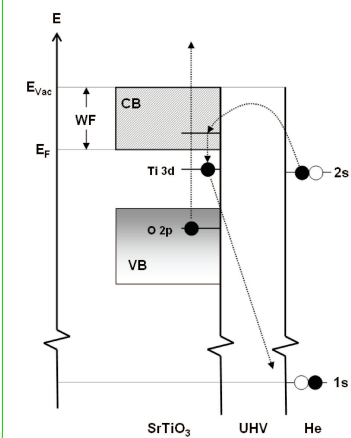


via the following mechanism: Our results however show that combined diffusion of <sup>18</sup>O and D does not occur. Thus we conclude that hydroxyl groups are not incorporated into SrTiO<sub>3</sub> in the manner above.

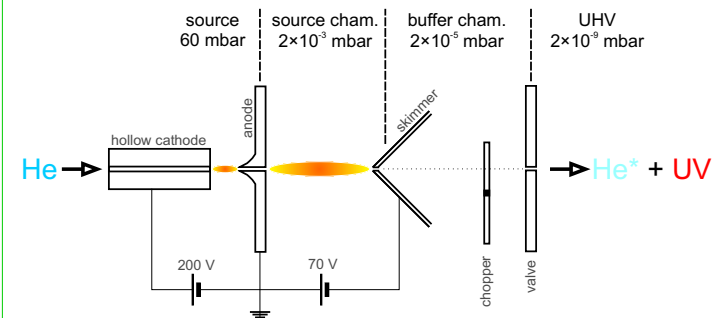
Our XPS results show two clearly different electronic states of the oxygen after treating the crystal with D<sub>2</sub><sup>18</sup>O though. The left one is due to lattice oxygen while the right one may be caused by the <sup>18</sup>O. It is possible that these results may be explained by another mechanism of diffusion, by assuming an oxygen atom with different electronic states caused by the dissociation or

## Experimental technique

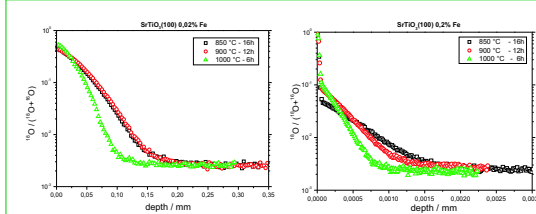
Metastable Impact Electron Spectroscopy (MIES) uses metastable He\*(1s<sup>2</sup>s<sup>1</sup>) to probe the surface of solids. The excitation potential of the He\* amounts to 19.8 eV. Because the He\* atoms interact with the surface in distances typically between 0.3 and 0.5 nm in front of it, MIES is extremely surface sensitive and displays the SDOS of the uppermost layer of the sample only. The interaction may proceed via different mechanisms.



During Auger Deexcitation (AD), an electron from the sample surface fills the 1s orbital of the impinging He\*. Simultaneously the He2s electron is emitted carrying the excess energy. The resulting spectra directly display the surface density of states (SDOS). To distinguish surface from bulk effects, AD-MIES and Ultraviolet Photoelectron Spectroscopy (UPS) can be compared directly. For SrTiO<sub>3</sub>, the He\* interacts with the surface via the process shown on the left. The 2s electron of the impinging He\* is resonantly transferred into the surface of the sample and localizes at near surface Ti 3d states. Subsequently, a Ti3d electron fills the hole in He<sup>1</sup>s in an interatomic Auger Neutralization (AN) process, followed by the emission of an O2p surface electron carrying the excess energy. The energy of the resulting MIES peak is shifted by 1.2 eV toward higher binding energies compared to AD due to a diminished local ionization potential. A detailed discussion of this process is given in [1]. Our experimental setup is shown below. It produces He\* for MIES as well as ultraviolet light for UPS, thus allowing to measure MIES and UPS simultaneously.

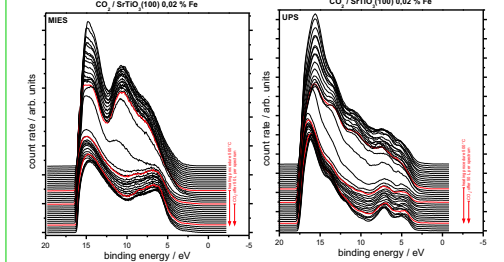


## Carbon dioxide



The interaction of carbon dioxide with SrTiO<sub>3</sub>(100) is rather weak. Under the conditions applied by us, no adsorption could be detected on the surface. Additionally, no carbon uptake could be detected with XPS.

These findings are backed up by SIMS, no carbon can be found



apart from small surface contaminations. Experiments with <sup>13</sup>C<sup>18</sup>O<sub>2</sub> show <sup>18</sup>O being incorporated into the crystal though. So the interpretation of a SrTiO<sub>3</sub> sensor's signal will have to account for oxygen incorporation from this source as well. For some applications like the analysis of automobile exhaust, this will be quite challenging.

Experiments with other gases present in the exhaust flow like carbon monoxide or methane as well as corrosive components like nitric oxide have been performed, too. These species do not show a degradation of the crystal, neither, at least not on the scale of gas offers investigated by us. These results give rise to the prospect that gas sensors made of Fe-doped SrTiO<sub>3</sub> will exhibit a long-lasting stability in application.

This is in contrast to donor-doped SrTiO<sub>3</sub>, where secondary phases made up of SrO grow on the crystal's surface when heated for longer periods under oxidising conditions, that are not easily removed.

## Acknowledgements

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