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14. ABSTRACT Investigations were performed with a view to making such devices in the surface, or in thin crystals, of vanadium dioxide. This required developing suitable crystals, testing techniques to shape, pattern and dope them, improving understanding of the electrical and optical properties of the phases and the metal-insulator transition (MIT) between them, and establishing control of the MIT. We found several improved ways to grow, manipulate, clean, pattern and dope VO ₂ nanobeams, rods and plates, and epitaxial VO ₂ films on TiO ₂ . We studied the competition between					
15. SUBJECT TERMS vanadium dioxide, nanowire, metal insulator transition, Mott transition					
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Report Title

Mesoscopic effects and metal-insulator transition in vanadium oxide nanowires: final progress report

ABSTRACT

Investigations were performed with a view to making such devices in the surface, or in thin crystals, of vanadium dioxide. This required developing suitable crystals, testing techniques to shape, pattern and dope them, improving understanding of the electrical and optical properties of the phases and the metal-insulator transition (MIT) between them, and establishing control of the MIT. We found several improved ways to grow, manipulate, clean, pattern and dope VO₂ nanobeams, rods and plates, and epitaxial VO₂ films on TiO₂. We studied the competition between the two insulating phases, M1 and M2, and the metallic phase using near-field scanning optical techniques and Raman spectroscopy. Also, using scanning photocurrent microscopy we investigated for the first time the photoresponse of this correlated material. We determined that the response is purely photothermal, meaning that carrier relaxation to thermal equilibrium in the insulating phase is much more efficient than in band semiconductors, consistent with strong correlations.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

"New aspects of the metal-insulator transition in single-domain vanadium dioxide nanobeams", J. Wei, Z. Wang, W. Chen, and D.H. Cobden, Nature Nanotechnology 4, 420 (2009)

Number of Papers published in peer-reviewed journals: 1.00

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

(d) Manuscripts

<u>Received</u>	<u>Paper</u>
2012/07/08 2: 2	T. Serkan Kasirga, D. Sun, Jae H. Park, Jim M. Coy, Zaiyao Fei, Xiaodong Xu, David H. Cobden. Photoresponse of a strongly correlated material determined by scanning photocurrent microscopy, Nature Nanotechnology (06 2012)

TOTAL: 1

Number of Manuscripts: 0.00

Books

<u>Received</u>	<u>Paper</u>
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TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Jiang Wei	0.50
Jae Park	0.50
FTE Equivalent:	1.00
Total Number:	2

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
David Cobden	0.05	No
FTE Equivalent:	0.05	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Vincent J. Roma	0.10	Physics
FTE Equivalent:	0.10	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	1.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	1.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	1.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):.....	1.00
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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	1.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>
Jiang Wei
Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachment

Technology Transfer

Statement of the problem studied

Vanadium dioxide has a dramatic first-order metal-insulator transition above room temperature which could in principle be exploited to make electrical and optical switches and sensors. Under this one-year grant, investigations were performed with a view to making such devices in the surface, or in thin single crystals, as opposed to granular films, of VO_2 . This required developing suitable crystals, testing techniques to shape, pattern and dope them, improving understanding of the electrical and optical properties of the phases and the metal-insulator transition (MIT) between them, and establishing better control of the MIT.

Summary of the most important results

1. Nano-optical investigations

In collaboration with M.B. Raschke (University of Colorado), using mid-IR s-SNOM (scattering-scanning near-field optical microscopy) above room temperature in air, we analyzed the domain behavior in substrate-bound VO_2 nanobeams at down to 10 nm spatial resolution. The results were published in Nano Letters¹. Fig. 1 indicates the experimental setup and representative s-SNOM results, showing sudden appearance and growth of metallic domains with high resolution. By combining the measurements with micro-Raman spectroscopy we identified the presence of the M2 insulating phase in competition with the M1 insulating phase in a range of temperatures below T_c . We interpret this as a result of the relationship between the lattice constants of the three phases, which is such that placing M2 at a boundary between M1 and the rutile metal (R) reduces the elastic energy. This observation combined with those of other recent studies implies that M2 is generically present in thin films and bulk samples below T_c , though this fact has not been taken into account in most of the literature on VO_2 . Ours may be the first investigation of a correlated electron material where the volume fraction and real space domain pattern of three competing phases were revealed.

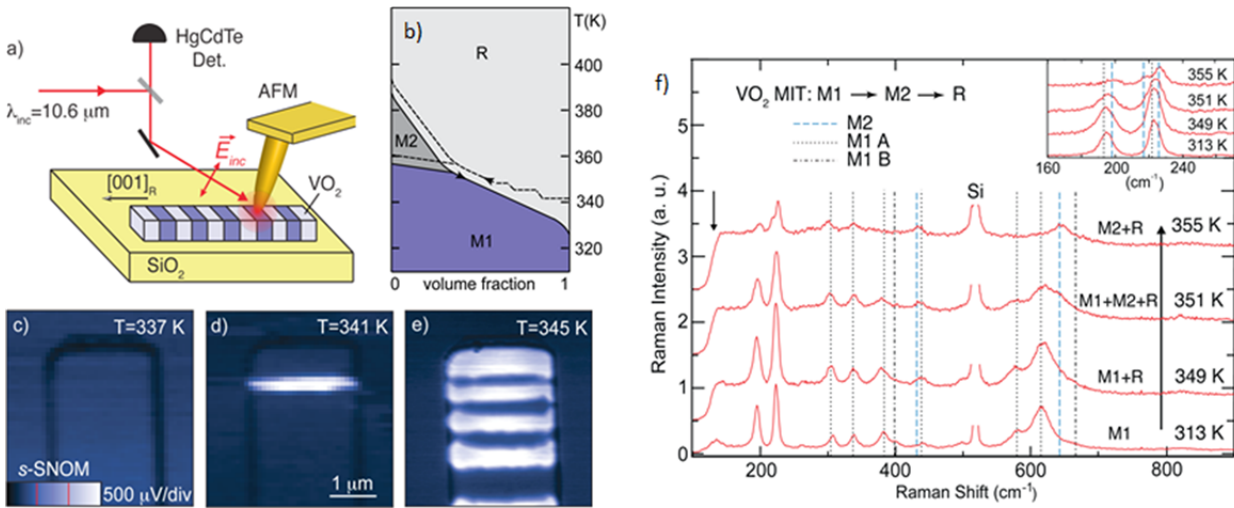


Figure 1. (a) IR s-SNOM technique applied to a VO_2 nanobeam attached to a substrate. (b) Volume fraction of M1, M2, and R phases for a nanobeam derived from the combination of s-SNOM imaging, as illustrated in (c)-(e), and micro-Raman measurements as illustrated in (f).

2. Photoresponse

Using scanning photocurrent microscopy (SPCM), in collaboration with Xiaodong Xu (UW Physics Department) we have investigated photocurrent and ultrafast response in suspended VO_2 nanobeams² in ambient atmosphere, as depicted in Fig. 2. The results demonstrate the potential of SPCM applied to

this system and others. They are currently under review in Nature Nanotechnology³. The scanning laser reflection images 2a-c reveal the I-M interface, and show how the temperature rise due to laser heating produces a shift of the interface. A laser power of 5 μW ($\sim 120 \text{ W/cm}^2$) produces about 10 $^\circ\text{C}$ warming, deduced from the interface shift. Figs. 2d-f are reflection images of a device at 30 $^\circ\text{C}$, well below the MIT, and at 75 and 95 $^\circ\text{C}$, in I-M coexistence. Below are measurements of the photocurrent I_{ph} and photoconductance $G_{ph} = (I_{ph} - I_0)/V$, where V is the bias and I_0 is the zero-bias photocurrent, at laser power 1 μW . Below T_c , we find that I_0 is small and the finite G_{ph} is caused by the temperature dependence of the insulator resistivity. Well above T_c , both I_0 and G_{ph} are larger and peaked at the I-M interface. The sign, magnitude and variation of I_0 is consistent with a thermoelectric origin, $V_{th} = -\Delta S_{IM} \delta T_b$, where $\Delta S_{IM} = S_I - S_M \approx -280 \mu\text{V}/^\circ\text{C}$ is the difference in Seebeck coefficients between the I_{M2} and M phases. δT_b is the rise in interface temperature which is maximum when the laser is directly incident on it. By fitting the data we can also deduce that the ratio of the thermal conductivities $\kappa_M/\kappa_{I_{M2}} = 2$ and the fraction of the incident laser power absorbed, ~ 0.5 . The peak in G_{ph} is at the same place because G_{ph} is dominated by the change in resistance due to the decrease in the amount of I_{M2} on laser warming which is also proportional to δT_b . In summary, we determined the relationship between the optical and dc electrical properties of VO_2 . The photoconductance and zero-bias photocurrent generation are entirely of photothermal origin, consistent with very efficient electron-lattice relaxation in the strongly correlated insulating phase and in stark contrast with the response of uncorrelated band insulators.

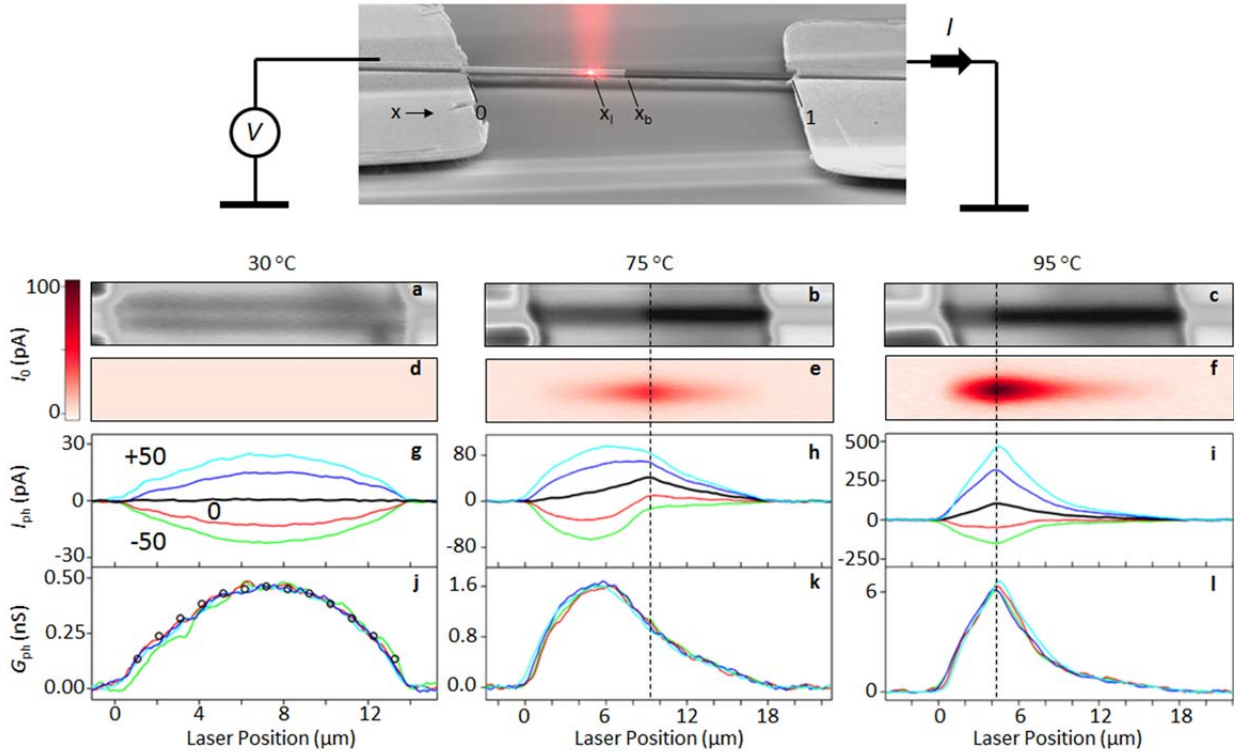


Figure 2. Top: Rendering of a laser spot (800 nm, continuous wave) superimposed on an SEM image of a suspended VO_2 nanobeam. A bias voltage is applied to the left contact and the current I is measured from the right. The photocurrent I_{ph} is the component of I at the laser chopping frequency, measured using a lockin amplifier. Bottom: (a)-(c) Reflection images using a silicon photodiode, comparing the effects of a stage temperature increase (middle) and laser power (bottom) on the I-M interface. (d)-(f), Corresponding photocurrent images. (g)-(i), Photocurrent traces along the center-line of the nanobeam in each case, at a series of biases ($V = -50, -30, 0, +30, +50$ mV). (j)-(l), Derived photoconductance along the same line.

3. Crystal growth, patterning, doping and gating

Fig. 3 illustrates some of the results of our extensive efforts to tune the growth of VO_2 , using different substrates, catalysts and growth conditions, to dope it, and to make versatile electrical contacts. For example, we succeeded in growing high quality epitaxial VO_2 films, by physical vapor transport using a V_2O_5 source, on rutile TiO_2 which showed an MIT [unpublished]. Fig. 3a shows the MIT occurring in such a film on (100) TiO_2 .

We succeeded in doping VO_2 nanobeams and platelets to the metallic state at room temperature by either tungsten incorporation in the source (Fig. 3b) or exposure to hydrogen gas above 200 °C (Fig. 3c). The latter was investigated in detail by Jiang Wei, who was the first graduate student on this project and who performed the detailed follow-up experiments⁴ after graduating while working as a postdoc with Doug Natelson at Rice University.

An absolutely key question in the field of VO_2 devices is whether the MIT can be controlled by an electric field. Essentially no effect of an insulated solid-state gate has ever been reported, and we have not detected any. Moreover, tests of gating⁵ using an ionic liquid by Wei in Natelson's group exhibited no electrical gating effects and only showed metallization resulting from injection of protons from the liquid. In our opinion, the accumulated evidence points to the facts that (a) the screening length is very short in insulating VO_2 – no more than 5 nm – and (b) the MIT cannot be induced without a structural change which costs too much elastic energy to occur only at the surface. Nevertheless the complete inability to significantly gate the surface carrier density reported in Ref. 5 and others remains puzzling.

We also made excellent contacts to VO_2 nanobeams using indium, graphite flakes (Fig. 3d), and single-layer graphene [unpublished]. The nanobeams are manipulated into place in the graphene using a piezo-controlled nanomanipulator. Graphene has the advantages of being very smooth and inert, thus minimizing the effects of strain and substrate chemistry.

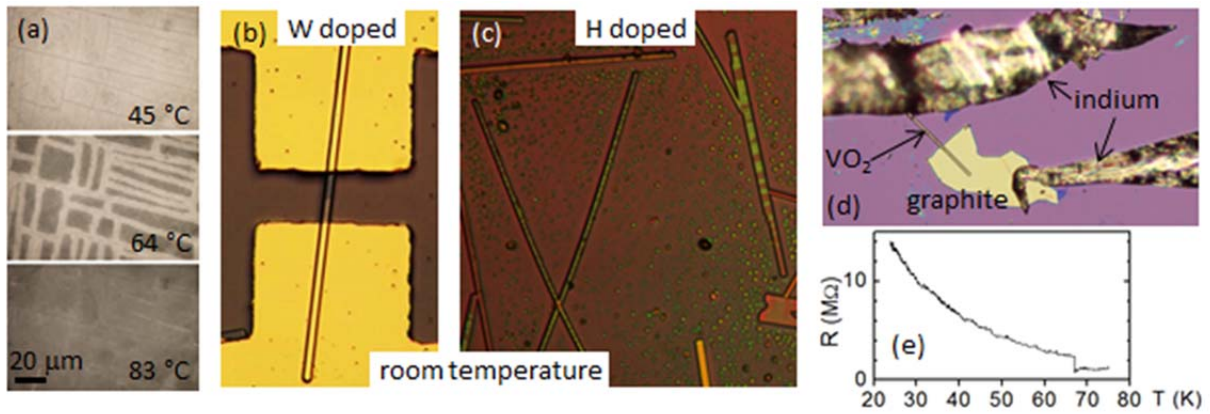


Figure 3. (a) MIT seen optically in an epitaxial film of VO_2 grown on crystalline rutile (c-axis) TiO_2 . (b) A suspended W-doped nanobeam, with a single I-M boundary, at room temperature. (c) As-grown H-doped VO_2 nanobeams attached to SiO_2 , also showing I-M coexistence stripes at room temperature. (d) VO_2 nanobeam connected with an indium contact at one end and a graphite contact at the other, and (e) temperature dependence of its resistance (up sweep only).

Bibliography

- 1 Jones, A. C., Berweger, S., Wei, J., Cobden, D. & Raschke, M. B. Nano-optical Investigations of the Metal-Insulator Phase Behavior of Individual VO₂ Microcrystals. *Nano Lett.* **10**, 1574-1581, doi:Doi 10.1021/Nl903765h (2010).
- 2 Wei, J., Wang, Z. H., Chen, W. & Cobden, D. H. New aspects of the metal-insulator transition in single-domain vanadium dioxide nanobeams. *Nature Nanotechnology* **4**, 420-424, doi:Doi 10.1038/Nnano.2009.141 (2009).
- 3 Kasirga, T. S. *et al.* Photoresponse of a strongly correlated material determined by scanning photocurrent microscopy. *Nature Nanotechnology* **under review** (2012).
- 4 Wei, J., Ji, H., Guo, W. H., Nevidomskyy, A. H. & Natelson, D. Hydrogen stabilization of metallic vanadium dioxide in single-crystal nanobeams. *Nature Nanotechnology* **7**, 357-362 (2012).
- 5 Ji, H., Wei, J. & Natelson, D. Modulation of the Electrical Properties of VO₂ Nanobeams Using an Ionic Liquid as a Gating Medium. *Nano Lett.* **12**, 2988-2992 (2012).