UV induced photochromism in Fe-doped $SrTiO_3$ caused by oxygen stoichiometry changes

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In the last decades Fe-doped $SrTiO_3$ (Fe:STO) has become one of the best investigated mixed conducting materials. Nevertheless, the effect of UV irradiation at elevated temperatures on the material's composition, more precisely on its oxygen content, has hardly been examined so far. UV illumination in oxygen causes an enhanced oxygen incorporation rate [1] and therefore a decreased oxygen vacancy concentration of $SrTiO_3$. [2] Consequently, Fe^{3+} in Fe:STO is oxidized to Fe^{4+} to preserve charge neutrality. This oxidation may cause color changes in Fe:STO and a decline in the AC and DC resistivity, which can be investigated by UV-vis spectroscopy, in-plane impedance spectroscopy, van der Pauw measurements respectively. Oxygen can also be released again from Fe:STO by annealing without UV exposure. Therefore, reversibly switching between these described states can be obtained.

Before UV illumination the Fe:STO single crystal is brownish/ transparent. It turns black after 19 h under UV illumination at 440 °C. Another 12 h at 700 °C without UV exposure turns the single crystal into its original color. The oxygen incorporation process is diffusion limited, since when covering one side of the sample during UV treatment a color gradient is obtained. Moreover, Pt electrodes seem to accelerate the release of oxygen (compare Fig. 1 c).

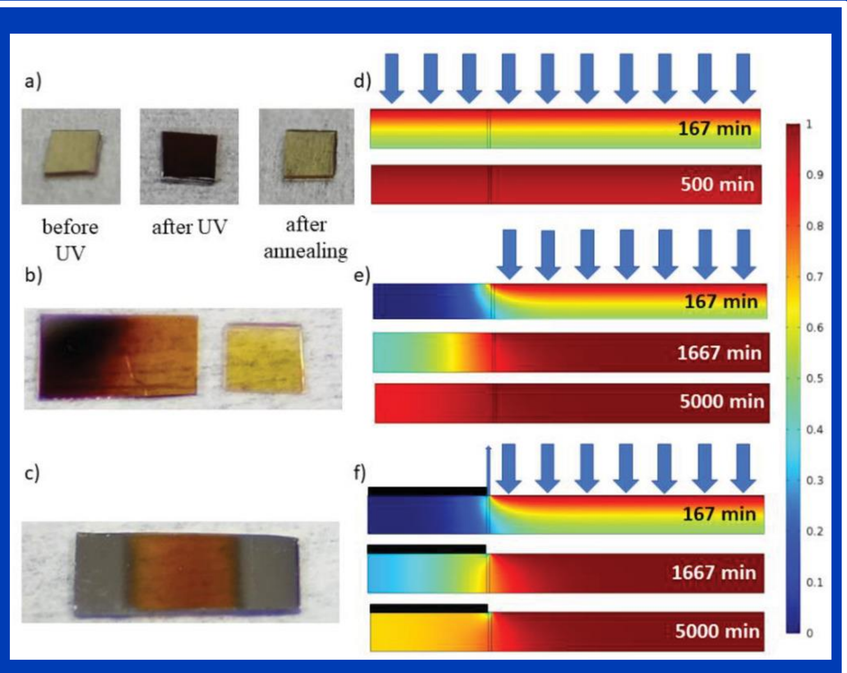


Fig. 1: a)-c) Fe:STO single crystals during various states of UV illumination and annealing. d)-f) finite element calculation describing the situation in a)-c).

DC Conductivity Change of Fe:STO under UV Illumination

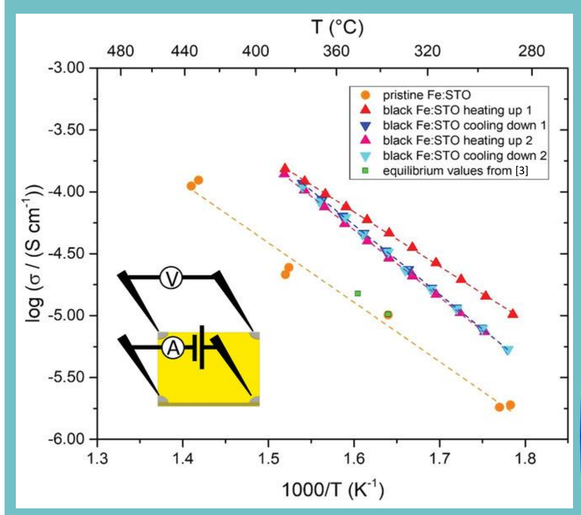
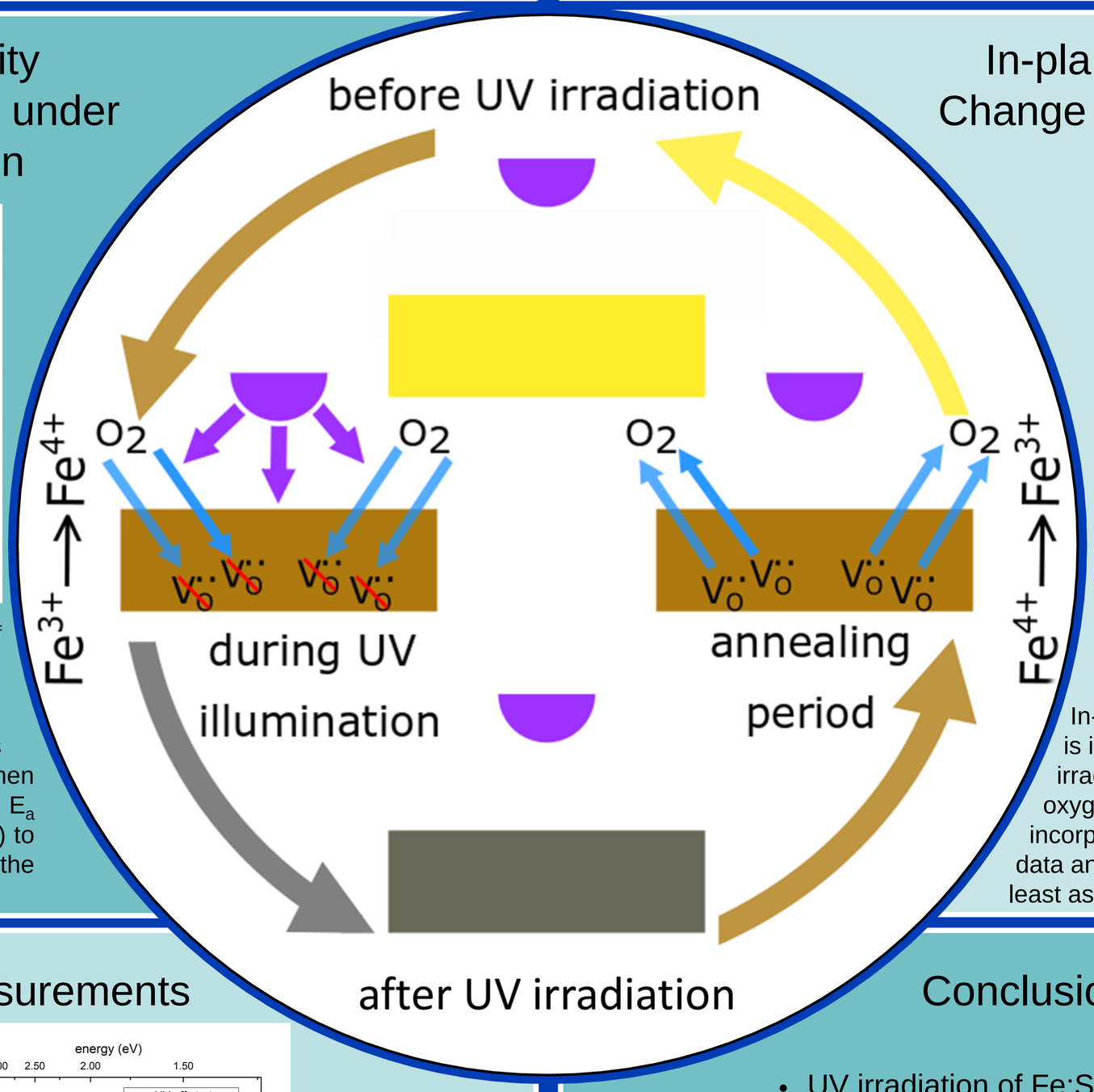


Fig. 2: Van der Pauw measurements of Fe:STO before and after UV illumination.

After UV illumination at 440 °C the DC conductivity is increased. Slight changes of the resistivity of the black specimen occurs after the first temperature cycle. E_a changes from 0.9 eV (pristine specimen) to 0.87 eV and 1.09 eV respectively after the exposure to UV light.



In-plane AC Conductivity Change of Fe:STO under UV Illumination

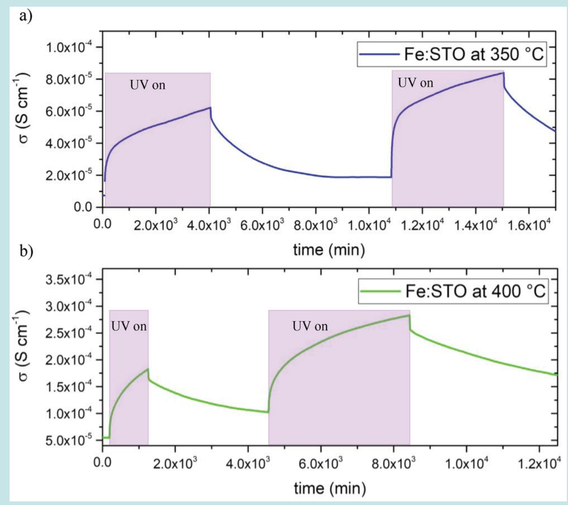


Fig. 3: In-plane AC conductivity without an under UV illumination at 350 °C (a) and 400 °C (b).

In-plane AC conductivity of Fe:STO samples is increased by a factor of 10 during UV irradiation at 350 °C and by 4 at 400 °C. The oxygen chemical potential causing the oxygen incorporation can be calculated from these data and turned out to be equal to a $p(O_2)$ at least as high as 10^8 Pa.

In-situ UV-vis Measurements

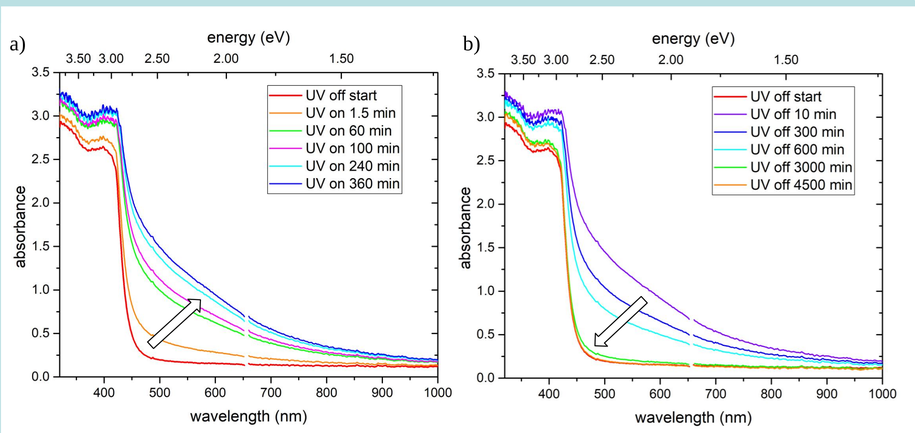


Fig. 4: In-Situ UV-vis measurements during UV exposure (a) and after (b) at 440 °C.

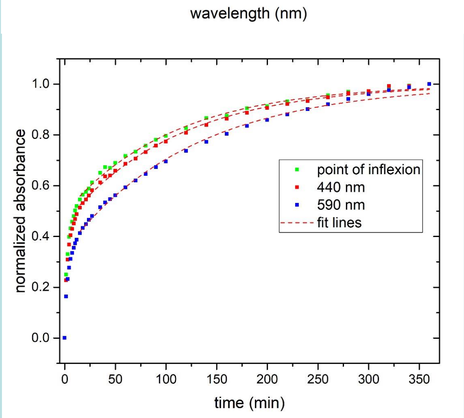


Fig. 5: Evolution of the normalized absorbance at 432, 440 and 590 nm

$$A' = \frac{A(t) - A(0)}{A(\infty) - A(0)} = \frac{c(t) - c(0)}{c(\infty) - c(0)}$$

$$= 1 - B * \exp\left(-\frac{\pi^2 * D_0^{\delta}}{4\,L^2} * t\right)$$

Absorbance of the specimen increases during UV exposure and decreases again during the annealing period, reaching nearly its origin absorbance after 4500 min. By using the equation above and the normalized absorbance the diffusion coefficient of Fe:STO at 440 °C can be calculated. A diffusion coefficient of 1.4-1.6 × 10^{-7} cm^2 s^{-1} was obtained.

Conclusion

- UV irradiation of Fe:STO at elevated temperatures causes oxygen incorporation
- Fe:STO single crystals turn black due to the oxidation of Fe^{3+} to Fe^{4+}
- AC and DC conductivity is increased after long term UV exposure
- Using UV-vis spectroscopy an oxygen diffusion coefficient of ca. 1.5 × 10^{-7} cm^2 s^{-1} is found at 440 °C

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FOXSI Functional Oxide Surfaces and Interfaces

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