Phase control of bistable metal-insulator states in vanadium dioxide

K. Shibuya
Where is RIKEN and AIST?

RIKEN: the institute of physical and chemical research

National Institute of Advanced Industrial Science and Technology

Narita airport

City center

60km
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Background of vanadium dioxide

Metal $\rightarrow$ Insulator

$T_{MI} = 340$ K

Rutile $P4_2/mnm$

Monoclinic $P2_1/C$

$T_{MI}$ above room temperature

Resistivity ($\Omega \text{cm}$)

Temperature (K)

Chemical substitution

Metal $\rightarrow$ Insulator

Metal

Insulator

$\sim 0.5$ eV

$V_{0.91}W_{0.09}O_2$

~0.5 eV
Sneak current

Oxide Double-Layer Nanocrossbar for Ultrahigh-Density Bipolar Resistive Memory

Seo Hyoung Chang, Shin Buhm Lee, Dae Young Jeon, So Jung Park, Gyu Tae Kim, Sang Mo Yang, Seung Chul Chae, Hyang Keun Yoo, Bo Soo Kang, Myoung-Jae Lee, and Tae Won Noh*

Background of vanadium dioxide

**Smart window**

After AIST press lease (2005)

Winter (<30°C)  
Summer (>30°C)

**Photo switch**

λ=1.55 µm  
Metal

Sapphire


Thermochromic property

**Thermal control ⇒ Electric-field, photo, pressure control**
Outline

1. Phase control by chemical substitution
2. TiO$_2$/VO$_2$ superlattices
3. VO$_2$/Nb:TiO$_2$ junctions
4. Electric-field-induced phase transition
5. X-ray photo-induced phase transition
6. High-pressure-induced phase transition
Acknowledgements

Overall supervision
- RIKEN & U. Tokyo: M. Kawasaki & Y. Tokura

X-ray Diffraction
- RIKEN: D. Okuyama, Y. Taguchi, & T. Arima
- KEK: Y. Yamasaki, K. Kobayashi, H. Nakao, R. Kumai, & Y. Murakami

Photoemission spectroscopy
- U. Tokyo: E. Sakai, K. Yoshimatsu, H. Kumigashira, & M. Oshima

Optical study
- GIST: J. S. Lee

Electric Double Layer Transistor (ELDT)
- RIKEN: M. Nakano, T. Hatano, & Y. Iwasa

High pressure measurement
- RIKEN: C. Terakura
1. Phase control by chemical substitution
Electron-doping in VO$_2$ thin films

The dimerization is destabilized with electron-doping

**Spin-singlet formation vs. kinetic energy**

Electron-doping can control the transition temperature and the metallic state is stabilized.

Optical study for $V_{1-x}W_xO_2$ thin films

- Lower doping ($x=0.05$)

**Charge and lattice dynamics**

Photoemission study for $V_{1-x}W_xO_2$ thin films

Electronic structure

Spin-Peierls

Lower doping

Electron correlation

Higher doping

Mott insulator

E. Sakai, K. Shibuya et al, PRB 84, 195132 (2011)
2. TiO$_2$/VO$_2$ superlattices
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TiO$_2$/VO$_2$ superlattices

Motivation:
Interface properties in rutile

Prediction:
VO$_2$ metallic ground state

A superlattice of rutile-type layers ($m=5$)

3$d^1$/3$d^0$ interface

<table>
<thead>
<tr>
<th>Layer</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>m</td>
<td>n</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>m</td>
<td>n</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>m</td>
<td>n</td>
</tr>
<tr>
<td>VO$_2$</td>
<td>m</td>
<td>n</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>m</td>
<td>n</td>
</tr>
<tr>
<td>TiO$_2$(001)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PRL 102, 166803 (2009)

Half-Metallic Semi-Dirac-Point Generated by Quantum Confinement in TiO$_2$/VO$_2$ Nanostructures

Victor Pardo$^{1,2}$ and Warren E. Pickett$^1$

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$^2$Departamento de Física Aplicada, Universidade de Santiago de Compostela, E-15782 Santiago de Compostela, Spain

(Received 10 February 2009; published 22 April 2009)
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**TiO$_2$/VO$_2$ superlattices**

- Robust V-V dimerization
- Neither metallic nor ferromagnetic

**Diagram:**
- Low temp structure with TiO$_2$ and VO$_2$
- High temp structure with TiO$_2$ and VO$_2$

**Graphs:**
- Structural change vs. temperature
- Resistivity vs. temperature for different samples
The inherently metallic electron-doped VO₂ layer was alternatively utilized.

K. Shibuya et al, PPB 82, 205118 (2010).

The revival of the insulating ground state was observed.

Both W:VO₂ and TiO₂ layers are rutile.
Spin-singlet state is favored at the interfaces due to strong electron-lattice interaction.

The bulk-like metallic phase is stabilized when the film thickness exceeds 6 ML.
3. $\text{VO}_2$/Nb:TiO$_2$ junctions
**V_{1-x}Cr_{x}O_{2} thin films**

![Graph showing resistivity versus temperature for V_{1-x}Cr_{x}O_{2} thin films]

- Thin film
  - Metal
  - Insulator

![Color map showing resistivity ratio (Resistivity/\(\Omega\) cm) versus log temperature (K) for different compositions of V_{1-x}Cr_{x}O_{2}]

- Bulk

Phys. Rev. B 8, 1323 (1973)
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VO$_2$/Nb:TiO$_2$ junction

Electron-doping  Hole-doping

\[ \frac{1}{C^2} = \frac{2(V_{BI} - V)}{q\varepsilon_0} \left( \frac{1}{\varepsilon_T N_{DT}} + \frac{1}{\varepsilon_V N_{DV}} \right) \]

\[ = \frac{2(V_{BI} - V)}{q\varepsilon_0 \varepsilon_T N_{DT}} \left( 1 + \frac{\varepsilon_T N_{DT}}{\varepsilon_V N_{DV}} \right) \]

\[ N_{DT}' = N_{DT} \left( 1 + \frac{\varepsilon_T N_{DT}}{\varepsilon_V N_{DV}} \right) \]

No indication of depletion layer in VO$_2$

TiO$_2$  VO$_2$

Nb:0.05wt%
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**VO\textsubscript{2}/Nb:TiO\textsubscript{2} junction**

- **VO\textsubscript{2} work function**
  - $\sim 5$ eV

- **ΔV\textsubscript{BI} ≈ ΔZ(eV)**
  - $x = 0.01$
  - $x = 0.05$
  - $x = 0.09$
  - $x = 0.14$
  - $y = 0.20$
  - $y = 0.10$
  - $y = 0.30$

A. Sawa *et al*, APL 90, 252102 (2007)
4. Electric-field-induced phase transition
Electric-field induced phase transition


a,b, A schematic (a) and an optical micrograph (b) of an EDLT with a coplanar gate electrode. A small droplet of an ionic liquid, DEME-TFSI, covers both a channel and a gate electrode so that ions can freely move between these areas back and forth depending on a gate voltage, enabling electrical switching.
The temperature dependence of the sheet resistivity under different $V_G$. Once a positive gate bias is applied, the metal-insulator transition temperature decreases drastically. Above $V_G = 0.8$ V, the sample shows almost metallic behavior.
Electric-field induced phase transition

Carrier injection by $E$

5. X-ray photo-induced phase transition
Femtosecond Structural Dynamics in VO$_2$ during an Ultrafast Solid-Solid Phase Transition

A. Cavalleri,* Cs. Tóth, C. W. Siders, and J. A. Squier
University of California San Diego, La Jolla, California 92093-0339

VO$_2$ single crystal at 300 K

Photo-induced phase transition at room temperature
But not persistent
X-ray induced phase transition

\[
V_{0.935}W_{0.065}O_2
\]

X-ray induced

\[x = 0.04\]

\[x = 0.065\]

\[x = 0.08\]

Metal

Insulator

Transition temperature (K)

0.00 0.02 0.04 0.06 0.08 0.10

X-ray induced

\[t = 80 \text{ nm}\]

\[h\nu = 9.8 \text{ keV}\]

K. Shibuya et al, PRB 84, 165108 (2011)
A negligible relaxation process was seen without X-ray irradiation. The persistent phase transition was confirmed.
The insulator-metal transition is well-scaled with the time-integrated photon density, independent of flux density.
6. High-pressure-induced phase transition
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External-Strain Induced Insulating Phase Transition in VO$_2$ Nanobeam and Its Application as Flexible Strain Sensor

By Bin Hu, Yong Ding, Wen Chen, Dhaval Kulkarni, Yue Shen, Vladimir V. Tsukruk, and Zhong Lin Wang$^*$


[100]$_{M2}$ // [001]$_{R}$

more insulating
Hydrostatic pressure induces an insulator-metal transition.
Electric Pulsed Induced Changes in Oxides 2012

X-ray diffraction under high pressure

With use of DAC and synchrotron X-ray

$V_{0.94}W_{0.06}O_2/TiO_2(001)$

$W:VO_2(101)$

$T_{MI}$

Insulator

Metal
Hall measurements for $V_{0.933}W_{0.067}O_2$ under hydrostatic pressures

With use of a piston-type pressure cell

High pressure induces a correlated metal.
Pressure-induced insulator-metal transition was seen at the phase boundary.
Summary

- The metallic state is stabilized by chemical substitution. The collective dimerization is robust even at the interfaces.
- Electronic phases of VO$_2$ can be controlled by external stimuli such as electric field, X-ray, and high-pressure. The electronic state is closely interrelated with the lattice-structural change. The electric-field control is the most powerful perturbation for device application.
Back-up
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VO$_2$(001)/TiO$_2$(001)

<table>
<thead>
<tr>
<th></th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2$</td>
<td>0.4552</td>
<td>0.2846</td>
<td>Rutile</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.4593</td>
<td>0.2959</td>
<td>Rutile</td>
</tr>
</tbody>
</table>

$Lattice$ $mismatch$ (%) \(-0.89\) $-3.82$

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Y. Muraoka et al., APL 80, 583 (2002).

All thin films were grown on TiO$_2$(001) surfaces by PLD.
**X-ray diffraction**

The out-of-plane lattice constants change linearly against W-doping concentration.

The out-of-plane lattice constants change linearly against W-doping concentration.
Optical study for $V_{1-x}W_xO_2$

The V-V dimerization is systematically weaken with W concentration.

Comparing with V magnéli phases: $V_nO_{2n-1}$

Vanadium magnéli phases

![Graph showing metal-insulator transition temperatures and magnetic ordering temperatures of compounds belonging to the Magnéli phases.](image)

Figure 1. Metal to insulator transition temperatures and magnetic ordering temperatures of compounds belonging to the Magnéli phases [10]. Points related to the compounds under study in the present work have been highlighted.

A. Perucchi et al.

A similar picture can be applied to W:VO$_2$?
Fig. 3 Electrical resistivity vs reciprocal temperature

Fig. 5 Magnetic susceptibility curves for $V_{nO_{2n-1}}$

$V_{0.85}W_{0.15}O_2$ polycrystal

The magnetic inflection point corresponds to the metal-insulator transition temperature.
TiO$_2$/V$_{1-x}$W$_x$O$_2$ ($x = 0$ or $0.08$) superlattices

Motivation:
Interface properties in rutile

Strong e-lattice coupling?

3$d^1$/3$d^0$ superlattices in Perovskite
- SrVO$_3$/SrTiO$_3$ (metal-insulator transition)

A superlattice of rutile-type layers ($m=5$)

3$d^1$/3$d^0$ interface

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Robust V-V dimerization

\[
\text{(TiO}_2\text{)}_m/\text{(W:VO}_2\text{)}_n
\]

Neither metallic nor ferromagnetic

K. Shibuya et al, PPB 82, 205118 (2010)
Electric-field induced phase transition
Electric-field induced phase transition
Electric-field induced phase transition

- $V_{0.925} W_{0.075} \text{O}_2$
- $E_s \sim 0.3 \text{ eV}$
- $E_F$
- $T = 285 \text{ K}$
- $n_s$ from $Q = C_i V_G$ ($C_i = 10 \mu \text{Fcm}^{-2}$)
- Bulk effect
- Surface effect
The X-ray induced phase transition is accompanied with the revival of metallic conduction. The conductivity is strongly coupled with lattice.

X-ray was irradiated at 9 K, and off during heating.

\[ 5.4 \times 10^{14} \text{ photon/cm}^2 \text{ s} \]
The metal volume fraction was estimated, assuming that two phases exist which form a nanoscale phase separation. The threshold difference between conductivity and metal volume fraction was observed, indicating a percolative conduction.
Possible mechanism

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Or coupling with optical phonon?

Structural change?

The d electron comes back.

Electronic change?

Photo-excitation

Transiently d electron is removed.

Core-level excitation

The spin-singlet dimmer is deformed
Previous studies on pressure effect on VO$_2$

**VO$_2$ single crystal**

**Fig. 2.** Hydrostatic-pressure dependence of the transition temperature of VO$_2$ for increasing and decreasing temperature.


**Fig. 2** (color online). Optical conductivity $\sigma_1(\omega)$ of VO$_2$ at different pressures. Dashed lines are guides to the eyes. Inset: normalized spectral weights $SW_L(P)$ and $SW_H(P)$.

Composition dependence

The insulating phase remains in $x = 0$ and $0.02$. 

(a) $x = 0$

(b) $x = 0.02$
Evidence of pressure induced compressibility enhancement in pure and Cr-doped vanadium dioxide

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