Liquid electrolyte gating in oxide thin films: VO_2 and WO_3 as smart materials

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Novel materials whose properties can be controlled by external stimuli are the foundation of emerging cognitive technologies. An example of such systems is the new phase originating from the interface between polarized ionic liquids and insulating oxides. The intense electric field produced by the ionic liquid reversibly induces a phase that supports high conductivity in the oxides. Spectroscopic studies characterized and unveiled the properties of those high-conducting phases in gated VO_2 and WO_3 oxides.

In material sciences, novel phases have been found under extreme conditions of pressure and temperature. Recently, intense electric fields were also used as a pathway to induce unusual phase transitions. This can be realized by applying liquid electrolytes as a gate dielectric on thin films. Here, we report liquid electrolyte gating of VO_2 and WO_3 thin films. The experiments were performed using an electric double-layer transistor structure as shown in Fig 1. The design and electrical characterization of the devices were performed in collaboration with IBM Almaden Research Center (San Jose, USA) and MPI of Microstructure Physics (Halle, Germany). We performed material characterization to correlate the electronic- and atomic-structure changes induced by the gating process.

Vanadium dioxide (VO_2) was the first system studied. VO_2 exhibits a temperature-driven metal to insulator transition accompanied by a structural transformation from a rutile structure (high-temperature metallic phase) to a monoclinic structure (low-temperature insulator phase). Using an ionic liquid electrolyte as a gate dielectric, it is possible to reversibly induce a metallic state below the metal-to-insulator transition temperature. Hard X-ray photoelectron spectroscopy (HAXPES) was performed in the monoclinic, rutile, and gated phases using the experimental geometry depicted in Fig.1. The valence band (VB) of the VO_2 film was measured in the pristine insulating monoclinic (120 K) and metallic rutile (350 K) phases as well as in the gated (120 K) state, as shown in Fig. 2(a). Note that the valence band of the gated state cannot be decomposed into a combination of valence band spectra from the rutile and monoclinic phases. This confirms that the *gate-induced metallic phase is distinct from the temperature-induced rutile phase*. The intensity at the peak maximum in photoemission of the vanadium 3*d* band in the monoclinic phase is higher than that in the rutile and gated phases. This behavior can be explained as a consequence of coupling between the light electric field vector and the electronic orbital arrangements in this compound.

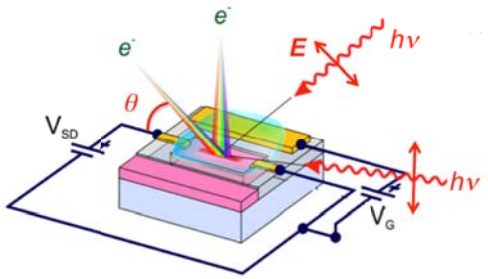

Fig.1. *Experiment and device schematic. The Au gate electrode and electrical contacts are shown in yellow. The oxide film is shown in pink and is set at a distance 0.5 mm from the gate. The turquoise droplet is the ionic liquid.*

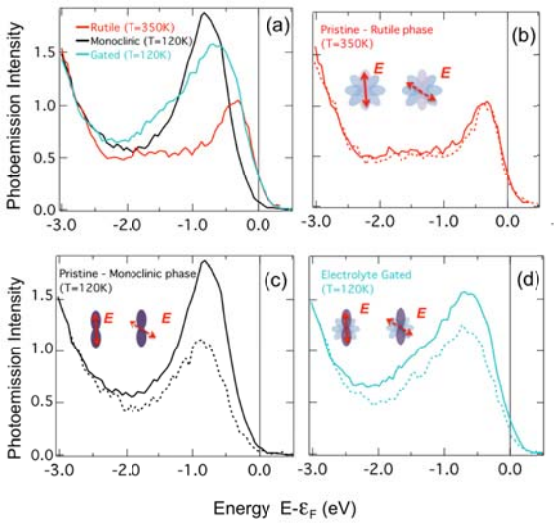

Fig 2*. (a) VB spectra measured at 3.0 keV for VO_2 in the rutile, gated, and monoclinic states. (b-d) show the dependence of the spectra intensity on the orbital polarization for the three phases. Solid (dashed) lines represent the incidence angle of 5°(60°).*

Fig. 2(b)-(d) explores the dependence of the 3*d* band photoemission intensity on the light incident angles. The vanadium *3d* states form two bands near E_F: the $d_{||}$-band, originating from the overlap of the *d*-orbitals oriented along the c_R-axis; and the π^*-band, an antibonding state arising from the hybridization of *d*-orbitals and oxygen 2*p* states. In the rutile phase, both bands are filled resulting in a homogeneous spatial distribution of 3*d* states, as sketched in the inset of Fig 1b. Therefore, the photoemission intensity does not present a strong dependence on the light electric field direction. By contrast, the monoclinic phase has a strong dimerization of vanadium atoms resulting in a strong orbital polarization. That is, only the $d_{||}$ band is occupied at energies near E_F. The light electric field at low incident angles couples with the $d_{||}$ states resulting in an enhanced photoemission intensity (Fig. 1c). In the gated phase, the angular dependence is smaller, which can be ascribed to a partial orbital polarization (Fig. 1d). *A smaller orbital polarization is a direct consequence of the reduced vanadium-vanadium dimerization*, as shown schematically in Fig. 3.

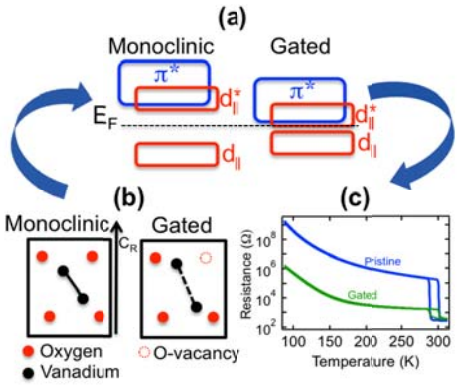

Fig 3. I*nterconnection between crystal and electronic structure of monoclinic and gated VO_2.* ***(a)*** *Modifications in the band diagram can be described by a reduction of $d_{||}$ band splitting* ***(b)*** *Structural changes induced by electrolyte gating: in the gated structure, the V-V distances are larger than that in the monoclinic phase* ***(c)*** *Temperature-dependent resistances of pristine and gated films.*

In contrast with the VO_2, tungsten trioxide (WO_3) does not exhibit a temperature-driven insulator-metal transition. It is a transparent insulator with a large band-gap. The liquid electrolyte gating of WO_3 thin films can still reversibly induce a high conductivity phase in this material. HAXPES measurements on the *gated* state show a significant change of the core level spectra and VB states. Fig 4 a-d show the decomposition of the O1s and W4f spectra before (*pristine*) and after that gating (*gated)* state. The experiment showed that gating reversibly modifies the atomic coordination of W and O atoms without a substantial change in the stoichiometry. The changes in the W and O core spectra might be correlated with a symmetrization of W–O bond lengths upon gating. This is in agreement with the Raman spectroscopy measurements performed on the *gated* state.

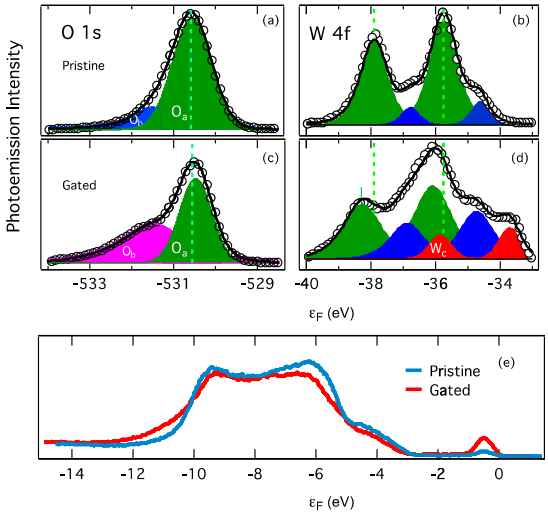

Fig. 4. (a-d) *Core levels spectra measured at 5.9 keV for WO_3 in the pristine and gated state. The symbols represent the experimental data, and the solid black lines represent the fit by the Voigt components.* ***(e)*** *VB spectra for pristine and gated states.*

We observed an enhancement of the spectral intensity near the Fermi edge, which explains the high conductivity of the *gated* phase.

In summary, we investigated the new phases induced by liquid electrolyte gating of VO_2 and WO_3. A more general mechanism that explains the induced phase transition is still under investigation. Nevertheless, we can point that, in both systems, the enhancement of conductivity is mainly driven by structural transformations, rather than by simple chemical doping. The full understanding of these systems will open a new avenue for the creation and control of new phases in oxides and might have an impact on the understanding of superconducting oxides.

References

[1] J. Karel, CE ViolBarbosa, J. Kiss, J. Jeong, N. Aetukuri, M. Samant, X. Kozina, E. Ikenaga, GH. Fecher, C. Felser, S. SP Parkin. *ACS Nano, 8, 5784, (2014)*

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