Physical origins of current and temperature-controlled negative differential resistances in NbO$_2$

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Negative differential resistance behavior in oxide memristors, especially those using NbO$_2$, is gaining renewed interest because of its potential utility in neuromorphic computing. However, there has been a decade-long controversy over whether the negative differential resistance is caused by a relatively low-temperature non-linear transport mechanism or a high-temperature Mott transition. Resolving this issue will enable consistent and robust predictive modeling of this phenomenon for different applications. Here we examine NbO$_2$ memristors that exhibit both a current-controlled and a temperature-controlled negative differential resistance. Through thermal and chemical spectromicroscopy and numerical simulations, we confirm that the former is caused by a ~400 K non-linear-transport-driven instability and the latter is caused by the ~1000 K Mott metal-insulator transition, for which the thermal conductance counter-intuitively decreases in the metallic state relative to the insulating state.
negative differential resistance (NDR) in NbO$_2$ is a manifestation of local activity that underlies threshold switching, generation of an action potential (in a neuristor), self-oscillations, and chaotic behavior, which are all being intensely researched for potential applications in neuromorphic or non-Boolean computing$^{1-9}$. However, for several decades, there has been a controversy on whether the NDR is caused by a low-temperature (usually <500 K) non-linear-transport-driven thermal instability$^{4, 16-18}$, or a high-temperature Mott metal-insulator transition (MIT)$^{1, 5, 13-17}$. This issue is crucial for development of compact predictive models to study behaviors of larger computational systems constructed with NDR elements. Although accurate modeling of the low-current behavior consisting of the current-controlled NDR has been achieved recently$^{4, 5, 11, 12}$, a direct physicochemical measurement of the material temperature and localization effects during different NDR events have not been reported.

Here we examine nano and microscale NbO$_2$ memristors that exhibit both a current-controlled and a less frequently observed temperature-controlled NDR. Through in operando thermoreflectance, in operando synchrotron X-ray transmission spectromicroscopy, transmission electron microscopy, and numerical simulations, we confirm that the current-controlled NDR is caused by a ~400 K non-linear Poole–Frenkel-transport-driven instability and the temperature-controlled NDR is caused by the ~1000 K Mott MIT. We highlight that temperature is the state variable for both types of NDRs, whereas they are driven by completely different physical mechanisms and occur at very different temperatures. We also show that the temperature and current density are spatially uniform over the memristor area through both NDRs when using a current source, whereas there is localized conduction channel/filament-formation when the memristor is biased in an unstable regime with a voltage source, recalling a long-standing and debated hypothesis$^{18, 19}$.

Results

Fabrication and transmission electron microscopy. We fabricated nanometer-scale NbO$_2$ devices using a sub-100 nm diameter metallic TiN plug to contact a blanket thin film of amorphous NbO$_2$ (Fig. 1a, b), the construction of which is described elsewhere (“Methods” section and Supplementary Figs. 2–4)$^{11}$. The repeatable current–voltage curve (Fig. 1c) obtained by sweeping the applied current exhibits a region of current-controlled NDR (“NDR-1”), wherein the curve is single-valued for any value of current, and has been routinely observed in NbO$_2$ before$^{1, 4, 5, 11, 18}$. However, at higher currents, this was followed by a rectangular hysteretic region consisting of a pair of sharp NDRs (“NDR-2”), which is neither current-controlled nor voltage-controlled. Current–voltage curves similar to the rectangular hysteresis have been observed in VO$_2$ before and attributed to a Joule-heating-driven Mott MIT$^{25}$. By studying the electron diffraction patterns of the initially amorphous active NbO$_2$ layer across multiple devices, we observed irreversible crystallization only in devices that had been subject to current levels beyond those required to trigger NDR-2 (Fig. 1d). Since crystallization occurs at temperatures$^{21, 22}$ in the range 800–1100 K, this observation suggests that NDR-2 is related to the MIT$^{23, 24}$ ($T_{\text{MIT}}$ is in the range of 1000–1100 K). Thus, NDR-1 was observed in both amorphous and crystalline NbO$_2$, while NDR-2 was observed only in crystalline NbO$_2$ (Supplementary Fig. 10).

Temperature mapping using thermoreflectance. In order to directly map the NbO$_2$ temperature throughout the range of current–voltage operation, we employed in operando synchronous time-multiplexed pump-probe thermoreflectance with a spatial resolution of 290 nm (using incident light of wavelength 530 nm, Fig. 2a)$^{25}$. While the nanometer-scale devices described above were suitable for transmission electron microscopy measurements, we required different structures for the thermoreflectance and synchrotron X-ray measurements. For these, we fabricated 2.0 × 2.5 µm crosspoint devices on 150-nm-thick silicon nitride membranes suspended over holes etched into a silicon substrate, with a material stack consisting of Pt (15 nm) (bottom electrode)/NbO$_2$ (15 nm)/TiN (10 nm) (top contact)/Pt (15 nm) (top electrode). These devices exhibited similar quasi-static electronic behavior to the nanometer-scale devices examined previously when driven with a current source$^{26}$, but there was only a single pinched hysteresis loop that encompassed both NDR-1 and NDR-2 when the device was driven with a voltage source (Supplementary Fig. 1). The thermal isolation of the structure resulted in insignificant temperature gradients normal to the membrane/device surface during the Joule heating due to the electrical operation of the devices, thereby enabling the thermoreflectance measurements on the device stack (of thickness...
<50 nm) to accurately represent the temperature of the active NbO2 layer (Supplementary Notes 1 and 2, Supplementary Figs. 6 and 7). The temperature maps (Fig. 2b) and the corresponding average temperatures within the crosspoint area (Fig. 2c) at different current levels (obtained using a current sweep) are shown. The black dashed lines would occur upon a parametric temperature sweep. Black arrows indicate hysteresis and temperature jumps predicted by the model. Pink solid line-segment indicates an abrupt jump in current that would occur upon a parametric temperature sweep. Green dashed-line-segment is an abrupt jump in the current-voltage curve upon a parametric temperature sweep. Black dashed lines in e, c, are used to indicate the temperature at the onset of the two regions of negative differential resistances (NDRs), namely, NDR-1 and NDR-2.

While these estimates are obtained by crude simplifications of the values and functional forms of \( R_{th} \) and \( C_{th} \), they nonetheless agreed well with experimental data and provide a good starting point for further detailed modeling.

Numerical modeling. To model the experimentally observed quasi-static current-voltage behavior, we adapt and extend a recently proposed modified three-dimensional Poole-Frenkel conduction mechanism with temperature as the state variable, represented by Eq. 2.

\[
\frac{dT}{dt} = \frac{i_m v_m}{C_{th}} - \frac{T - T_{amb}}{C_{th} R_{th}(T)},
\]

where \( T_{amb} \) is the ambient temperature of 300 K; \( C_{th} \) is the thermal capacitance; and \( R_{th} \) is the effective thermal resistance. We determined that \( R_{th} \) for a steady-state temperature of ~490 K was \( 1.4 \times 10^6 \pm 0.2 \text{KW}^{-1} \) (\( T < T_{MIT} \), current levels within NDR-1) and that for a steady-state temperature of ~1100 K (\( T > T_{MIT} \), current levels above NDR-2) was \( 1.9 \times 10^6 \pm 0.3 \text{KW}^{-1} \) (while we used the same \( C_{th} \) of 1.25 \times 10^{-11} \text{WsK}^{-1} \) in both cases).
The predicted hysteretic jumps during current-source operation across NDR-2 (black arrows) are too small to be observed experimentally, given the measurement uncertainty. They would change to a single-valued function of temperature (pink solid line) upon a parametric T sweep as displayed in Fig. 2c. Thus, NDR-2 is a temperature-controlled instability that manifests as a rectangular hysteresis during current-source operation. This behavior is similar to the Chua Corsage current–voltage characteristic. Further, the counter-intuitive increase in $R_h$ in the metallic state ($T > T_{MIT}$) relative to the insulating/semiconducting state ($T < T_{MIT}$), which is consistent for both temperature and electrical measurements (Supplementary Note 3, Supplementary Figs. 8 and 11), is opposite to that expected from the Wiedemann–Franz law. A recent report also described such anomalous behavior of $R_h$ across the Mott transition in VO$_2$ and provided plausible explanations that may cover the behavior observed here as well, although a comprehensive theory remains unexplored.

**Synchrotron X-ray spectromicroscopy.** To further analyze the uniformity and the chemical nature of the NbO$_2$ material changes in operando, we employed synchronous time-multiplexed scanning transmission X-ray microscopy (STXM) (Fig. 3a, Supplementary Note 4, Supplementary Fig. 12) using synchrotron radiation, which has been described elsewhere. This technique provided a spatial resolution of <30 nm and spectral resolution of 70 meV using X-ray energies tuned to the O K-edge, and the synchronous measurements enabled the detection of very low signal differences. For these experiments, we were able to use devices that were identical to the ones used for thermoreflectance, wherein the suspended thin silicon nitride membrane enabled transmitted X-ray detection. The X-ray maps of the crosspoint area (Fig. 3b) without a current ($M_0$) and that with a current sufficient to exceed NDR-2 (<1 mA) and, its corresponding histograms, similar to those in (d). g X-ray absorption spectra of the material within the crosspoint, along with the component bands marked. The spectral differences between the material with current and that with no current are also shown for two different currents, as marked (arbitrarily offset, horizontal dashed lines indicate zero difference for respective colors).
corresponding to the Ti–O bond energies likely arise from a non-linear conduction mechanism in the TiO formed at the interface of TiN and NbO₂ (Supplementary Figs. 2 and 3). Beyond NDR-2, a similarly obtained spectral difference displays prominent features consistent with downshifting of both the π* and σ* bands, in agreement with theoretical predictions of an increased conductivity at the MIT and an accompanying Peierls distortion in the crystal structure. The Mott + Peierls transitions in NbO₂ responsible for NDR-2 are similar to those in VO₂ causing a behaviorally similar NDR (discussed further in Supplementary Note 5 and Supplementary Fig. 13).

**Filament formation using a voltage source.** Following the observations of spatially uniform temperature and chemical changes during current-source measurements, we studied such responses when the devices were biased directly by a voltage source (with no external series resistance to limit the current; there was a series electrode resistance of about 300 Ω). Upon applying 1 V pulses (estimated current higher than 1.5 mA from applying 1 V across, which persisted even after the voltage was removed, likely due to irreversible stoichiometry changes caused by the high temperatures (Fig. 4b, Supplementary Fig. 9). The post-O K-edge-absorption intensity within the channel was lower relative to its surroundings (Fig. 4c), revealing a lower O concentration. At the O K-edge, significant downshifting in energy of the component bands of NbO₂ within the channel also indicated chemical reduction of the oxide. The spectral differences between the material with a 1 V and with zero bias also revealed a higher current density inside the channel. The formation of a high current density “filament” or channel in a background of lower current density resulting from a symmetry-breaking instability in the NDR region was first proposed by Ridley based on entropy-production minimization arguments, which were later questioned by Landauer. Numerical simulations of NDR by Funck et al. also showed a high-current density channel within a lower-current density region, but this was enforced by the cylindrical symmetry of the model and the radial boundary conditions for heat flow. In our voltage source experiments, the NbO₂ experienced irreversible material changes due to the high temperatures that were reached, so an unambiguous determination of the mechanism responsible for the channel formation is not possible from our data. Resolution of this interesting and important issue that is critical for robust modeling of NDR and other electrical instabilities will require further research.

**Discussion**

Using spectromicroscopic characterization techniques to measure temperature and chemical spatial distributions, along with numerical simulations, we confirmed that the current-controlled NDR-1 in NbO₂ is caused by a Joule-heating-driven thermal runaway in strongly nonlinear conduction at relatively low temperatures (~400 K) and further demonstrated that NDR-2 is a temperature-controlled MIT-driven hysteresis at high temperature (~1000 K). Both types of NDR within the same material are Joule-heating driven, and thus have T as a state variable, but they are caused by distinctly different physical mechanisms at very different temperatures. In addition, we showed that using a current source yields, a spatially uniform current density over the device area, while operating the devices with a voltage source causes the formation of a localized high current density channel, highlighting an outstanding problem on the subject of filament formation during electrical instabilities. These results definitively resolve the question of whether the NDR of NbO₂ is caused by nonlinear temperature-dependent conduction or by a MIT—the answer is both mechanisms are distinct and present, which provides a rich set of nonlinear behaviors for potential exploitation.

**Methods**

**Film growth.** Si₃N₄ of 150 nm was grown using low-pressure chemical vapor deposition on double side-polished Si wafer with low p-doping. Holes were etched into the Si wafer to allow free suspension of Si₃N₄ membranes. Crosspoint cells were lithographically patterned onto these membranes. The Pt electrodes were evaporated from a Pt target. The layers of NbO₂ and TiN were sputter-deposited.

**Spectral processing.** Spectra were first normalized to background absorptions in the vacuum chamber, measured through a blank Si₃N₄ membrane (with no other material on it). The resulting spectra were corrected for a linear background in the pre-absorption-edge region. Peak fitting was done using the software Sigmaplot PeakFit. The pre-edge of the oxygen K-edge was aligned to zero, a linear background in the pre-edge region was subtracted, and the data was smoothed by 1% using Savitzky–Golay smoothing. The peaks were composed of a convolution of a Lorentzian component (to account for the broadening of spectral lines due to excited electron lifetime) and a Gaussian component (to account for the resolution of the spectrometer, mostly due to the beamline monochromator). For each spectrum, the component bands were allowed to vary in width, amplitude, and...
