INTRINSIC DEFECTS IN TiO$_2$ TO EXPLAIN RESISTIVE SWITCHING DEVICES

Dieter Schmeißer, Matthias Richter, Massimo Tallarida

BTU Cottbus, Angewandte Physik – Sensorik, Konrad Wachsmann-Allee 17, 03046 Cottbus, Germany.

We use resonant photoemission spectroscopy to study the valence and conduction band partial density of states in TiO$_2$ films and single crystals. We distinguish between covalent contributions of O2p and Ti3d4s states (Fig.1, upper panel) and localized defect states (Fig.1, lower panel). The latter are not related to oxygen vacancies but attributed to polaronic, oxygen based intrinsic defects. They form a continuous band which appears throughout the electronic band gap and which is identified by Fano type resonant behaviour of the valence electrons when passing the O1s resonance, see CIS(-4.3eV) in Figure 1.

In addition we identify O2p-Ti3d4s charge transfer states. These are localized around the Fermi energy and are attributed to cause the n-type electronic behaviour. They show up as a peak in the CIS (-9eV) as shown in Fig.1. They are associated to a particular Auger decay at the resonance, which involves these localized O2p-Ti3d4s CT-states. Thereby, the states at the lowest oxygen resonance show a different Auger profile, which proceeds with a slope of 67.5° in a 2-dim plot of all valence band data vs. the excitation energies around the O1s threshold [1-3]. These findings contrast the common Auger process which is also evident in our data but can be observed only at photon energies above 535eV and proceeds under 45°. We explain such behaviour by a multiple Auger process, which causes a 3h final state. It is shown schematically in Figure 2. The starting point for this resonant mechanism is the existence of the localized O2p$^5$ state of the CT complex (O in Fig.2).

Figure 1: The combined partial density of states of the valence band and conduction band as determined from the XPS and XAS data, respectively. In the lower part we compare to the CIS data of the valence feature and the CIS spectrum at the onset of the Auger process at the O1s threshold as marked by arrows. The common energy is referred to E$_F$ by shifting the absorption spectra by the binding energy of the corresponding core levels. The positions of the VBM and of E$_F$ are indicated by dashed lines.
In our model we describe the role of these two different intrinsic defect mechanisms to account for the resistive switching mechanism observed in titania based devices. In the normal (high resistivity) state the transport properties are based on the energy difference between the VBM and the CT-band (2eV). In the low resistivity state the band gap is filled by field assisted charged polarons. In this state the transport is by hopping conductivity and is enabled by the fluctuating charge density waves of the polaronic states. They also enable a field assisted reversible phase separation. The polaronic states are originally neutral and intrinsic states with a very short life time. However, an increase of their life time and dissociation into charged polaronic states can be achieved by both, the introduction of structural defects (preconditioning) and the application of external fields.