***Doping-controlled Coherent Electron-Phonon Coupling in
Vanadium Dioxide***

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Broadband femtosecond transient spectroscopy and density functional calculations reveal that substitutional tungsten doping of a VO₂ film changes the coherent phonon response compared to the undoped film due to altered electronic and structural dynamics.

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To design and fabricate optoelectronic and photonic devices operating at terahertz speeds, it is crucial to understand how ultrafast optical pulses couple to the microscopic degrees of matter. Recently, coherent phonons – quantized atomic lattice vibrations – have attracted considerable interest as a tool to probe [1] and modify [2] non-equilibrium properties of matter. Here we demonstrate how elemental doping – even at 2 at. % – can provide a viable route to modifying coherent phonon modes, which causes drastic changes in the energy requirements in the ultrafast switching properties of a phase-change material (PCM), vanadium dioxide.

Vanadium dioxide exhibits a reversible solid-solid phase transformation that combines an insulator-to-metal transition (IMT) with a structural phase transition from the monoclinic insulating (M1) phase to a rutile, tetragonal (R) form at near-room temperature (68°C). When triggered optically, its transformation, clocked by its band gap collapse, occurs within 100 fs [3]. When the phase-transformation is driven well above the fluence threshold for the IMT or by charge injection, a catastrophic phonon collapse also occurs [1, 4].

Here, we demonstrate how elemental doping modulates the delicate electron-phonon-orbital coupling that exists in this class of phase-change materials. As a proof-of-principle, we compare pristine VO₂ thin film to its tungsten-doped counterpart, both grown by pulsed laser deposition to about 60nm thick [5]. Fig. 1 shows a representative broadband ultrafast VO₂ response when excited *at near-threshold*. Within the first picosecond, one observes strong

Figure 1. (a) Representative ultrafast broadband absorption response of VO₂ at near threshold. Note the data is not chirp corrected. (b, c) Kinetic traces at ~ 425 nm and ~ 600 nm for pristine VO₂ and W-doped VO₂ plotted on the same 1 ps timescale and optically excited at the same energy fluence. Note the change in oscillatory behaviour, with a dominant 6THz mode for pristine VO₂ while an additional 4 THz mode is present for the W:VO₂, associated with the W-ion vibration.

modulation of the coherent phonon modes that decays rapidly. Kinetic traces at key wavelengths corresponding to the O2p-V3d transition bands, accompanied by Fourier transform reveals the presence of the strong 6 THz characteristic mode in both films. Additionally, the W:VO₂ shows an additional frequency component at 4THz. As revealed by density functional theory, this mode corresponds to the W vibration as it couples to the surrounding VO₂ unit cells, thus upsetting the charge ordering. Together with two additional electrons from the W⁶⁺ ions compared to the V⁴⁺, this modifies the energy requirements for switching VO₂. Fluence-dependent measurement shows that this 2 at.% doping level reduces the threshold by about 1 mJ/cm².

In order to understand how this doping affects the electronic properties of the VO₂, we also study their broadband ultrafast response in the near-infrared region, which is close to the VO₂ band gap (0.69 eV). Figure 2 displays the VO₂ response when triggered at the pristine VO₂ *near-switching threshold* (semiconductor like response). Two important differences are observed: (i) the W:VO₂ domains have already switched below the fluence needed to switch pristine VO₂ and (ii) the change in W:VO₂ absorption (transmission contrast) is less than that of the pristine VO₂. The former can be attributed to the additional electrons in the conduction band in W:VO₂ while the decrease in optical contrast is potentially due to fast electron-hole recombination, following ultrafast excitation. Density functional calculations show that the additional charges (either holes or electrons) are localized near the W-dopant. Thus, this enhanced electron-hole interaction can produce an overall decrease in the absorption changes.

Figure 2. (a) Broadband near-IR ultrafast response of pristine and W-doped VO₂ excited at the *same* optical fluence and plotted on the same intensity scale. The VO₂ film shows semiconductor-like response while the W:VO₂ film is already in its switched state. (b) Induced electron energy difference of the W:VO₂ lattice displaying that the electron is localized near the W-ion. Similar figures were obtained with holes.

In summary, we have shown the rich ultrafast dynamics of PCM VO₂ and how coupling with its various microscopic degrees of freedom can be tuned by doping. More importantly, we conclude that doping, even at quite low concentrations, can affect the energy requirements for the ultrafast switching of phase-change material, modifying both its electronic and coherent phonon dynamics.

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