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Time-dependent UHV-IR investigation on ZnO(10-10): probing excitations of electrons trapped in shallow states

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A better understanding of photo-chemistry and photo-physics on metal oxide surfaces is urgently required for a number of applications. In particular, it is mandatory to obtain a better and more detailed information on the path of photoexcited charge carriers. Recording the transients of photostimulated charge accumulation and dissipation kinetics, and studying the charge transfer to molecular species adsorbed on oxides surfaces will eventually allow us to understand phenomena governing photocatalysis, solar energy harvesting, electrochemical fuel cells, etc.

Here we study an important intermediate state in chain of events which leads from photon absorption to chemical modification of molecular adsorbates, namely the trapping of photoexcited electrons in polaronic trap states, which can be either intrinsic (self-trapping of electrons) or localized at defects like O-vacancies. On TiO_2 such states have been shown to have lifetimes from seconds to several hours. For this material the electron trapping in a polaronic state has been already successfully observed for rutile TiO_2(110) single crystal surfaces by using an ultra-high vacuum compatible grazing incidence infrared spectroscopy (UHV-IR) [1].

In this contribution we extend our studies to ZnO. For this important oxide IR studies on trapped charge carriers have not yet been reported. By applying the UHV-IR technique to probe photoexcited electrons in a reflection geometry for the mixed terminated ZnO(10-10) surface we are able to study the kinetics of populating and de-populating processes of the polaronic states. In pronounced contrast to TiO_2, we find that the lifetime of these states is rather short, which requires the application of a time-resolved variant of IR-spectroscopy, the so-called rapid scan method. In our experiments we observe after irradiation with a UV lamb a broad infrared absorbance band which is attributed to present of trapped electrons in intrinsic shallow and self-trapped states of ZnO. The evaluation of the state and its kinetic behaviors under different environment conditions will be discussed.

In the second part of talk, we shall briefly present new developments and research capabilities of the ESCAmicroscopy endstation in Elettra Synchrotron Light Laboratory (Italy, Trieste).

References

[1] H. Sezen, M. Buchholz, A. Nefedov, C. Natzeck, S. Heissler, C. Di Valentin, C. Wöll, Scientific Reports 4, 3808 (2014).

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