Polaron-phonon interaction in charge intercalated tungsten oxide thin films

UNIVERSITY OF NEBRASKA-LINCOLN

MoP.48

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Our message

We observe no unbound (free) charge carriers upon charge intercalation but increasing polaron mode absorption.

We observe that water and O-H vibration modes remain unaltered with increasing charge intercalation while distinct changes in the phonon mode spectrum indicate annihilation of W-O-W and creation of W=O bonds .

We present a dielectric function model near-IR to UV spectral range based on two oscillators with Gaussian and Lorentzian line shapes which precisely describes our ellipsometric data. The oscillators with resonance energies at 1.75 and 1 eV are assigned to the $W^{4+} \leftrightarrow W^{5+}$ and $W^{5+} \leftrightarrow W^{6+}$ polaron transitions.

Experiment and model

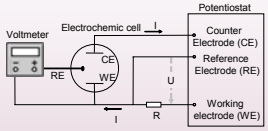
- ✓ Electrochemical ion intercalation (0 to 20 mC/cm²).
- ✓ Spectroscopic Ellipsometry (SE) in N_2 atmosphere at RT from 300 - 2000 cm^{-1} and from 0.75 - 3.34 eV.
- ✓ Model Dielectric Function (MDF) for WO_3 thin films: Lorentz and Gaussian terms account for the contribution of the $W^{4+} \leftrightarrow W^{5+}$ (4-5) and the $W^{5+} \leftrightarrow W^{6+}$ (5-6) polaron transition.

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 intercalated charge density.

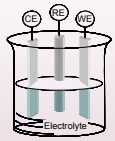
Setup

Sample structure
270 nm thick magnetron sputtered WO_3 thin film on ITO with glass substrate (Flabeg)

Electrochemical charge intercalation

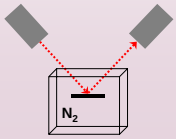


Electrochemic cell



SE Spectral range
mid-IR to near-IR
300 – 4800 cm^{-1}

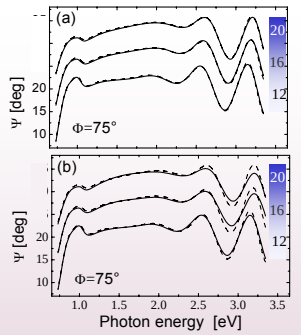
near-IR to UV
0.75 – 3.34 eV



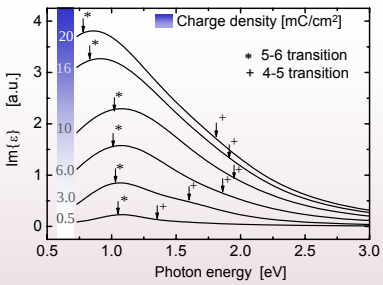
Charge density range
[mC/cm²]
0 to 20

Results and Discussion

Polaron properties

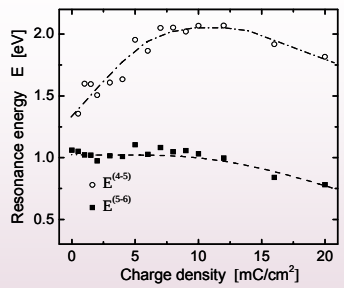


Experiment and best-match model calculated ellipsometry data in the VIS-UV range at various intercalation states. (a) Gaussian and Lorentz, and (b) single-Lorentz lineshape approximation for the polaron contribution. The double oscillator model describes precisely the expermental data.



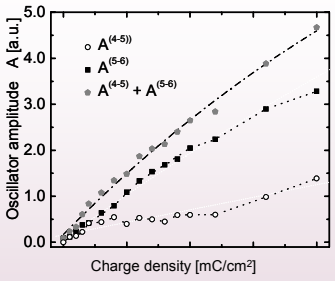
Imaginary part of the dielectric function. The vertical arrows indicate the hopping energy of the polaron 4-5 and 5-6 transitions. The hopping energy is reduced due to the W-O-W bond polarity decrease upon charge intercalation observed by the phonon mode reduction in band II (see graph „Vibration modes frequencies")

Polaron resonance energy parameters Vs charge density



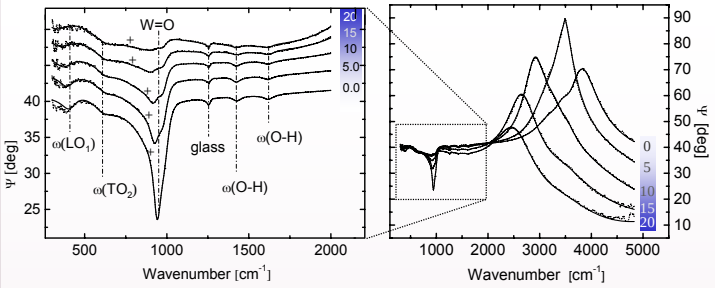
Oscillator resonance energy parameters of the 4-5 and 5-6 polaron transition. For charge densities higher than 10 mC/cm², the hopping energy is reduced with increasing charge density. The dotted lines are a guide to the eye .

Polaron amplitude parameters Vs charge density



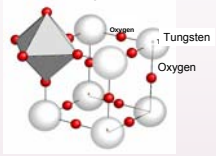
Oscillator amplitude parameters in dependence of the charge density for the 4-5 and 5-6 polaron transition. The sum of the oscillator amplitude follows an asymptotic saturation behavior characteristic from polaron hopping.

Phonon properties

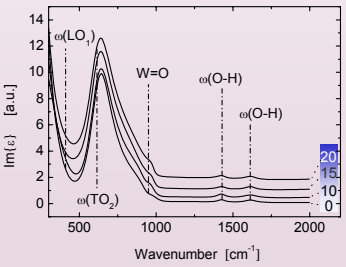


Experiment and best-match model ellipsometry data (Ψ) in the MIR range of tungsten oxide thin films with various intercalated charge densities. The phonon modes of interest for structural information are found below 2000 cm^{-1}. The cross symbols denote the position of the LO_2 mode.

Structure of the WO_3 (ideal) unit cell

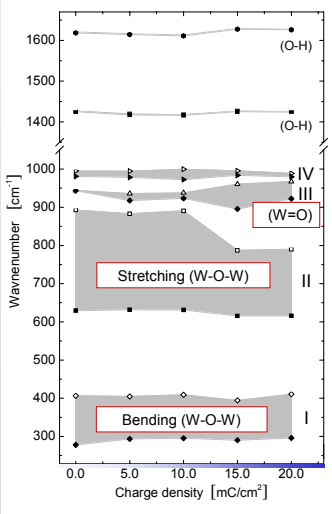


Below: Imaginary part of the dielectric function of WO_3 which reflects the change of the phonon mode contribution of the tungsten oxide film.



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

Vibration modes frequencies



Support: UNL Startup, NSF MRSEC, JAWF