Polaron and phonon properties in WO_3 thin films

Mario Saenger[1,*], Thomas Höing[2], Tino Hofmann[1], and Mathias Schubert[1]

[1] *Department of Electrical Engineering, and Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln, NE 68588-0511, U.S.A.*

[2] *FLABEG GmbH. und Co. KG, Glasserstr. 1, D-93437, Furth i. Wald, Germany*

*Email: saenger@engr.unl.edu ellipsometry.unl.edu

Our message

We analyze the dielectric function of electrochemically intercalated tungsten oxide thin films by spectroscopic ellipsometry, and model approach by Drude, Lorentz and Cauchy lineshape functions, accounting for possible free charge carriers, bound (polaron) charge carriers, phonon modes, and near-band-gap dispersion

We observe NO unbound (free) charge carrier but increasing polaron mode absorption upon electrochemical intercalation.

We can excellently verify the validity of the polaron hopping transport in WO thin films

We further observe distinct changes in the phonon mode spectrum, which is indicative for new bond formation, tentatively assigned to reduction of W-O-W bonds with increasing charge intercalation accompanied by creation of W=O bonds.

Experiment and model

- ✓ Electrochemical ion intercalation of samples between 0 and 20 mC/cm².
- ✓ Variable Angle Spectroscopic Ellipsometry (VASE) in nitrogen atmosphere at RT from 300 to 2000 cm^{-1} (MIR) and from 0.75 to 3.34 eV (VIS-UV).
- ✓ Transmission measurements from 0.75 to 3.34 eV.
- ✓ Model Dielectric Function (MDF) for WO_3 thin films in the NIR-UV spectral range (Lorentz and Cauchy terms).

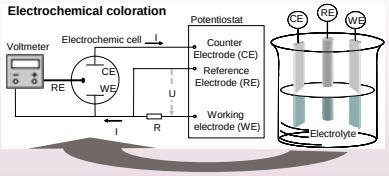
New:

Polaron and Phonon mode contributions quantified for WO_3 thin films in the VIS-UV and MIR spectral regions, respectively, as a function of electrochemical ion intercalation density.

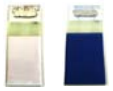
Setup

Sample structure:
Magnetron sputtered amorphous WO_3 on ITO (Flabeg)

Electrochemical coloration

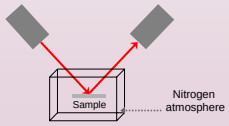


Before and after coloration



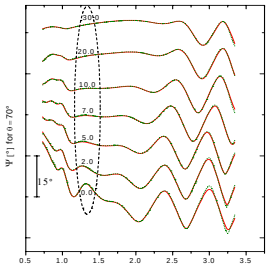
VASE
Spectral range:
MIR – NIR: 300 – 4800 cm^{-1}
NIR-UV: 0.75 – 3.34 eV

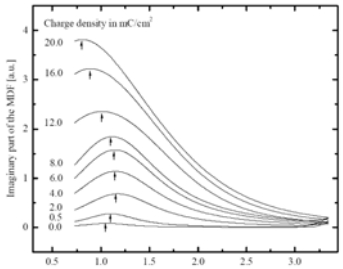
Transmission at normal incidence
NIR – UV: 0.75 – 3.34 eV



Results and Discussions

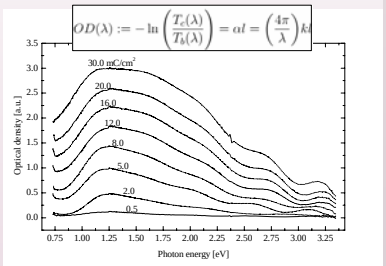
Polaron properties

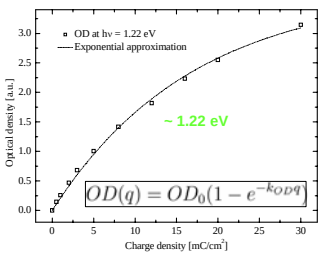


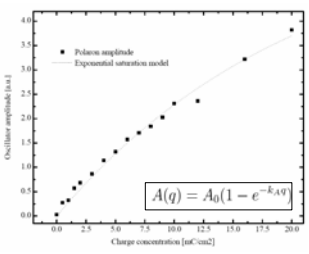


Above left: Experiment and best-match model calculated ellipsometry data in the VIS-UV range of a tungsten oxide thin film at various intercalation states. The labels on the graphs denote the intercalated charge densities in mC/cm². **Above right:** Imaginary part of the dielectric function determined from the ellipsometry measurements. The vertical arrows indicate the spectral position of the polaron mode. The W-O bond polarity decrease - observed by the phonon mode softening in band II (see Fig. E) - causes a polarity reduction of the lattice, which facilitates polaron displacement, i.e., the hopping energy is reduced.

Rigth: Optical density spectra calculated from transmission intensity measurements (intercalated versus unintercalated).
Below left: Optical density at 1.22 eV plotted as a function of charge intercalation density. The OD follows an exponential behavior, predicted by the polaron hopping model, with k_{OD}= 0.059 +/- 0.004.
Below right: Amplitude of the Polaron absorption (at the vertical arrow position above right) as a function of charge intercalation density, which follows an exponential law with k_A= 0.048 +/- 0.007 cm²/mC.

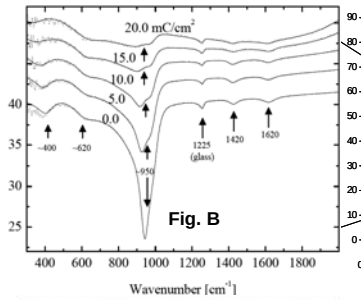


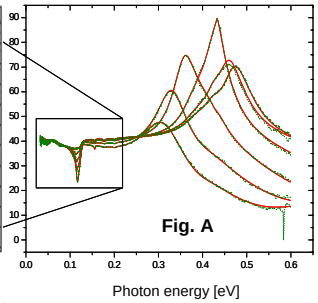


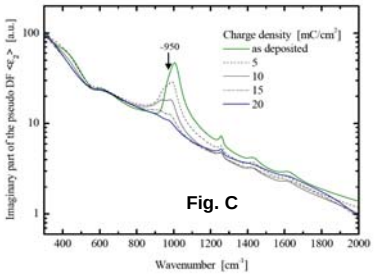


The exponential dependencies indicate hopping as the polaron transport mechanism!

Phonon properties







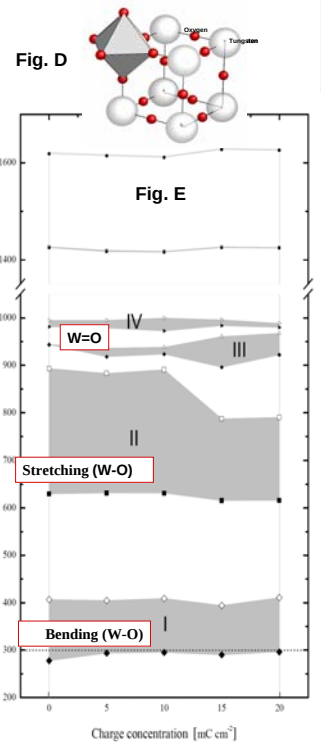


Fig. A: Experiment and best-match model calculated ellipsometry (Psi) data in the MIR range of a tungsten oxide thin film at various intercalation states. The labels on the graphs denote the intercalated charge densities in mC/cm². The phonon modes of interest for structural information are found below 2000 cm^{-1}.

Fig. B: Expanded view of the inset in Fig. A. The arrows indicate the tungsten oxide phonon modes. **Fig. C:** Pseudo-dielectric function of the entire sample (including the conductive ITO substrate), which reflects the change of the phonon mode contribution of the tungsten oxide film. **Fig. D:** Structure of the unit cell (ideal) tungsten oxide, with octahedron.

Fig. E: Bands of total reflection (TO-LO phonon bands) for the tungsten oxide films versus charge intercalation density. The shaded areas are proportional to the bond polarity. **The stretching W-O mode is loosing polarity upon intercalation, while the double-bond modes gain strength. This is indicative for intercalation-induced bond reformation.**

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