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as of 28-Jan-2020

Agency Code:

Proposal Number: 67239PHREP

Agreement Number: W911NF-15-1-0448

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DUNS Number: 175303262

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Report Date: 30-Nov-2019

Date Received: 30-Nov-2019

Final Report for Period Beginning 01-Sep-2015 and Ending 31-Aug-2019

Title: Nonlinear Plasmon, Rayleigh Scattering and Terahertz Dynamics in Phase-Change Correlated Oxides

Begin Performance Period: 01-Sep-2015

End Performance Period: 31-Aug-2019

Report Term: 0-Other

Submitted By: Sergiy Lysenko

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STEM Degrees: 4

STEM Participants: 20

Major Goals: THE RESEARCH OBJECTIVES OF THE PROJECT

The major research objectives of this project are to investigate fundamental processes in ultrafast light-induced insulator-to-metal (I-M) and metal-to-insulator phase transition (M-I PT) dynamics in correlated vanadium oxides and elucidate the evolution of nonequilibrium phases upon photoexcitation. Different single-layer epitaxial films, multilayer plasmonic structures and also several phase-change oxide heterostructures will be synthesized during the program.

The research effort is organized into three separate thrust areas:

- (1) Synthesis of vanadium oxide thin films and complex multilayer structures
- (2) Time- and angle-resolved hemispherical elastic light scattering and surface plasmon-polariton (SPP) spectroscopy of photoexcited oxides
- (3) Time-domain terahertz spectroscopy

The synthesis of a broad range of phase-change oxides, including highly nonlinear VO₂, V₂O₃ complexes, is one of the major goals of the project. Pulsed laser deposition (PLD) and pulsed-dc magnetron sputtering techniques will be applied to prepare thin epitaxial and non-epitaxial films. While the main research focus of the project is centered on VO₂ and V₂O₃ oxides, we also focus on the development of reliable protocols for the fabrication of V₆O₁₃, V₃O₅, V₄O₇, V₅O₉ and V₆O₁₁. The study of light-induced PT dynamics is applied for all successfully synthesized oxides. We note that the light-induced PT in V₃O₅, V₄O₇, V₅O₉, V₆O₁₁, V₆O₁₃ was never studied before and it is a completely unexplored phenomenon for these oxides.

In order to elucidate pathways of excited state dynamics in vanadium oxide complexes, the research focuses on ultrafast light-induced PT dynamics in oxides with different stoichiometries and morphologies. Different methods of femtosecond spectroscopy will help to separate the charge and lattice dynamics upon PT and to reconstruct the evolution of electronic and structural material properties.

SPECIFIC AIMS

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- To separate and characterize the electronic and structural components of nonequilibrium dynamics upon optical excitation, and to obtain characteristic relaxation times of these processes in vanadium oxides. Some experimental techniques will be based on the analysis of light polarization for scattered, reflected or transmitted light.
- To realize the surface plasmon-polariton excitations in single- and multilayer vanadium oxide structures and to elucidate the surface wave dynamics when high-intensity SPP or evanescent surface waves are applied to induce the PT, and also when low-intensity surface waves are used as a probe.
- To realize time-domain terahertz detection of transient optical conductivity, and to obtain characteristic THz response of synthesized materials upon light-induced PT.
- To understand the role of electronic correlations in photoexcited state dynamics. To find relations between 3D light scattering field measured by tr-ARHELS technique, THz and SPP spectroscopy data and photoinduced PT in vanadium oxides, size of grains in thin epitaxial films, morphology, a structural disorder of materials and level of optical excitation. A significant research effort is aimed at understanding the influence of structural characteristics of the material and laser radiation (i.e. SPP or ordinary homogeneous light wave excitation, level, polarization, etc.) onto temporal evolution of nonequilibrium phase after photoexcitation.
- To find critical parameters controlling the light-induced phase transition dynamics in vanadium oxide structures (laser fluence threshold level for PT versus particle size, stoichiometry, structural disorder and parameters of plasmon wave interaction with vanadium oxides). This knowledge can bring an understanding of the PT mechanism in different oxides.
- To develop and enhance new research capabilities at the University of Puerto Rico, Mayaguez (UPRM). A non-collinear optical parametric amplifier (NOPA) and a fundamental-frequency-pumped collinear OPA (compressors of ultrafast optical pulses) will be assembled. It will allow us to compress laser pulse below 20 fs and to use broadband spectral ultrafast measurements. Also, a terahertz ultrafast setup will be assembled in order to monitor transient optical conductivity during insulator-to-metal PT.

Activities of the project (completion rate):

- A1. Pulsed laser deposition and magnetron sputtering of vanadium oxide films and multilayer plasmonic structures (100% of completion);
- A2. Time- and angle-resolved hemispherical elastic light scattering, tr-ARHELS, measurements (100% of completion);
- A3. Ultrafast pump-probe transient-grating measurements (100% of completion);
- A4. Ultrafast measurements of SPP reflection, transmission, and scattering (100% of completion);
- A5. Assembling of non-collinear optical parametric amplifier NOPA: compressor of ultrafast optical pulses for the visible region) (100% of completion);
- A6. Assembling of THz spectrometer (100% of completion);
- A7. Assembling of and fundamental-frequency-pumped collinear OPA: compressor of ultrafast optical pulses for NIR region (50% of completion);
- A8. Nonlinear optical Z-scan measurements of third-order susceptibility (100% of completion);
- A9. Conventional absorption/reflection spectroscopy; luminescence measurements 100% of completion;
- A10. Time-domain THz optical measurements (100% of completion) and THz conductivity measurements (50% of completion);
- A11. X-ray diffraction, including in-plane and off-plane geometries (100% of completion);
- A12. Atomic force and another microscopy (100% of completion);
- A13. Installation of elliptical mirror and alignment of SPP-tr-ARHELS (100% of completion).

Accomplishments: see attachment

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Training Opportunities: This ARL ARO DoD project significantly stimulated student activities in the area of physical optics. Very recently, our students from Advanced Materials Dynamics Group together with the PIs founded the first OSA Student Chapter in Puerto Rico. Starting from August 2018 the OSA student chapter is located in the Physics Department of UPR-Mayaguez. PI, Dr. S. Lysenko is the advisor of the Chapter. This is a huge leap for Puerto Rico to promote Optical Science on the island, to attract most talented students to STEM programs in the area of Optics, Photonics and related disciplines. The participation of STEM students in our programs is a solid foundation for their training. While this chapter was founded very recently, the PIs and their students have organized one OSA student conference on the island and several outreach activities for high-school students. Information about these activities is available on

Twitter: <https://twitter.com/OsaUpr>

Facebook: <https://www.facebook.com/uprosa.chapter.75>

OSA UPR website: <https://osa.uprm.edu/>

During the project period, PI, Dr. S. Lysenko, organized special trainings for undergraduate and graduate students in assembling of THz setup and noncollinear optical parametric amplifier (NOPA), in interferometry, LabVIEW programming, GPU (graphical processing unit) CUDA® programming of NVIDIA Tesla K80 card, conjugation of "National Instruments" data acquisition/control electronic board with optical detectors and optomechanical systems, in electrical wiring of electronic equipment controlling optical systems, in how to improve data acquisition with analog-to-digital converters and how to integrate digital CCD cameras in ultrafast optical setup. Students received special training in how to use lock-in amplifiers, how to modulate and demodulate the optical signal and how to design the setup for an optical experiment to obtain the highest signal-to-noise ratio without artifacts. This knowledge is highly important for students who are working in the area of condensed matter and optical physics.

Co-Investigator, Dr. F. Fernandez, conducted workshops for students on topics such as X-ray diffraction (XRD), atomic force microscopy (AFM), electric conductivity measurements, optical ellipsometry, magnetron sputtering and pulsed laser deposition (PLD). These are at an accessible level and cover fundamentals as well as practical aspects related to the application in the research project. These workshops were attended by students working on the project.

For all students working in the lab, the PIs provided special training in laser safety, electrical safety and safety with laser dyes and other chemicals in the lab. Students received information about the responsibilities of persons operating lasers of Class II, Class III and Class IV. Students are allowed to work with lasers in the lab only after receiving this training.

Two Summer 2019 Apprenticeship Programs for High-School Students and for Undergraduate Students (HSAP/URAP) were funded by this DoD project during two summer months of 2019. These research opportunities were given for one high school student (Sofia Sanchez) from Robinson School of Puerto Rico, and for one undergraduate UPRM student (Angel Reyes). Both students conducted summer research in the group of Advanced Materials Dynamics in the Department of Physics, UPRM. The work is sponsored by the U.S. Army Research Office DoD and directed by Prof. Sergiy Lysenko.

Five graduate students (Jose Figueroa, Jennifer Aldama, Juan Pastrana, Karla Echeverria and Larry Theran) and seven undergraduate students (Angel Reyes, Bryan Ayala, Lee Roger Chevres, Christian Plaza, Jorge Morales, Thais Santiago Pabon, and Tiahra Aviles) and one high school student (Sofia Sanchez) received a stipend provided by the project, and they were deeply involved in the project research activities. Along with these students, four non-funded graduates (Camilo Verbel, Ivan Castillo, William Rojas, and Leonardo Ramos) and four undergraduate (Felix Rivera, Dashleen Gonzalez, Manuel Lozano, and Christian Nieves) students have also participated in the project. Students received the appropriate training in one or more of different tasks, including film growth of vanadium oxides and other materials by PLD or sputtering, film characterization techniques, and performing electrical or optical measurements. Students were working with the assembly of mechanical and optical components of experimental setups and performed required optical/electrical measurements and computer programming.

Graduate student Jennifer Aldama received training in experimental optical techniques to study surface plasmon-polariton (SPP) propagation and scattering. Jennifer's experimental data were included in numerous conference presentations as well as in the paper Opt.Expr.26,13773,2018. Jennifer received a Travel Grant from OSA to attend OSA Siegman International School on Lasers which was held on the Island of Hven, Backafallsbyn, Sweden, 29 July – 4 August 2018. She presented there a poster titled "Surface Plasmon Polariton Scattering in

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photorefractive VO₂/Au bilayer." In 2018 she defended her master thesis "Light scattering and surface plasmon polaritons in thin films of phase-change materials." Jennifer Aldama was accepted for a Ph.D. program at the Institute of Photonic Sciences, ICFO, Barcelona, Spain.

Graduate student Jose Figueroa has received deep training in nonlinear optics and condensed matter physics. His research was strictly focused on optical Z-scan measurements of NLO properties of different vanadium oxides. Part of his work was also devoted to transient light scattering measurements of photoexcited phase-change materials. He presented his work "Optical Nonlinearity of VO₂ and V₂O₃" on the 2015 Workshop On Frontiers in Electronics (WOFE) and Workshop on Multifunctional Nanomaterials (WMN) in San Juan, Puerto Rico, USA December 15-18, (2015). Also, he presented his work in the 1st Physics Symposium, a departmental event organized by the Physics Department of UPRM, on April 26-28. In July 2016 he successfully defended his master thesis "Nonlinear Spectroscopy of Vanadium Dioxide". He was accepted for a Ph.D. program at Michigan State University at East Lansing.

Graduate student Juan Pastrana. Master student Juan Pastrana was supported by DoD during the previous reporting period of DoD project. He graduated in December 2017. The thesis title is "Fabrication of VO₂(B) Thin Films by Pulsed DC Reactive Magnetron Sputtering and Characterization at Low and High Temperatures". During his study in UPRM, he received deep training in the synthesis of vanadium oxide materials by DC magnetron sputtering, in developing of new sputtering deposition protocols for different vanadium oxides, and in film characterization by different optical/electrical techniques. He also received special training in the assembly of several experimental setups which require a vacuum environment. Juan Pastrana is now pursuing a Ph.D. in Electrical Engineering at Michigan State University.

Graduate student Karla Echeverría. Master student Karla Echeverría has received training in the area of synthesis of vanadium oxide materials by PLD and DC magnetron sputtering techniques, as well as training in Raman scattering techniques. She is a co-author of several conference presentations and papers (Opt.Expr. 26,13773,2018, JAP 124, 205301). She is now pursuing a Ph.D. at UPRM.

Postdoctoral researcher, Dr. Nardeep Kumar, received special professional training in ultrafast optical spectroscopy, ultrafast optical diffraction, in SPP linear and nonlinear optics and experimental study of plasmonic materials. Though his research tasks in the field of nonlinear optical spectroscopy and condensed matter physics, Dr. Kumar receives deep training for his professional development as an independent researcher. In May 2018 he left UPRM to work as a researcher/engineer at Veeco Instruments, Inc.

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Results Dissemination: Dissemination of the research findings was done via publishing research papers in national and international journals. Fifteen peer-reviewed papers were published during the project period, including publications in major physics journals, such as Phys. Rev. Lett., Phys. Rev. B, Phys. Rev. Appl, J. Appl. Phys, Opt. Express and Optics Letters. One manuscript now is under review in Nature Communications and one is just submitted to Nature Communications. Additionally, at least three new papers are almost complete and will be published with the results obtained in this project.

In 2016, we created the website of our group "Advanced Materials Dynamics" [<http://fisica.uprm.edu/light>]

Pls' research group organized the OSA Conference "Beyond the Optics", University of Puerto Rico-Mayaguez, PR, USA, April 11, 16, 2019. <https://osa.uprm.edu/> The Workshop "Beyond the Optics" was a student-oriented conference supported by OSA Foundation.

In 2018, PI together with his students founded the first OSA (The Optical Society) Student Chapter in Puerto Rico, which is now located in the Physics Department at UPR-Mayaguez.

OSA UPR website: <https://osa.uprm.edu/>

Twitter: <https://twitter.com/OsaUp>

Facebook: <https://www.facebook.com/uprosa.chapter.75>

Outreach presentations:

1. at "Weather Festival", UPRM on March 8, 2019. We prepared a section called Sky Light, where OSA Members answered different questions about optics of nature, such as why the sky is blue or what is halo, when and why we can see a rainbow, etc.

2. at "Zirconia Camp", UPRM, April 6, 2019. This activity was aimed at girls from ninth to eleventh grade, organized by the Material Advantage Student Association, attached to the Department of Materials Science and Engineering. OSA Chapter Members demonstrated different optical phenomena in order to inspire students and motivate them towards Physics careers.

3. at International Day of Light, May 16, 2019. The "Art of Light" was an optical exhibition from the UPR OSA Chapter at Plazas las Americas, San Juan, Puerto Rico. Our exhibition was part of the Oceanic exhibition (Science Museum of Puerto Rico), UMET-PRPI and the EcoExploratorio. Different schools from different parts of Puerto Rico were participating and also people from around the island. "Art of Light" presentation included the art of lasers, diffraction, polarization, geometrical optics, waveguiding and holography. The International Day of Light 2019 organized in EcoExploratorio at Plazas las Americas, San Juan, Puerto Rico has been chosen as one of the SPIE winners of IDL2019 giveaways.

THE RESEARCH WAS DISSEMINATED VIA PRESENTATIONS AT INTERNATIONAL AND LOCAL CONFERENCES:

[1]. Sergiy Lysenko, Armando Rua, Felix Fernandez, Joaquin Aparicio, Jose Figueroa, Kevin Vargas, Joseph Y Cordero, "Ultrafast insulator-to-metal phase transition dynamics of VO₂ monitored by elastic light scattering," Workshop on Multifunctional Nanomaterials, Caribe Hilton Hotel, San Juan, Puerto Rico, USA, 14-16 January, (2015).

[2]. J. Figueroa, L. Chevres, A. Rúa, F. Fernández, S. Lysenko, "Optical Nonlinearity of VO₂ and V₂O₃" 2015 Workshop On Frontiers in Electronics (WOFE) and Workshop on Multifunctional Nanomaterials (WMN), DOI: 10.13140/RG.2.1.3965.2723, Caribe Hilton Hotel, San Juan, Puerto Rico, USA December 15-18, (2015).

[3]. Sergiy Lysenko, Armando Rua, Jose Figueroa, Felix Fernandez, "Strain-dependent ultrafast dynamics of insulator-to-metal phase transition in VO₂," APS March Meeting 2016, Baltimore, Maryland, P27.00009, March 14-18, (2016).

[4]. Sergiy Lysenko, Armando Rua, Félix Fernández, "Effects of Strain in Mesoscale VO₂ Grains on Light-Induced Insulator-Metal Transition". (full length article is accepted for publication in 2016 Ultrafast Phenomena proceedings), OSA International Conference on Ultrafast Phenomena, 17 - 22 July 2016, Santa Fe Community

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Convention Center, Santa Fe, New Mexico, US

[5]. J. Aldama-Guardia, L. Chevres-Fernandez, Z. Shi, R. Romañach, S. Lysenko, "Development of motorized goniometer for high-resolution angle-resolved optical measurements." 1st Physics Symposium, University of Puerto Rico, Mayagüez, April 26-28, 2016.

[6]. Sergiy Lysenko, Armando Rua, José Figueroa, Lee Chevres, Félix Fernández, "Ultrafast Light Scattering by Transient Inhomogeneities in Vanadium Dioxide". (full length article is accepted for publication in 2016 Ultrafast Phenomena proceedings), OSA International Conference on Ultrafast Phenomena, 17 - 22 July 2016, Santa Fe Community Convention Center, Santa Fe, New Mexico, US

[7]. Kumar, Nardeep, Armando Rúa, Ramón Díaz, Iván Castillo, Brian Ayala, Sandra Cita, Félix Fernández, and Sergiy Lysenko. "Time-resolved light scattering by photoexcited V₂O₃." 2017 MRS Fall Meeting & Exhibit (2017).

[8]. N. Kumar, A. Rua, L. R. Chevres, L. Theran, B. Ayala, F. E. Fernandez, S. Lysenko, "Photoinduced optical dynamics of phase-change vanadium oxides," SPIE Nanoscience + Engineering, San Diego, California, USA, 6 - 10 August, 2017.

[9]. B. Ayala, "Thermal Treatment Effects on Electrical Properties of V₂O₃ Thin Films," Emerging Researchers National (ERN), Washington DC, February 22-24, 2018.

[10]. N. Kumar, A. Rúa, J. Aldama, K. Echeverría, F. Fernández, S. Lysenko, "Degenerate Four-Wave Mixing of Surface Plasmon Polaritons and Volume Waves in Au/VO₂," Abstract: T60.00369, APS March Meeting 2018, Los Angeles, California, March 5–9, 2018.

[11]. B. Ayala, "Thermal Treatment Effects on Electrical Properties of V₂O₃ Thin Films," 7th Puerto Rico Interdisciplinary Scientific Meeting and 52nd ACS Junior Technical Meeting, Gurabo Puerto Rico, April 28, 2018.

[12]. J. Aldama, A. Rua, N. Kumar, K. Echeverría, F. Fernandez, S. Lysenko, "Surface Plasmon Polariton Scattering in photorefractive VO₂/Au bilayer," OSA Siegmán International School on Lasers, Island of Hven, Backafallsbyn, Sweden, July 29 – August 4, 2018.

[13]. L. Theran, A. Rua, F. Fernandez, S. Lysenko, "Parallel GPU computing in light scattering metrology of ultrafast surface dynamics," OSA Frontiers in Optics & Laser Science: FIO+LS Conference, Washington, DC United States, 16–20 September 2018.

[14]. C. Nieves, K. Echeverría, F. Fernández, S. Lysenko, A. Rúa, "Measurement of the Young's Modulus of V₃O₅ Thin Films," Emerging Researchers National (ERN) Conference in STEM, Washington, D. C. February 21-23, 2019

[15]. L. Theran, A. Rúa, F. E. Fernandez, S. Lysenko, "Time-Resolved Surface Dynamics of Phase Transition Materials Visualized by Light Diffraction," 2019 Junior Technical Meeting (JTM) and the Puerto Rico Interdisciplinary Scientific Meeting (PRISM), University of Puerto Rico-Mayaguez, PR, USA, May 4, 2019.

[16]. S. Lysenko, "Ultrafast Optical Spectroscopy of Phase-Change Materials" Beyond the Optics, OSA Conference, University of Puerto Rico-Mayaguez, PR, USA, April 11-16, 2019

[17]. L. Theran, A. Rua, F. Fernandez, S. Lysenko, "Light scattering metrology of ultrafast surface dynamics", International OSA Network of Students (IONS), CREOL, The College of Optics & Photonics, Orlando, FL, USA, March 10-13, 2019.

[18]. L. Theran, A. Rúa, Nardeep Kumar, F. E. Fernandez, S. Lysenko, "Photoinduced surface dynamics of V₃O₅: visualization of autocorrelation function from light scattering data." OSA Frontiers in Optics & Laser Science: FIO+LS Conference, Washington, DC, USA, 15-19 Sep 2019.

[19]. S. Lysenko, "Pathways of Photoinduced Insulator-Metal Transition in VO₂ and V₃O₅," Abstract: D01.00007, 86th Annual Meeting of the APS Southeastern Section, Wrightsville Beach, North Carolina, USA, November 7–9, 2019.

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[20]. (Invited) S. Lysenko, "Ultrafast Angle-Resolved Light Scattering Metrology of Quantum Materials," Abstract: B02.00003, 86th Annual Meeting of the APS Southeastern Section, Wrightsville Beach, North Carolina, USA, November 7–9, 2019.

Honors and Awards: Two master students received OSA Travel Grants to attend different OSA Conferences.

Jennifer Aldama has received a Travel Grant from OSA to attend "OSA Siegman International School on Lasers" which was held on the Island of Hven, Backafallsbyn, Sweden, 29 July – 4 August 2018. She presented there a poster titled "Surface Plasmon Polariton Scattering in photorefractive VO₂/Au bilayer" with novel results on angle-resolved light scattering of photorefractive plasmonic materials for ultrafast optoelectronics. After considering Jennifer's application letter and abstract which were submitted to OSA student competition, OSA granted her for the full possible amount required to participate in the Siegman School.

Larry Theran has received two times a Travel Grant from OSA to attend FIO 2018 and FIO 2019 conference "Frontiers in Optics: OSA Annual Meeting and Exhibit/Laser Science Conference", Washington Hilton, Washington, DC, USA, Sep 2018 and Sep 2019. He presented posters titled "Parallel GPU computing in light scattering metrology of ultrafast surface dynamics." and "Photoinduced surface dynamics of V₃O₅: visualization of autocorrelation function from light scattering data."

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI

Participant: Sergiy Lysenko

Person Months Worked: 11.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Co-Investigator

Participant: Felix Fernandez

Person Months Worked: 10.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: Nardeep Kumar

Person Months Worked: 15.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Jennifer Aldama

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Person Months Worked: 11.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Karla Echeverria

Person Months Worked: 6.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Larry Theran

Person Months Worked: 1.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Juan Pastrana

Person Months Worked: 14.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Graduate Student (research assistant)

Participant: Jose Figueroa

Person Months Worked: 8.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

Participant: Lee Chevres

Person Months Worked: 5.00

Funding Support:

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Participant Type: Undergraduate Student

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Participant: Jorge Morales

Person Months Worked: 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Undergraduate Student

Participant: Christian Plaza

Person Months Worked: 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Undergraduate Student

Participant: Bryan Ayala

Person Months Worked: 12.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Undergraduate Student

Participant: Thais Santiago

Person Months Worked: 2.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Undergraduate Student

Participant: Tiahra Aviles

Person Months Worked: 1.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

Participant Type: Undergraduate Student

Participant: Angel Reyes

Person Months Worked: 2.00

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: N

Other Collaborators:

Funding Support:

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Participant Type: High School Student

Participant: Sofia Sanchez

Person Months Worked: 2.00

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Other Collaborators:

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Date Published:

Publication Location:

Article Title: Semiconductor-insulator transition in VO₂ (B) thin films grown by pulsed laser deposition

Authors:

Keywords: Oxides, Insulator-metal transitions, Electrical conductivity, Crystal structure, Surface morphology

Abstract: Thin films of B-phase VO₂ were grown by pulsed laser deposition on glass and (100)-cut MgO substrates in a temperature range from 375 to 425° C and using higher gas pressures than usual for this technique. The films were strongly oriented, with ab-planes parallel to the substrate surface. Detailed study of surface morphology through Atomic Force Microscopy images suggest significant differences in evolution as a function of growth temperature for films on the two types of substrates. Measurements of conductivities through cooling-heating cycles from room temperature to 120 K showed changes of five orders of magnitude, with steeper change between room temperature and ~150 K, which corresponds with the extended and reversible phase transition known to occur for this material. At lower temperatures conductivities exhibited Arrhenius behavior, indicating that no further structural change was occurring. No hysteresis was found between the cooling and heating branches of the cycles, which is

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Publication Location: Optical Society of America, 2016

Article Title: Ultrafast Light Scattering by Transient Inhomogeneities in Vanadium Dioxide

Authors: Sergiy Lysenko, Armando Rua, Jose Figueroa, Lee Chevres, Felix Fernandez

Keywords: Imaging ultrafast phenomena; Linear and nonlinear light scattering from surfaces; Ultrafast processes in condensed matter, including semiconductors

Abstract: The VO₂ morphology and structural defects both affect the light-induced insulator-to-metal phase transition dynamics on the mesoscale. Angle-resolved light scattering reveals substantial differences in transient statistics of optical inhomogeneities for non-epitaxial and crystalline epitaxial films.

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Journal: Conference Proceedings: OSA UP

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Article Title: Effects of Strain in Mesoscale VO₂ Grains on Light-Induced Insulator-Metal Transition

Authors: Sergiy Lysenko, Armando Rua, Felix Fernandez

Keywords: Linear and nonlinear light scattering from surfaces; Ultrafast processes in condensed matter, including semiconductors; Imaging ultrafast phenomena

Abstract: Ultrafast light diffraction measurements show strong influence of local strain in multiscale VO₂ grains on initial phase of coherent lattice oscillations accompanying the light-induced insulator-metal transition. Anisotropy of strain field in epitaxial film significantly affects the transition rate.

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Peer Reviewed: Y

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Date Submitted: 6/30/17 12:00AM

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Publication Location:

Article Title: Ultrafast diffraction conoscopy of the structural phase transition in VO₂: Evidence of two lattice distortions

Authors: Nardeep Kumar, Armando Rua, Felix Fernandez, Sergiy Lysenko

Keywords: Photoinduced phase transitions in cooperative condensed-matter systems, Insulator-Metal transitions, Ultrafast spectroscopy, Linear and nonlinear light scattering from surfaces, Imaging ultrafast phenomena

Abstract: Photoinduced phase transitions in complex correlated systems occur very rapidly and involve the interplay between various electronic and lattice degrees of freedom. For these materials to be considered for practical applications, it is important to discover how their phase transitions take place. Here we use a novel ultrafast diffraction conoscopy technique to study the evolution of vanadium dioxide (VO₂) from biaxial to uniaxial symmetry. A key finding in this study is an additional relaxation process through which the phase transition takes place. Our results show that the biaxial monoclinic crystal initially, within the first 100-300 fs, transforms to a transient biaxial crystal, and within the next 300-400 fs converts into a uniaxial rutile crystal. The characteristic times for these transitions depend on film morphology and are presumably altered by misfit strain. We take advantage of Landau phenomenology to describe the complex dynamics of VO₂ phase transition in the femtosecond.

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Journal: Journal of Applied Physics
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Volume: 121 **Issue:** 23 **First Page #:** 235302
Date Submitted: 6/19/17 12:00AM **Date Published:** 6/20/17 2:50AM
Publication Location:

Article Title: Metal-insulator transition and nonlinear optical response of sputter-deposited V3O5 thin films

Authors: Armando Rua, Ramon Diaz, Nardeep Kumar, Sergiy Lysenko, Felix Fernandez

Keywords: Magneli phases, Insulator-Metal transitions, Photoinduced phase transitions in cooperative condensed-matter systems

Abstract: Thin films of V3O5, one of the vanadium Magnéli series phases, were deposited on glass substrates by DC magnetron sputtering, without any post-deposition treatment. Characterization by x-ray diffraction and atomic force microscopy showed that the films are polycrystalline, with randomly oriented crystallites and ~300 nm grains. Some content of V2O3 was detected in long-count scans. Film resistivity was measured from room temperature to 500 K and found to follow behavior of single-crystal V3O5, including the metal-insulator transition near 425 K, except that resistivity was much lower throughout the range, which is attributed to the V2O3 in the samples. Results of small-polaron conduction theory were used to model conductivity at temperatures under ~400 K. Ultrafast nonlinear optical response of the films was explored using a pump-probe scattering technique. It was found that this material exhibits clear nonlinear response within 800 femtoseconds from the pump excitation.

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: MRS Advances
Publication Identifier Type: DOI **Publication Identifier:** 10.1557/adv.2017.91
Volume: **Issue:** **First Page #:** 1
Date Submitted: 2/7/17 12:00AM **Date Published:** 1/28/17 2:53AM
Publication Location: Cambridge, United Kingdom

Article Title: Time-resolved light scattering by photoexcited V2O3

Authors: Nardeep Kumar, Armando Rua, Ramon Díaz, Ivan Castillo, Brian Ayala, Sandra Cita, Felix Fernandez, :

Keywords: Metal-Insulator Transition; Ultrafast processes in condensed matter, including semiconductors; Linear and nonlinear light scattering from surfaces; Imaging ultrafast phenomena

Abstract: Using ultrafast angle-resolved light scattering technique, we were able to trigger a photoinduced, paramagnetic metal to paramagnetic insulator, phase transition processes in V2O3 film grown on a glass substrate. The phase transition is caused by photoacoustic wave in the film and appears as coherent oscillations of scattering signal at various time scales. These processes strongly depend on the size of microstructures constituting the V2O3 film. One of the key findings of our study is the presence of a size dependent phase transition threshold for V2O3 microstructures, where small size structures (<0.5µm) have lowest contribution to the phase transition. The presence of this threshold can be well described by considering uneven internal strain in the films which is one of the key parameters controlling phase transition dynamics in various vanadium oxides.

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Volume: 42

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Date Submitted: 6/4/17 12:00AM

Date Published: 5/26/17 4:00PM

Publication Location: Optical Society of America

Article Title: Super-resolution in diffractive imaging from hemispherical elastic light scattering data

Authors: SERGIY LYSENKO, VALERIY STERLIGOV, MANUEL GONÇALVES, ARMANDO RÚA, IAROSLAV GF

Keywords: Inverse scattering; Image reconstruction techniques; Superresolution; Scattering, rough surfaces.

Abstract: Angle-resolved hemispherical elastic light scattering techniques have been used to reconstruct the surface profile of two-dimensional photonic crystals with submicron resolution and metrological precision. Iterative algorithms permit subsequent calculation of surface autocorrelation function with additional numerical approximation of power spectrum and then yield final reconstruction of the surface shape. The proposed method enables filtering out unwanted scattering background which precludes the convergence of phase-retrieval algorithms. The estimation of higher harmonics in power spectrum provides the reconstruction of a realistic surface achieving subwavelength resolution.

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Journal: Physical Review Letters

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Date Submitted: 8/2/17 12:00AM

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Publication Location:

Article Title: Ultrafast Excited-State Dynamics of V3O5 as a Signature of a Photoinduced Insulator-Metal Phase Transition

Authors: Nardeep Kumar, Armando Rua, Junqiang Lu, Felix Fernandez, Sergiy Lysenko

Keywords: Strongly correlated systems; Metal-insulator transition; Electronic structure; Lattice dynamics; Ultrafast phenomena; Nonequilibrium lattice models; Time-resolved light scattering spectroscopy; Ultrafast pump-probe spectroscopy

Abstract: The ultrafast elastic light scattering technique is applied to reveal photoinduced insulator-metal phase transition in V3O5. Observation of time-domain relaxation dynamics suggests several stages of structural transition. We discuss the nonequilibrium processes in V3O5 in terms of photoinduced melting of polaronic Wigner crystal, coalescence of V-O octahedral and photogeneration of acoustical phonons in the low-T and high-T phases of V3O5. A molecular dynamics computation supports experimentally observed stages of V3O5 relaxation dynamics. Calculation of low-T band structure shows its insulating nature.

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Publication Location:

Article Title: Ultrafast Structural Dynamics of VO₂

Authors: Sergiy Lysenko, Nardeep Kumar, Armando Rua, Jose Figueroa, Junqiang Lu, Felix Fernandez

Keywords: Strongly correlated systems, Ultrafast pump-probe spectroscopy, First order phase transitions, Mesoscopics, Metal-insulator transition, Time-resolved light scattering spectroscopy

Abstract: Distinct contribution of acoustic and optical phonons in light-induced lattice transformation was resolved at different time scales by monitoring the insulator-to-metal phase transition in epitaxial and non-epitaxial VO₂ films. Applying the ultrafast angle-resolved light scattering technique we demonstrate a significant influence of internal misfit strain in epitaxial films on sub-picosecond phase transition dynamics. This technique also allows observing a contribution of structural defects in the evolution of the transient state. The ultrafast structural phase transition dynamics is discussed in terms of the Ginzburg-Landau formalism. Using a set of experimental data we reconstruct the thermodynamic potential of photoexcited VO₂ and provide a phenomenological model of ultrafast light-induced structural phase transition.

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Journal: Conference Proceedings: SPIE

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Volume: 10345

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Date Submitted: 8/26/17 12:00AM

Date Published: 8/24/17 4:00PM

Publication Location:

Article Title: Photoinduced optical dynamics of phase-change vanadium oxides

Authors: Nardeep Kumar, Armando Rúa, Lee R. Chevres, Larry Tharan, Brian Ayala, Félix E. Fernández, Sergiy

Keywords: Strongly correlated systems, Ultrafast pump-probe spectroscopy, First order phase transitions, Mesoscopics, Metal-insulator transition, Time-resolved light scattering spectroscopy

Abstract: Using time- and angle-resolved hemispherical elastic light scattering technique we reveal complex pathways of photoinduced nonlinear optical dynamics in VO₂, V₂O₃ and V₃O₅ thin films. The structural dynamics was monitored by using an ultrafast diffraction conoscopy technique. The evolution of phases in these correlated oxides is substantially different and significantly depends on optical excitation, temperature and size of grains and domains. Strong optical nonlinearity along with its complex transient dynamics makes vanadium oxides attractive for high-contrast all-optical switches, high-speed optical data storage and holographic devices. The characteristic time of optical nonlinearity can be tuned from several femtoseconds to picoseconds by altering the excitation fluence and size of grains and domains. Additional control of ultrafast phase transition dynamics can be achieved by photoacoustical generation of strain waves.

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Journal: Optics Express
Publication Identifier Type: DOI **Publication Identifier:** 10.1364/OE.26.013773
Volume: 26 **Issue:** 11 **First Page #:** 11068
Date Submitted: 8/18/18 12:00AM **Date Published:** 5/14/18 12:00PM
Publication Location:

Article Title: Photoinduced surface plasmon switching at VO₂/Au interface

Authors: Nardeep Kumar, Armando Rúa, Jennifer Aldama, Karla Echeverría, Félix Fernández, Sergiy Lysenko

Keywords: Surface plasmons; Photorefractive materials; Ultrafast processes in condensed matter, including semiconductors; Nonlinear optics; Integrated optics; Scattering, rough surfaces.

Abstract: Angle-resolved reflection, light scattering and ultrafast pump-probe spectroscopy combined with a surface plasmon-polariton (SPP) resonance technique in attenuated total reflection geometry was used to investigate the light-induced plasmonic switching in photorefractive VO₂/Au hybrid structure. Measurements of SPP scattering and reflection shows that the optically-induced formation of metallic state in a vanadium dioxide layer deposited on a gold film significantly alters the electromagnetic field enhancement and SPP propagation length at the VO₂/Au interface. Obtained results demonstrate high potential of photorefractive vanadium oxides as efficient plasmonic modulating materials for ultrafast optoelectronic devices.

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Journal: Physical Review Applied
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Volume: 11 **Issue:** 1 **First Page #:** 014054
Date Submitted: 11/30/19 12:00AM **Date Published:** 1/28/19 4:00PM
Publication Location:

Article Title: Ultrafast Insulator-Metal Transition in Nanostructures Assisted by Picosecond Strain Pulses

Authors: Ia. A. Mogunov, F. Fernandez, S. Lysenko, A. J. Kent, A. V. Scherbakov, A. M. Kalashnikova, A. V. Akin

Keywords: Ultrafast phenomena, Acoustic phonons, Metal-insulator transition, Phase transitions, Strain

Abstract: Strain engineering is a powerful technology that exploits the stationary external or internal stress of specific spatial distribution for controlling the fundamental properties of condensed materials and nanostructures. This advanced technique modulates in space the carrier density and mobility, the optical absorption, and in strongly correlated systems, the phase, e.g., insulator-metal or ferromagnetic-paramagnetic. However, while successfully accessing nanometer-length scales, strain engineering is yet to be brought down to ultrafast time scales allowing strain-assisted control of the state of matter at THz frequencies. We demonstrate control of an optically-driven insulator-to-metal phase transition by a picosecond strain pulse, which paves the way to ultrafast strain engineering in nanostructures with phase transitions. This is realized by simultaneous excitation of VO₂ nanohillocks by a 170-fs laser and picosecond strain pulses finely timed with each other.

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Journal: Journal of Applied Physics

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Volume: 124 Issue: 20

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Date Submitted: 12/13/18 12:00AM

Date Published: 11/27/18 8:00PM

Publication Location:

Article Title: Towards reproducible metal-insulator transition characteristics in V₂O₃ thin films sputter-deposited on glass

Authors: Armando Rua, Karla Echevarria, Brian Ayala, Gabriel A Goenaga, Sergiy Lysenko, Félix E Fernández

Keywords: Magneli phases, Insulator-Metal transitions, Correlated oxides

Abstract: Vanadium sesquioxide (V₂O₃), a Mott insulator which exhibits remarkable property changes through its metal-insulator transition near 150 K, is a very interesting candidate for device applications, either in pure form or with dopants known to significantly alter its characteristics. Thin films of V₂O₃, which would be required for most applications, have been successfully produced by many different techniques. However, as is the case for other vanadium oxides, before devices can be feasible beyond the laboratory setting, reproducibility of characteristics for the resulting materials must be achieved. Stoichiometric deviations and residual stresses very strongly affect V₂O₃ electrical characteristics, so that very tight control of these parameters will be required. The focus of this work was this issue, specifically when applying deposition techniques appropriate for industrial scale production, with standard control features. Thin V₂O₃ films were deposited on SiO₂ glass by reactive DC ma

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Journal: Frontiers in Optics / Laser Science

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Volume: Issue: First Page #: JTU3A.123

Date Submitted: 12/13/18 12:00AM

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Publication Location:

Article Title: Parallel GPU computing in light scattering metrology of ultrafast surface dynamics

Authors: Larry Theran, Armando Rua, Felix Fernandez, Sergiy Lysenko

Keywords: Ultrafast phenomena, Diffraction imaging, Parallel GPU computing, Metal-insulator transition

Abstract: Phase-retrieval algorithms are developed for parallel computing of surface autocorrelation function (ACF) and for solving the inverse problem of light scattering. A real-time visualization of ACF was achieved for transient spectroscopy of materials.

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Publication Location:

Article Title: Non-thermal generation of picosecond strain pulses during ultrafast photo-induced phase transition in vanadium dioxide

Authors: Iaroslav Mogunov, Sergiy Lysenko, Anatolii Fedianin, Felix Fernandez, Armando Rua, Anthony Kent, Ar

Keywords: Ultrafast phenomena, Acoustic phonons, Metal-insulator transition, Phase transitions, Strain

Abstract: Strain pulses of picosecond duration are a versatile tool for investigation of mechanical properties of meso- and nano-scale objects with high temporal and spatial resolutions. The traditional methods of generating picosecond strain pulses using ultrafast lasers are based on the excitation of the electron system in a metallic or semiconductor transducer. This excitation results in the generation of instantaneous stress due to thermoelastic effect or deformation potential. These approaches unavoidably lead to the heat dissipation and temperature rise which ultimately results in the destruction of the transducer. Here we propose to exploit ultrafast structural changes during photo-induced first-order phase transitions (PIPTs) in strongly correlated media for generating a high-amplitude non-thermal contribution to picosecond strain pulses. To verify this principle, we perform experiments on vanadium dioxide VO₂, which exhibits a first-order phase transition accompanied by drastic changes

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Journal: Nature Communications

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Publication Location:

Article Title: Phonon softening in V₃O₅: view from quasi-equilibrium and ultrafast time scales

Authors: Sergiy Lysenko, Armando Rua, Nardeep Kumar, Junqiang Lu, Jia-An Yan, Larry Theran, Karla Echeverri

Keywords: Ultrafast phenomena, Phonons, Metal-insulator transition, Phase transitions

Abstract: Raman scattering spectroscopy and hemispherical angle-resolved elastic light scattering (ARHELS) techniques are applied to study thermal and photoinduced insulator-to-metal (IMT) phase transition dynamics in V₃O₅ films and microcrystals. We show that phonon mode softening observed near transition point T_c can be classified as a special class of first-order phase transition close to second-order ones. Ultrafast photoinduced mode softening was resolved by time-resolved tr-ARHELS technique with distinct contribution of optical and acoustic phonons in phase transition dynamics. Ultrafast scattering imaging of surface autocorrelation function shows rise of optical homogeneity in the lateral direction of the surface on subpicosecond time scale. Theoretical modeling of V₃O₅ lattice dynamics shows good agreement with experiment. ARHELS shows the principal difference in phonon dynamics across IMT for thermally and ultrafast light-induced phase transition: the ultrafast IMT is accompanied

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CONFERENCE PAPERS:

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Conference Name: 2nd Workshop on Multifunctional Nanomaterials (WMN)
Date Received: 07-Feb-2017 Conference Date: 15-Dec-2015 Date Published:
Conference Location: San Juan, Puerto Rico
Paper Title: Optical Nonlinearity of VO₂ and V₂O₃
Authors: J. Figueroa, L. Chevres, A. Rúa, F. Fernández, S. Lysenko
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: APS March Meeting 2016
Date Received: 07-Feb-2017 Conference Date: 14-Mar-2016 Date Published:
Conference Location: Baltimore, MD, USA
Paper Title: Strain-dependent ultrafast dynamics of insulator-to-metal phase transition in VO₂
Authors: Lysenko, Sergiy, Armando Rua, Jose Figueroa, Felix Fernandez
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: APS March Meeting 2018
Date Received: 13-Mar-2018 Conference Date: 05-Mar-2018 Date Published: 05-Mar-2018
Conference Location: Los Angeles, California, USA
Paper Title: Degenerate Four-Wave Mixing of Surface Plasmon Polaritons and Volume Waves in Au/VO₂
Authors: Nardeep Kumar, Armando Rúa, Jennifer Aldama, Karla Echeverria, Félix Fernández, Sergiy Lysenko
Acknowledged Federal Support: **Y**

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Conference Name: 2018 Siegmán International School on Lasers
Date Received: 13-Dec-2018 Conference Date: 28-Jul-2018 Date Published: 29-Jul-2018
Conference Location: Island of Hven, Backafallsbyn, Sweden
Paper Title: Surface Plasmon Polariton Scattering in photorefractive VO₂/Au bilayer
Authors: Jennifer Aldama, Armando Rua, Nardeep Kumar, Karla Echeverría, Felix E. Fernandez, Sergiy Lysenko
Acknowledged Federal Support: **Y**

Publication Type: Conference Paper or Presentation **Publication Status:** 1-Published
Conference Name: 86th Annual Meeting of the APS Southeastern Section
Date Received: 30-Nov-2019 Conference Date: 07-Nov-2019 Date Published: 07-Nov-2019
Conference Location: Wrightsville Beach, North Carolina, USA
Paper Title: Ultrafast Angle-Resolved Light Scattering Metrology of Quantum Materials
Authors: Sergiy Lysenko
Acknowledged Federal Support: **Y**

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Conference Name: 86th Annual Meeting of the APS Southeastern Section
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Conference Location: Wrightsville Beach, North Carolina, USA
Paper Title: Pathways of Photoinduced Insulator-Metal Transition in VO₂ and V₃O₅
Authors: Sergiy Lysenko
Acknowledged Federal Support: **Y**

DISSERTATIONS:

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Publication Type: Thesis or Dissertation

Institution: University of Puerto Rico-Mayaguez

Date Received: 27-Jul-2016

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Title: Nonlinear Spectroscopy of Vanadium Dioxide

Authors: Jose Figueroa

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: University of Puerto Rico-Mayaguez

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Title: Fabrication of VO₂ (B) Thin Films by Pulsed DC Reactive Magnetron Sputtering and Characterization at Low and High Temperatures

Authors: Juan Pastrana

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: University of Puerto Rico at Mayagüez

Date Received: 13-Dec-2018

Completion Date: 12/4/18 2:27AM

Title: Fabricación y caracterización de películas delgadas de sesquióxido de vanadio dopado con cromo

Authors: Karla Andrea Echeverría Altamar

Acknowledged Federal Support: **Y**

Publication Type: Thesis or Dissertation

Institution: University of Puerto Rico-Mayaguez

Date Received: 13-Dec-2018

Completion Date: 12/3/18 4:00AM

Title: Light scattering and surface plasmon polaritons in thin films of phase-change materials

Authors: Jennifer Diana Aldama Guardia

Acknowledged Federal Support: **Y**

WEBSITES:

URL: <http://fisica.uprm.edu/light/>

Date Received: 27-Jul-2016

Title: Advanced Materials Dynamics

Description: This web page was created in September 2015. Here we report our previous, current and future research. It is under continuous development. In next few months we are going to provide there a description of our very new achievements in nonlinear ultrafast spectroscopy of different vanadium oxides.

Accomplishments Under Goals

1. Major activities

During the project period we proceeded according to the plan outlined in the original proposal. The project was an excellent fit for our expertise and capabilities at the Ultrafast Laser Spectroscopy Laboratory. This is a well-established entity in our campus for the study of ultrafast photodynamic processes of correlated materials. It functions also in an independent research role for development of *quantum materials*, including phase-change vanadium oxides.

Fifteen peer-reviewed papers were published during the project period [1-15], including publications in major physics journals, such as *Phys. Rev. Lett.*, *Phys. Rev. B*, *Phys. Rev. Appl.*, *J. Appl. Phys.*, *Opt. Express* and *Optics Letters*. One manuscript now is under review in *Nat. Commun.* [16]. and one is just submitted to *Nat. Commun.* [17]. Additionally, at least three new papers are almost completed and will be published with the results obtained in this project.

Using pulsed laser deposition (PLD) and dc sputtering we synthesized epitaxial and non-epitaxial thin films of several vanadium oxides, as planned. Along with VO_2 and V_2O_3 materials, a significant part of the work was dedicated to development of synthesis protocols for other vanadium oxide materials which have been little studied so far. Among these we were able to synthesize V_3O_5 , V_4O_7 , V_6O_{13} , V_6O_{14} and V_6O_{11} films. We have emphasized development of protocols for reproducible thin film growth, which is an important topic in relation to industrial applicability of these materials. In particular, we performed an in-depth study of V_2O_3 thin film production, achieving highly reproducible metal-insulator transition characteristics in comparison with previously known work [13]. Thin V_2O_3 films were deposited on SiO_2 glass by reactive DC magnetron sputtering, followed by thermal treatment under equilibrium conditions for V_2O_3 , but without degrading the film's electrical continuity. The focus of our work was to achieve high reproducibility of electronic and optical characteristics, specifically when applying deposition techniques appropriate for industrial scale production, with standard control features. The successful approach developed for V_2O_3 is suitable for other vanadium oxides in thin film form, and our work continues along the same lines, particularly for the cases of V_3O_5 and VO_2 . The latter material, while it is by far the best studied of these oxides, presents to this day well known reproducibility issues which curtails its prospective industrial applications.

Several new preparation protocols were developed for synthesis of photorefractive plasmonics structures. The first type of these samples is a two-layer plasmonic structure for attenuated total reflectance (ATR) experiments, where VO_2 thin films or nanoparticles are synthesized by PLD method on top of a 40 nm gold film. Gold films were deposited by magnetron sputtering. The second type of plasmonic structure employs VO_2 films with embedded Au nanoparticles of different sizes. We also deposited single VO_2 thin films on the surface of a prism for ATR measurements, and were then able to excite the surface-plasmon-polaritons in these films in the near-infra-red (NIR) optical region.

During the project period, we performed a set of rigorous optical and electrical measurements of photoinduced phase transition (PIPT) as well as thermally induced transition in VO_2 , V_2O_3 and V_3O_5 thin films. For major nonlinear optical (NLO) studies we used pump-probe time- and angle-resolved hemispherical elastic light scattering setup (*tr*-ARHELS) [Fig.1(a,b)], time-resolved reflection/transmission [Fig.1(c)], degenerate four wave mixing (DFWM) technique [Fig.1(d)] optical Z-scan, and Raman scattering. Most of these measurements included light polarization control.

This project had significant impact on development of new ultrafast research equipment in our lab, especially the *tr*-ARHELS setup [Fig.1(a)] [5]. This is a unique optical system, not available elsewhere, which enables monitoring transient hemispherical distribution of light scattering for different phase-change materials. Along with a previously existing ultrafast scattering setup widely used in this project, we built a new high-resolution one which can operate at cryogenic temperatures [Fig.1(e)]. The construction of this new *tr*-ARHELS setup was funded by NSF (Award# DMR-1531627).

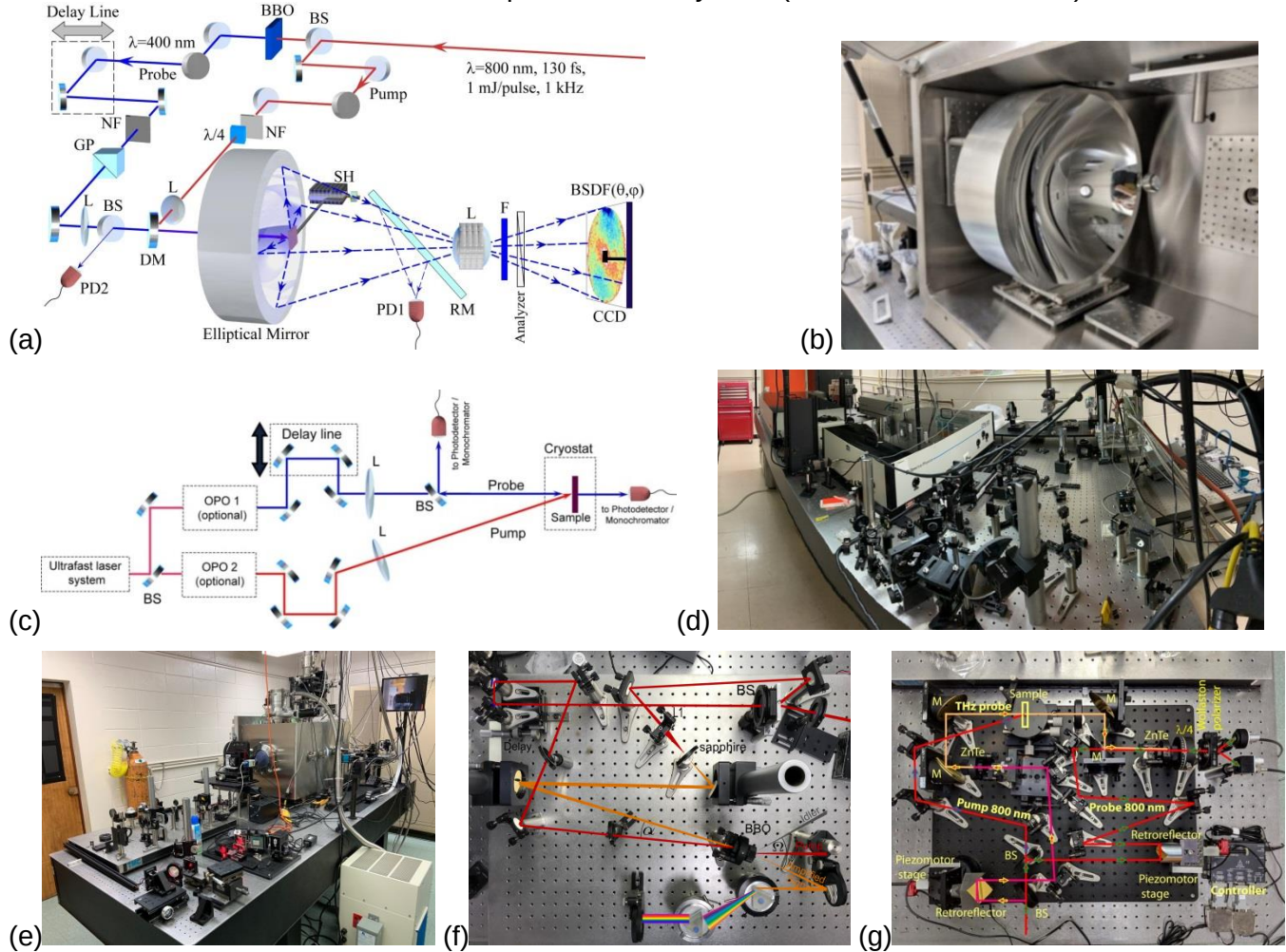


Figure 1: (a) Experimental setup for ultrafast angle-resolved light scattering measurements within the hemisphere. BS, beam splitter; DM, dichroic mirror; GP, Glan-type polarizer; NF, neutral density filter; F, color filter; L, lens; $\lambda/4$, quarter-wave plate; SH, sample holder; PD1 and PD2, silicon photodetectors to measure transient reflection and integrated scattering signal; RM, removable mirror. (b) 50-cm-diameter elliptical mirror of new *tr*-ARHELS apparatus. (c) Conventional optical pump-probe experimental setup for transient reflection/transmission measurements. OPO – optical parametric oscillator, L-focusing lenses, BS-beam splitter. (d) Femtosecond laser system: DFWM setup for transient grating measurements at cryogenic temperatures. (e) *tr*-ARHELS multifunction apparatus for 4D (space+time) scattering measurements at cryogenic temperatures. (f) OPO: Non-Collinear Optical Parametric Amplifier (NOPA). (g) THz spectrometer.

The reconstruction of nonequilibrium processes by ultrafast optical scattering not only shows how fast these phenomena occur, but also what is really happening on the surface. Data obtained during the project show that the *tr*-ARHELS measurements yield new insights on the grain-size-dependent electron-lattice interactions, role of electronic correlations in nonequilibrium quantum phases of matter, multi-scale insulator-to-metal phase transition (PT) dynamics in different functional materials and correlated oxides under strong laser field.

We were able to complete construction and alignment of a *tr*-ARHELS setup for ultrafast diffraction conoscopy (UDC). A new sample holder with precision sample positioning was built. In order to increase the sensitivity (signal/noise ratio) of light scattering measurements by CCD camera, we installed a computer-controlled fast electromechanical shutter with pulse counter to select a desired number of fs pulses.

As a part of our pump-probe femtosecond setup [Fig.1(c,d)], we have built a new non-collinear optical parametric amplifier (NOPA) [Fig.1(f)] and THz spectrometer [Fig.1(g)]. Also, during the project period we assembled a FROG setup to characterize the ultrashort pulses. An ultrafast THz spectrometer was built to study phase-change materials, which is a conventional time-domain THz spectrometer. Here THz pulses are generated via optical rectification in a ZnTe crystal. The measured signal is suitable for Fourier analysis in order to provide transient spectral information within several THz. The probing of strongly correlated materials in the THz spectral range is critical for the study of optical conductivity, to reach exciton and polaron binding energies and optical phonon frequencies, and to understand the nature of photoexcited states (i.e. excitons, polarons, unbounded electron-hole plasma, etc.) For the THz spectrometer we built and programmed optomechanical delay lines (Newport® optomechanics) with 30-nm-step resolution by installing and programming closed-loop Picomotor translation stages with retroreflectors. We use Labview programming to control the optomechanical stages, providing fine tuning and absolute positioning of the mechanical components.

During the project we performed a set of complex experiments on photoinduced phase transitions and plasmon dynamics in thin films of phase-change materials VO_2 , V_2O_3 and V_3O_5 . These experiments, using time- and angle-resolved hemispherical elastic light scattering technique, revealed complex pathways of photoinduced nonlinear optical dynamics in these materials. The structural dynamics in VO_2 and V_2O_3 were also monitored by using an ultrafast diffraction conoscopy technique invented in our lab. It was clearly shown that the characteristic time of optical nonlinearity can be tuned from several femtoseconds to picoseconds by altering the excitation fluence and size of grains and domains. Additional control of ultrafast phase transition dynamics was achieved by photoacoustical generation of strain waves in all the three oxides: VO_2 , V_2O_3 and V_3O_5 . Depending on material morphology and level of optical excitation, we observed coherent oscillations of the optical signal caused by photoacoustic wave at picosecond and nanosecond time scales. We found that the complex nonlinear dynamics of correlated vanadium oxides can provide a way for precise tuning of transient optical and electronic properties in photonic devices. Nonlinear optical Z-scan measurements were performed for VO_2 thin films with different morphologies. New and important results were obtained for VO_2 and V_3O_5 in insulating and also in metallic state.

Raman "soft-mode spectroscopy" measurements were performed for high-quality V_3O_5 samples. This was the first ever Raman scattering study of V_3O_5 material. We detected clear mode softening and phonon mode behavior near the metal-insulator phase transition point.

We performed a new set of experiments on ultrafast surface-plasmon-polariton (SPP) dynamics in VO_2/Au films [11], including degenerate-four-wave-mixing measurements (DFWM) [18]. We built an optical setup to study a degenerate-four-wave mixing process with excitation of SPPs and/or evanescent surface waves in thin films [in ATR geometry]. This setup includes an optical goniometer for excitation of SPPs in the samples at different angles. Also, we ran experiments on photoinduced PT in nanocomposite plasmonics structures: VO_2 films with embedded Au nanoparticles. Angle-resolved reflection, light scattering and ultrafast pump-probe spectroscopy combined with a SPP resonance technique in ATR geometry was used to investigate the light-induced plasmonic switching in photorefractive Au/VO_2 hybrid structure. Measurements of SPP scattering and reflection showed that the optically-induced formation of metallic state in a vanadium dioxide layer deposited on a gold film significantly alters the electromagnetic field enhancement and SPP propagation length at the Au/VO_2

interface. Obtained results demonstrate high potential of photorefractive vanadium oxides as efficient plasmonic modulating materials for ultrafast optoelectronic devices.

We performed many angle-resolved reflection and scattering measurements for plasmonic structures by using a motorized goniometer and conventional CW (continuous wave) semiconductor lasers with wavelengths $\lambda=405$ nm, $\lambda=635$ nm and $\lambda=800$ nm. These data were obtained in steady-state regime of SPP excitation in photorefractive materials. The photo-refractivity of these materials was controlled by thermally induced PT produced by a CW high-intensity laser (used as a sample heater). These data are very important for comparison with experimental data from ultrafast SPP dynamics obtained for femtosecond light-induced PT in VO₂.

We developed new techniques for real-time computation of surface autocorrelation function and for the reconstruction of surface profile from light scattering data. We programmed a "Tesla K80" card for High Performance Computing. A set of programs was written for data analysis using Igor-Pro software. The Igor-Pro programs use dll files written in C++ using CUDA (Compute Unified Device Architecture) technology. The development of the parallel programs has been carried out on distributed memory of an NVIDIA Tesla K80 card. Our specific interest in this instance concerns the development of new numerical methods to solve the phase retrieval problem for the case of angle-resolved light scattering. The error-reduction (ER) and hybrid input-output (HIO) phase-retrieval algorithms provide correct calculation of the autocorrelation function (ACF) of the surface and result in additional reconstruction of surface power spectral density (PSD) function. Using advanced parallel CUDA[®] programming of a NVIDIA Tesla K80, we found a way to speed up our existing algorithms by *a factor of more than twenty*.

A large effort was made to understand the influence of photoacoustic strain waves on light-induced insulator-to-metal phase transition in VO₂ [14, 16]. This work we performed in collaboration with our colleagues from Nottingham University, UK. We have performed very sophisticated experiments on optical generation of acoustic waves in a 140-nm thick Al film, serving as an opto-acoustic transducer. An aluminum film was sputtered on the back side of a VO₂ / sapphire sample. Acoustical pulses, generated in the Al film, were injected into the VO₂ film through the sapphire crystal. We demonstrated control of an optically-driven insulator-to-metal phase transition by a picosecond strain pulse, which paves a way to ultrafast strain engineering in nanostructures with phase transitions. We found excellent agreement between complex experimental data obtained in these experiments on the photoacoustically-assisted phase transition and a theoretical model of photoinduced structural phase transition in VO₂ developed previously by our group.

We performed many angle-resolved reflection measurements for vanadium oxide films using motorized goniometer and conventional CW semiconductor lasers with wavelengths $\lambda=405$ nm and $\lambda=635$ nm. Obtained experimental data were used to calculate optical constants of studied materials.

In order to select high-quality stoichiometric samples for NLO measurements, the structure and morphology of synthesized vanadium oxide materials was characterized by X-ray diffraction (XRD) and by atomic force microscopy (AFM).

2. Specific objectives:

The research objectives of this project are to investigate fundamental processes in ultrafast light-induced insulator-to-metal (I-M) and metal-to-insulator phase transition (M-I PT) dynamics in correlated vanadium oxides and elucidate the evolution of nonequilibrium phases upon photoexcitation.

Specific objectives of the project are

- To separate, visualize and characterize the electronic and structural components of nonequilibrium dynamics of phase-change materials upon optical excitation of epitaxial films and to obtain information about ultrafast dynamics of these materials using novel light diffraction techniques.
- To elucidate pathways of excited state dynamics in vanadium oxide complexes. To find thermodynamics potential of photoexcited phase-change material and to reconstruct different pathways of ultrafast insulator-metal PT. To develop a theoretical model for the light-induced PT in studied vanadium oxides.
- To find critical parameters controlling the light-induced phase transition dynamics in vanadium oxide structures, to reveal details and propose the model of ultrafast photoinduced phase transition dynamics in vanadium oxides synthesized in our lab. The main objectives of this study were (i) experimental observation of light-induced insulator-to-metal phase transition of vanadium oxides on an ultrafast time scale; (ii) semi-classical calculation of the ultrafast molecular dynamics of the lattice in order to understand the role of electron-electron correlations in photoexcited state dynamics and in insulator-metal PT
- To understand the influence of structural characteristics of synthesized vanadium oxides onto photoinduced temporal evolution of nonequilibrium phase.
- To understand the role of electronic correlations in structural phase transition and in photoexcited state dynamics of studied vanadium oxides.
- To realize the SPP excitations in vanadium oxide structures and to elucidate the ultrafast SPP dynamics and interaction with composite phase-change materials.
- To find relations between 3D light scattering, SPP dynamics and THz structural dynamics upon photoinduced phase transition in vanadium oxides; To find relations between photoexcited state dynamics and size of grains in thin epitaxial films, morphology, structural disorder of materials and level of optical excitation. To develop new numerical methods to analyze 3D light diffraction patterns.
- To develop and enhance new research capabilities at the University of Puerto Rico, Mayaguez. To assemble a THz spectrometer. To assemble a compressor of ultrafast optical pulses: non-collinear optical parametric amplifier (NOPA) (compressors of ultrafast optical pulses).
- To synthesize VO_2 , V_2O_3 and, other oxides (V_3O_5 , V_4O_7 , V_6O_{13} , V_6O_{14} , and V_6O_{11}) of very high-quality and to develop new deposition protocols. To synthesize plasmonic structures: VO_2/Au -based plasmonic materials.

3. Significant results

For major nonlinear optical studies of photoinduced phase transition (PIPT) we used numerous experimental techniques, including pump-probe time- and angle-resolved hemispherical elastic light scattering setup *tr*-ARHELS, DFWM, time-resolved reflection/transmission, and optical Z-scan. Most of these measurements include light polarization control. Among different techniques, the *tr*-ARHELS is a unique method available on our lab, which helped us uncovering hidden features and pathways of phase transition dynamics.

3.1 Reconstruction of thermodynamic potential and pathways of structural phase transition dynamics in phase-change materials.

The ultimate goal of this project was the **reconstruction of pathways** of excited state dynamics in vanadium oxide complexes. In order to achieve this goal, we developed new original experimental technique for experimental **reconstruction of thermodynamic potential** of the materials far from equilibrium as a function of photoexcitation level.

PIs developed new technique of femtosecond spectroscopy which enables straightforward experimental reconstruction of the free energy landscape of photoexcited material, applying it to correlated oxide VO₂ [5] (Fig.2). This reconstruction enables quantitative modeling of ultrafast phase transition processes, uncovering observed and potentially possible pathways of the phase transition dynamics versus material morphology, size and statistical distribution of domains on the mesoscale. By using this technique, PIs obtained also evolution of activation energy of the PIPT for another oxide V₃O₅ [4]. This PI's work has important didactic value with boarder impact on experimental study of different phase-change materials.

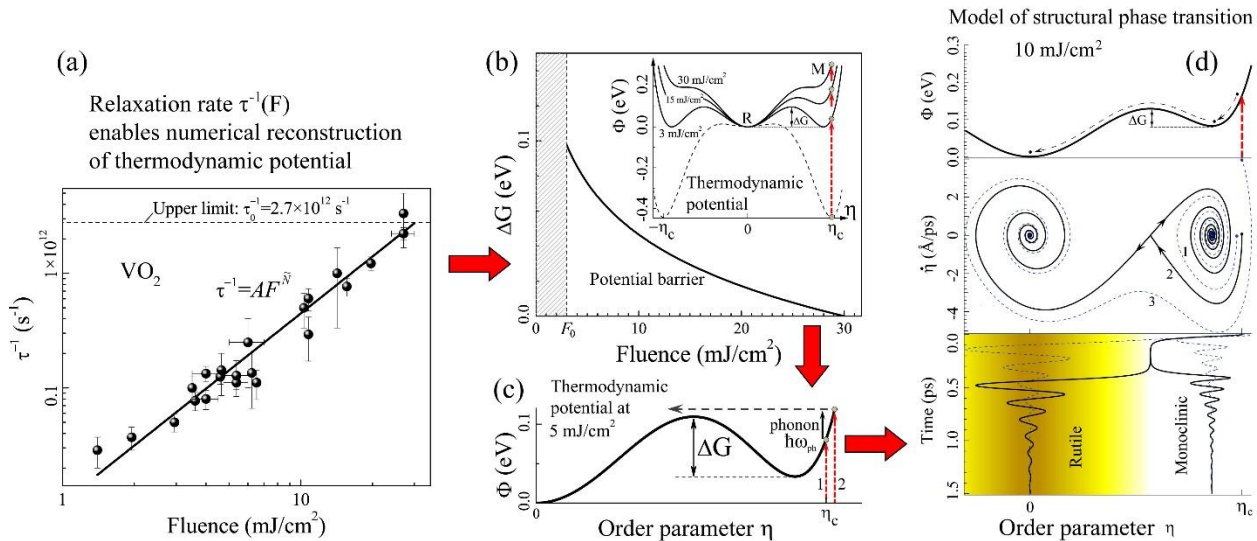


Figure 2: (a) The relaxation rate for picosecond component of photoinduced phase transition of VO₂ versus laser pump fluence. (b) Potential barrier between monoclinic and rutile phases. The inset shows the reconstructed thermodynamic potential. (c) The photoexcitation of VO₂ at moderate laser fluence: thermodynamic potential and phase transition process. (d) Reconstructed thermodynamic potential at 10 mJ/cm² laser fluence, phase trajectories on the $\eta\eta$ phase plane, and evolution of $\eta(t)$ [5].

PIs found that the observation of relaxation rate versus excitation fluence within ~40 ps timescale enables the calculation the potential barrier which separates monoclinic and rutile phases of VO₂. The relaxation rate τ^{-1} of the material [Fig.2(a)] derived from transient change of VO₂ reflectivity versus

excitation fluence F enables numerical reconstruction of potential barrier $\Delta G(F)$ [Fig.2(b)] which separates monoclinic and rutile phases of VO_2 . It was found that rate τ^{-1} depends on the laser excitation level and can be well approximated by

$$\tau^{-1} = AF^{\tilde{N}}, \quad (1)$$

where A and $\tilde{N}$ are fitting parameters. Above some maximal fluence $F_{\max}$ the rate τ^{-1} becomes to be constant and independent on pump fluence. One of the most significant results of our study is the expression to calculate potential barrier $\Delta G(F)$ which separates monoclinic (M) and rutile (R) phases. We for the first time have *derived* the expression

$$\Delta G(F) = -\tilde{N}k_B T \ln[F/F_{\max}], \quad (2)$$

where k_B is Boltzmann constant, T is temperature. Equations (1) and (2) represent important discovery of this work, critical for the reconstruction of thermodynamics potential [inset in Fig.2(b), Fig.2(c)] . The details of the reconstruction procedure are described in [5]. This knowledge provides solid background for the quantitative modeling of transient dynamics of order parameter on an ultrafast time scale [Fig.2(d)]. The modeling is based on the numerical integration of the equation of motion for the effective displacement of lattice ions in terms of Ginzburg-Landau formalism. The model describes the ultrafast structural dynamics within several picoseconds after photoexcitation and agrees with numerous experimental observations of the structural phase transition in VO_2 .

3.2 Ultrafast diffraction conoscopy: new approach to detect hidden, artificial or metastable transient structural phases.

To achieve the project goals, the first challenging specific aim of the project was to separate and characterize the electronic and structural components of nonequilibrium dynamics upon optical excitation, and to obtain characteristic relaxation times of these processes in vanadium oxides. In the case of light-induced solid-to-solid phase transition, it was always an immense problem to monitor by optical techniques only lattice relaxation or only relaxation of electronic subsystem. Conventional optical pump-probe methods provide information about the collective response of lattice plus electronic subsystems, and usually it is impossible to separate these two contributions in optical signal. In order to monitor only the lattice distortion (neglecting electronic dynamics), PIs developed ultrafast diffraction conoscopy (UDC) technique. UDC is novel time-resolved optical technique for reliable separation and characterization of the electronic and structural components of nonequilibrium dynamics upon optical excitation. The experimental setup is described in Ref. [6].

It was shown that UDC method reliably detects structural dynamics separately from electronic dynamics in epitaxial films of phase-change materials: VO_2 and V_2O_3 . UDC technique employs polarization analysis of scattered light and enables detection of photoinduced artificial or metastable transient phases on ultrashort time scales. The UDC method is based on the fact that the crystal anisotropy produces optical birefringence and splits linearly polarized light into two mutually orthogonal components with different phase velocities. Due to cumulative phase difference of these components, the scattered light becomes elliptically polarized. The degree of elliptical polarization and the shape of conoscopy pattern are monitored by a CCD detector placed after a linear polarizer (analyzer). In UDC a noticeable contribution in light depolarization arises from Rayleigh scattering, which allows monitoring birefringence of microcrystals with sizes *much less than the light wavelength*. This is an important advantage of this technique.

Considering that the role of ultrafast diffraction conoscopy to study phase transition in complex correlated systems is yet to be reported, our current work has the capability to provide answers to the outstanding mechanistic questions about the photoinduced phase transition in complex correlated phase-change materials.

3.2.1 Intermediate state of VO₂: evidence of two lattice distortions upon ultrafast insulator-metal phase transition.

Applying UDC to study structural phase transition of VO₂, we were able to clearly separate signals related only to the lattice symmetry transformation from other types of signals (band filling, change of optical constants during I-M PT, etc.) [6]. The evolution of conoscopy pattern [Fig.5(a)] provides precise monitoring of structural evolution of the photoexcited crystal. This allowed the discovery of an *intermediate transition state* of VO₂. With UDC we studied the evolution of VO₂ crystal birefringence from biaxial type to uniaxial type, and we showed that the UDC technique opens up the possibility to visualize the pathway of the PT dynamics with extraordinary detail.

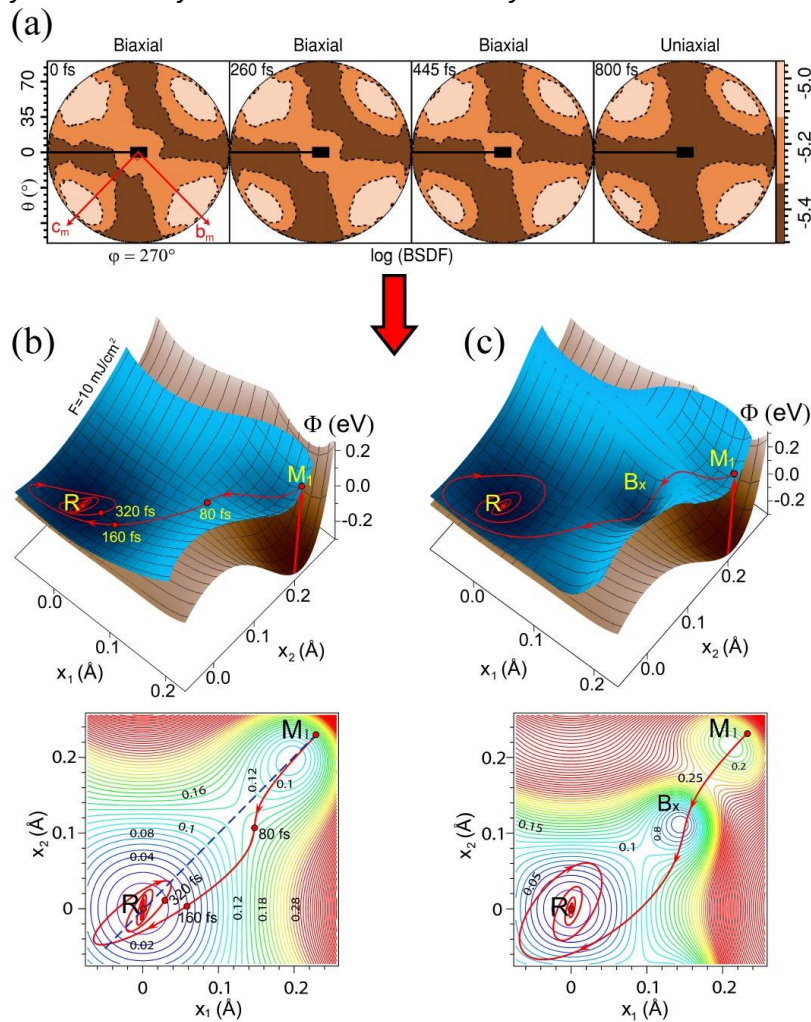


Figure 3: (a) Ultrafast diffraction conoscopy patterns of VO₂ crystal (epitaxial film). (b) and (c): Phase trajectory of photoexcited VO₂. The red solid line shows the pathway of the energy relaxation. Two potential-energy surfaces correspond to unperturbed and photoexcited states of VO₂ respectively. (a) A double-well potential case. This model implies the presence of only M_1 and R phases. Dashed line indicates the phase trajectory for the case of equal relaxation rates for antiferroelectric distortion (x_1) and V-V bonding (x_2). (b) A triplewell thermodynamic potential. The possible intermediate phase is denoted by B_x [6].

This allowed the discovery of an **intermediate phase transition state** of VO_2 . Our results reveal that the monoclinic biaxial crystal initially, within the first 250-300 fs, transforms to an intermediate biaxial crystal, and within the next 300-400 fs converts into a uniaxial crystal. This study is a step forward to resolve the long-standing debate over the structural PT dynamics of VO_2 . It is shown that the first stage of the PIPT is highly influenced by the film morphology and, most likely, by internal strain in the sample. By applying Ginzburg-Landau formalism we reconstructed thermodynamic potential [Fig. 5(b)] and modelled two-stage SPT dynamics, which is originated from two lattice distortions x_1 and x_2 with different relaxation times on subpicosecond time scale.

UDC data analysis suggests the presence of an intermediate biaxial phase and additional third potential well on the thermodynamic potential landscape denoted by B_x , as shown in Fig. 5(c). Upon light-induced phase transition, the lattice symmetry changes from monoclinic to rutile via B_x , moving along some complex phase trajectory. In the case of photoinduced structural transition, the initial excited state corresponds to the M_1 phase, while the transient biaxial phase B_x can be the M_2 or orthorhombic phase.

The presence of the two components in ultrafast I-M PT reveals a resemblance between light-induced and thermally induced crystallographic transition in terms of Goodenough's model.

3.2.2 Ultrafast diffraction conoscopy of V_2O_3

It has been shown that the photoexcitation significantly changes electronic properties of V_2O_3 . However, very little is known about structural transitions of V_2O_3 during photoexcitations at temperatures beyond the metal-insulator transition temperature ($T_c \sim 150\text{K}$). One way to study structural dynamics of V_2O_3 upon photoexcitation is by collecting data related only to the structural properties. By employing the UDC technique, we can just focus on properties of V_2O_3 related to structural dynamics. For this study, we kept the sample at room temperature, which is well above the T_c point. Hence, the collected nonlinear signal is solely due to the photoexcitation.

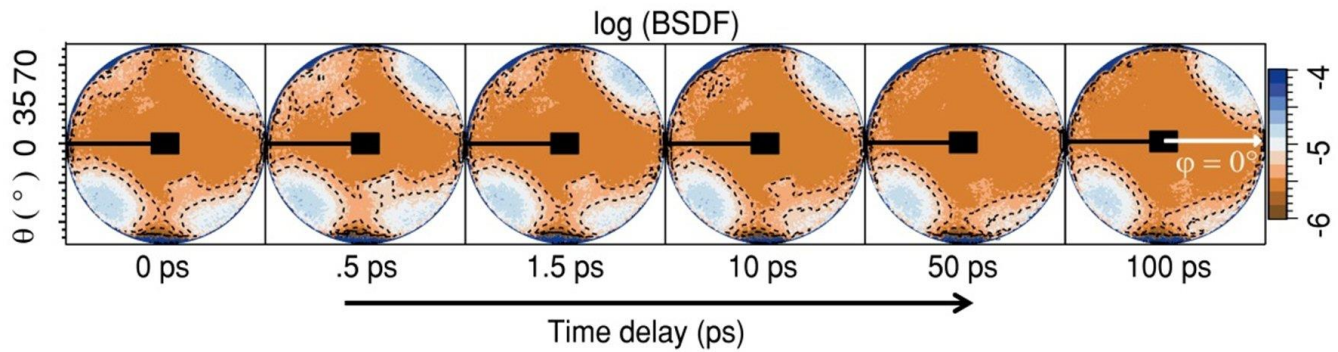


Figure 4: Evolution of the transient ultrafast conoscopy indicatrix for V_2O_3 epitaxial film [10].

Figure 4 shows the time-resolved ultrafast diffraction conoscopy indicatrices at various time scales from 0 ps to 100 ps. There is a clear change in the scattering signal for different polar angles when time changes from 0 ps to 100 ps, indicating a strong photoinduced nonlinear response. With the help of UDC technique we can answer whether this photoinduced nonlinear change is related to the structural change or not. Evolution of $\log(\text{BSDF})$ indicatrices show that, compared to VO_2 [Fig. 3], the V_2O_3 results [Fig. 4] do not indicate any change in the symmetry of the crystal on the timescale from 0 ps to 100 ps. This is an important result indicating that the strong photoinduced scattering response we see is not related to the structural phase transition.

3.3 Phase transition dynamics of V_3O_5

3.3.1 Discovery of light-induced insulator-to-metal phase transition in V_3O_5

Many of vanadium oxides can undergo phase transition by applying a pressure, strain or heat, but only two of them (VO_2 and V_3O_5) show metal-insulator phase transition above room temperature. This makes these two vanadium oxides extremely promising for novel optoelectronic applications. However to date, the light-induced transition was discovered for a few oxides only. While the first observation of photoinduced phase transition and optical nonlinearity of VO_2 was made in 70s, for V_3O_5 these features were not discovered until now. First results on strong optical nonlinearity and nonequilibrium excited-state dynamics of V_3O_5 were recently obtained in Pls' lab. This discovery was published in *Phys. Rev. Lett.* [4] and *J. Appl. Phys.* [7] as well as in SPIE Proceeding [10], and new paper on ultrafast Raman mode softening was submitted recently to *Nat. Commun.* [17]

In series of measurements it was confirmed that the optical nonlinearity is originated from light-induced insulator-metal phase transition. It was found that the formation of metallic phase occurs within an ultrafast timescale of ~ 1 picosecond.

The evidence of photoinduced phase transition in V_3O_5 was presented by measuring the temporal evolution of transient integral scattering on sufficiently long, 2-nanosecond, time scale vs pump fluence F [Fig.5(a)]. This behavior, along with observation of transient NLO dynamics on picosecond time scale [Figs.5(b)] shows that at $F \geq 16 \text{ mJ/cm}^2$ the complete insulator-metal transition of V_3O_5 is triggered by light within 1 ps and temperature increase does not produce any further phase transition. The observed NLO dynamics within 2 ns at different pump fluences evidences an ultrafast *non-thermal* photoinduced insulator-metal transition in V_3O_5 .

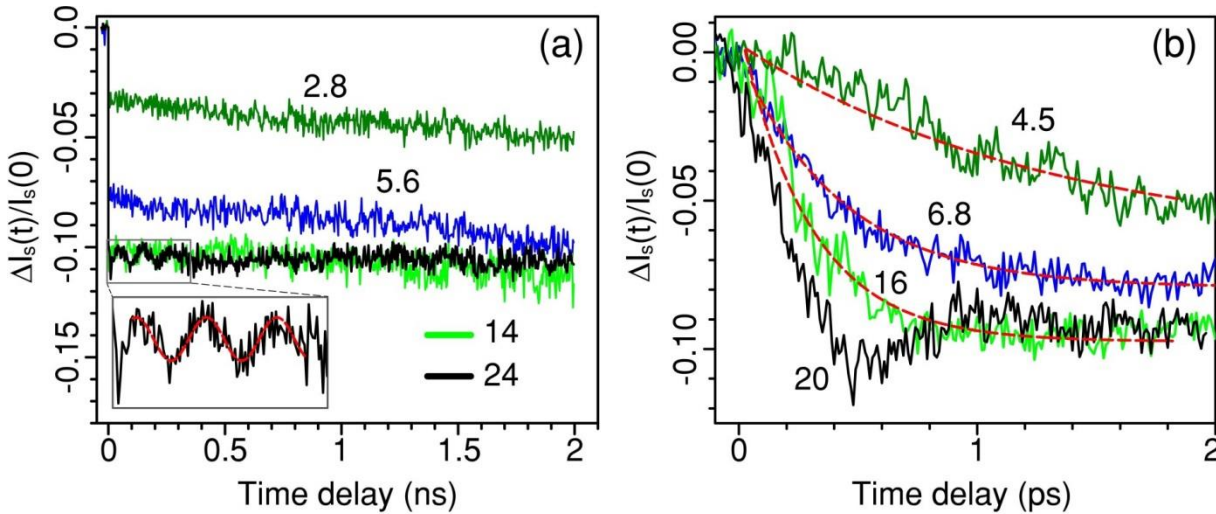


Figure 5: Fluence dependence of differential scattering signal $\Delta I_s(t)/I_s(0)$ as a function of pump-probe delay within (a) 2 ns and (b) 2 ps. Numbers specify the laser pump fluence in mJ/cm^2 . [4]

The nature of stable insulating phase of V_3O_5 can be understood in terms of Wigner crystallization of small polarons due to strong correlations between carriers. However this stability of insulating phase can be destroyed by light. A photogeneration of dense electron-hole plasma can produce a screening of electron correlations to the level when electrostatic interaction cannot provide segregation and localization of charges. As a result, the polaronic crystal melts into non-correlated polaronic states. Photoinduced oscillations of the optical signal were observed due to excitation of coherent acoustical phonons in the material.

3.3.2 Ultrafast surface dynamics in V_3O_5

3D Raleigh scattering allows detecting structural transformation of V_3O_5 material on the mesoscale. The spatial distribution of light diffraction signal is highly sensitive to internal strain, domain formation, and interaction of grains during insulator-metal phase transition. Therefore, angle-resolved hemispherical elastic light scattering measurements (ARHELS) were performed to allow observation of internal strain influence on V_3O_5 surface roughness versus temperature for thermally induced transition, and versus time for light-induced transition (Fig.6).

Thermally induced phase transition. To observe the evolution of surface morphology in a V_3O_5 film across thermally induced phase transition, we recorded the 3D scattering field by mapping BSDF(θ, φ) data versus sample temperature for polar θ and azimuthal φ scattering angles, as shown in Figs.6(a), 6(b) [17]. Isotropic distribution of V_3O_5 grains on amorphous SiO_2 substrate results in a nearly isotropic scattering indicatrix. Increasing the sample temperature from 320 K to 480 K results in a decreased integral scattering signal, as V_3O_5 switches to its metallic state.

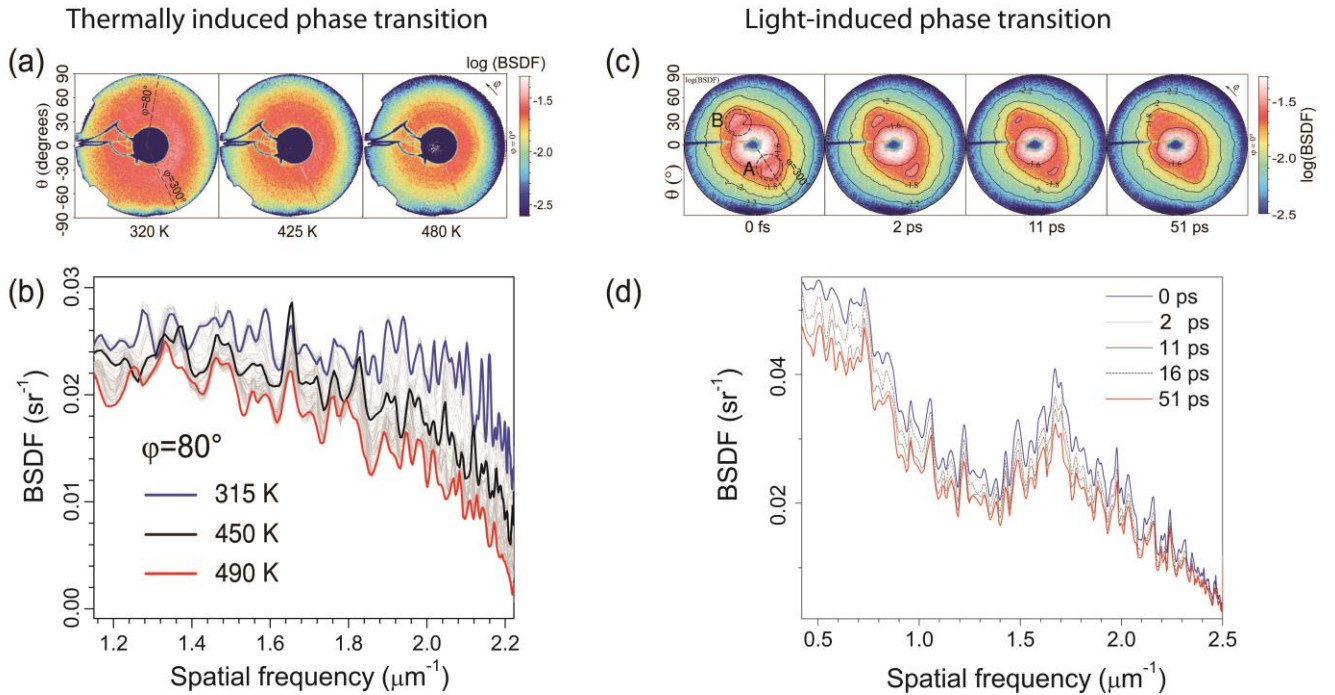


Figure 6: (a) Thermal evolution of light scattering indicatrices BSDF(θ, φ) during IMT of V_3O_5 . (b) Cross-sections BSDF(θ) at $\varphi = 80^\circ$ taken at different temperatures. The curves are plotted for 70 temperatures in the temperature interval from 315 K to 490 K. (c) Transient BSDF(t, θ, φ) scattering signal within 51 ps. The signal was collected at a pump fluence of 10 mJ/cm². (d) Cross-sections of BSDF(t) indicatrices at $\varphi = 300^\circ$ [17].

Fig.6(a) shows the BSFD light scattering indicatrices at three different temperatures for a 100 nm V_3O_5 film, revealing thermal evolution through the IMT. Fig.6(b) shows axial cross sections of the indicatrix for $\varphi = 80^\circ$ and at three different temperatures as well, revealing numerical detail of the changes in BSDF(f) through the transition. Here continuous domains formation and alteration of film optical properties both result in growth, suppression and/or shift of numerous tiny diffraction peaks.

Light-induced phase transition. In order to gain a deeper insight into the problem of V_3O_5 phase transition, we performed a set of time- and angle-resolved hemispherical elastic light scattering, *tr*-ARHELS measurements. Figure 6(c) shows the transient evolution of BSDF(θ, φ) indicatrices upon light-induced phase transition of V_3O_5 by a pump fluence of 10 mJ/cm². The light scattering by self-organized domains shows an anisotropy with the presence of two strong diffraction peaks, marked as

"B" and "A", superimposed onto isotropic scattering background caused by stochastic surface roughness.

The evolution of BSDF(θ, ϕ) indicatrices within a 51 ps time scale [Fig.6(c)] and their cross-sections [Fig.6(d)] at $\phi = 300^\circ$ show rapid drop of the signal for all scattering angles (and, a consequence, all spatial frequencies). However, positions of all numerous small local peaks in diffraction pattern remain the same during the transition. This fact indicates that the surface geometry during PIPT on the ultrashort time scale remains unchanged. Here we note the principal difference in the evolution of V_3O_5 diffraction pattern for ultrafast light-induced phase transition and for thermally induced transition, where positions of the majority of tiny diffraction peaks change continuously with temperature [Fig.6(b)].

Additional analysis of the surface autocorrelation function (ACF) calculated from power spectral density (PSD) of the surface inhomogeneities [Fig.7(a)] shows the increase of ACF(t) amplitude for the metallic phase [Fig.7(b,c,f,g)], which is due to higher uniformity in the distribution of surface dielectric constant [15, 17]. Figure 7(e,f,g) shows the filtered autocorrelation function ACF^* of V_3O_5 slab domains for unexcited surface, and the evolution of ACF^* within a 50 ps time scale. The cross-section of the ACF^* [Fig.7(g)] along the dashed line in Fig.7(f) at $t = 0$ ps shows noticeable growth of ACF^* amplitude due to the evolution of surface optical properties with time, as the V_3O_5 switches into its metallic state. The inset in Fig.7(g) shows that the amplitude of the oscillatory maximum at $0.6 \mu m$ lag length builds up within less than 5 ps, indicating that the main structural surface dynamics associated with light-induced phase transition completes within this time scale. Increase of the $ACF^*(0.6 \mu m)$ amplitude by 20% is associated with a noticeable increase of optical homogeneity of each surface domain. This result matches well with the growth of ACL for the isotropic component of the V_3O_5 surface [Fig.7(d)].

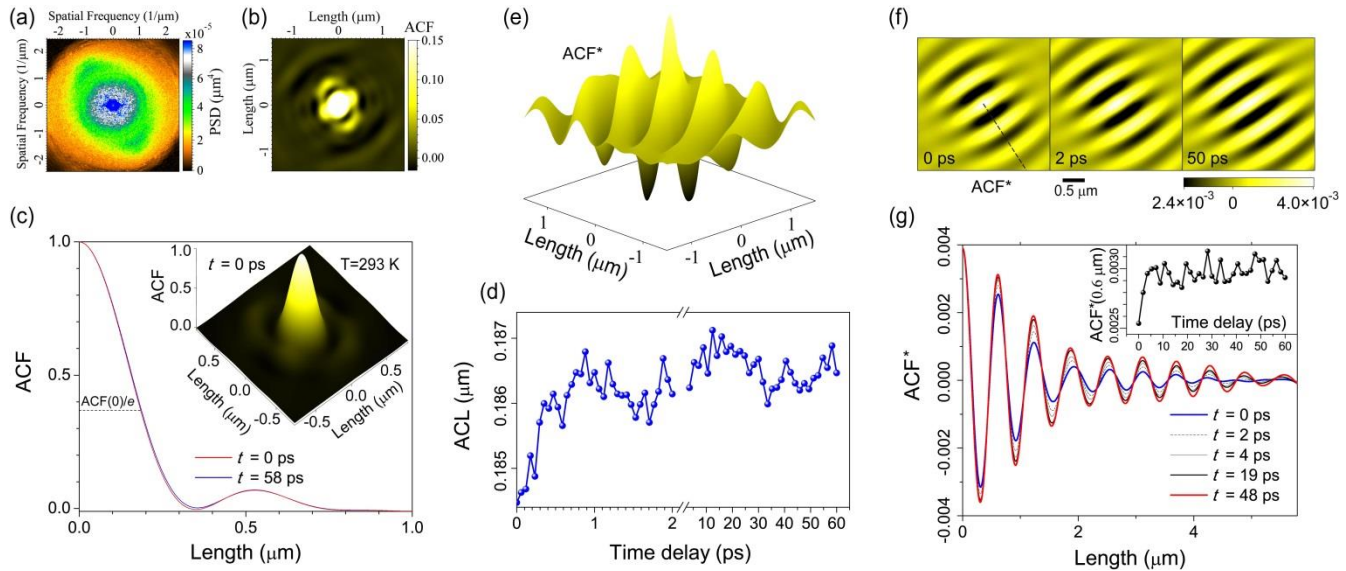


Figure 7: (a) PSD function of V_3O_5 surface calculated from light scattering data. (b) Autocorrelation function of V_3O_5 calculated from PSD data shown in (a). (c) ACF cross-sections at $\phi = 300^\circ$. Inset shows 3D ACF which consists of a bell-shaped maximum due to stochastic roughness, and a periodic component caused by self-organized slab domains. (e) Autocorrelation function of periodic domain structure: ACF^* of unexcited V_3O_5 . (f) Evolution of ACF^* upon photoexcitation. (g) Cross-sections of ACF^* at $\phi = 300^\circ$, as marked by dashed line in (f) at $t = 0$ ps. Inset: amplitude of ACF^* at $0.6 \mu m$ lag length [15,17].

3.3.3 Electronic and phonon band structure of V_3O_5

Pls' group performed first quantum calculation of electronic and phonon band structure as well as computation of molecular dynamics (MD) for V_3O_5 . This result is included as supplement in *Phys. Rev. Lett.* [4] and in recently submitted paper to *Nat. Commun.* [17]. The information about electronic energy

bands and density of states (DOS), along with phonon dispersion curves and vibrational DOS, is of prime importance for unified understanding of insulator-metal transition dynamics in V_3O_5 .

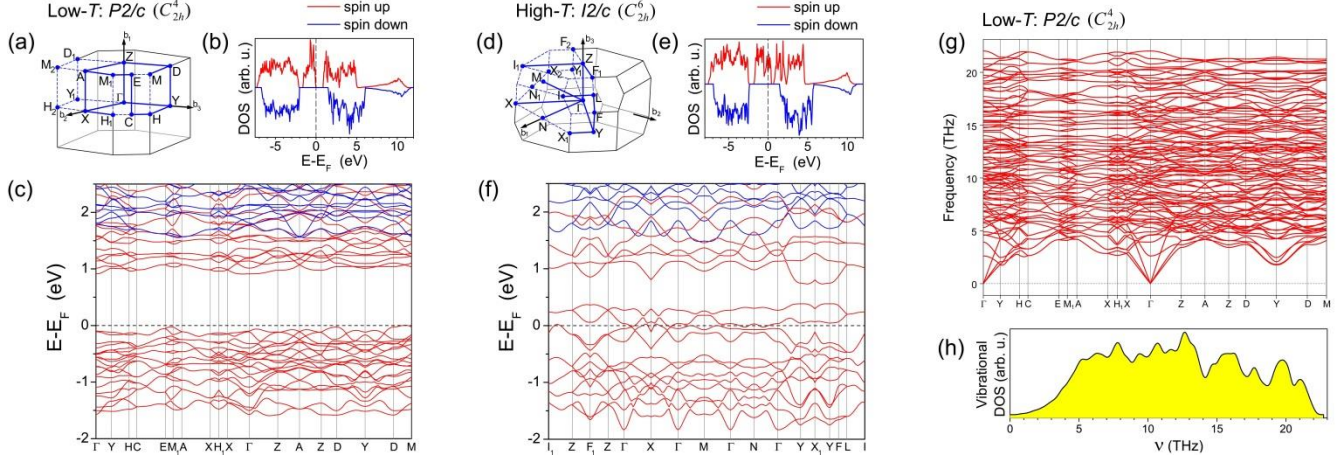


Figure 8: Low- T V_3O_5 : (a) Brillouin zone; (b) density of electronic states; (c) electronic energy bands. High- T V_3O_5 : (d) Brillouin zone. (e) density of electronic states; (f) electronic energy bands. (g) Phonon band structure and (h) vibrational DOS of Low- T V_3O_5 . [4, 17]

We calculated electronic DOS and bandstructures for Low- T and High- T V_3O_5 by using density functional theory based on plane-wave technique implemented in Vienna Ab-initio Simulation Package (VASP). Our calculations use the projector-augmented wave approach for the core-valence interaction and the Perdew-Burke-Ernzerh generalized gradient approximation (GGA-PBE) for the exchange and correlation functional.

Figure 8(a) shows the Brillouin zone for monoclinic Low- T V_3O_5 (space group $P2/c$ or C_{2h}^4). The obtained electronic DOS and bandstructure [Figs. 8b, 8c] show that Low- T V_3O_5 is insulating in nature, with an energy bandgap $E_g \sim 0.9$ eV. Figure 8(d) shows the Brillouin zone for monoclinic High- T V_3O_5 (space group $I2/c$ or C_{2h}^6). Electronic DOS [Fig. 8(e)] and bandstructure [Fig. 8(f)] of High- T V_3O_5 show that the high-temperature structure is metallic and the DOS near the Fermi energy E_F is spin-polarized.

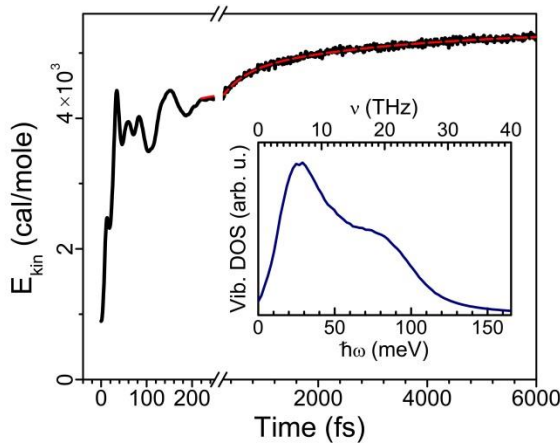


Figure 9: Kinetic energy relaxation for V_3O_5 lattice. A double exponential fit (dashed line) yields two relaxation times: $\tau_1=405$ fs and $\tau_2=3.1 \times 10^3$ fs. Inset: vibrational density of states of all V_3O_5 atoms [4].

Calculations of the phonon dispersions and density of states of Low- T V_3O_5 were performed using the projected augmented wave (PAW) method as implemented in VASP. The phonon band structure and vibrational DOS of Low- T V_3O_5 are shown in Figs. 8(g) and 8(h) correspondingly. In all calculations of phonon properties, we employed the spin-polarized local-density approximation (LSDA) with valence electron configurations $3d^4 4s^1$ and $2s^2 2p^4$ for V and O, respectively.

In order to gain deeper insight into the ultrafast structural dynamics of V_3O_5 , we modeled the lattice relaxation by the semi-classical computational method of molecular dynamics (MD) using QuantumWise software package. Figure 9 shows the adiabatic relaxation dynamics of kinetic energy for V_3O_5 lattice. The relaxation dynamics of kinetic energy E_{kin} reveals significant instability of the V_3O_5 lattice. Here the initial rise of E_{kin} within 100 fs can

be associated with melting of polaronic Wigner crystal after photoinduced screening of electron correlations. The inset in Fig. 9(e) shows the vibrational density of states calculated for all atoms of the V_3O_5 cluster. MD computation shows a broad resonance with maximum at ~ 6.5 THz.

3.3.4 Phonon softening in V_3O_5 : view from quasi-equilibrium and ultrafast time scales

Raman spectra. A good agreement was found between Raman experiment and calculated phonon spectra [17]. Figure 10 shows the calculated DOS spectrum of V_3O_5 , as well as Raman spectra of microcrystals in insulating phase at $T=339$ K, and near T_c at $T=421$ K. As can be seen, the total DOS range agrees well with experimental Raman data, while the calculated DOS spectrum shows similar structure although there is no exact coincidence. Some modes at ~ 180 , 220 , 420 , 560 and 590 cm^{-1} match closely with calculated DOS peaks. We also note that the intensity and position of some peaks depend on crystallinity and temperature of the V_3O_5 sample, which can be the origin of observed mismatch between experimental and theoretical data.

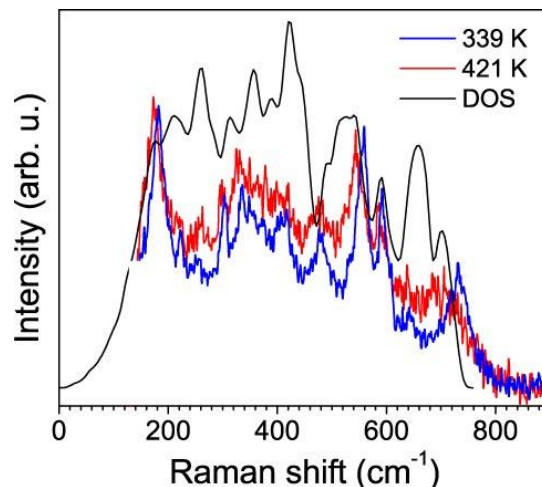


Figure 10: Vibrational DOS of Low- T V_3O_5 and Raman spectra of microcrystals near IMT and at room temperature. [17]

The Raman measurements are an important tool to identify and track active vibrational modes during the structural transition. Here we note that despite the technological importance of V_3O_5 for potential practical applications, the group-theory analysis for this material has not been performed yet, and this is an attractive subject for future investigations of V_3O_5 vibrational modes. The Raman spectra in Fig. 11(a) clearly show softening of several lines with broadening and noticeable decay for those initially at frequencies ~ 183 , 561 , 593 , 739 cm^{-1} and also ~ 222 cm^{-1} , (correspondingly marked as A, B, C, D and E), as the temperature approaches the transition point T_c . The softened lines B, C and D are entirely suppressed as the structure transforms into High- T phase V_3O_5 .

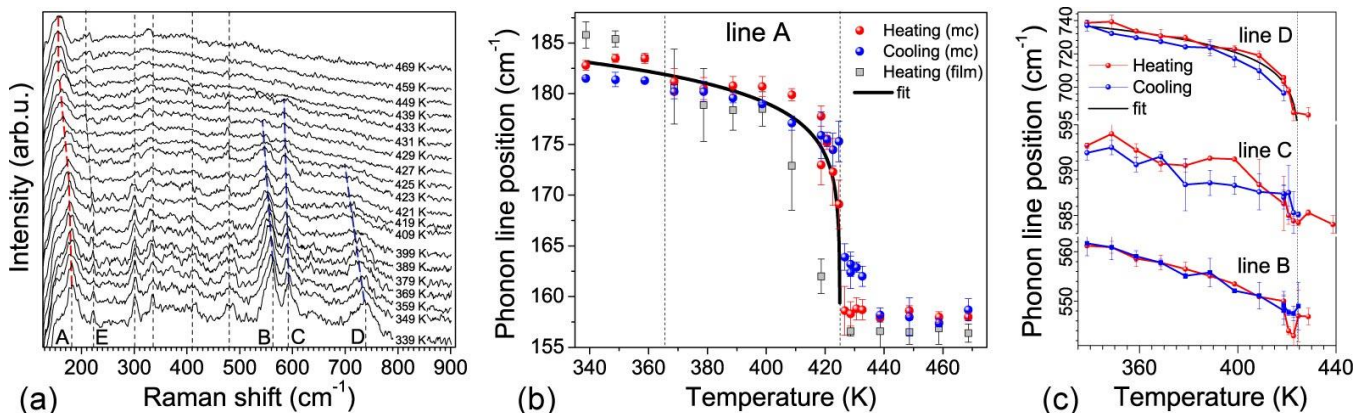


Figure 11: (a) Raman spectra of V_3O_5 microcrystals at different temperatures across insulator-metal phase transition. (b) Phonon line position for the soft mode A for microcrystals (mc) and continuous film. The position shows noticeable change starting from $T=365$ K. (c) Phonon line positions for active Raman modes B, C, and D, as identified in (a).

The temperature dependencies of the position of phonon line A [Fig.11(b)], and line C [Fig.11(c)] show a signature of small hysteretic behavior, although a clear hysteresis loop was not resolved. The lowest frequency phonon line A is dominant in all spectra and is determined as a “soft mode” of V_3O_5 . As the temperature approaches T_c , line A clearly shows noticeable broadening and the decrease of its position frequency from 183 cm^{-1} for Low- T V_3O_5 to 158 cm^{-1} for High- T V_3O_5 microcrystals [Fig.11(b)]. The evolution of phonon line A for the film and for microcrystals shows two distinctive temperature ranges of the phase transition: 365-405 K range, which is associated with V_3O_5 lattice softening near T_c , and 405-435 K range, associated with the insulator-metal phase transition.

The observed first-order transition in V_3O_5 was classified as a special class close to second-order ones.

Ultrafast mode softening. One of the main objectives for V_3O_5 ultrafast measurements was to enable time-resolved observation of coherent phonon dynamics. By applying *tr*-ARHELS technique we were able to detect oscillatory behavior of the optical signal with maximal modulation at azimuthal direction $\varphi = 300^\circ$ (Fig.12) [17].

The cross-sections of V_3O_5 scattering indicatrices for temporal range of 2 ps [Fig.12(a)] and 60 ps [Fig.12(b)] show complex dynamics of coherent oscillations with some dependence on spatial frequency of the surface. Here one can see that the 2 ps-range signal is dominated by THz oscillations due to excitation of optical phonons of 3 THz on a 1 ps time scale, and 7 THz on a 1-2 ps scale, while the 60 ps-range signal shows 50 GHz oscillations.

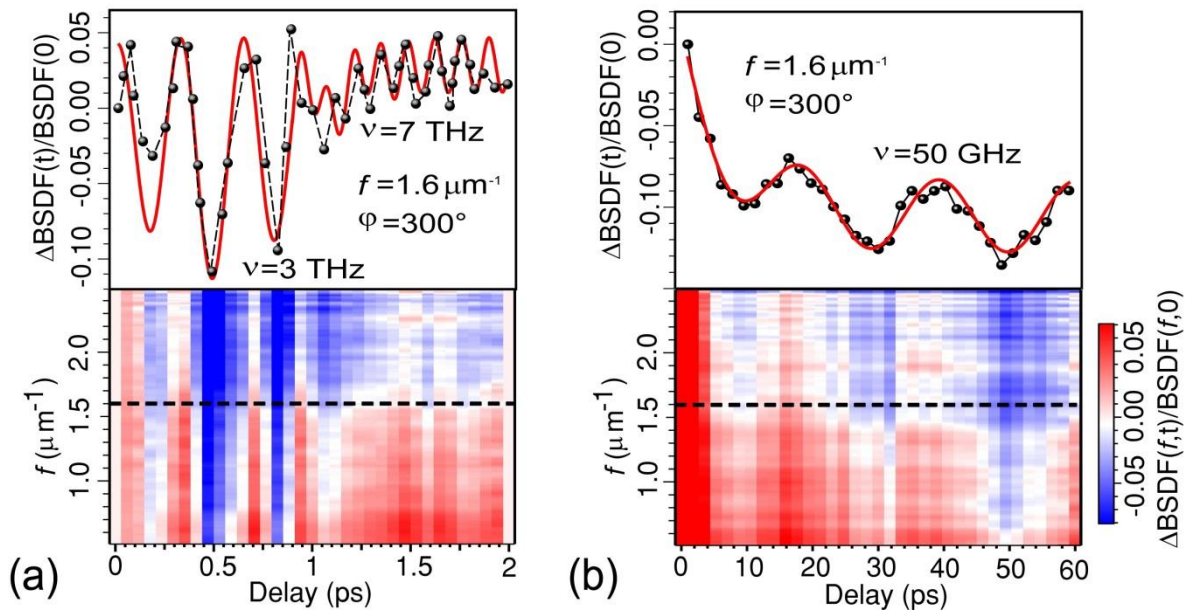


Figure 12: Upper panels show the cross-sections corresponding to spatial frequency $f = 1.6\text{ }\mu\text{m}^{-1}$ for 2 ps (a) and 60 ps (b) probe delays. Lower panels show the time-dependent cross-sections of the scattering indicatrices [17].

Nonequilibrium lattice dynamics can be understood in terms of Wigner crystallization of small polarons in V_3O_5 . In the Low- T insulating phase this crystallization originates from strong electron correlations which provide spatial ordering of polarons and corresponding ions of different valences in the lattice. The complex electron-phonon interactions of this correlated system stabilize the Low- T phase with low mobility of polarons and, as a result, low conductivity of V_3O_5 . Upon photoexcitation of V_3O_5 , the screening of electron correlations by dense electron-hole plasma initiates the melting of a polaronic Wigner crystal into noncorrelated polaronic states on the time scale of 130 fs pump pulse. This process

appears as instantaneous mode softening and lattice instability, where the phonon frequency drops to 3 THz, subsequently rising to 7 THz within less than 2 ps. This is a signature of lattice hardening, as V_3O_5 switches into its equilibrium metallic phase, and can originate from partial recovery of electronic correlations, which were initially suppressed by photoexcitation.

Theoretical modeling of molecular dynamics shows good agreement with observed ultrafast lattice dynamics, where the maximum of DOS spectrum approaches a 7 THz frequency position after 1 ps [17].

3.4 Phase transition dynamics of VO_2

3.4.1 Computation of subpicosecond molecular dynamics

To compute the molecular dynamics (MD) we used the QUANTUMWISE software package. The transient lattice distortion was modeled by using semi-classical computational MD methods which neglect electron-electron correlations. The MD method provides a meaningful estimation of quantitative parameters of molecular dynamics [i.e., root-mean-square (*rms*) atomic displacements, vibrational density of states, kinetics of energy relaxation, etc.].

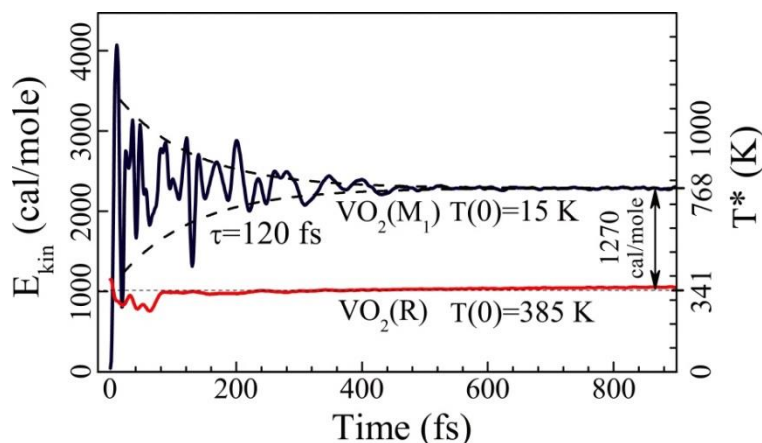


Figure 13: The time evolution of kinetic energy and effective transient temperature T^* for pure monoclinic $\text{VO}_2(\text{M}_1)$ at $T = 15\text{K}$ and for rutile $\text{VO}_2(\text{R})$ at $T = 385\text{ K}$. [5]

The computational study of adiabatic lattice dynamics reveals significant instability of the VO_2 lattice with monoclinic symmetry, while the rutile phase was found to be relatively stable [5]. Figure 5 shows the time evolution of kinetic energy E_{kin} and effective transient temperature T^* for $\text{VO}_2(\text{M}_1)$ and $\text{VO}_2(\text{R})$. A comparison of kinetic energy evolution for monoclinic and rutile phases shows that E_{kin} for $\text{VO}_2(\text{M}_1)$ increases within 900 fs by two orders of magnitude, from 45 to 2.29×10^3 cal/mole, while for $\text{VO}_2(\text{R})$ this change is noticeably less. For $\text{VO}_2(\text{R})$ E_{kin} changes from 1.15×10^3 to 1.05×10^3 cal/mole: After a small drop it returns to nearly the same level.

A significant difference in the relative change of E_{kin} for the correlated low- T monoclinic phase and for the noncorrelated high- T rutile phase was *a priori* expected as the result of photoinduced screening of electron correlations, and eventually reliably confirmed by the MD simulation. Thus, a screening of Coulomb repulsion for noncorrelated rutile VO_2 does not provide a considerable change of E_{kin} , while for the correlated low- T monoclinic phase the screening results in an instantaneous rise of kinetic energy followed by lattice instability. Also, this indicates that the electron correlations in the low- T phase are the major factor in stabilizing the VO_2 monoclinic symmetry.

It was shown that in terms of thermodynamics, the photoinduced screening of electron-electron correlations triggers an exothermic reaction which guarantees the thermally induced phase transition of VO_2 , even if the initial temperature of the material is near absolute zero.

3.4.2 VO₂ surface dynamics: strain influence

During the project we discovered strong and very complex influence of internal strain in VO₂ on the surface reconstruction during thermally induced phase transition and on the evolution of optical inhomogeneities and the rate of light-induced phase transition. While we published only a short report of this study in [3] and made several conference presentations [3] on this matter, during the last period of the project we obtained much more experimental data and made a concentrated effort to understand this very sophisticated evolution of the surface upon phase transition in VO₂. We intend to publish the results of this study in a few months in *Phys.Rev.B* [19].

In order to study the influence of internal strain on the insulator-metal phase transition we used non-epitaxial and epitaxial VO₂ films deposited on Al₂O₃(c-cut) sapphire crystal. The advantage of VO₂/Al₂O₃(c-cut) samples is the occurrence of several-fold twinning of VO₂ film due to lattice mismatch between film and substrate. This provides high local inhomogeneity of the strain field.

3.4.2.1 Surface reconstruction upon thermally induced insulator-metal transition

It was found that the light scattering technique is highly sensitive to monitor strain effects during the insulator-metal phase transition. We prepared two sets of VO₂ samples: non-epitaxial VO₂ films deposited on amorphous SiO₂ substrates and epitaxial films on Al₂O₃(c-cut) sapphire crystal substrates. In these samples the level of strain was controlled by the type of the substrate and by the film thickness. Figures 14 and 15 show very recent results of the thermally induced transition in epitaxial VO₂/Al₂O₃(c-cut) films, and Figs. 16 and 17 show results for VO₂/SiO₂ films of different thicknesses [19].

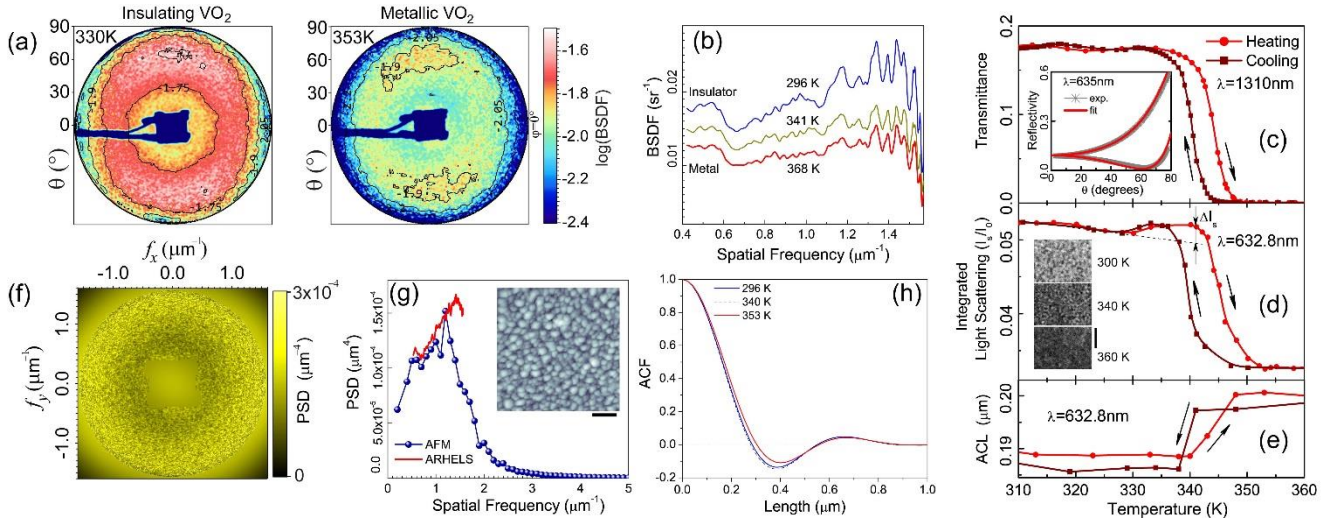


Figure 14: Thermally induced PT of 145-nm-thick epitaxial film VO₂/Al₂O₃(c-cut) with reduced strain. (a) Scattering indicatrix in the insulating and metallic state. (b) Cross-sections of BSDF indicatrix at different temperatures. (c) Hysteretic evolution of transmittance, (d) scattering signal I_{scatt}/I_0 integrated within the hemisphere and (e) autocorrelation length of the surface. (f) Surface PSD calculated from scattering data. (g) Averaged PSD obtained from AFM and scattering data. Inset: 5×5 μm AFM surface topography. (h) Surface ACF.

Figure 14 shows the data for VO₂/Al₂O₃(c-cut) film with low level of internal misfit strain. The relatively high 145 nm thickness of this film is above the misfit dislocation threshold, and numerous dislocations in the film reduced the internal strain. While the scattering indicatrix shows significant change in its intensity [Fig.14(a)], the weak elastic interaction between VO₂ domains does not have a noticeable influence on surface geometry. As a result, nearly all features and positions of tiny diffraction peaks in scattering pattern remain the same within the full studied temperature range [Fig.14(b)]. Upon insulator-

metal phase transition the transmittance of the sample changes monotonically [Fig.14(c)] and in the total integrated scattering signal [Fig.14(d)] we can detect only a small rise of the signal due to relatively small structural disorder of VO₂ near T_c. The autocorrelation length of the surface, calculated from the surface ACF [Fig.14(h)], increases in the metallic phase, indicating a higher level of optical homogeneity. The ACF was calculated from PSD data [Fig.14(f)] for each temperature using phase retrieval algorithms. The PSD data were obtained from BSDF scattering indicatrices. Precision of PSD calculation from scattering data was verified by comparison of extracted function with PSD obtained directly from profilometric AFM measurement of the surface [Fig.14(g)]. This comparison showed excellent coincidence.

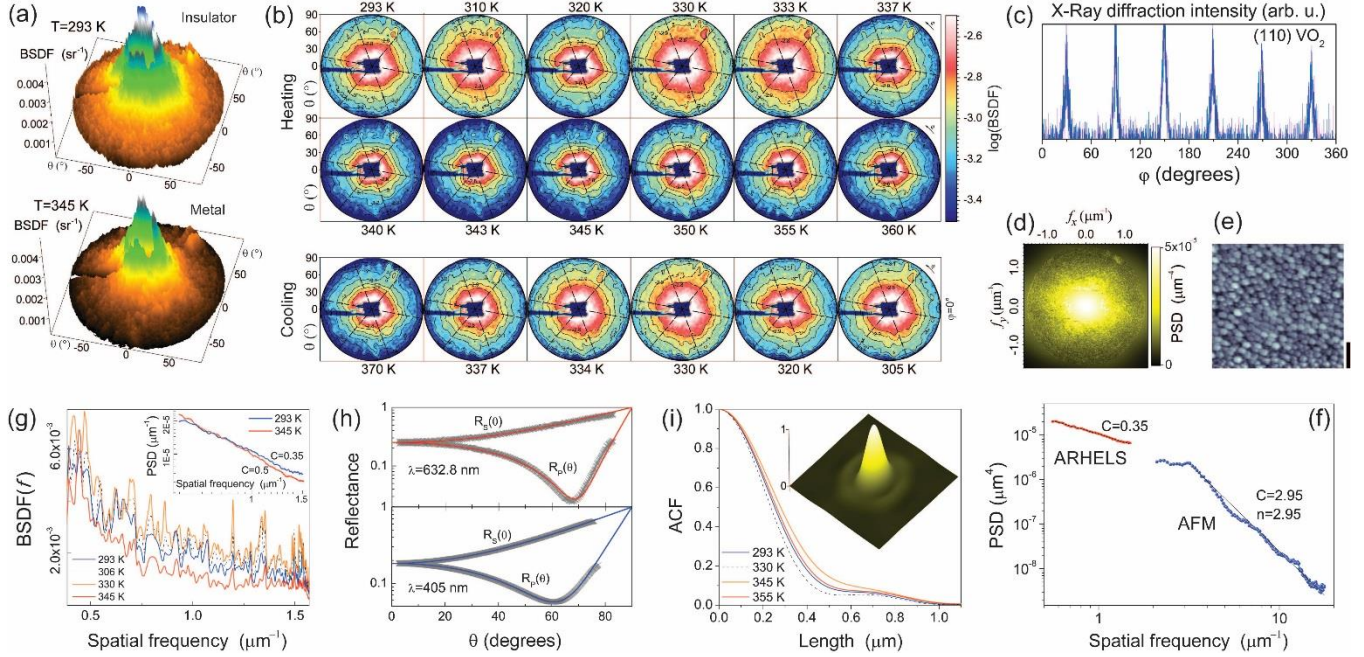


Figure 15: Thermally induced PT of 55-nm-thick epitaxial film VO₂/Al₂O₃(c-cut) with high misfit strain. (a) Scattering indicatrix in the insulating and metallic state and (b) the evolution of scattering indicatrix versus temperature. (c) XRD signal versus azimuthal orientation of the sample. (d) Surface PSD calculated from scattering data. (e) 5×5 μm AFM surface topography. (g) Cross-sections of BSDF indicatrix at different temperatures. (h) Angle-resolved reflectance. (i) Surface ACF. (f) Averaged PSD obtained from AFM and scattering data.

Significantly different and more complex evolution of mesoscale structural dynamics was observed for the VO₂/Al₂O₃(c-cut) films, which have a high level of internal misfit strain [Fig.15]. The 55 nm thickness of this epitaxial film is below the threshold for introduction of misfit dislocations which would release internal strain. As a result, the level of this strain is sufficiently high to have a considerable effect during surface reconstruction, as compared to 145 nm film in Fig.14. Thus, the evolution of BSDF scattering indicatrix versus temperature does not show a monotonic change of scattering intensity as the VO₂ switches from insulating to metallic phase [Fig.15(a,b)]. The hexagonal pattern in BSDF indicatrices clearly demonstrate fractal properties of scattering, where the VO₂ epitaxial film is twinned along 3 equivalent directions with 60° symmetry, as confirmed by XRD study [Fig.15(c)]. Furthermore, the majority of numerous diffraction peaks in BSDF scattering pattern undergo continuous change with temperature, even when the sample temperature is quite far from the T_c point, as can be seen from scattering indicatrix cross-section in [Fig.15(g)]. This behavior evidences continuous reconstruction of the surface profile due to the film twinning and new domains formation. The origin of this behavior was associated with nonuniform misfit strain in the 55-nm-thick epitaxial VO₂ film, since in a substantially thicker (145-nm-thick) VO₂/Al₂O₃(c-cut) film, with relatively low internal strain, this behavior was not observed [see Fig.14(b)].

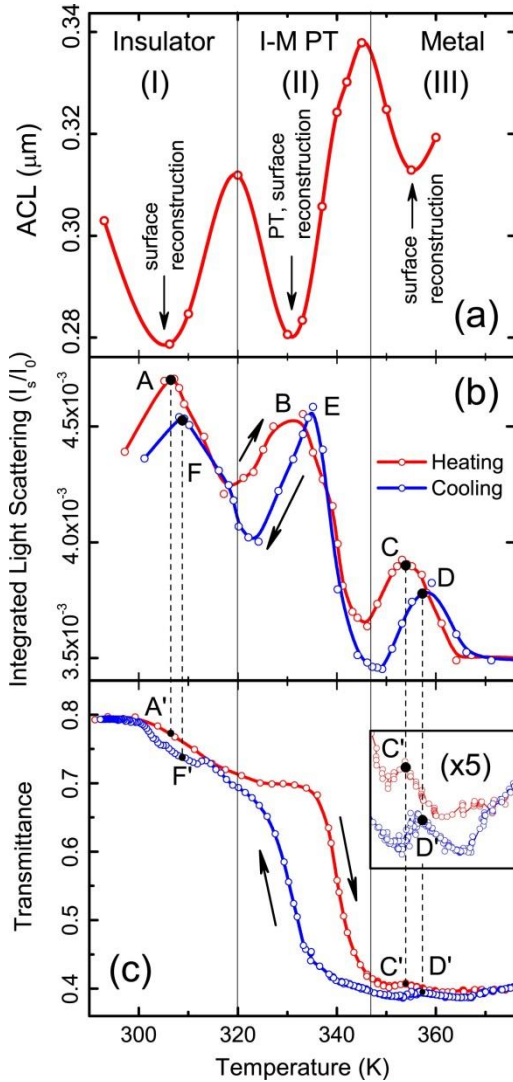


Figure 16: (a) Hysteretic evolution of surface autocorrelation length of 55-nm-thick $\text{VO}_2/\text{Al}_2\text{O}_3$ (c-cut), (b) scattering signal integrated within the hemisphere and (c) transmittance.

BSDF scattering indicatrix [Fig.17(b,c)] shows significant transformation of the scattering pattern due to surface reconstruction. The evolution of integrated light scattering [Fig.17(d)] is nearly the same as for the thin epitaxial film with high misfit strain [Fig.16(b)]. For non-epitaxial VO_2/SiO_2 the observed evolution of the scattering pattern is also related to the strain, but this strain appears at the boundary of large neighboring grains due to thermal expansion and due to change of elastic constants of the material upon phase transition. By monitoring the differential scattering signal [Fig.17(e)] we identified different evolution of scattering signal at polar scattering angles $\theta < 40^\circ$ and $\theta > 40^\circ$. The scattering signal for $\theta < 40^\circ$ shows rather common hysteretic evolution of typical VO_2 without noticeable fluctuations, as shown in [Fig.17(e)], while the evolution of the scattering signal for $\theta > 40^\circ$ fully coincide with this behavior. The scattering signal at $\theta > 40^\circ$ is caused by surface inhomogeneities with sizes less than $1\mu\text{m}$. It is clearly seen in microscopy images for the phase transition range [Fig.17(a)] that these sizes correspond to the boundaries of VO_2 grains.

After extraction of optical constants from angle-resolved reflectivity measurements [Fig.15(h)], we calculated ACF [Fig.15(i)] and PSD [Fig.15(d)] functions of surface relief. Direct measurements of surface topography by AFM [Fig.15(e)] enabled us to compare PSD data obtained from AFM and light scattering [Fig.15(g)] showing a very good match [Fig.15(f)].

Light scattering data for two different epitaxial $\text{VO}_2/\text{Al}_2\text{O}_3$ (c-cut) films revealed that the thermal hysteresis for the film with no internal strain (145 nm thick film with misfit dislocations, [Fig.14(d)]) is completely different from that of the film with internal strain (55 nm thick film without misfit dislocations, [Fig.16(b)]). For the strained film [Fig.16] the I-M PT occurs within the region II and noticeably affects optical transmission [Fig.16(c)], scattering [Fig.16(b)], and autocorrelation length ACL [Fig.16(a)] of the surface. Within region I and III only light scattering undergoes significant change. Here the net elastic strain reaches a threshold, introducing a new domain pattern which minimizes the elastic energy of the film. It is also possible that the intermediate M_1 - M_2 lattice transformation occurs within the region I of insulating VO_2 . When the structural disorder is maximal, the $\text{ACL}(T)$ function shows minima, while the scattering intensity is maximal.

The observed behavior of the scattering signal for VO_2 surface may seem peculiar. However, we found similar behavior for several films, indicating that this is rather common behavior for strained thin epitaxial VO_2 films on Al_2O_3 (c-cut) substrates. Moreover, the same evolution of scattering signal was also found for relatively thick (160 nm) non-epitaxial film VO_2/SiO_2 [Fig.17], where the internal strain was produced at the boundary of large neighboring grains. These grains have lateral sizes of several microns and can be clearly observed in an optical microscope when the VO_2/SiO_2 film approaches the phase transition point T_c [Fig.17(a)]. The thermal evolution of

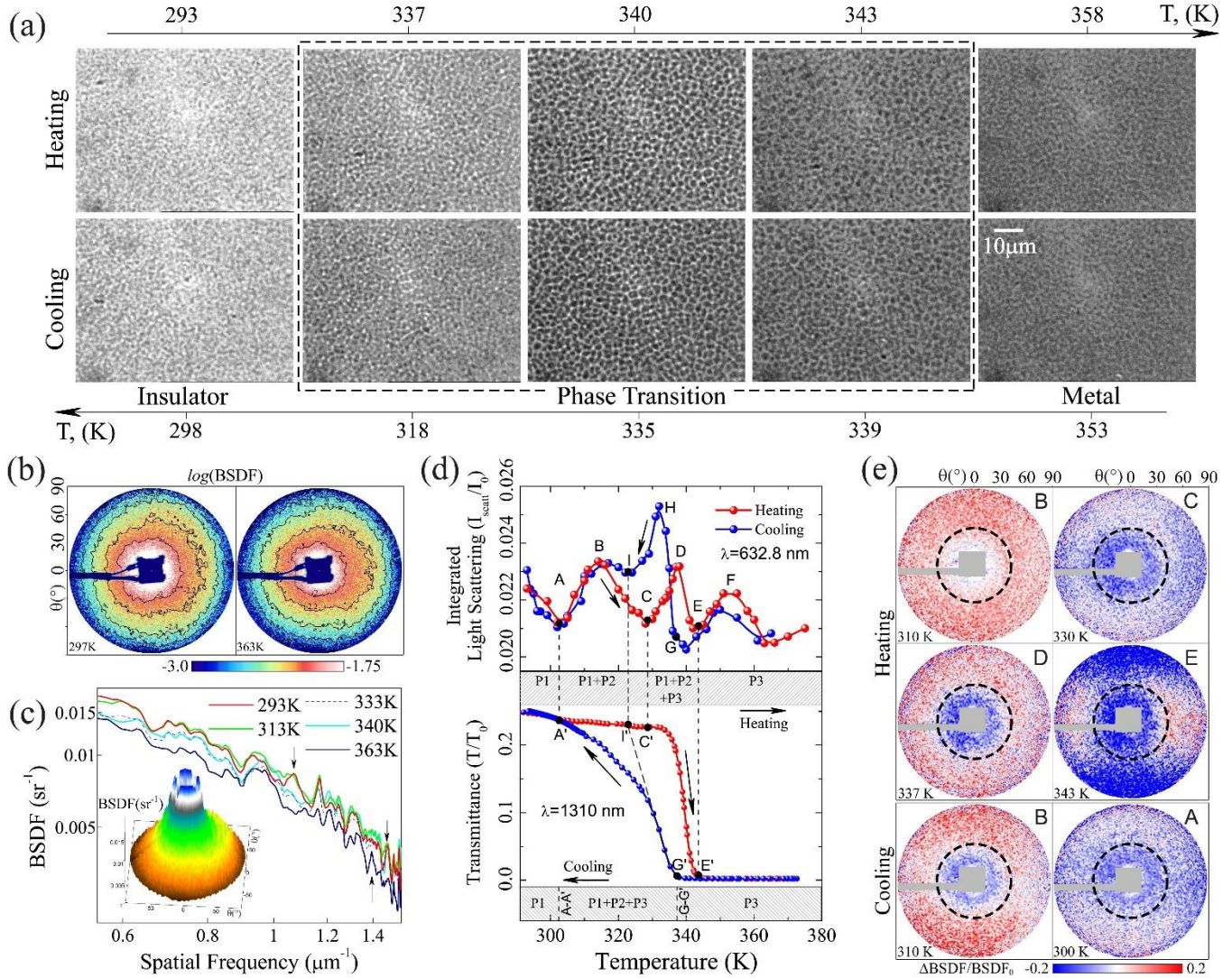


Figure 17: Thermally induced PT of 160-nm-thick non-epitaxial film VO_2/SiO_2 with high internal strain: (a) Optical image of the sample surface upon phase transition. (b) Scattering indicatrix in the insulating and metallic state. (c) Cross-sections of BSGF indicatrix at different temperatures. Inset: the 3D image of scattering indicatrix. (d) Hysteretic evolution of scattering signal integrated within the hemisphere and transmittance. (e) Evolution of differential signal $\Delta\text{BSGF}(T)/\text{BSGF}_0(293\text{K})$ versus temperature.

3.4.2.2 Photoinduced subpicosecond phase transition dynamics in the presence of anisotropic misfit strain

$\text{VO}_2/\text{Al}_2\text{O}_3(\text{c-cut})$. In order to detect ultrafast light-induced phase transition dynamics within strained regions we observed light scattering from highly twinned areas of two epitaxial 55-nm-thick and 30-nm-thick $\text{VO}_2/\text{Al}_2\text{O}_3(\text{c-cut})$ films with low concentration of misfit dislocations and high misfit strain. The first results of angle-resolved light scattering indicatrix for 55-nm-thick VO_2 film were published in Ref.[3]. However, during the last period of the project we obtained a significant amount of new experimental data, particularly for the 30-nm-thick $\text{VO}_2/\text{Al}_2\text{O}_3(\text{c-cut})$ film, which demonstrate how misfit strain affect the rate of the phase transition and also the phase of coherent phonon oscillations of the VO_2 lattice. These results will be published within the next few months in [19].

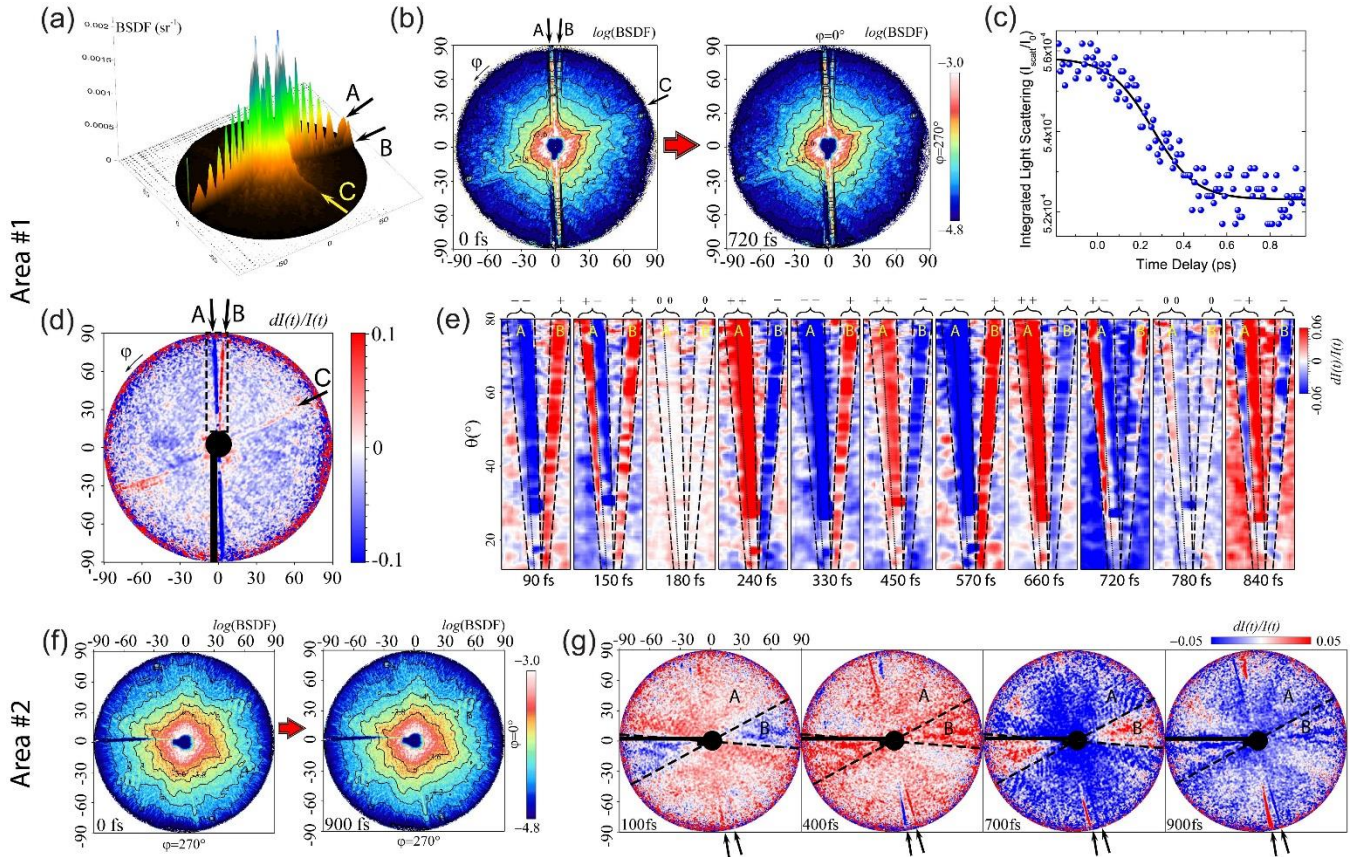


Figure 18: Photoinduced phase transition of 30-nm-thick epitaxial film $\text{VO}_2/\text{Al}_2\text{O}_3$ (c-cut) with high misfit strain. (a) 3D image of scattering indicatrix and its transient change upon light-induced PT at $F = 10 \text{ mJ/cm}^2$ for Area#1 (b), and for Area#2 (f). (c) Time-dependence of integrated scattering signal. (d) Differential scattering signal $dI(t)/I(t)$ and its evolution for (e) strained part of Area#1 and (g) for Area#2.

Figure 18(a) shows the light scattering by a highly twinned area of the 30-nm-thick $\text{VO}_2/\text{Al}_2\text{O}_3$ (c-cut) sample, where twinned domains produced specific diffraction patterns along azimuthal directions marked as 'A', 'B' and 'C'. The local strain has produced twinning where the group of domains is turned by 4° with respect to the 'A' direction, contributing to a satellite diffraction along 'B' direction [Figs.18(a,b)]. While the total integrated light scattering signal drops within 600 fs due to PIPT [Fig.18(c)], the scattering signal along 'A', 'B' and 'C' directions shows complex oscillatory behavior affected by the internal strain, as shown in Figs.18(d,e). The distribution of normalized $dI(t)/I(t)$ scattering signal in Fig.18(e) shows nearly antiphase oscillatory dynamics, associated with the twinned structure of the film. However the oscillation does not show strict antiphase behavior, probably due to superposition of different phonon modes. The observation of another area in the same 30-nm-thick $\text{VO}_2/\text{Al}_2\text{O}_3$ (c-cut) sample [Figs.18(f,g)] confirms that the phase of photoinduced oscillations of strained VO_2 domains has complex behaviour and is not exactly antiphase [scattered light from the two groups of these domains is marked by 'A' and 'B' in Fig.18(e)]. The exact information about the magnitude and sign of lattice strain is unknown. However it is very likely that the phase of oscillations within the region with numerous elastic deformations depends on the magnitude and direction of compressive and tensile strain.

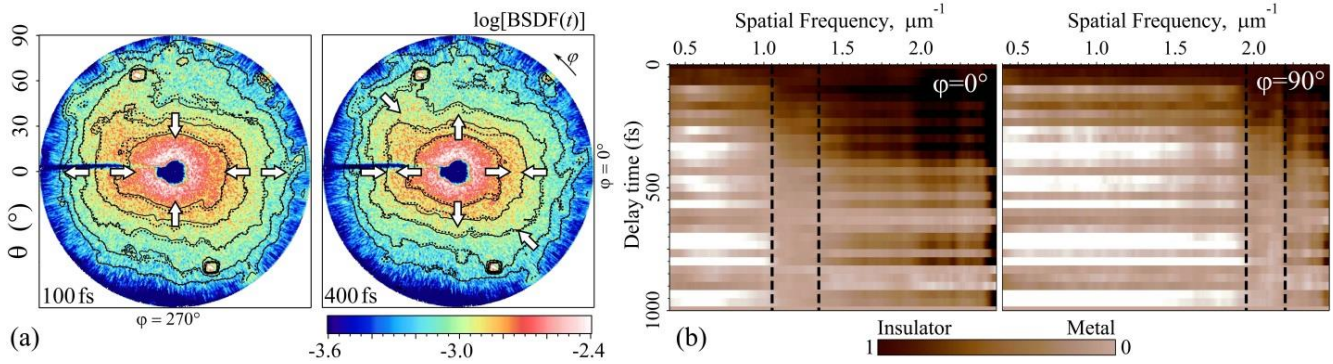


Figure 19: (a) Evolution of light scattering $\log(\text{BSDF})$ for the strained $\text{VO}_2/\text{Al}_2\text{O}_3(\text{c-cut})$ film. Dotted isophotes correspond to $\log(\text{BSDF})$ measured at 65 fs before the time specified on the figure. Arrows indicate the temporal change of isophotes. (b) Normalized scattering intensity for different spatial frequencies at $\phi=0^\circ$ and $\phi=90^\circ$ during the light-induced phase transition. The scattering intensity is scaled between 0 and 1, with a unit value for insulating and zero value for the metallic phase [3].

The ultrafast evolution of the light scattering indicatrix for 55-nm-thick $\text{VO}_2/\text{Al}_2\text{O}_3(\text{c-cut})$ [Fig.19(a)] reveals noticeable influence of internal strain inside VO_2 grains on the initial phase of coherent phonon oscillations during the insulator-metal phase transition [3, 19]. The phase of coherent phonon oscillations depends on the level of misfit strain and is nearly π -shifted [Fig.19(b)] for this film within areas of structural deformations and strained regions. It is likely that the tensile and compressive strain in different domains results in nearly antiphase oscillation of VO_2 lattice of these domains. The higher misfit strain in smaller grains of epitaxial VO_2 film presumably decreases the rate of insulator-metal transition.

$\text{VO}_2/\text{Al}_2\text{O}_3(\text{A-cut})$. In order to obtain new information about how internal strain affects the femtosecond SPT, we used an 80-nm-thick epitaxial $\text{VO}_2/\text{Al}_2\text{O}_3(\text{A-cut})$ film with anisotropic misfit strain [5]. To enhance the influence of anisotropic misfit strain on SPT dynamics in VO_2 grains/domains with different spatial frequencies, the pump fluence was set near the PT threshold, at $F = 7 \text{ mJ/cm}^2$. Figure 20(a) shows that the photoexcitation of VO_2 with this fluence results in activation of coherent phonon mode at $\sim 6 \text{ THz}$. This allows us to observe clearly the influence of film morphology on amplitude and evolution of these oscillations. Transient scattering signal $\Delta\text{BSDF}(t)/\text{BSDF}(0)$ shows strong oscillatory behavior associated with photoexcitation of active Raman modes in monoclinic VO_2 due to stretching and tilting of V-V dimers. In the central part of scattering indicatrix, the amplitude of oscillations is relatively high, but it decreases at larger polar angles and the transient signal decays rapidly. Due to epitaxial orientation of the film, oscillatory response of grains/domains contributes to symmetric diffraction pattern outlined by dashed rhomb in the center of scattering indicatrix.

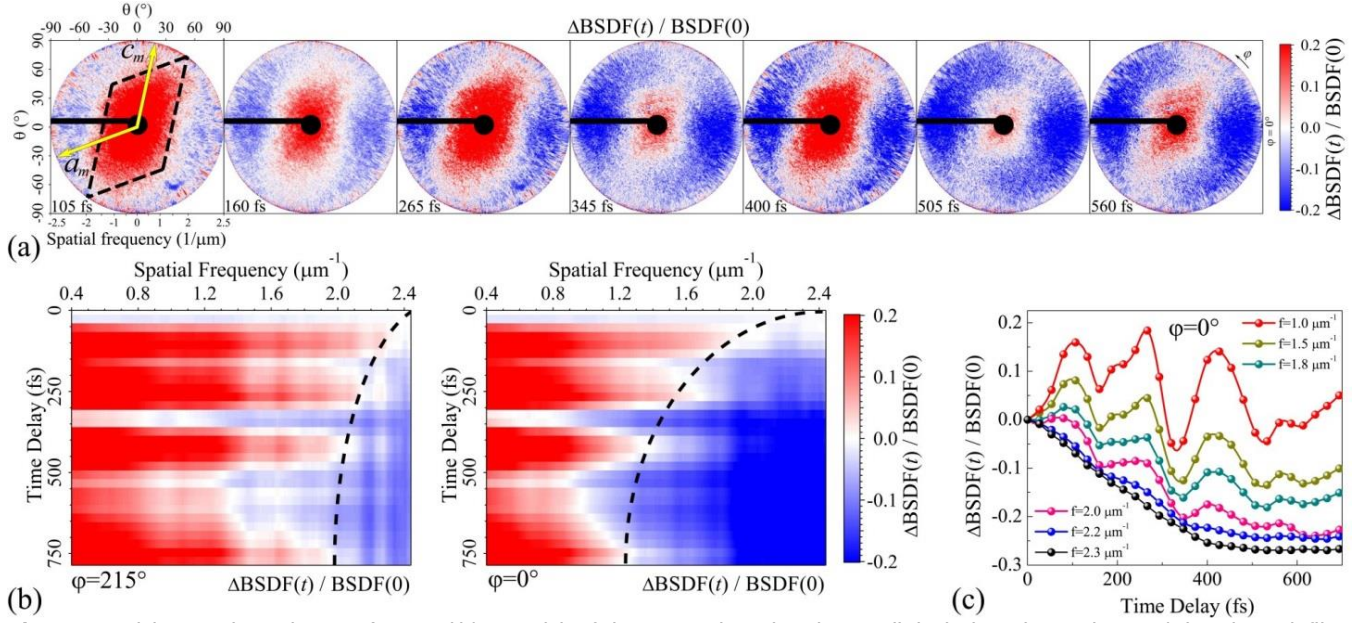


Figure 20: (a) Transient change $\Delta\text{BSDF}(t)/\text{BSDF}(0)$ of the scattering signal upon light-induced SPT in $\text{VO}_2/\text{Al}_2\text{O}_3$ (A-cut) film; $F = 7 \text{ mJ/cm}^2$. Arrows show the orientation of a_m and c_m axes of $\text{VO}_2(\text{M}_1)$. Dashed rhomb identifies the oscillatory area of scattering indicatrix. (b) Time-dependent cross sections of the data mapped in (a) at $\phi = 215^\circ$ and $\phi = 0^\circ$ versus spatial frequency of surface relief. (c) The cross sections of the data mapped in (b) at $\phi = 0^\circ$ shows gradual change of oscillatory dynamics versus spatial frequency [5].

Figure 20(b) shows the cross section of the scattering indicatrix at two azimuthal directions $\phi = 215^\circ$ and $\phi = 0^\circ$. The dashed line in the figures separates two mainly different areas for the SPT process. These data reveal anisotropy in the evolution of coherent lattice oscillations which accompany the SPT. This also evidences the size-dependent and anisotropic SPT dynamics, which rate depends on size and orientation of VO_2 grains/domains in the film. The cross-section in Fig. 20(c) shows that the oscillation of $\Delta\text{BSDF}(t)/\text{BSDF}(0)$ for larger crystallites is anharmonic and contains several oscillatory modes [see $f = 1.0 \mu\text{m}^{-1}$], while for smaller grains [$f \geq 1.5 \mu\text{m}^{-1}$] the oscillations become harmonic.

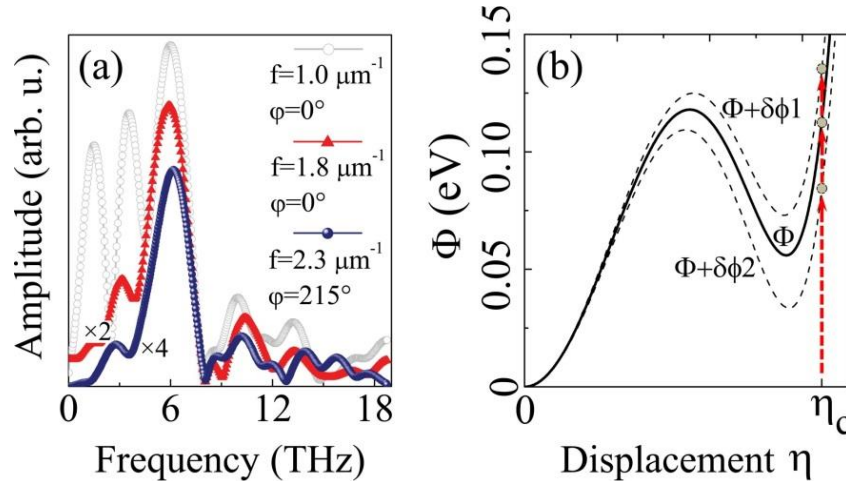


Figure 21: (a) The Fourier transform of the oscillatory component in the scattering signal for different spatial frequencies. (b) The thermodynamic potential of photoexcited VO_2 is altered by internal strain in the film. Strain contributes in additional positive $\delta\phi_1$ or negative $\delta\phi_2$ component of the potential. Dashed arrows indicate the initial energy of the VO_2 system right after photoexcitation. Here the same level of photoexcitation switches the grains/domains with different thermodynamic potential into different excited states [5].

The Fourier transform of the oscillatory component for the scattering signal at $f = 2.3 \mu\text{m}^{-1}$ shows a single frequency centered at $\nu_0 = 6.1 \text{ THz}$ [Fig. 21(a)], while for lower spatial frequency $f = 1.0 \mu\text{m}^{-1}$ the Fourier spectrum is more complex. The strong dependence $\Delta\text{BSDF}(t)/\text{BSDF}(0)$ oscillations versus spatial frequency is attributed to the influence of the misfit strain on thermodynamic potential of photoexcited VO_2 . Different strain in VO_2 grains/domains of different size and orientation alters thermodynamics potential Φ as shown in Fig. 21(b). As a result, the same level of photoexcitation switches these grains/domains into different excited states. In consequence, nonequilibrium dynamics of VO_2 becomes grain-size dependent.

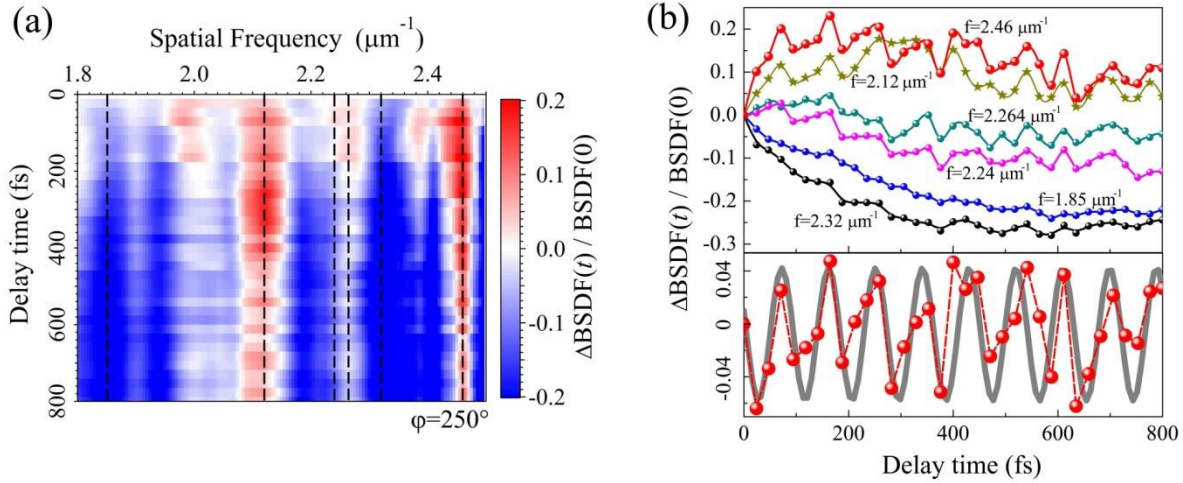


Figure 22: (a) Transient change $\text{BSDF}(t)/\text{BSDF}(0)$ of the scattering signal at $\phi = 250^\circ$ versus spatial frequency of surface relief; $F = 6 \text{ mJ/cm}^2$. (b) (Upper panel) The cross sections of the data mapped in (a) along the time axis marked by dashed lines. (Lower panel) The oscillatory part of $\text{BSDF}(t)/\text{BSDF}(0)$ obtained by high-pass filtering of the signal at $f = 2.46 \mu\text{m}^{-1}$ (circles). Solid line is the fit to equation $A_0 \sin(2\pi\nu t + \phi_0)$ with $\nu = 11.2 \text{ THz}$ [5].

It is important to note that at certain scattering angles we were able to resolve oscillations with nearly doubled frequency $\sim 2\nu_0$. Figure 22(a) shows that the oscillations are localized at certain spatial frequencies and represent nonequilibrium dynamics of certain groups of VO_2 grains. The cross sections of Fig. 22(a) at different spatial frequencies [Fig. 22(b)] show noticeable oscillatory behavior with frequency with $\nu \approx 2\nu_0 = 11.2 \text{ THz}$.

3.4.3 Subpicosecond phase transition in the presence of structural defects

Using femtosecond *tr*-ARHELS technique, we showed that the transient surface statistics and mesoscale structural phase transition are noticeably different for epitaxial and non-epitaxial films [2, 5]. Nonstoichiometry and higher concentration of structural defects in smallest VO_2 grains of non-epitaxial films both result in nonuniform metallic phase nucleation and strong phonon scattering on the subpicosecond scale.

The comparison of light scattering for strained epitaxial $\text{VO}_2/\text{Al}_2\text{O}_3$ films with low concentration of misfit dislocations and for disordered non-epitaxial VO_2/SiO_2 films shows distinctive principal differences in the pathways for light-induced phase transition [Fig. 23]. In nonstoichiometric VO_2 grains with VO_x inclusions ($1 \leq x \leq 2.5$), VO_2 sites undergo the insulator-metal phase transition upon light illumination while VO_x inclusions remain in the same phase or show nonlinear optical response different from the VO_2 transition. As a result, system disorder rapidly increases. Since light scattering depends on system disorder, its intensity also increases, as was detected for VO_2/SiO_2 for spatial frequencies above $f = 2.36 \mu\text{m}^{-1}$ [Figs. 23(d,e) and Figs. 24(b-d)] [2, 5].

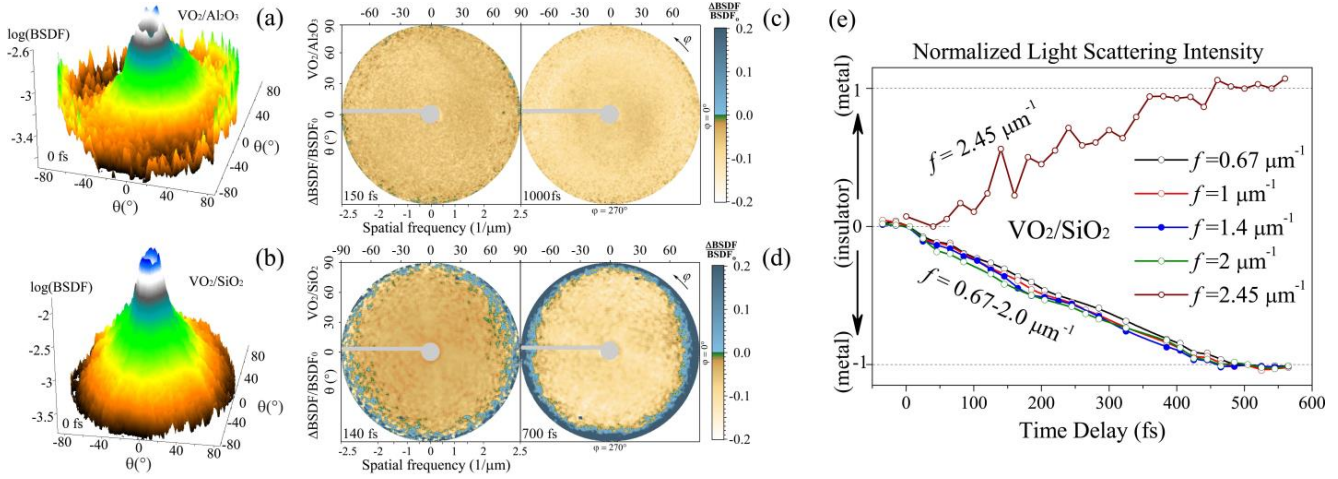


Figure 23: Ultrafast light scattering. BSDF indicatrix for (a) $\text{VO}_2/\text{Al}_2\text{O}_3$ and (b) VO_2/SiO_2 . Relative change $\Delta\text{BSDF}(t)/\text{BSDF}(0)$ of the scattering signal upon light-induced PT for (c) $\text{VO}_2/\text{Al}_2\text{O}_3$ and (d) VO_2/SiO_2 ; $\Delta\text{BSDF}(t) = \text{BSDF}(t) - \text{BSDF}(0)$. (e) Normalized transient scattering signal for VO_2/SiO_2 at different spatial frequencies at $\phi = 0^\circ$. '0'-level corresponds to initial insulating phase and ± 1 corresponds to metallic one. [2]

We also note that the transient optical response due to presence of heterogeneous VO_x phase is hidden for transient reflection and transmission measurements, since the main contribution to the optical signal here originates from structures with almost zero spatial frequencies. Only spatially-resolved techniques, such as angle-resolved light scattering, can reveal signatures of heterogeneous VO_x inclusions inside of the smallest grains of the film.

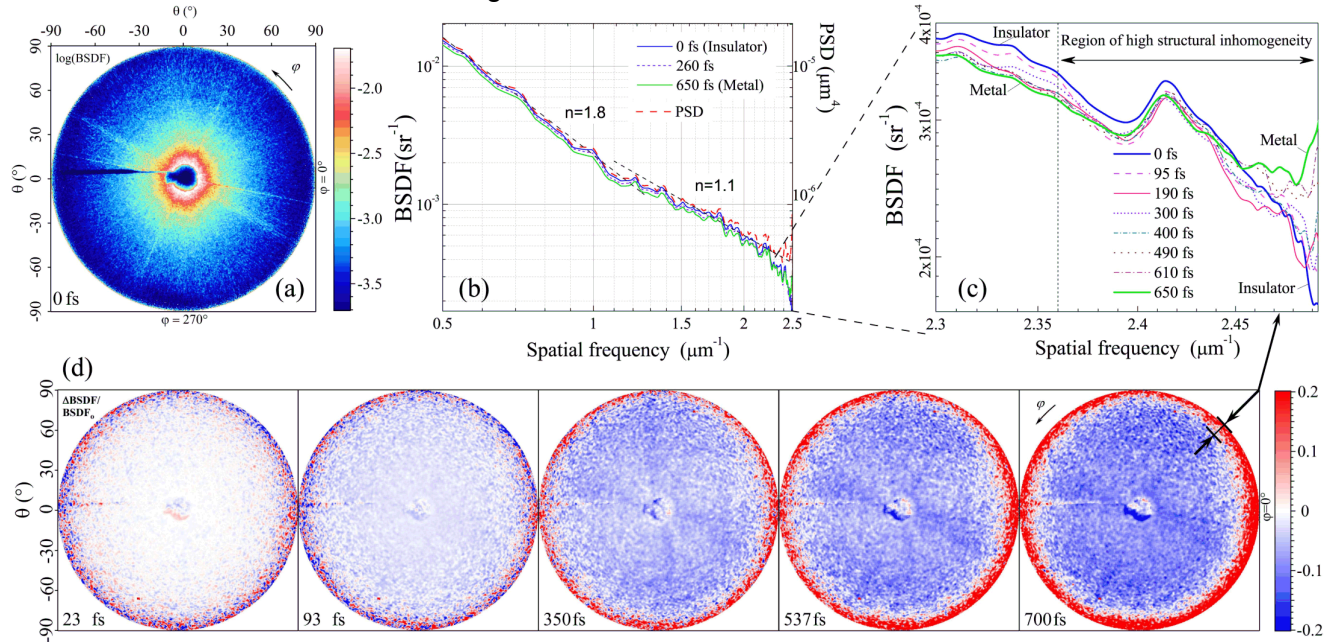


Figure 24: Transient light scattering by VO_2/SiO_2 . (a) BSDF indicatrix. (b) Cross-section of $\text{BSDF}(f)$ at $\phi = 45^\circ$. $\text{BSDF}(f)$ function shows multifractal behavior and can be approximated as $\text{BSDF}(f) = K/f^{n+1}$, where K and n are fractal parameters of surface inhomogeneity. (c) Part of $\text{BSDF}(f)$ with noticeable contribution of surface inhomogeneities. (d) Relative change $\Delta\text{BSDF}(t)/\text{BSDF}(0)$ of the scattering signal upon light-induced PT. For $f > 2.36 \mu\text{m}^{-1}$ the scattering signal unusually increases, instead of decrease as for pure VO_2 . This indicates a presence of structural defects and high level of VO_2 nonstoichiometry [5].

The advantage of *tr*-ARHELS technique is that these measurements provide the bidirectional scatter distribution function (BSDF). The shape of $\text{BSDF}(f)$ strongly depends on surface statistics and provides

information about power spectral density of surface inhomogeneities. During the light-induced transition the main shape of BSDF(f) does not change significantly for all studied films, since surface morphology remains the same. However, we were able to observe minor changes of the BSDF(f) for non-epitaxial VO₂/SiO₂ film due to size-dependent evolution of the dielectric constant and transient optical inhomogeneity within non-stoichiometric VO₂ grains at $f > 2.36 \mu\text{m}^{-1}$ [Figs. 23(d,e) and Figs. 24(b-d)] [2, 5].

3.4.4 The role of photoacoustic excitations in phase transition dynamics on nanosecond time scale

Along with internal misfit strain in the epitaxial film, the light-induced phase transition can be altered by photoacoustical effect in VO₂. We found the first evidence that the strain field produced by photoacoustical wave triggers the phase transition in photoexcited VO₂ on the nanosecond time scale (Fig. 25(a) [5]) at relatively low excitations with pump fluence below 6 mJ/cm², when thermal effects on ns time scale are small. At fluence above 6 mJ/cm² the VO₂ temperature probably exceeds T_c, the metallic state is stabilized by temperature and, therefore, cannot be altered by photoacoustical strain. The oscillatory behavior of transient transmittance due to photoacoustically assisted phase transition in different areas of the film was found to be different. For a 100 nm thick VO₂/SiO₂ film we found clear repeatable oscillatory dynamics of transient transmittance [Fig. 25(b)] assigned with coherent excitation of standing acoustic waves in VO₂ cluster of 5 μm size. Standing acoustical wave modulates the strain field inside the VO₂ cluster and alternately induces the structural phase transition.

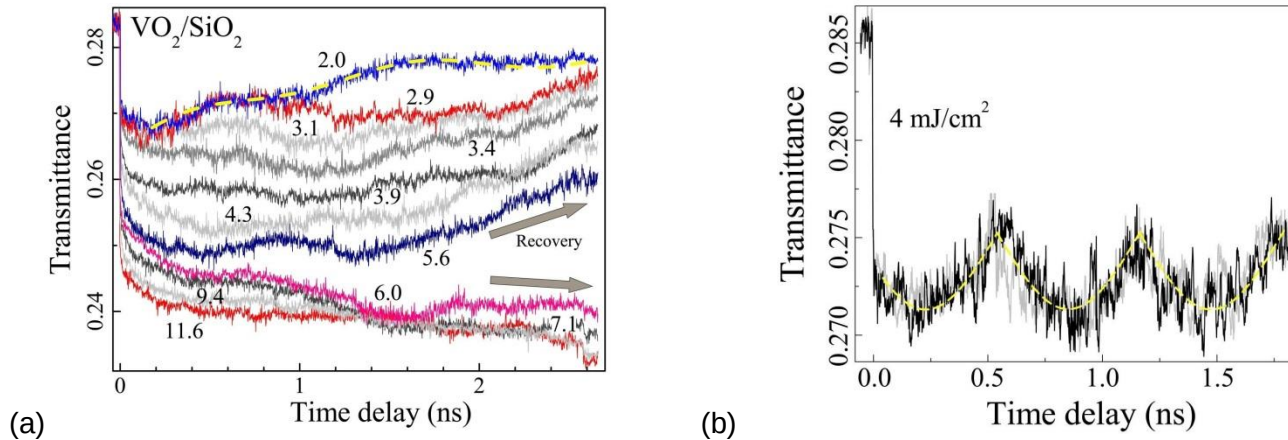


Figure 25: (a) Evolution of transient transmittance at different laser excitation levels. (b) Oscillatory signal proportional to $-\sin(2\pi vt + \phi)$. This dynamics can be modeled by photoacoustically-assisted PT in VO₂ clusters [5].

Observed photoacoustically-assisted phase transition is a fundamental property of ferroelastic VO₂. However, this phase transition was hardly observed before for thin epitaxial films. Owing to epitaxial nature of the VO₂/Al₂O₃ film, generated acoustical phonons freely propagate from the film to the substrate. The study of photoacoustically-assisted phase transition in VO₂ now are in progress, and we observed this effect for several non-epitaxial VO₂/SiO₂ films, while for epitaxial VO₂/Al₂O₃ we did not see oscillatory dynamics on nanosecond time scale.

3.4.5 Nonlinear optical properties of VO₂ observed by picosecond Z-scan

During the project we performed a set of optical Z-scan measurements for VO₂ in insulating and metallic phase using picosecond laser (30 ps pulses, $\lambda = 532 \text{ nm}$). During the time of ps pulse interaction, strong photorefractive is caused by rapid change of lattice symmetry and by generation of dense electron-hole plasma. Figures 26(a-d) show closed and open aperture Z-scan signal obtained at different fluences for 30-nm-thick and 100-nm-thick VO₂ films. Optical constants and effective values of

third-order nonlinear susceptibility where obtained using Z-scan technique in closed and open aperture scanning mode [20]. Using standard approach, we obtained effective values of nonlinear index of refraction n_2 , two-photon absorption coefficient β and the third order non-linear susceptibility $\chi^{(3)}$. Figure 26(e,f) shows the on-axis phase shift $\Delta\Phi_0$ at the focus and normalized peak and valley transmittance ΔT_{p-v} as a function of fluence. Obtained data clearly indicate two different nonlinear responses of VO₂.

The main conclusion from the optical Z-Scan measurements is that the ps laser excitation of VO₂ results in complex two-component optical nonlinearity due to light-induced phase transition and due to Kerr Effect in insulating and metallic VO₂.

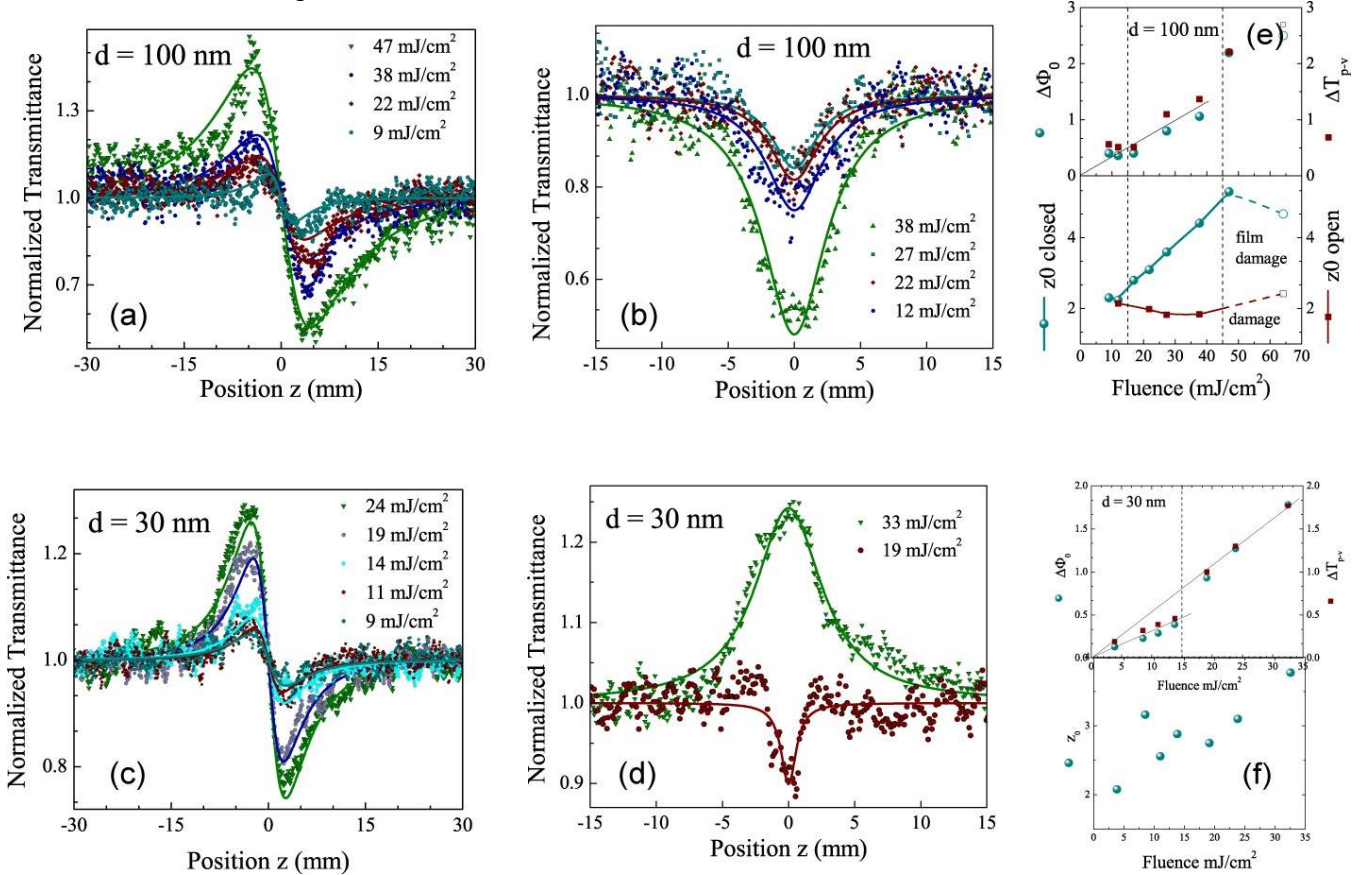


Figure 26: (a) Closed aperture Z-scans for 100-nm-thick VO₂ film. (a) Open aperture Z-scans for 100-nm-thick VO₂ films. (a) Closed aperture Z-scans for 30-nm-thick VO₂ film. (a) Open aperture Z-scans for 30-nm-thick VO₂ films. (b) $\Delta\Phi_0$ and ΔT_{p-v} as a function of laser fluence for (e) 100-nm-thick and (f) 30-nm-thick VO₂ film.

3.5 Light-induced metal-to-insulator phase transition of V₂O₃

Using ultrafast angle-resolved light scattering technique, we were able to trigger a photoinduced, paramagnetic metal-to-paramagnetic insulator (PM-PI), phase transition processes in V₂O₃ film grown on a glass substrate [8,10]. At room temperature the phase transition is caused by photoacoustic wave in the film and appears as coherent oscillations of scattering signal at various time scales. These processes strongly depend on the size of microstructures constituting the V₂O₃ film. One of the key findings of our study is the presence of a size dependent phase transition threshold for V₂O₃ microstructures, where small size structures ($\lesssim 0.5 \mu\text{m}$) have lowest contribution to the phase transition. The presence of this threshold can be well described by considering uneven internal strain in the films which is one of the key parameters controlling phase transition dynamics in various vanadium oxides.

Figure 27(a) shows the light-induced transient change in V_2O_3 scattering versus pump-probe delay within 20 ps at fluence of 22 mJ/cm^2 . The transient nonlinear optical response of V_2O_3 can be divided into three main processes: (i) an ultrafast generation, within 1ps, of a long-lasting photoexcited state, marked as T1, (ii) a relaxation process within the few picosecond time scale, denoted by T2, and (iii) transient processes T3 visible within 20 picoseconds. The initial process T1 is assigned to excitation of transient electronic states. The process T2 corresponds to electron-phonon thermalization and strongly depends on the level of optical excitation. The characteristic time of this process was defined as a time between the peak point "R" in the Fig. 27(c) and the point where scattering signal starts to increase (starting point of the process T3). The process T3 is assigned to the coherent acoustic phonon process accompanied by photoacoustical strain-induced PM-PI phase transition. As can be seen from Fig. 27(c), the starting point of this process is affected by the rate of electron-phonon thermalization. Thus, electron-phonon thermalization is an intermediate step between initially generated photoexcited electronic state T1 and the process T3. The recovery process starts after several hundred picoseconds and completes in several hundred nanoseconds (not shown here), after damping of acoustical phonons and heat transfer to the substrate.

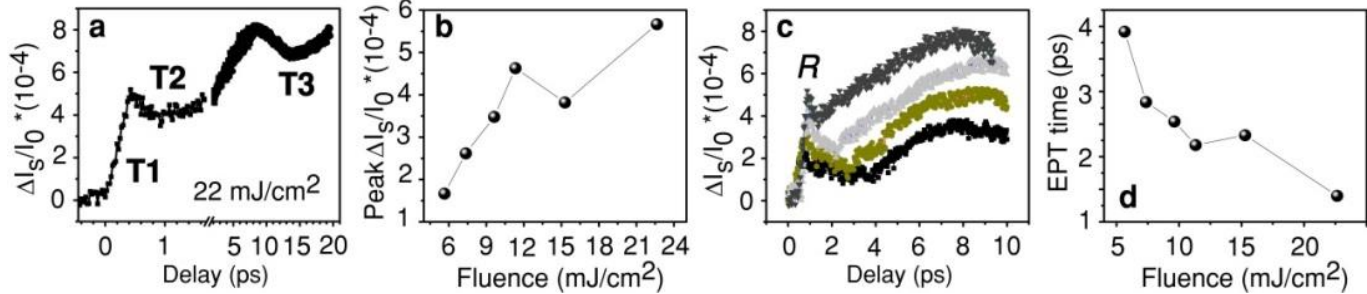


Figure 27: Panel (a) shows differential scattering signal versus probe delay for fluence 22 mJ/cm^2 . Panel (b) shows the peak intensity of the scattering signal within 1 ps as a function of the pump fluence. Panel (c) shows evolution of differential scattering signal within 10 ps for 6 mJ/cm^2 (dark gray curve), 7 mJ/cm^2 (light gray curve), 15 mJ/cm^2 (gray curve), and 22 mJ/cm^2 (black curve) pump fluence. Panel (d) summarizes the characteristic times of electron-phonon thermalization (EPT) process with pump fluence. [8]

With increasing fluence, the transient signal starts to show an oscillating behavior [Fig. 28(a)]. Fitting $\Delta I_s(t)/I_s(0)$ with a sinusoidal function gives a period of 18 ps. The oscillatory response of V_2O_3 at relatively high pump fluence is very different from NLO response of VO_2 , which shows coherent oscillations at low fluence levels. To investigate the V_2O_3 phase transition dynamics with respect to characteristic size of film structural irregularities, we map the cross sections of scattering patterns [Fig. 28(b)] for different spatial frequencies of V_2O_3 sample (at azimuthal scattering angle $\phi=220^\circ$). There are four prominent oscillations visible for the microstructures up to $\sim 2 \mu\text{m}^{-1}$ spatial frequency. These prominent oscillations are marked by 1, 2, 3 and 4 white lines, respectively. The oscillations can be assigned to paramagnetic metal-to-paramagnetic insulator phase transition process induced by coherent acoustic phonons.

From the map of scattering cross-section, we clearly see a variation of scattering intensity, and hence V_2O_3 PT, with respect to different spatial frequencies. The sharp drop in the scattering intensity for smaller structures ($f \geq 2 \mu\text{m}^{-1}$, $\lesssim 0.5 \mu\text{m}$) indicates the existence of a size-dependent threshold for strain-induced PM-PI transition in photoexcited V_2O_3 . This fact has not previously been observed in V_2O_3 , and is an important finding. Since the PM-PI transition is directly related to photoinduced strain in V_2O_3 , one possible cause of the observed threshold for smaller grains is associated with a presence of uneven internal strain in the film. In this case the induced strain in smaller structures with sizes less than $\sim 0.5 \mu\text{m}$ is significantly lower as compared to larger structures. This implies that in V_2O_3 films the PM-PI phase transition does not take place uniformly over the entire photoexcited areas of the film.

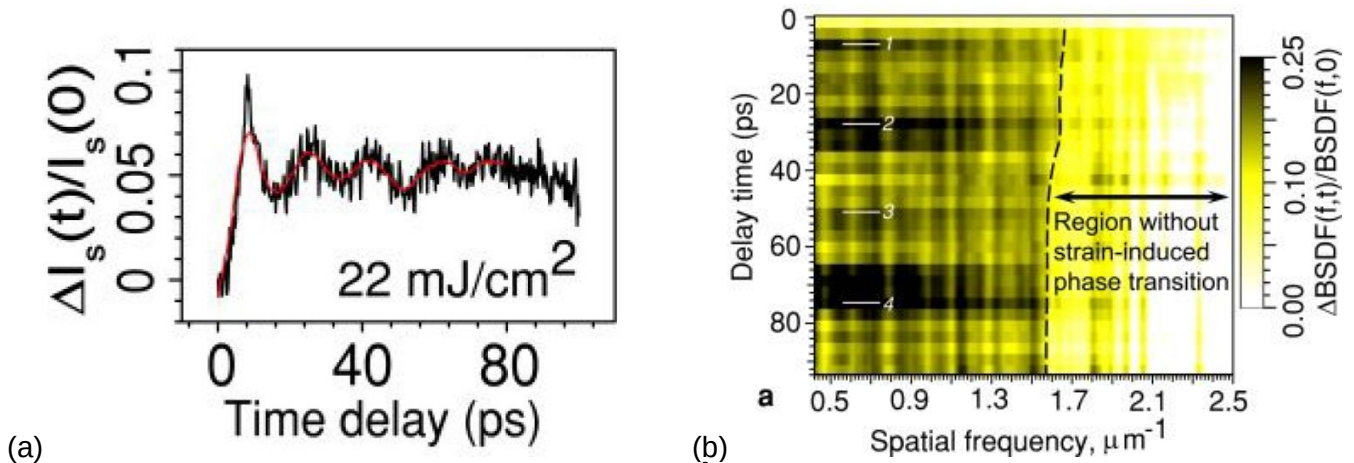


Figure 28: (a) Differential scattering signal at $F = 22 \text{ mJ/cm}^2$. Solid line indicates a sinusoidal fit of oscillatory signal component. (b) The evolution of normalized scattering intensity for different spatial frequencies for 100 ps temporal range. White lines and numbers represent four prominent oscillations visible in the signal. [8, 10]

3.6 Ultrafast spectroscopy of surface polaritons and evanescent surface waves in photorefractive VO_2/Au structures

Ultrafast photoinduced dynamics of surface plasmon polaritons (SPPs) as well as non-ultrafast SPP dynamics were investigated by attenuated total reflection (ATR) with Kretschmann-Raether configuration [11]. The multilayer VO_2/Au structure was synthesized on the hypotenuse face of a prism with average index of refraction $n=1.55$. The significance of this research lies in the fact that in recent years it has become urgent to find plasmonic structures for ultrafast optical control of SPP dynamics.

The effect of photoinduced surface plasmon switching was demonstrated for a VO_2/Au hybrid bilayer structure. Our results demonstrate that the ultrafast insulator-to-metal phase transition phenomenon in VO_2 significantly alters the SPP enhancement within femtosecond time frames at the VO_2/Au bilayer interface in ATR geometry. This opens possibilities to build fast all-optical plasmonic modulators by combining strongly correlated vanadium oxides with noble metals.

Our study demonstrates for the first time [11]:

- (1) All-optical (light-induced), thermal and non-thermal control of SPP dynamics in thin photorefractive bilayer structure in ATR geometry;
- (2) Ultrafast manipulation of SPP dynamics at VO_2/Au interface (in sophisticated femtosecond pump-probe spectroscopy experiment);
- (3) Angle-resolved polar diagrams of SPP scattering from a photorefractive plasmonic system;
- (4) The SPP scattering from photorefractive plasmonic structure, which is very different from ordinary volume wave scattering. We show that it is controlled by several competitive factors: by SPP enhancement, SPP propagation length, variable surface roughness and variable VO_2 optical constants.
- (5) The estimation of the SPP propagation length and its influence on SPP scattering in Au/VO_2 .
- (6) Numerical fitting of reflection in ATR geometry and extraction of Au and VO_2 optical constants for photorefractive VO_2/Au plasmonic system.

In two experiments with thermal and ultrafast non-thermal phase transition of the VO₂ layer it was shown that through excitation of SPPs, light reflection and scattering from the VO₂/Au interface can be noticeably altered by light on different time scales. It was shown that the resonance angle for excitation of SPPs depends on VO₂ film thickness and optical wavelength, and shifts markedly upon the PT of VO₂. Thus, a Au/VO₂ hybrid structure with different VO₂ film thicknesses provides different nonlinear SPP responses, making it suitable for multifunctional active plasmonic devices.

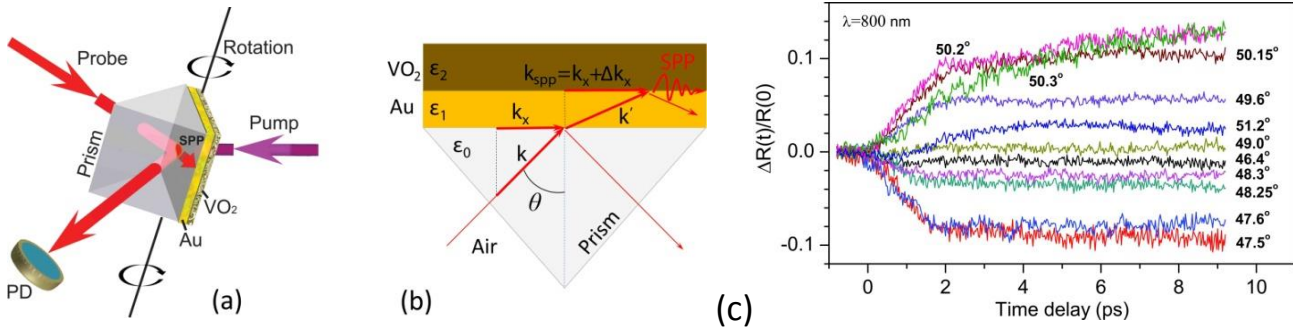


Figure 29: (a) Experimental geometry of ATR measurements. (b) Excitation of SPPs at VO₂/Au interface by ATR method, Kretschmann-Raether configuration. (c) Time-resolved evolutions of the differential reflectivity obtained for different incident angles of the probe. The incident angles are specified in the figure. [11]

The excitation of SPPs was produced at the VO₂/Au interface by ATR using the Kretschmann-Raether configuration as shown in Figs.29(a,b). For time-resolved reflectivity measurements a femtosecond Spectra-Physics pulsed laser system was used to excite and probe the samples.

The excitation of SPPs in ATR configuration takes place when the momentum vector of incident light in the film plane equals the momentum of SPP. This corresponds to the case when the projection of the incident light wave vector k onto the surface plane equals the wave vector of the SPP on the metallic films (k_{spp}) [Fig.29(b)]. The time-resolved SPP reflection measurements performed in ATR geometry shows high efficiency in all-optical modulation of SPP resonance, as evidenced in Fig.29(c).

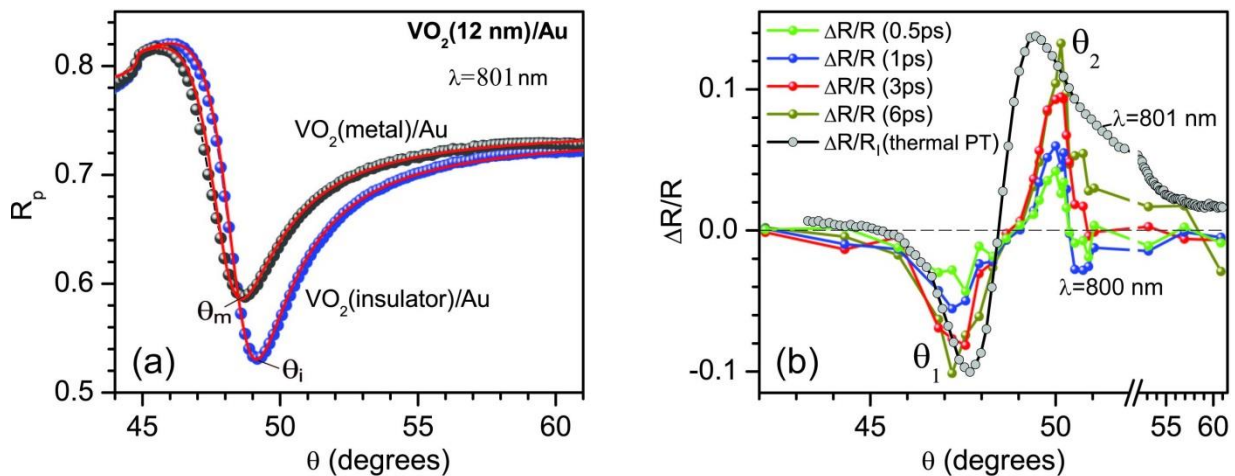


Figure 30: (a) Angle-resolved reflectivity R_p of VO₂/Au bilayer in ATR geometry for $\lambda = 801$ nm. (b) Relative change of the reflectivity $\Delta R/R$ for several probe delays as a function of incident angle. [11]

The ultrafast phase transition in VO_2 and, as a result, modulation of SPP resonance were induced by the femtosecond pulse impinging the sample surface from the air side, as shown in Fig.29(a). Figure 29(c) shows the temporal evolution of differential reflectance at different angles of probe pulse incidence. The transient optical reflectivity obtained at different angles of incidence have similar dynamics, but with different magnitudes of the signal. Within the monitored 9 ps timescale the reflectivity shows rapid change within 2 ps, followed by slower relaxation. These two-component transient dynamics of SPP excitation at VO_2/Au interface is similar to the nonlinear optical response of pure VO_2 .

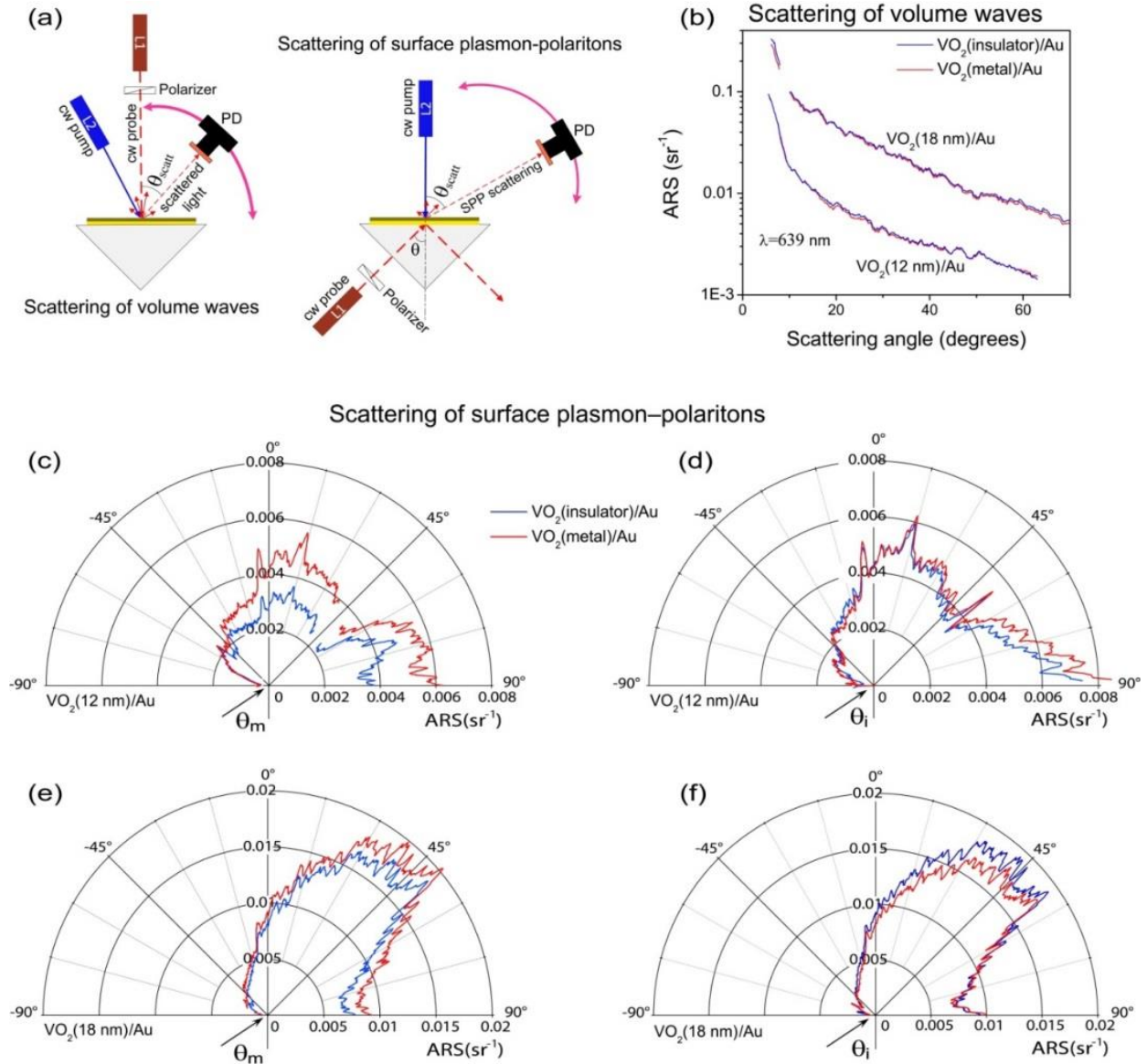


Figure 31: Angle-resolved light scattering for $\lambda=639$ nm. (a) Experimental configurations for measurements of homogeneous volume wave and SPP scattering. L1 and L2, probe pump and lasers, respectively; PD, photodetector. (b) ARS signal of the volume wave scattering. (c) SPP scattering from $\text{VO}_2/\text{Au}(12 \text{ nm})$ interface with excitation of SPPs at resonance angle θ_m and (d) at θ_i . (e) SPP scattering from $\text{VO}_2/\text{Au}(18 \text{ nm})$; excitation of SPPs is at θ_m and (f) at θ_i . [11]

To obtain information about transient enhancement of electromagnetic field at the VO₂/Au interface, the transient reflectivity was measured versus angle of incidence at various time delays. Figure 30(a) shows the angular dependence of the probe beam reflectivity for VO₂/Au film with insulating and metallic phases of the VO₂ layer. The phase transition of VO₂ changes the wave vector of the SPPs k_{spp} and, as a result, the resonance angle θ for ATR excitation of SPPs. Figure 30(b) shows the reflectance for the case of transient reflectivity at time $t=0.5$ ps, 1 ps, 3 ps and 6 ps as well as for static reflectivity. It is important to note that the magnitude of the transient differential reflectivity at $t > 3$ ps matches well with the variation of static reflectivity.

To obtain information about plasmon propagation length L_{spp} and its influence on SPP dissipation we performed angle-resolved scattering measurements. The SPP scattering data were obtained at two different incident angles, θ_i and θ_m , which correspond to the SPP resonance at VO₂/Au interface with, respectively, insulating and metallic phase of VO₂ (Fig. 31). It was shown that the characteristic propagation length of plasmons L_{spp} is an important parameter in SPP scattering phenomenon. Thus, the SPP scattering can be considered as a complex process which strongly depends on several competitive factors such as SPP enhancement, SPP propagation length, variable surface roughness and optical constants. The insulator-to-metal phase transition in VO₂ alters all these factors resulting in various changes of the $ARS(\theta_{scatt})$ function.

We believe that our work has the capability to provide answers to many important questions related to plasmonic dynamics in photorefractive systems. Considering that neither photoinduced nor time-resolved surface plasmon response in ATR geometry for VO₂-based plasmonic materials has been reported before, this work can further advance the field of plasmonics and provide an important contribution to ultrafast science. Thus, it should be of interest for a broad audience.

3.7 Degenerate-four-wave mixing process with excitation of surface-plasmon polaritons

Recently we built an optical setup to study a degenerate-four-wave mixing process with excitation of SPPs and/or evanescent surface waves in VO₂/Au composite structure [Fig. 32(a)] [18, 20]. Transient grating is formed by volume wave interference in the VO₂ film, and SPP diffracts on the nonstationary grating, as shown in the figure. In these experiments we show for the first time the following:

- (1) The ultrafast formation of transient grating in the VO₂ layer is accompanied by nonlinear wave interaction with SPPs excited by the ATR coupler at the VO₂/Au interface.
- (2) Optical mixing of SPPs and volume waves with same and different linear polarizations gives rise to surface plasmon waves by inducing nonlinear polarization.
- (3) Photoinduced diffraction grating in the photorefractive layer is also used to decouple the SPPs from the surface and to convert SPPs to volume optical waves, which were then directly detected by a photodetector [Fig. 32(b)].

We performed a full set of DFWM measurements and demonstrated the possibility of efficient tuning of enhancement, reflection and diffraction of optical waves in a photorefractive structure via excitation of surface plasmons within the visible and near-infrared region. Nonlinear energy transfers between different types of waves with the ability to manipulate and decouple SPPs from the surface open up new possibilities for future plasmonic devices. As soon as we complete analysis of the extensive data obtained, these new results on degenerate-four-wave mixing process of SPPs and volume (homogeneous) electromagnetic waves will be submitted for publication.

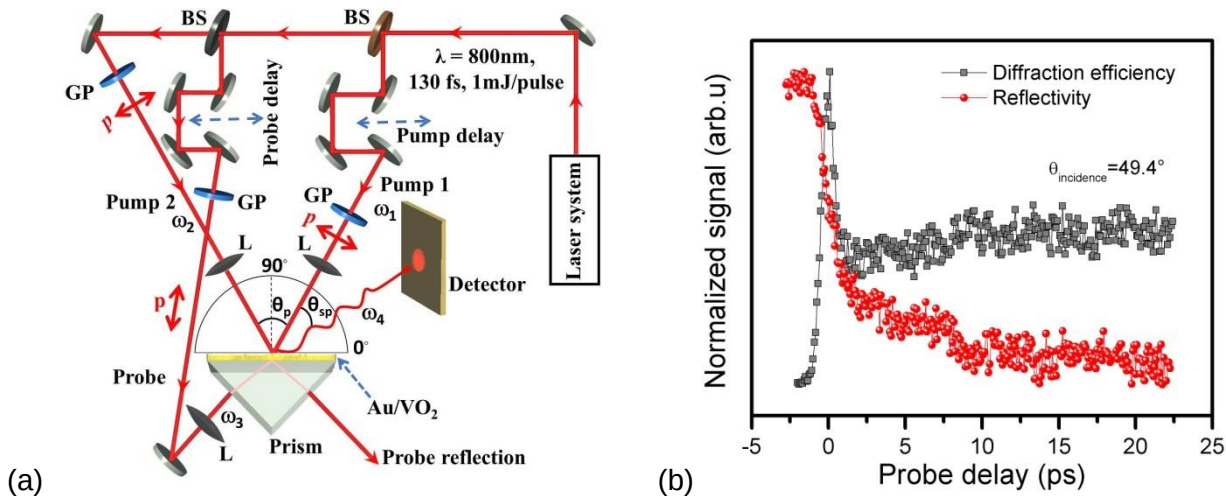


Figure 32: (a) Experimental setup for ATR measurements of Four-Wave-Mixing. (b) Diffraction (SPP decoupling signal) and Reflectivity of SPP in ATR geometry. [18]

3.8 Ultrafast strain engineering in nanostructures with insulator-to-metal phase transition

Our group, in collaboration with researchers from Nottingham University, UK, enabled pioneering experimental demonstration of ultrafast insulator-to-metal and structural transition under the combined action of femtosecond optical and picoseconds strain pulses [14]. The experiments were performed on a well-known and technologically-relevant model object – vanadium dioxide, VO_2 . It was shown that a picosecond strain pulse of moderate amplitude $\sim 10^{-3}$ injected into epitaxial VO_2 nanohillocks either assists or suppresses the optically-driven ultrafast phase transition depending on the sign of the strain present in the nanostructure at the moment of optical excitation. Importantly, it is shown unambiguously that only the transient strain present during the optical excitation affects the efficiency of the phase transition, while the strain present at other times has no effect on the phase transition.

The broader impact of these experiments is:

- Simultaneous excitation of phase transition with picosecond strain pulses is a novel technique which creates a new paradigm in strain engineering of phase transitions.
- It advances the established field of strain engineering into the field of ultrafast effects on picosecond time scales.
- This work spans the interests of several wide research communities working on strain-related phenomena, ultrafast electronic, structural and spin kinetics, phase transitions, and nanotechnologies.

Atomic force microscope (AFM) images [Figs. 33(a) and 33(b)] show the VO_2 hillocks grown on c-cut Al_2O_3 . Figure 33(c) shows the temperature hysteresis of the optical reflectivity R at a photon energy of 1.2 eV, and reveals the phase transition occurring at $T_c = 340$ K with coercivity of 20 K, which is typical for thin-film and nano-granular VO_2 samples.

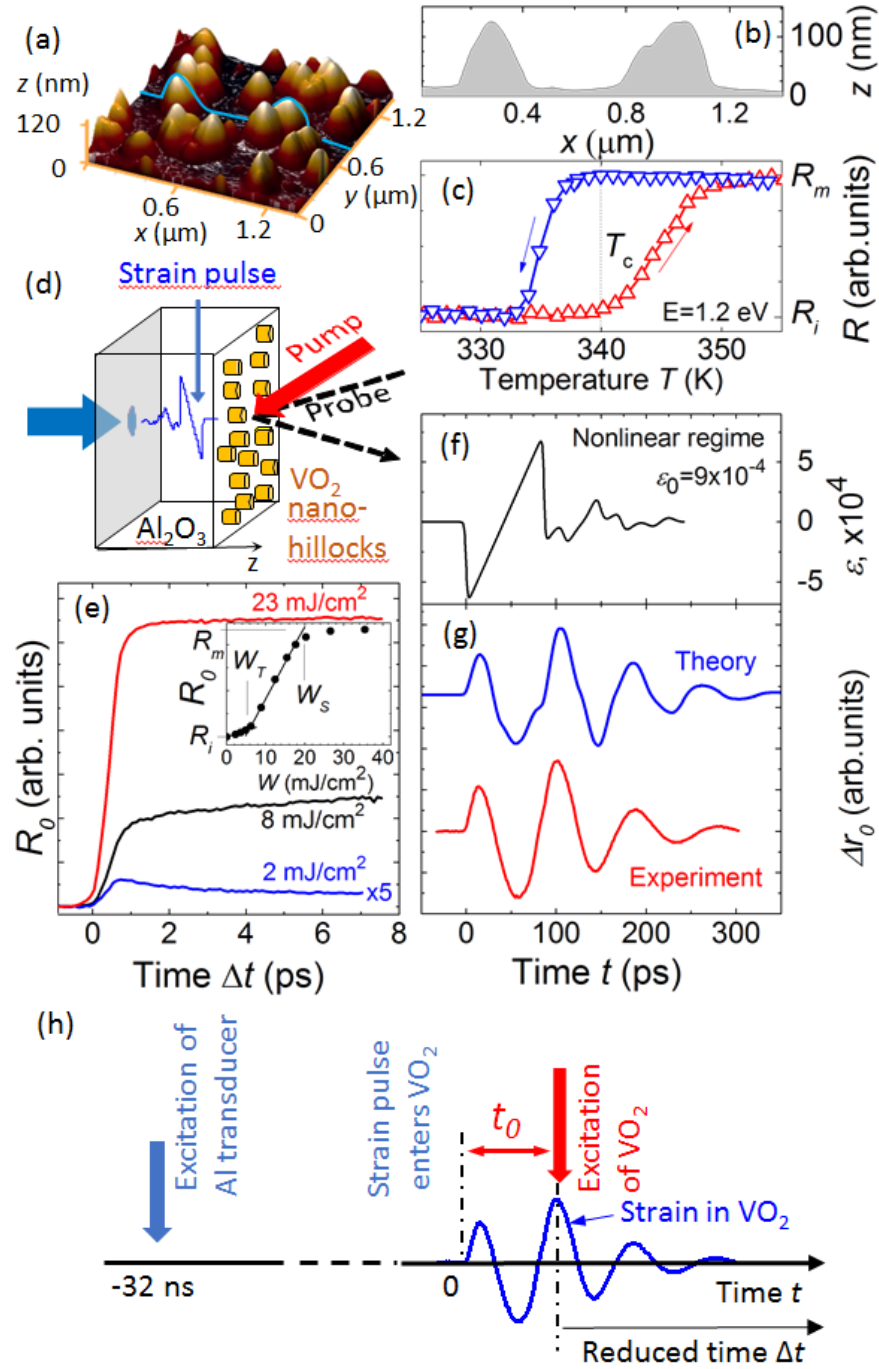


Figure 33: Sample properties and experimental schematic. (a) AFM image of the VO₂ nanohillocks and b its cross-section along the blue line in (a). (c) The temperature dependence of stationary reflectivity R at the photon energy 1.2 eV obtained upon heating (red symbols) and cooling (blue symbols). (d) Experimental scheme. (e) Transient reflectivity $R_0(\Delta t)$ signals obtained for three values of optical fluence W in the absence of the strain pulse. Inset shows the transient reflectivity at $t=1$ ps as a function of W . (f) Calculated strain pulse temporal profile $\varepsilon(t)$ in nonlinear propagation regime in the sapphire substrate in the vicinity of the VO₂ nanohillocks; (g) Calculated (blue line) and measured (red line) reflectivity evolution of strain-induced reflectivity signal $\Delta r_0(t)$ in the absence of the optical pump ($W=0$) corresponding to nonlinear input strain pulse shown in (f). (h) The diagram illustrating definitions of $t=0$, $t=t_0$, and Δt , and the instants for excitations of Al transducer and PIPT in VO₂. [14]

Figure 33(d) shows the pump-probe experimental scheme which allows combined excitation of a sample under study by femtosecond optical and picoseconds strain pump pulses. The optical pump pulse is incident on VO₂ nanohillocks. The *second pump pulse* is used to generate the strain pulse, shown by a blue arrow in the diagram. It is incident onto an Al transducer film on the back side of the sample, with fluence of $\sim 60 \text{ mJ/cm}^2$ and spot size of $110 \times 110 \text{ }\mu\text{m}^2$. The third one is a *probe pulse* controlled by a scanning delay line and used for monitoring the temporal evolution of the reflectivity $R(t)$ from the surface with VO₂ nanohillocks.

Figure 33(e) demonstrates the pump-probe temporal reflectivity signal $R_0(\Delta t)$ in the absence of the strain pulse for three different optical pump fluences. An example of the simulated temporal strain profile, $\epsilon_0(t)$, with strain amplitude $\sim 10^{-3}$ in sapphire in the vicinity of the VO₂ layer is shown in Fig. 33(f). Figure 33(g) shows the simulated and measured evolutions of strain-induced reflectivity changes $\Delta r_0(t)$ in VO₂ in the absence of the optical pump (fluence $W=0$).

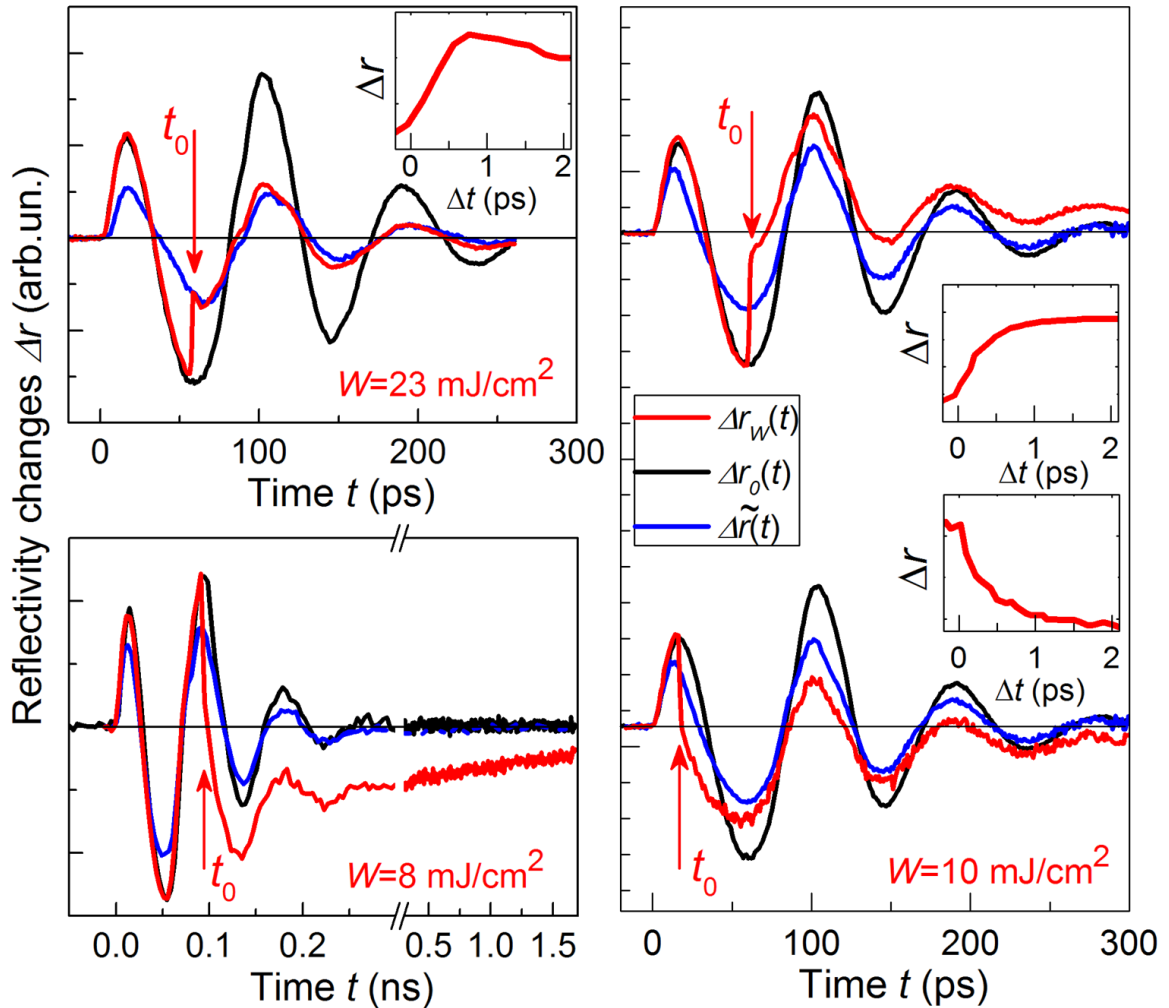


Figure 34: Temporal evolutions of the reflectivity changes in the VO₂ nanohillocks under the impact of a picosecond strain pulse measured in the time intervals 300 ps (a, b) and 1700 ps (c). Black and red curves are the signals measured without and with optical pump, correspondingly. Vertical arrows indicate the time $t_0 > 0$ when the optical pump is applied. Blue lines correspond to $\Delta r(t)$ when the optical pulse excited the VO₂ nanohillocks before the arrival of the strain pulse, $t_0 = -30 \text{ ps}$. In (b) and (c) the optical pump densities W are above the threshold, $W > W_T$, and below the saturation level, $W < W_S$, for light-induced phase transition; in (a) $W > W_S$. The insets in (a) and (b) show $\Delta r(t)$ vs. reduced time $\Delta t = t - t_0$ measured around t_0 with temporal resolution 200 fs. [14]

The diagram in Fig. 33(h) shows the sequence of incident optical pulses and strain pulses on the sample. By changing the delay t_0 we induce light-induced phase transition during the strain pulse present in VO₂ (i.e. $t_0 > 0$) or before the strain pulse reaches the interface between sapphire and nanohillocks (i.e. $t_0 < 0$). Since the duration of the strain pulse when it reaches VO₂ is ~ 100 ps (Fig. 33(e)), we can precisely adjust the temporal delay t_0 of the femtosecond optical pump

The effects of the strain pulses on the light-induced insulator-to-metal phase transition are presented in Fig. 34. The analysis of the transient signal behavior obtained for different delays t_0 and different optical pump fluences W leads us to the following conclusions:

- (i) Strain-induced decrease (increase) of the proportion of VO₂ hillocks undergoing light-induced phase transition takes place when out-of-plane compression (tension) takes place. In the experiments with strain pulses it is possible to control the sign and value of strain by choosing precisely the moment t_0 of optical impact inducing light-induced insulator-to-metal phase transition;
- (ii) Only at the moment of the optical pulse impact the magnitude and sign of acoustic strain define the strength of the strain-induced effect on light-induced phase transition.

The results described above unambiguously suggest that strain corresponding to out-of-plane compression (tension) applied at the moment of the optical pump impact, impedes (supports) the sub-picosecond insulator-to-metal transition and switching of the crystalline lattice to a new symmetry state (for VO₂, from monoclinic to rutile lattice cell) during light-induced phase transition.

To explain these findings, we employ the phenomenological model developed by our group of the first-order light-induced structural phase transition in a single domain of VO₂ and extend it to the case of combined laser and strain pulse impacts, as shown in Fig. 35.

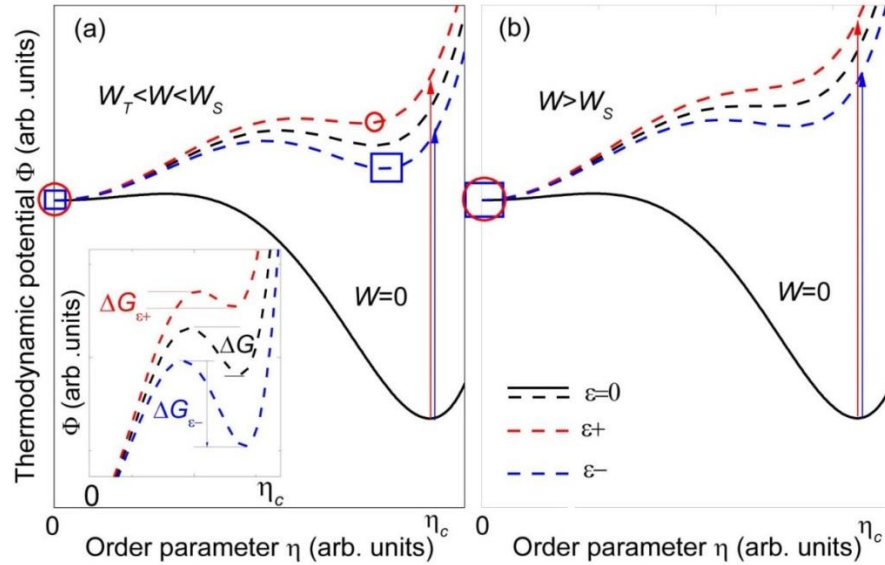


Figure 35: Thermodynamic potentials $\Phi(\eta)$ in the initial monoclinic phase (solid lines) and after the photo excitation (dashed lines) by a femtosecond pulse of intermediate fluence (a), and in the saturation regime (b). Black lines show the thermodynamic potential of the unstrained system. Red and blue lines are the potentials corresponding to the strain components which increase ($\epsilon+$) or decrease ($\epsilon-$) the free energy of the photoexcited system, respectively. Note that the distortion of $\Phi(\eta)$ due to strain is exaggerated for the sake of clarity. Vertical arrows show the photoexcitation process in the sample in the presence of strain. Symbols and their sizes indicate schematically a probability for the system to occur in the rutile ($\eta=0$) or metastable monoclinic ($0 < \eta < \eta_c$) state after ~ 1 ps following the photoexcitation of the sample subjected to the strain-induced increase (red circles) or decrease (blue squares) of $\Phi(\eta)$ at $\eta=\eta_c$. Inset shows the strain-induced change of the potential barrier ΔG between the photoexcited rutile and metastable monoclinic states. [14]

The demonstrated effect of photoacoustic strain is not limited to the particular material (VO_2) and type of phase transition studied here. Feasibility of the control of light-induced structural phase transition in VO_2 by picosecond strain pulses paves the way to ultrafast strain engineering in materials with magnetic phase transitions where femtosecond photo-induced changes the magnetic state. Ultrafast strain engineering may also facilitate yet-to-be-demonstrated laser-driven control of ferroelectricity in complex structures, i.e.: heterostructures and patterned nanolayers, which include optically opaque and transparent materials possessing phase transitions. Picosecond strain pulses may be generated selectively in space, thus allowing control of strain-induced effects on both nanometer and picosecond scales in space and time respectively.

3.9 Large non-thermal generation of picosecond strain pulses via ultrafast photo-induced phase transition in vanadium dioxide

It is proposed to exploit ultrafast structural changes during photo-induced first order phase transitions in strongly correlated media for generating a high-amplitude non-thermal contribution to picosecond strain pulses [16]. To verify this principle, the experiments were performed on vanadium dioxide VO_2 , which exhibits a first order phase transition accompanied by drastic changes of lattice and electronic structure. Upper panel in Fig. 36 shows the schematics of the experiment on detection of the strain pulses emitted into sapphire from the photoexcited VO_2 film. It was demonstrated that during femtosecond optical excitation of VO_2 the photo-induced phase transition alone contributes to ultrafast expansion of this material as large as 0.45 %, which is not accompanied by heat dissipation, and is 5 times higher than the contribution from the thermoelastic effect for the same excitation density of 8

mJ/cm^2 . We discuss ways of reducing the heat dissipation even further by utilizing spectral degrees of freedom available for PIPT, as well as by designing VO_2 transducers with a sharp transition.

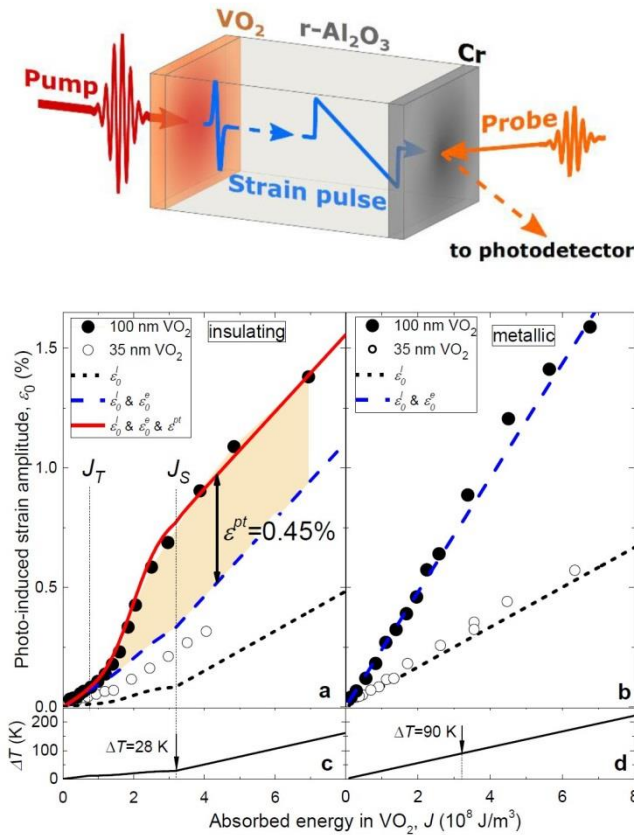


Figure 36: Strain generated in VO_2 transducers as a function of the energy deposited into transducers by laser pulses.

Strain magnitude ϵ_0 vs. the absorbed energy of the excitation laser pulses J , when the VO_2 film, initially in insulating (a) or metallic (b) phases, is excited. Data (symbols) are obtained from the experimental dependencies (Figs. 2c,d) and the calibration curves (Fig.1e) for the 35 nm (open symbols) and 100 nm (closed symbols) VO_2 transducers. Gray shaded areas in the panels a,b indicate the uncertainty ranges originating from the uncertainty in the calibration curves (Fig. 1e). The relation between the absorbed volume density J and incident fluence W is obtained from the reflection and transmission measurements performed under the corresponding experimental conditions [SOM]. Lines show results of calculations of the photo-generated strain using Eq.(3), under the assumption of only thermoelastic contribution ϵ^t (dotted black lines), thermoelastic and electronic contributions ϵ^t & ϵ^e (dashed blue lines), and all contributions (solid red line), including that from PIPT ϵ^{pt} (shaded area in a). Lower panels show calculated temperature increase in the 100 nm VO_2 film when excited in insulating (c) or metallic (d) phases. [16]

3.10 Super-resolution in diffractive imaging

We have developed a new experimental technique to study morphology of electronic materials, vanadium oxides, plasmonic structures and photonic crystals. Here the angle-resolved hemispherical elastic light scattering technique has been used to reconstruct the surface profile with submicron resolution and metrological precision [9]. Iterative algorithms permit subsequent calculation of a surface autocorrelation function with additional numerical approximation of the power spectrum and then yield final reconstruction of the surface shape. The estimation of higher harmonics in the power spectrum provides the reconstruction of a realistic surface achieving sub-wavelength resolution.

We have resolved very complex experimental problem of light scattering phase reconstruction for the case when the object of interest is superimposed onto a statistically random surface relief, which produces an unwanted scattering background. The proposed method enables filtering out unwanted scattering background, precluding the convergence of phase-retrieval algorithms. Figure 37 shows the steps to filter-out the diffuse scattering component for 2D photonic crystal and to calculate correct autocorrelation function (ACF) of the surface. The consecutive filtering of BSDF scattering function is shown in Figs. 37(a,b,d,e,g,h,j,k). The corresponding ACF function computed by Fourier transform of BSDF data is shown in Figs. 37(c, f, i, l). The algorithm is described in Ref.[9].

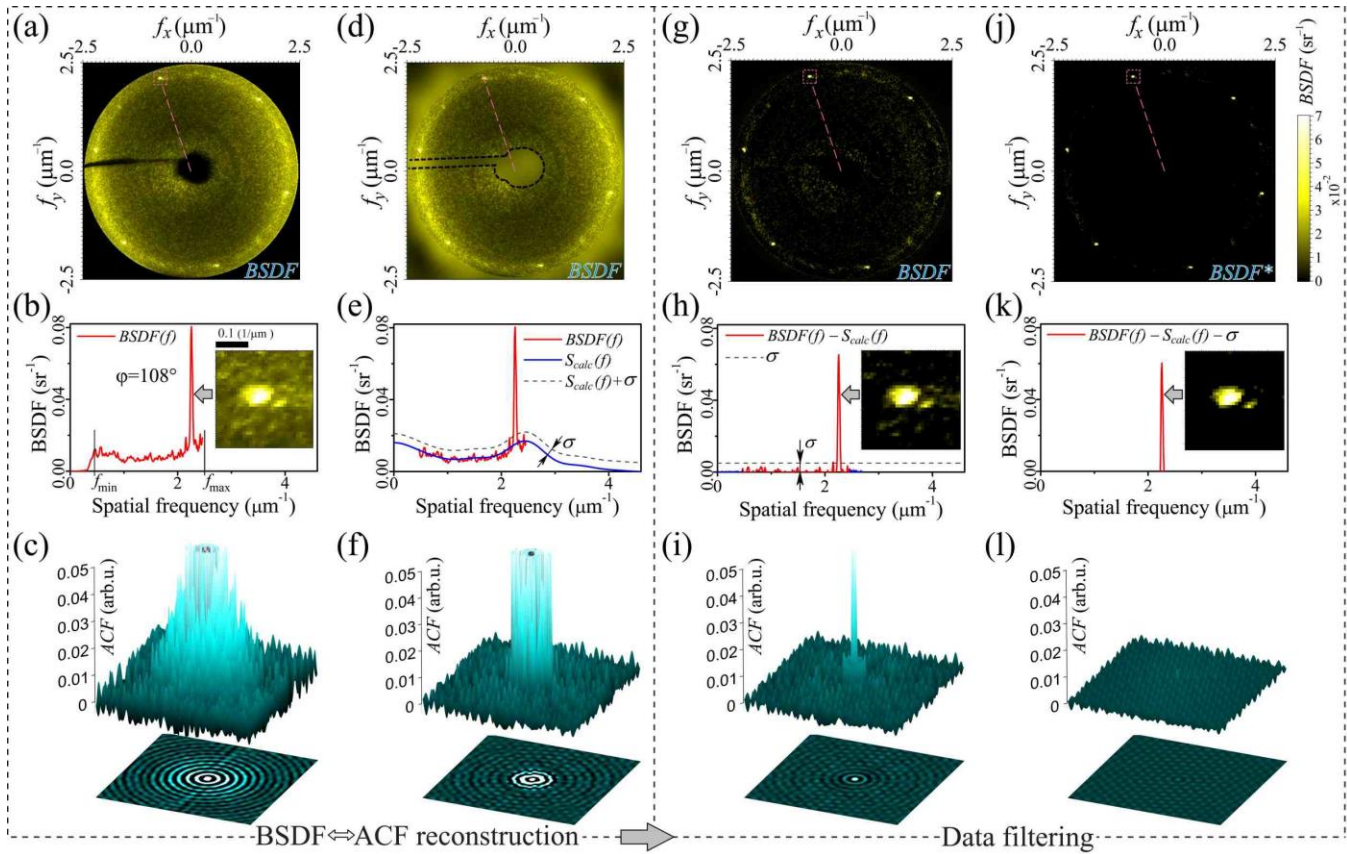


Figure 37: (a) BSDF as measured by light scatterometer versus spatial frequencies f_x and f_y for x and y Cartesian coordinate directions of the surface. (d) $S(f)$: BSDF with low-resolution approximation $S_{calc}(f)$. (g) Filtered BSDF with residual noise level σ . (j) Filtered BSDF without residual noise level σ . Dashed lines in BSDF indicatrices identify cross-sections shown in (b), (e), (h), (k). Insets in (b), (h), (k) show the structure of the single diffraction peak in BSDF indicatrix. (c), (f), (i), (l): the $4 \times 4 \mu\text{m}^2$ ACF images computed by applying inverse Fourier transform to BSDF data shown in (a), (d), (g), (j), correspondingly.

The quality of reconstructed topography h can be significantly improved by applying some predictions for distribution of power spectral density (PSD) function, achieving super-resolution. For 2D plasmonic crystal formed by gold nanopillars [Figs. 38(a) and 38(b)] we calculated the filtered power spectral density function PSD^* , as shown in Fig. 38(c). Using these data in the phase-retrieval algorithm, we obtained the surface topography h [Fig. 38(f)]. In order to achieve a super-resolution we reconstructed surface topography h from extrapolated PSD^* data into $f_{\max} < f < 2f_{\max}$ and $2f_{\max} < f < 3f_{\max}$ regions [Figs. 38(d) and 38(e)], as shown in Figs. 38(g) and 38(h), respectively. Achieved super-resolution in topography function h shows fairly close proximity to the topography h_{AFM} obtained by AFM [Figs. 38(a) and 38(b)].

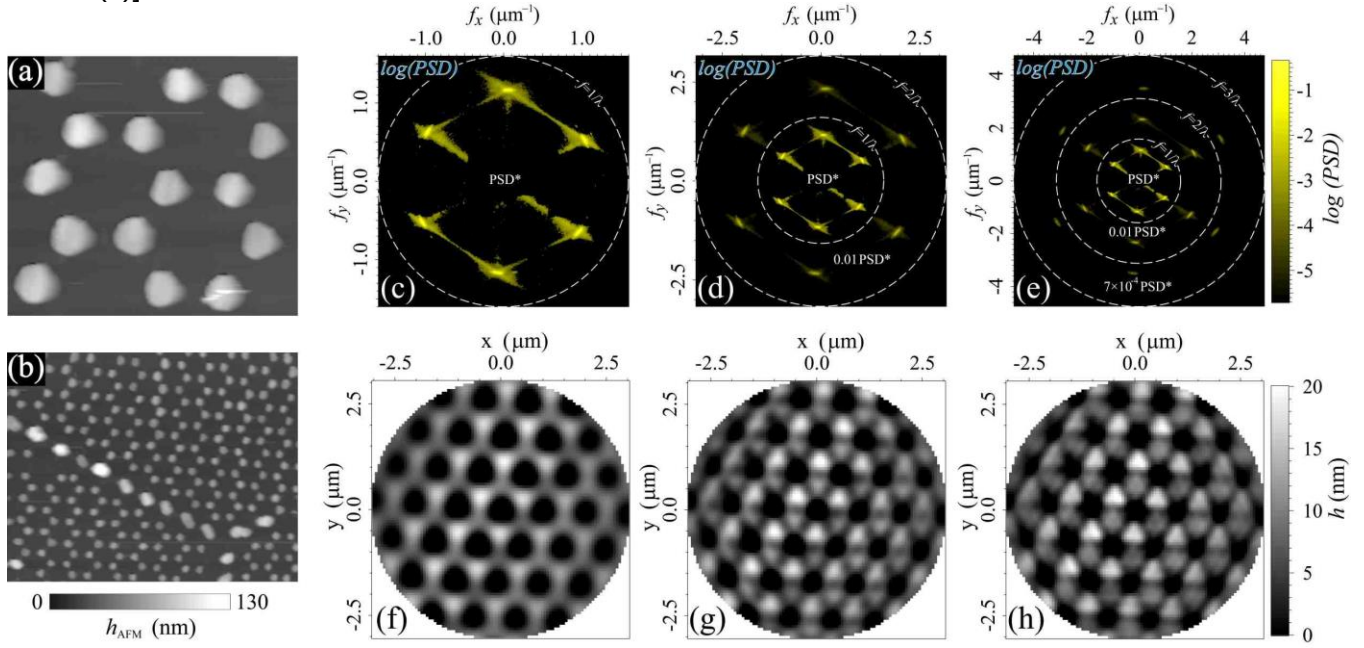


Figure 38: AFM images of 2D plasmonic crystal: (a) $2.7 \times 2.4 \mu\text{m}^2$ scan, (b) $12.3 \times 9.6 \mu\text{m}^2$ scan. (c) Filtered PSD^* as obtained from angle-resolved light scattering data. (d) PSD^* with reconstructed part at $f_{\max} < f < 2f_{\max}$ and (e) at $2f_{\max} < f < 3f_{\max}$. The correspondingly reconstructed surface topographies h are shown in (f), (g), (h).

3.11 Parallel GPU computing in light scattering metrology of ultrafast surface dynamics

Time- and angle-resolved hemispherical elastic light scattering measurements were performed to study surface dynamics of VO_2 , V_2O_3 and V_3O_5 upon photoinduced insulator-metal phase transition. The imaging of ultrafast optical diffraction by *tr*-ARHELS technique provides statistical information about the evolution of surface irregularities of different sizes. The information on the correlation of the surface irregularities was obtained from the surface power spectral density (PSD) and autocorrelation function (ACF). However, the absence of experimental data for BSDF or PSD regions introduces significant artifacts in the calculation of ACF.

In order to overcome these limitations, we applied Gerchberg-Saxton error reduction (ER) and hybrid input-output (HIO) phase-retrieval iterative algorithms, which produce a robust and precise reconstruction of the ACF and PSD pair [12]. For this purpose we developed a parallel computing procedure written for graphics processing unit (GPU, NVIDIA Tesla K80) by using the parallel computing platform CUDA. For the analysis of scattering data, we use the scientific data analysis software “Igor Pro”. By applying the data transfer operation, the scattering data were linked with

external computational procedures written in C++. An important feature of the current implementation is the application of high-performance GPU CUDA computing, which increases the calculation speed by about 20 times. Here the “Igor Pro” software was used only for data visualization, while the main computations were performed in external procedures. As shown in Fig. 39, the synchronization of GPU CUDA computing with “Igor Pro” software was performed via XOP toolkit and a dynamic-link library DLL.

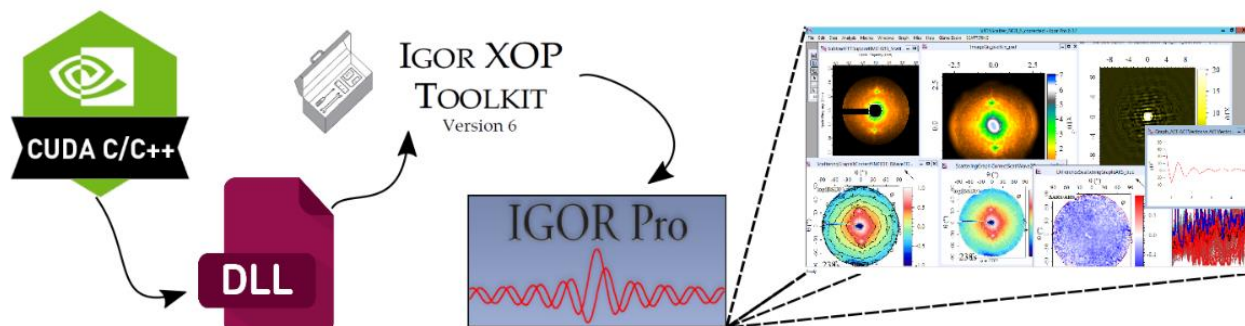


Figure 39: Interaction of GPU CUDA procedures with “Igor Pro” data analysis software. [12]

Figure 40 shows the main procedure for rigorous computation of ACF along with reconstruction of PSD within regions where the experimental data are absent. The scattering BSDF indicatrix obtained for photoexcited VO₂ was recalculated into PSD function by using Elson’s scattering theory. The region blocked by the sample holder was cut, and the obtained PSD* data were scaled and reoriented to PSD** indicatrix suitable for the Gerchberg-Saxton ER procedure. The ACF was calculated by using ER iterative algorithm. This algorithm implements the CUDA Fast Fourier Transform library (cuFFT) for parallel computing in the NVIDIA Tesla K80 card. A similar procedure was applied also to solve the inverse scattering problem for the reconstruction of VO₂ surface shape and phase of scattered light.

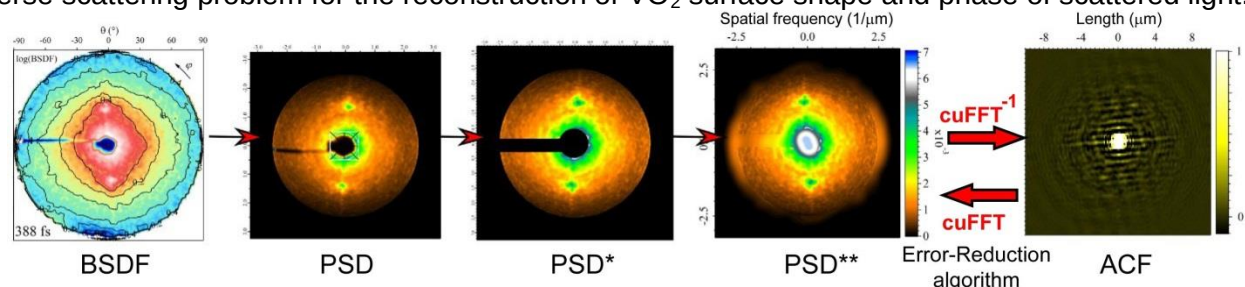


Figure 40: Computations of ACF along with partial reconstruction of PSD function for photoexcited VO₂ surface. [12]

In summary, the multiprocessing programming of GPU significantly speeds-up the reconstruction of PSD function and provides accurate calculations of ACF, allowing real-time numerical analysis of diffraction data.

3.12 Synthesis of vanadium oxides

VO₂, V₂O₃, V₆O₁₃

Figure 41 shows the XRD patterns for different vanadium oxides recently synthesized in the lab. XRD data for VO₂/SiO₂ [Fig.41(a)] is obtained at grazing incidence and shows several diffraction peaks all assigned to single M₁ phase, indicating pure stoichiometric VO₂. The PLD as well as DC sputtering protocols for VO₂ thin films synthesis are well established in our lab. We were able to synthesize also a set of epitaxial VO₂ films on single crystal Al₂O₃ (R-cut, A-cut, M-cut and C-cut substrates). Strong in-

plane orientation of VO_2 lattice of these films was very important to complete polarization-sensitive ultrafast light diffraction experiments.

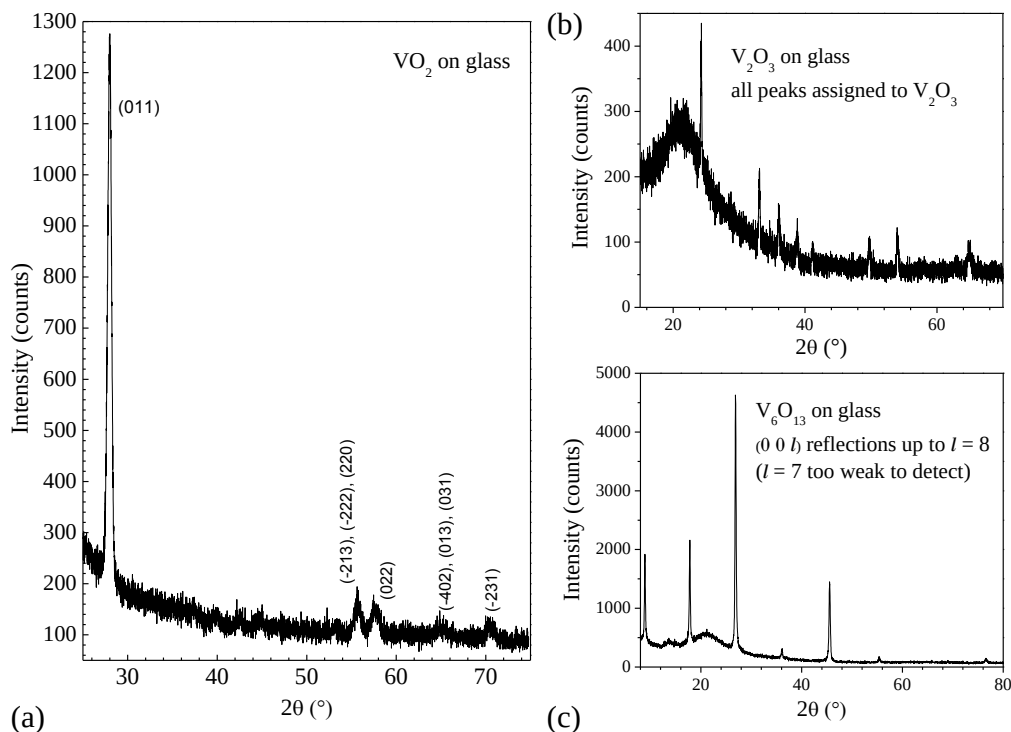


Figure 41: X-ray diffraction scans for vanadium oxides deposited on SiO_2 substrate. (a) VO_2 PLD film. Reflections for VO_2 are labeled according to Powder Diffraction File JCPDS 82-0661. (b) V_2O_3 film obtained by DC sputtering (c) V_6O_{13} PLD film. All XRD peaks for (a-c) can be assigned to pure stoichiometric vanadium oxide phases.

Along with VO_2 , a significant amount of work was aimed to develop new protocols to synthesize other oxides. During the first year of the project we made significant progress in synthesis of V_2O_3 , V_6O_{13} [Figs.41(b,c)] and VO_2 (B-phase). Several tens of epitaxial and non-epitaxial VO_2 , VO_2 (B-phase), V_2O_3 and V_6O_{13} thin films were prepared by PLD on single-crystal Al_2O_3 (R-cut, A-cut, M-cut and C-cut substrates), MgO , SrTiO_3 and also on amorphous SiO_2 substrates. Typical thickness of the films ranges from 30 nm to 300 nm.

VO_2 (B). Having a robust PLD technique to synthesize VO_2 films, we made a step forward towards synthesis of polymorphs, particularly VO_2 B-phase, which seems interesting from the point of view of applications. As a result, a new protocol for PLD process was developed to grow nearly pure B-phase VO_2 [1]. Thin films were grown on SiO_2 glass and (100)- MgO substrates. For samples grown on glass substrates strong (00 l) reflections for VO_2 (B) were observed, with l at least up to third order [Fig.42(a)]. Compared with reference powder diffraction reflections, all (00 l) peaks for samples on glass were shifted to higher angles, more so for higher order reflections, indicating *tensile strain* in the films. Figure 43(b) shows the XRD data for the VO_2 (B)/glass sample grown at the 425 $^\circ\text{C}$. The fact that only (00 l) reflections were present demonstrates that the films had very strong out-of-plane orientation with (001) planes parallel to the sample surface. These planes correspond to the VO_2 (B) layered structure. It is noted that although forces between these layers (actually, pairs of layers) are relatively weak, the responsible mechanism is not that of van der Waals type forces; instead, there are interlayer covalent bonds, but the bond density per unit area is small. As a result, this material can intercalate small ions (e.g, Li^+) between the bilayers.

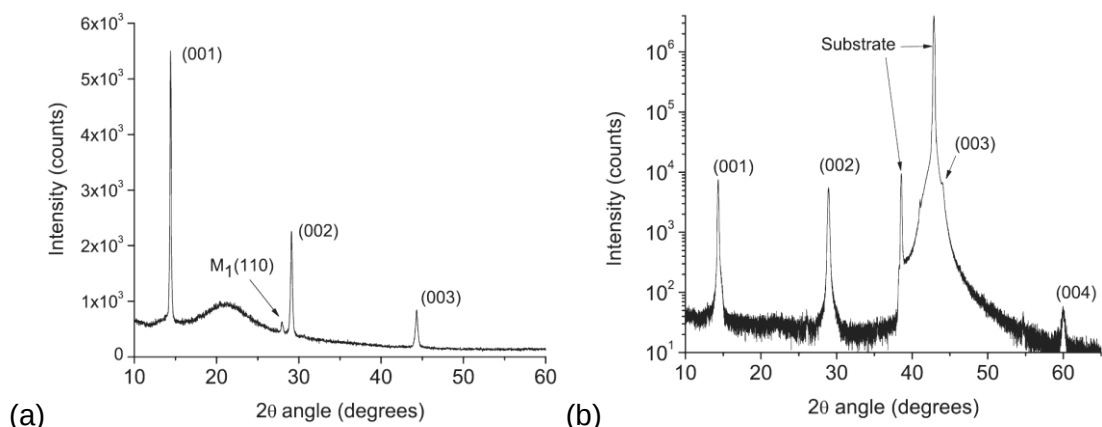


Figure 42: X-ray diffraction scan for (a) $\text{VO}_2(\text{B})$ sample deposited on glass at 425°C . Main reflections correspond to the B phase. (b) $\text{VO}_2(\text{B})$ sample deposited on (100)-MgO at 400°C . Reflections for $\text{VO}_2(\text{B})$ are labeled. Substrate peaks correspond to MgO (200) reflections for CuK_α and CuK_β radiation.

$\text{VO}_2(\text{B})$, which is monoclinic at room temperature, has a reversible transition to a lower temperature phase. Starting from near room temperature, the material undergoes a gradual transition to a different monoclinic structure. Previous work by other researchers has shown that the transformation is never complete and the fraction of the low temperature phase saturates at 70% below 150 K. Figure 43 shows the conductivity of $\text{VO}_2(\text{B})$ vs. inverse temperature for samples deposited on glass at 425°C and on MgO at 400°C . The most remarkable difference found with respect to the few published studies of electrical conduction for $\text{VO}_2(\text{B})$ films is the lack of detectable hysteresis observed in the present work for all samples grown on either glass or MgO substrates. This was repeatedly observed for all samples produced within the range of growth conditions we used. It is possible that the high defect density in the films reduces the energy barrier for the phase transformation. The "extended" and gradual nature of the transition between high-temperature and the low-temperature $\text{VO}_2(\text{B})$ phases already suggests that transformation energy must be distributed in some fashion over a very large temperature range (~ 150 K).

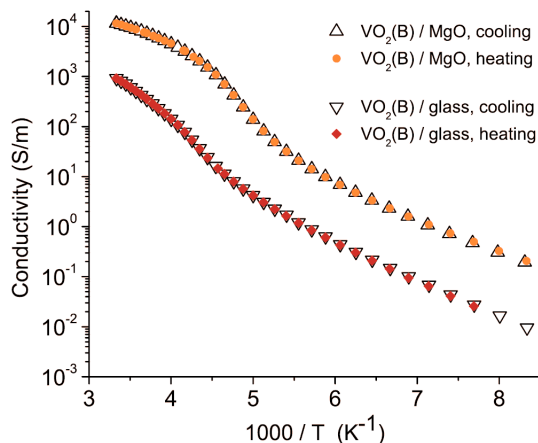


Figure 43: Conductivity (log scale) vs. inverse temperature for samples deposited on glass at 425°C (lower curves) and for sample deposited on (100) MgO at 400°C .

V_3O_5

We synthesized high quality V_3O_5 oxide films and performed the first ever experiment on light-induced I-M PT in this material [4,7,17]. V_3O_5 thin films were deposited on glass (SiO_2) substrates by reactive DC magnetron sputtering from a vanadium target, without subsequent annealing. The very narrow stoichiometric range of V_3O_5 makes this one of the least promising candidates for growth by reactive sputtering. However, with appropriate selection and control of growth conditions we have been able to deposit nearly pure phase as-grown V_3O_5 films, as confirmed by XRD measurements [Fig.44(a)]. In the figure, the lower curve is a standard θ - 2θ scan, which evidences, besides the V_3O_5 peaks, one single peak which may possibly be assigned to V_2O_3 . To verify this, the same sample was run in a fixed grazing-incidence angle ($\alpha = 4.4^\circ$) detector scan, since this technique allows detection of reflections

corresponding to lattice planes which may not be parallel to the sample plane. The result is shown in the upper curve in Fig.44(a), where three V_2O_3 peaks are indicated. These correspond to the strongest V_2O_3 reflections, and confirm that the other phase present in the film, aside from V_3O_5 , is indeed V_2O_3 . This result is not surprising, since V_2O_3 is just next to V_3O_5 in the V-O phase diagram. It shows, however, that the V_3O_5 film is slightly oxygen-deficient, and points to the small changes in growth conditions we will need to make in order to approach pure-phase V_3O_5 later on.

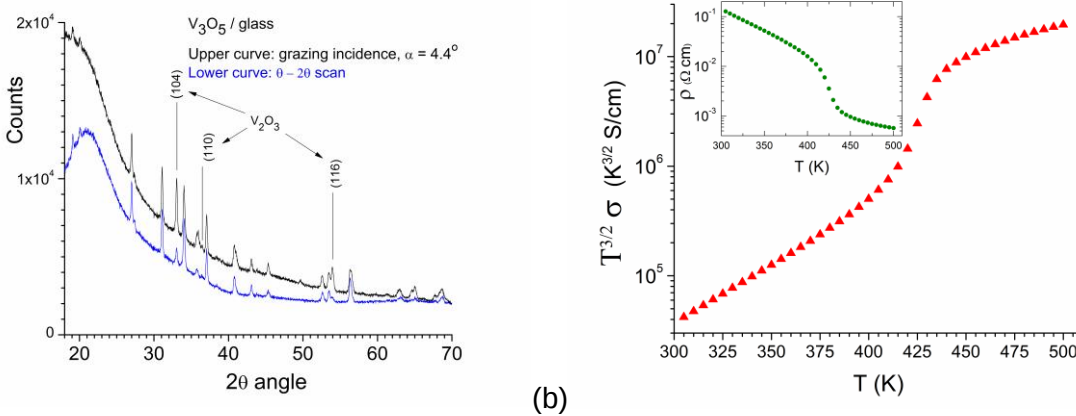


Figure 44: (a) XRD scans for 240 nm thick sample deposited on glass. Lower graph is for a θ - 2θ scan. Upper graph is for 2θ scan taken at a fixed grazing incidence angle ($\alpha = 4.4^\circ$). All peaks can be assigned to V_3O_5 except for the three indicated ones, which are assigned to V_2O_3 . (b). Inset: Resistivity (log scale) vs. temperature for V_3O_5 thin film; note phase transition near $T \sim 425$ K. Main graph: Product of conductivity $\times T^{3/2}$ (log scale) vs. T ; note linearity for $T < 400$ K.

V_3O_5 sample resistivity was measured from room temperature to 500 K, using a 4-point van der Pauw configuration. The result is shown in the inset of Fig.44(b). No hysteresis was observed between heating and cooling branches of the cycle, so only the heating branch is presented. Lack of observable hysteresis is consistent with some of the previous results for V_3O_5 single crystals. The transition region is broad, extending from ~ 395 K to ~ 455 K. For temperatures above $T \sim 460$ K the conduction data is linear in an Arrhenius plot and activation energy of 0.17 eV was determined. The main graph in Fig.44(b) shows the product $T^{3/2} \times \sigma$ (in a logarithmic scale) as a function of temperature. From room temperature up to ~ 40 degrees less than the phase transition this curve is linear, and is a better fit than either an Arrhenius plot or a $\log \sigma$ vs. T plot. Data analysis in [7] shows that the concept of *small polaron* is applicable to describe V_3O_5 conductivity in the sub- T_c range.

V₂O₃

Synthesis of V₂O₃ thin films with reproducible metal-insulator transition characteristics. We performed systematic studies on synthesis of V₂O₃ thin films with reproducible optical, electronic and structural characteristics near the critical point [13]. We developed a new synthesis protocol for reactive DC magnetron sputtering with posterior thermal treatment under reducing conditions. The thermal treatment is a key process which corrects the composition of V₂O₃ thin films without causing extensive morphological changes. The resulting films consistently show a 5 order of magnitude change through the MIT, with transition temperature essentially equal to the bulk value and repeatable characteristics for different samples. Fabrication via DC sputtering ensures also compatibility with standard large-scale industrial processing. As can be observed in Fig. 45, small shifts in x-ray diffraction peak positions were positive or negative with respect to the PDF reference, evidencing anisotropic distortion of the unit cells.

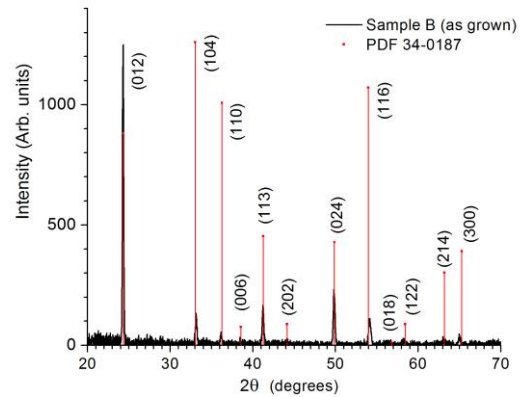


Figure 45: XRD θ - 2θ scan for sample B (as-deposited), along with PDF reference pattern for V₂O₃. Intensities of the reference have been normalized to the maximum observed intensity, that of (012) reflection

Resistivities were measured for the three samples before and after annealing, using a 4-point van der Pauw configuration, from room temperature down the lowest possible temperatures before sample resistance becomes too high to allow accurate results (Fig. 46). For the high-temperature phase (corundum structure), from room temperature to the onset of the metal-insulator transition (MIT), by ~ 175 to 165 K, measured resistivities have values $\sim 10^{-3} \Omega \cdot \text{cm}$, are almost constant at temperatures near 300 K, and increase slightly with decreasing temperatures. That is, conduction cannot be typified as metallic.

For films deposited under nominally identical conditions significant differences were found in terms of transition temperature and width of hysteresis loops. Naturally, the effect of stress can shift the transition temperature in each “as-deposited” case (Fig. 46). Nevertheless, it is most likely that small variations of oxygen partial pressure and vanadium deposition rate were the main factors responsible for the differences observed. However, after thermal treatment of the three samples, the new resistivity curves have all shifted up to higher values, but they still exhibit a five order of magnitude

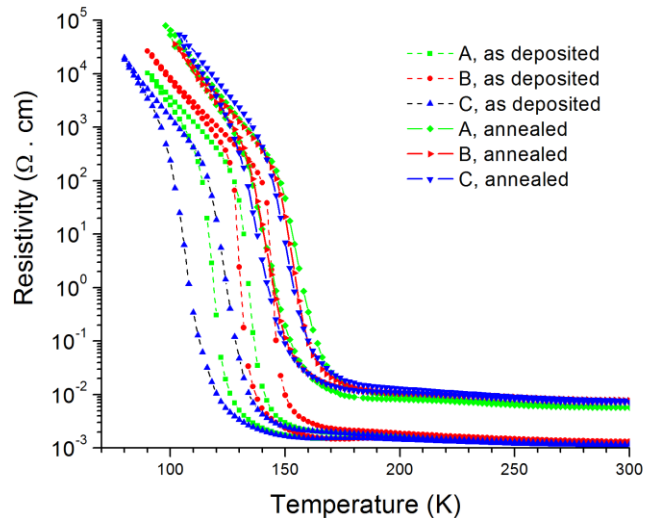


Figure 46: . Resistivity as a function of temperature for samples A, B, and C, before and after annealing.

increase through the phase transition. The most remarkable change observed with respect to the “as-deposited” samples is that transition regions have all shifted to higher temperatures and are now all nearly, although not exactly, coincident.

The resulting films are under high tensile stress and are not expected to be fully stoichiometric, but despite this do exhibit characteristics similar to those of bulk crystals in terms of T_c value and hysteresis width. Our group is currently extending this work to Cr-doped V_2O_3 , which is particularly interesting because of the possibility of tailoring the phase transition temperatures and bringing them closer to room temperature.

The procedure established for the V_2O_3 films is entirely compatible with standard thin film processing techniques allowing fast growth rates, no need for ultra-high vacuum conditions, and reasonable temperatures and processing times for post-deposition annealing. With proper adjustment of annealing times, it is applicable to films of any required thickness. Since SiO_2 glass substrates were employed, the results are extensible to silicon-based technology. Work remains to be done in fully characterizing the effect of residual tensions and non-stoichiometry, but we expect that the results presented will increase interest in development of practical devices based on the remarkable properties of pure and doped V_2O_3 . Naturally, *mutatis mutandis*, the same approach is applicable to other vanadium oxides of high interest on account of their MIT characteristics.

V_4O_7 and V_6O_{14}

During the second year of the project we developed new DC magnetron sputtering protocol for synthesis of V_4O_7 and V_6O_{14} thin films. High-quality vanadium oxide film samples were grown on SiO_2 glass substrates by reactive DC magnetron sputtering from vanadium target with 99.95% purity in argon and oxygen atmosphere. Chamber background pressure was $\sim 1 \times 10^{-5}$ Torr and sputtering pressure was maintained at 2×10^{-2} Torr. Sputtering power was 300 W and target-substrate distance was 10 cm. With these conditions the vanadium target was kept in its “metallic” surface condition and the resulting deposition rate was 16 nm/min. Figure 47 shows XRD patterns of materials recently synthesized in our lab. The positions of diffraction peaks evidence a high-quality of vanadium oxide structures. Currently we are working on synthesis of these materials by PLD method in order to obtain high-quality thinner films suitable for ultrafast nonlinear optical measurements.

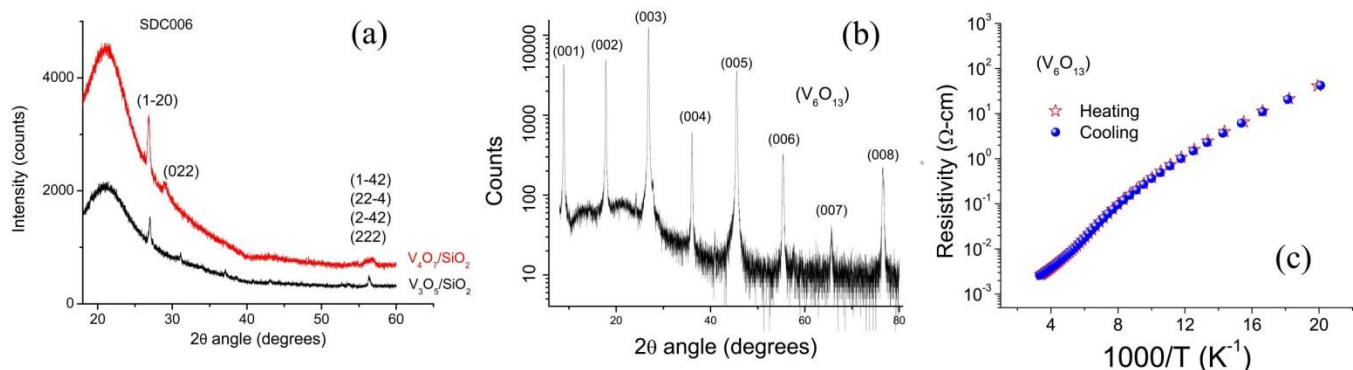


Figure 47: . (a) The XRD pattern of V_4O_7 and V_3O_5 thin films on SiO_2 substrate. (b) XRD pattern of V_6O_{13} on SiO_2 substrate (c) Resistivity of V_6O_{13} film as $1000/T$ function of sample temperature.

V_6O_{11}

During the third year of the project we developed a new DC magnetron sputtering protocol for synthesis of V_6O_{11} thin films. High-quality samples were grown on SiO_2 glass substrates by reactive DC magnetron sputtering from vanadium target with 99.95% purity in argon and oxygen atmosphere. Chamber background pressure was $\sim 1 \times 10^{-5}$ Torr and sputtering pressure was maintained at 1×10^{-2} Torr. Sputtering power was 150 W and target-substrate distance was 10 cm. Figure 48 shows XRD patterns of materials recently synthesized in our lab. Grazing incidence measurements and positions of diffraction peaks evidence a high-quality of vanadium oxide structures. Further characterization and studies of these samples are currently underway

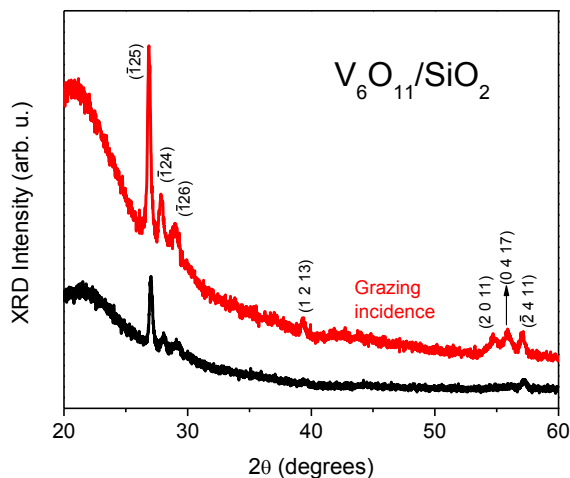


Figure 48: The XRD pattern of V_6O_{11} thin films on SiO_2 substrate.

4. Key outcomes or other achievements

4.1 Synthesis of vanadium oxides

Over one hundred high-quality epitaxial and non-epitaxial thin films of VO_2 , V_2O_3 , V_3O_5 , V_6O_{13} , V_4O_7 , V_6O_{14} and V_6O_{11} were synthesized. New deposition protocols to synthesize these complex oxides were developed for either PLD or DC magnetron sputtering techniques.

4.2 Experimental technique for the reconstruction of thermodynamic potential and pathways of ultrafast structural phase transition in photoexcited phase-change materials

PIs demonstrated, for the first time, how to reconstruct a free energy landscape (thermodynamic potential Φ of photoexcited VO_2) from experimental data. Our method enables straightforward reconstruction of the potential barrier between two phases of photoexcited material. This work has immense didactic value. Thus, we derived, for the first time, the equation for the potential barrier which separates different phases of material upon photoexcitation [5]:

$$\Delta G(F) = -\tilde{N}k_B T \ln[F/F_{max}]$$

PIs show the technique how to model ultrafast processes in VO_2 in terms of a phenomenological Ginzburg-Landau model. This model provides a reliable explanation of experimentally observed structural dynamics, where the phase trajectories depend on the excitation level. Developed theoretical approach gives clear explanation of VO_2 dynamics and, we believe, will provide significant impact on experimental study of other phase-change materials.

4.3 Novel optical technique to detect hidden, artificial or metastable transient structural phases: *Ultrafast Diffraction Conoscopy*

A novel ultrafast diffraction conoscopy (UDC) setup and measurement technique were developed and successfully tested using epitaxial VO_2 thin films as a test object. UDC setup allows visualizing and separating structural lattice dynamics from electronic dynamics of phase-change materials. This fully optical technique can be applied to detect hidden, artificial or metastable transient structural phases. Thus, by applying the UDC technique, it was discovered that the ultrafast structural phase transition in VO_2 passes via specific metastable state B_x and accompanied by two lattice distortions.

4.4 V_3O_5

We for the first time provide results on

- (1) ultrafast nonlinear pump-probe optical response of V_3O_5 material in its insulating phase.
- (2) ultrafast nonlinear optical dynamics of V_3O_5 material in its metallic phase.
- (3) photoinduced oscillations of the optical signal due to excitation of coherent phonons in V_3O_5 ;
- (4) evidence of light-induced insulator-to-metal phase transition in V_3O_5 .
- (5) Raman measurements of V_3O_5 across insulator-metal phase transition.
- (6) evidence that the observed behavior is indeed the *first-order* phase transition in V_3O_5 .
- (7) semi-classical calculation of the ultrafast molecular dynamics of V_3O_5 lattice within 6 ps. These calculations show remarkable coincidence with experimentally observed nonlinear relaxation of V_3O_5 .
- (8) quantum calculations of electronic band structure and density of states of V_3O_5 .

(9) quantum calculations of phonon band structure and density of states of V_3O_5 .

We have to underline that the V_3O_5 is a correlated oxide with very exotic and interesting physical properties. V_3O_5 shows metal-insulator phase transition above room temperature (similar to VO_2 but with $T_c \sim 425$ K) which makes V_3O_5 extremely promising for novel optoelectronic applications. In our work we show, for the first time, that the V_3O_5 is also very promising for *ultrafast* optoelectronic applications.

We confirmed in a series of measurements that this NLO dynamics is originated from light-induced insulator-to-metal phase transition in V_3O_5 . We found that the formation of the metallic phase occurs within ~ 1 ps, producing very strong nonlinearity of V_3O_5 : the signal of elastic light scattering changes within 10-15%. *These measurements are the first published measurements of nonlinear optical properties of V_3O_5 .*

Experimentally observed nonlinear optical dynamics was fully supported by the calculation of molecular dynamics of V_3O_5 lattice. The relaxation process of V_3O_5 shows several stages, interpreted as order-disorder structural transition triggered by photoinduced melting of polaronic Wigner crystal. We also show that in the metallic phase as well as in the highly excited insulating phase a photoacoustic strain produces coherent oscillations of the light scattering signal. Furthermore, in order to better understand electronic and optical properties of V_3O_5 , using density functional theory we calculated the band structure of V_3O_5 , which gives an energy band gap of $E_g = 0.91$ eV. These are the first-ever made calculations of band structure for V_3O_5 .

4.5 VO_2

(1) We presented fundamental experimental discovery (supported by our theoretical calculations) of different pathways in the photoinduced structural phase transition of VO_2 . We revealed critical contributions of optical and acoustical phonons, material morphology and strain on phase trajectories. Resulting dynamics strongly depends on the excitation level, film morphology, internal strain, and strain induced by the optical pulse.

(2) We showed a new approach to push ultrafast spectroscopy into a new direction. In this work, we apply a novel 4D light diffraction technique to observe size-dependent structural transitions on the mesoscale. This unique state-of-the-art technique was recently developed in our lab. This technique enabled us to reveal new very interesting mesoscale phase transition dynamics that had been never observed before. A comparison of experimental data with theoretical calculations shows a remarkable coincidence.

(3) Using ultrafast diffraction conoscopy we discovered a two-stage subpicosecond structural phase transition in VO_2 with the formation of an intermediate metastable state accompanied by two different lattice distortions.

(4) Performing *tr*-ARHELS measurements for epitaxial VO_2 films we discovered the influence of internal misfit strain on the initial phase and rate of light-induced I-M PT.

(5) Performing pump-probe transient transmission measurements we found evidence of photoacoustically-induced PT in photoexcited VO_2 on the nanosecond time scale.

(6) We obtained a significant amount of information about characteristic relaxation times of VO_2 for different time scales versus pump power. This information allowed us to reconstruct quantitatively the thermodynamic potential of VO_2 lattice.

(7) We for the first time successfully applied phenomenological Ginzburg–Landau theory to model the pathways of the *first-order insulator-to-metal phase transition in the femtosecond regime* in vanadium dioxide. This model was developed using recently obtained key information about critical parameters (pump power, relaxation time, surface morphology, strain and concentration of structural defects) that control the light-induced phase transition in VO_2 .

(8) Semiclassical computation of molecular dynamics for VO_2 reveals significant instability of the monoclinic phase in the absence of electron-electron correlations.

(9) It was shown that the internal misfit strain in epitaxial film noticeably alters the rate of phase transition within ~ 500 fs. For epitaxial films with the anisotropic strain, the phase transition rate depends on the size and in-plane orientation of VO_2 grains/domains. This evidences that the strain alters the potential energy landscape of photoexcited VO_2 and, as a result, changes the phase trajectory of ultrafast structural dynamics.

(10) First measurements on photoinduced SPP dynamics in VO_2/Au multilayer structures are performed. Excitation of surface plasmons results in a very complex NLO response of the VO_2/Au material.

4.6 V_2O_3

(1) It was shown that the ultrafast optical excitation results in an instantaneous change of V_2O_3 optical properties within ~ 500 fs. However, an optical response associated with paramagnetic metal to paramagnetic insulator phase transition induced by photoacoustic strain was observed on the picosecond time scale.

(2) The evolution of scattering the signal reveals coherent oscillations of material optical properties.

(3) The scattering experiments herein demonstrate a key feature of V_2O_3 which nonlinear optical dynamics significantly depends upon the size of film microstructures. A pronounced characteristic size-dependence in scattering response was resolved.

(4) No noticeable variation in the conoscopy patterns has been detected from V_2O_3 , indicating no structural phase transition.

4.7 Ultrafast spectroscopy of SPPs

We for the first time provide results on:

(1) All-optical (light-induced), thermal and non-thermal control of SPP dynamics in thin photorefractive bilayer structure in ATR geometry.

(2) Ultrafast manipulation of SPP dynamics at the Au/VO_2 interface (in a sophisticated femtosecond pump-probe spectroscopy experiment).

(3) Angle-resolved polar diagrams of SPP scattering from the photorefractive plasmonic system;

(4) The SPP scattering from photorefractive plasmonic structure, which is very different from ordinary volume wave scattering. We show that it is controlled by several competitive factors: by SPP

enhancement, SPP propagation length, variable surface roughness, and variable VO₂ optical constants.

(5) The estimation of the SPP propagation length and its influence on SPP scattering in Au/VO₂.

(6) Numerical fitting of reflection in ATR geometry and extraction of Au and VO₂ optical constants for photorefractive Au/VO₂ plasmonic system.

4.8 DFWM process with excitation of SPP and volume waves

We for the first time provide results on:

(1) The ultrafast formation of the transient grating in the VO₂ layer. This process is accompanied by nonlinear wave interaction with SPPs excited by the ATR coupler at the VO₂/Au interface.

(2) Optical DFWM of SPPs and volume waves with the same and different linear polarizations. This gives rise to surface plasmon waves by inducing a nonlinear polarization.

(3) Decoupling of SPPs from the surface and to convert SPPs to volume optical waves, which were then directly detected by a photodetector.

4.9 Ultrafast strain engineering in phase-change materials

Key outcomes:

(1) We for the first time provide results on pioneering experimental demonstration of ultrafast insulator-to-metal and structural transition under the combined action of femtosecond optical and picoseconds strain pulses.

(2) We show that a picosecond photoacoustic strain pulse injected into epitaxial VO₂ film assists or suppresses the optically-driven ultrafast phase transition depending on the sign of the strain present in the nanostructure at the moment of optical excitation.

(3) Only the transient strain during the optical excitation affects the efficiency of the phase transition.

(4) The phenomenological model developed by our group for the first-order light-induced structural phase transition in a single domain of VO₂ was employed to unambiguously explain experimental results.

The broader impact:

(5) Simultaneous excitation of phase transition with picosecond strain pulses is a novel technique which creates a new paradigm in strain engineering of phase transitions.

(6) It advances the established field of strain engineering into the field of ultrafast effects on picosecond time scales.

(7) This work covers the interest of several wide research communities working on strain-related phenomena, ultrafast electronic, structural and spin kinetics, phase transitions, and nanotechnologies.

4.10 Super-resolution in diffractive imaging

(1) New approach to numerical analysis of 3D light diffraction data allows obtaining a super-resolution of submicron objects.

(2) Metrological precision, submicron and subwavelength resolution were achieved by applying phase-retrieval algorithms and filtering of noisy experimental data which contains significant amount of diffuse scattering.

(3) Proposed technique is very promising for the monitoring of ultrafast photoinduced surface dynamics, where all scattered field can be recorded in single optical shot. Sophisticated but robust methods of diffractive imaging can be very useful for modern optics and condensed matter physics.

4.11 Parallel GPU computing of ACF for ultrafast scattering metrology of surface dynamics

The new method for rigorous parallel GPU computing (for NVIDIA Tesla K80) of ACF was developed for light scattering metrology of ultrafast surface dynamics.

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