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Photo-induced intrinsic defects in single crystalline TiO_2 (rutile)

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Abstract – Several intrinsic defects in fully oxidized and reduced TiO_2 (rutile) in dark and under above band gap illumination were examined by electron paramagnetic resonance (EPR) in the temperature range from 4K – 300K. In the oxidized samples under dark conditions EPR spectra due to uncompensated Fe^{3+} are observed. Above band gap illumination (375 nm, 16mW) induces several paramagnetic defect states that are detected at low temperatures. Their angular dependencies and properties are measured and compared with intrinsic defects in reduced TiO_2 (rutile) samples.

Titanium dioxide (TiO_2) is intensively investigated because of many interesting features and technological applications in nanotechnology as for example photocatalytic activity, sensors and the memristor. Nonstoichiometric, intrinsic defects play an important role for such applications; however, the analysis about these defects is still not conclusive.

In this work two fully oxidized synthetic TiO_2 (rutile) single crystals from MTI (USA) and CRYSTEC (Germany) were investigated by electron paramagnetic resonance (EPR). In dark, both crystals show low concentrations of uncompensated paramagnetic substitucional Fe^{3+} impurities. Under UV light (375 nm, 16 mW) at low temperatures (< 30K) at least five different paramagnetic defect states are observed which are partially thermally stable at these low temperatures. Samples from the same substrate were partially reduced at 850°C for two hours in reducing Ar/H atmospheres. Before reduction treatment samples are slightly yellow, whereas after they turned medium blue with strongly reduced electrical resistance.

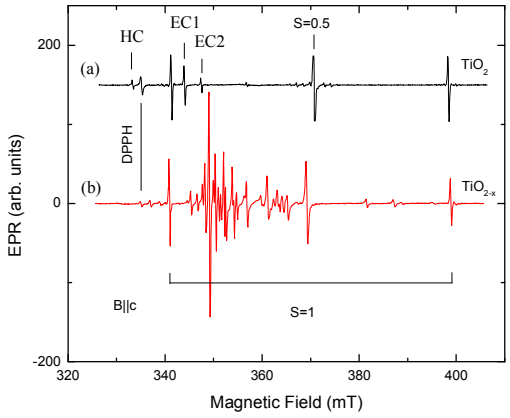

Figure 1: EPR spectra of (a) fully oxidized TiO_2 under UV light and (b) reduced TiO_2 measured at 25 K.

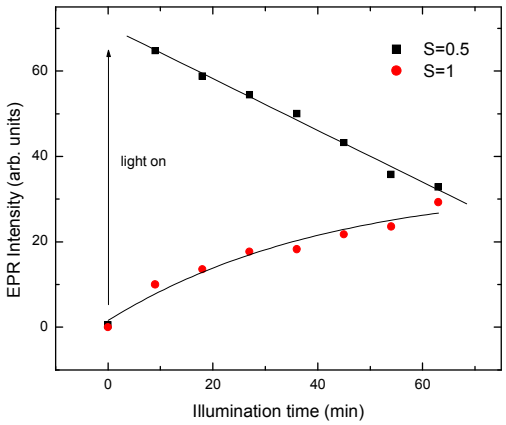

Figure 2: EPR signal intensity of two charge states of the oxygen vacancy (V^+) and $V(^O)$ under UV light at 25 K.

The EPR dependencies of the five different paramagnetic defect states are presented and analyzed. Two of them belong to two spin states of the same defect, S = 0.5 and S = 1, which was attributed recently to the oxygen vacancy in the charge states (V_O^+) and (V_O^0) [1]. In fully oxidized samples the paramagnetic states of this vacancy are populated by UV light by electrons from Fe^{3+} impurities. First, the one electron state (S=0.5) is occupied and second, the two electron state (S=1). These spectra have been observed before, however, not analyzed in detail [2]. The EPR spectra of the oxygen vacancy show superhyperfine interaction with two Ti ions in different symmetries that we attribute to relaxation effects of the vacancy. In addition, two other electron centers (EC1, EC2) and one hole center (HC) are observed in oxidized TiO_2 samples from MTI. The EPR spectra of all these defects are also observed in reduced TiO_2 samples in dark; however, not as the dominant defect species. In reduced TiO_2 samples, interstitial Ti ions are dominant [3].

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