

Nanoscale charge heterogeneity and chaotic resistive switching in VO₂-based Mott memristors



Thesis submitted in the partial fulfillment for the
Award of Degree

Doctor of Philosophy

By

Pawan Kumar Ojha

SCHOOL OF MATERIALS SCIENCE & TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI - 221005
INDIA

Roll No. 18111503

2024

Chapter 6

Conclusion and Future Plan

6.1 Results and Conclusions

A common resource material V_2O_5 is refined, $\frac{1}{2}V_2O_5 \rightarrow VO_2 + \frac{1}{4}O_2\uparrow$, that dispersed at a molecular scale in nanocolloids using poly(vinyl pyrrolidone) (PVP) in water, which is then uniformly coated at a substrate as thin VO_2 films. A nanogate SiO_2/TiO_2 is inbuilt to tune the interface VO_2 bonding, crystal structure, and functional properties. It is a simple user-friendly process to make quality controlled VO_2 films at a controlled thickness, $t \leq 100$ nm. The PVP - a biocompatible polymer serves as (i) a dispersoid to refine and finely disperse VO_2 at a molecular scale, (ii) a molecular template at the M_1 - VO_2 phase (a semiconductor) bind over in dimer chains, and (iii) a film former to cross-links the M_1 - VO_2 in a uniaxial (011) structure. As a dried hydrogel is duly annealed (in argon), the inbuilt M_1 - VO_2 is scaled up as nanoplates (single crystals) of an average size 15-40 nm is well-controlled at the interfaces. Fewer elongated shapes, ≤ 15 %, are built up on the nanoplates (seeds).

In **chapter 3**, we investigate the temperature induced phase transition in a nanostructured VO_2 thin film of M_1 - VO_2 with wide variations in sample morphology using thermal, Raman spectroscopy and I-V curve measurements. The experimental findings suggest that lowering the energy barrier between M_1 and R phases promote the growth of spatially inhomogeneous phases. The optical phase transition proceeds as described by Raman spectroscopy, with a transition from M_1 through some intermediate phase to R with a

characteristic time scale. Despite the variations in sample morphology, the simulated dependences indicate that variable sizes for charge puddles size between the phases are universally present in VO₂ samples. Thus, the metallic phase and optical switching that exploits this phase transition may be limited to switching behaviours independent of VO₂ morphology. Spatially inhomogeneous mixed-phase presence is manifested, which causes modulation in scattering cross-section that further explains the significant temperature shifts during optical transitions.

In **chapter 4**, we highlight a low-field memristor device is made from the VO₂ films to operate it in an ON/OFF switching mode in a prototype two-terminal device. The roles of a nanogate SiO₂/TiO₂ in charge transfer in the VO₂@(100) Si(*p*⁺⁺) films is studied in which a high-*k* TiO₂ efficiently controls and regulates field-induced output in a reversible I-V loop (current-voltage). In a low field 0 ↔ 5 V swipe, a threshold voltage as small as $V_t = 0.12$ V is achieved in a sharp peak. At wider swiping fields, such as 0 → 10, 20, and 30 V, it is shifted successively at 0.25, 0.50, or 0.74 V, in the field-induced charges order across the gate. An ion exchange, $V^{4+} \rightarrow V^{5+} + e^-$, in a pool, leads to streamline conduction in ‘conductive through channels’ in the itinerant $M_1 \rightarrow M_2/R_1/R$ -VO₂ metallic states. Thus, a smaller V_t lasts than ever reported before at low field, ≤ 1.0 V, devices; especially fast ON/OFF switches, logic gates, informatics, neurology, and many others. The results have a wide scope of developing the charge dynamics as well as the technology of VO₂-type metal oxide semiconductors.

In **chapter 5**, we describe that the nanostructured VO₂ of thin film (thickness $t \leq 100$ nm) executes a reversible transition of its structure and semiconductor to metallic states at a critical temperature $T_c \sim 343$ K. That is utilized to exchange energy in integrated electronics, optical memory, neuromorphic computing, and many other devices. Extensive studies are made on harvesting the T_c and emerging properties useful for the

applications. In fact, a series of $M_1 \rightarrow M_2/R_1/R_2/R\text{-VO}_2$ phases mediate the exotic features that are studied systematically in this chapter in terms of their impedance resistance R_o regulated at frequencies. The individual phases are shown to order at correlated charge order (metallizing) without a phase separation at VO_2 nanocrystals embedding in the films, as heated 303 K to 473 K at 10^2 Hz to 10^6 Hz frequencies. The frequency deprives coupled electron-phonon ‘e-p’ states and induce $3d^1\text{-V}^{4+}$ electrons (coupled to the holes ‘h⁺’ in the VB) filling up (metallizing) the bandgap across the Fermi surface. Thus, even near room temperature, a surface order $M_1 \rightarrow M_2/R_1/R_2/R\text{-VO}_2$ incurs over 10^2 to 10^6 Hz frequencies, respectively. The $R_1/R_2\text{-VO}_2$ (semi-metallics) extend well beyond T_c at the charge order prolongs at the metallic $R\text{-VO}_2$ states, well up to 473 K (or even more), over a frequency scale. All the five VO_2 phases are well mapped in MIR field s-SNOM images of the VO_2 films. The results anticipate a kinetic response of the T_c point at decoupled $3d^1$ electrons (orbitals) so that it is regularly shifted from 343 K at THz (5-10 meV) to 353 K at MIR (125 meV) fields used in the s-SNOM imaging at a nanoscale. Consistently, it is blue-shifted in the frequency modulated R_o (up to 10^5 times) as well at the charge order. The correlated phase-charge order delineates the strategy of exotic properties of thin VO_2 film technologies.

6.2 Future Scope of the Work

In the dazzling realm of technological innovation, the future scope of VO_2 is very, promising a symphony of transformative possibilities. Picture a world where windows are not mere panes of glass but gateways to adaptive environments, seamlessly transitioning between transparency and opaqueness at the whim of temperature fluctuations. VO_2 , with its enchanting ability to undergo a phase transition at a specific temperature, is poised to revolutionize smart materials and usher in an era of responsive

architecture. Imagine buildings that dynamically regulate their thermal properties, effortlessly adapting to the ever-changing climate, reducing energy consumption, and enhancing comfort. The future holds the promise of VO₂ unlocking unprecedented advancements in fields ranging from smart windows to energy-efficient structures, painting a mesmerizing portrait of a world where inanimate materials dance to the rhythm of technological ingenuity.

Embark on a journey into the uncharted territories of electronic and neuromorphic computing, where the future scope of vanadium dioxide transcends the boundaries of imagination. Envision a cybernetic landscape where traditional silicon-based processors yield to the mesmerizing allure of VO₂ unique properties. In this fantastical realm, the chameleon-like nature of VO₂, shifting between semiconductor and conductor states with temperature variations, becomes the cornerstone of a new era in computing. Picture neuromorphic devices that mimic the adaptive brilliance of the human brain, forging synaptic connections with unparalleled efficiency and speed. VO₂ emerges as the virtuoso conductor of this symphony, orchestrating a dazzling performance of cognitive computing, learning, and memory storage. As we navigate this electronic dreamscape, the future promises a tapestry of computational marvels, where VO₂ not only reshapes the landscape of traditional computing but also unveils a universe where machines possess an eerily human-like intelligence.
