Oxygen incorporation from CO₂ and H₂O in Fe-doped SrTiO₃ single crystals

Florian Voigts¹, Dominik Schwendl¹, Sebastian Dahle³, Pradyot Datta², J. Große-Brauckmann², Lars Dörre², Christos Argirusis² and Wolfgang Maus-Friedrichs¹

¹Institut für Physik und Physikalische Technikologie, TU Clausthal, Leibnizstrasse 4, 38678 Clausthal-Zellerfeld, Germany
²Institut für Metallurgie, TU Clausthal, Robert-Koch-Strasse 42, 38678 Clausthal-Zellerfeld, Germany

Introduction

Donor doped Strontium Titanate is well known for its capability as resistive high oxygen permeable 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 gases, thus lowering fuel consumption and pollution of the environment. Before this application can be implemented, preliminary studies aiming at the interpretation of the sensor's signal in such an environment will only be possible if an understanding of the cross-sensitivity of the sensor to other gases like water or carbon dioxide is achieved. We use Metastable Impact Electron Spectroscopy and Ultraviolet Photoelectron Spectroscopy to analyze the valence band structure of SrTiO₃, and display the SDOS of the uppermost layer of the sample only.

Experimental technique

Metastable Impact Electron Spectroscopy (MIES) uses metastable He⁺(1s2s) to probe the surface of crystals. 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 He⁺ electron is emitted carrying the excess energy. The resulting spectra 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 SrTiO₃, 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 a near surface Ti 3d state. Subsequently, a Ti3d electron fills the hole in He⁺'s 1s in an interband 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 the diminished localization 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.

References


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Oxygen

Oxygen tracer diffusion profiling using MIES as oxygen source show a strong dependency of the diffusion length of O atoms on the dopant concentration due to a change in the amount of oxygen vacancies.

Water

Water is interacting with the (100) surface of SrTiO₃ dissociated at least partly and forms surface hydroxyl groups which can be detected with MIES. The same experiments show however, that the coverage is quite low. A strong, irreversible oxidation of the surface, especially its chemical composition is not observed. Consequently, diffusion experiments using D₂, O₂ show a diffusion of O₂ into the bulk. Literature proposes the diffusion of hydroxyl groups HO⁻ + V⁺ → O₂⁻ + H₂O⁻, via the following mechanism:

Our results however show the mentioned diffusion of HO⁻ + D and D does not occur. Thus we conclude that hydroxyl groups are not incorporated into SrTiO₃, in the manner above.

Our XPS results show two clearly different electronic states of the oxygen after treating the crystal with D₂ or O₂. The left one is due to lattice oxygen whereas the right one may be caused by the "hydrated oxygen". 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 of stable O₂⁻.

Carbon dioxide

The interaction of carbon dioxide with SrTiO₃(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 based on experiments where we could not detect stable carbon dioxide on the sample. In experiments with CO₂ or CO, O⁺ being incorporated into the crystal though. So the interpretation of a SrTiO₃ sensor's signal will have to account for oxygen incorporation from CO₂ 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 to 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 SrTiO₃ will exhibit a long-lasting stability in application.

This is in contrast to donor-doped SrTiO₃, 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.

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