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XAS study of vanadium pentoxide thin films

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Vanadium oxides can exist with different formal vanadium valence states, ranging from 2+ to 5+. Among them, vanadium pentoxide is particularly noteworthy due to its outstanding physical and chemical properties. The aim of this work was study the electronic structure of V₂O₅ thin films and its changes with temperature by means of XAS technique.

V₂O₅ thin films have been deposited by rf reactive sputtering. XAS measurements were carried out at the PEEM/XAS beamline of Solaris National Synchrotron Radiation Centre, Poland. The total electron yield (TEY) detection mode was used and the spectra were collected in the V:L_{2,3} – O:K range at several temperatures from room temperature to 300°C. The effect of linear dichroism was studied with linearly polarized beam impinging along the normal, or at the angle of 60 degree to the normal of the sample plane and the spectra for the V₂O₅ thin film on the Si substrate are shown in Fig 1.

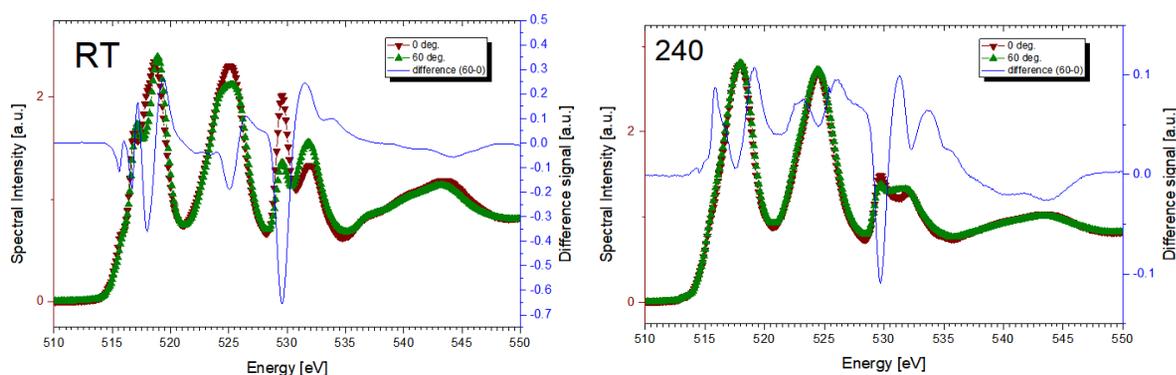


Fig. 1. The spectra for the V₂O₅ thin film on silicon substrate taken with linearly polarized beam impinging along the normal, or at the angle of 60 degree to the normal of the sample plane, together with their difference, i.e. the dichroic effect.

The room temperature Vanadium L_{2,3} spectrum of the VO_x thin film show the closest similarity to those of V₂O₅ powder, whereas the spectrum at 240°C is the closest to that of V₂O₃ powder reference (not shown). Cooling the sample down to room temperature and its exposure to air does not modify it noticeably. A similar behavior can be seen at the Oxygen K-edge spectrum (530 – 545 eV), Fig. 1 and reflects occurrence of deoxygenation and the corresponding change of the oxide stoichiometry from close to V₂O₅, towards V₂O₃. A significant dichroic effect is observed at room temperature, whereas it is much smaller at 240°C. It reveals a difference between occupation of in-plane and out-of-plane orbitals, much bigger at RT. The effect is particularly strong at the O:K XANES in the 530-534 eV double peak feature corresponding to O 2p orbitals hybridized with e_g and t_{2g} V states. It shows the difference between occupation of in-plane and out-of-plane O 2p orbitals hybridized with e_g and t_{2g} Ti states, varying with temperature and reveals deoxygenation and the resulting decreased oxidation state of the surface Vanadium ions. The results are discussed with respect to the explanation of the origin of the MIT-like effect observed in the V₂O₅ thin films and the implications for the catalytic and sensor applications.

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