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Ultrafast Phase Transition in Vanadium Dioxide Driven by Hot-Electron Injection

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Abstract. We present a novel all-optical method of triggering the phase transition in vanadium dioxide by means of ballistic electrons injected across the interface between a mesh of Au nanoparticles coveringd VO_2 nanoislands. By performing non-degenerate pump-probe transmission spectroscopy on this hybrid plasmonic/phase-changing nanostructure, structural and electronic dynamics can be retrieved and compared.

1 Introduction

Strongly correlated electron systems exhibiting interesting macroscopic quantum phenomena such as superconductivity, multiferroicity, colossal magnetoresistance or insulator-to-metal transition (IMT) have garnered widespread interest for their potential in providing reconfigurability in highly integrated nanophotonic devices. Vanadium dioxide (VO_2), a canonical phase-changing material, undergoes such a reversible IMT, accompanied by a structural modification from a M_1 monoclinic semiconducting phase to a metallic R phase with a tetragonal crystal structure one near 68 ^oC in bulk single crystals [1]. More relevant technologically is the fact that the IMT in VO_2 can also be triggered optically on a sub-100 fs timescale by an ultrashort laser pulse [2]. Recent ultrafast studies have consequently both focused on understanding the dynamics and threshold behavior of the *"switching on"* process [3] and also on determining the effect of substrate on the relaxation dynamics, that is the *"switching off"* process in VO_2 [4]. Such studies are crucial to optimizing the performance of VO_2-based devices that could be switched reversibly on an ultrafast timescale.

Here, we describe a novel all-optical method for triggering phase transition in VO_2 while additionally lowering the fluence threshold, a necessary requirement for reducing power consumption for phase-change technologies [5]. By fabricating a nanostructured Au/VO_2 hybrid nanomaterial, we show that hot electrons from the metal can be harnessed to trigger the transition. This ultrafast electron injection process not only lowers the fluence threshold behavior but also modifies the switching characteristics of the VO_2.

2 Experiment

The samples were grown by a combination of pulse laser deposition using a vanadium metal target followed by an annealing step in an oxygen background (450^oC, O_2 gas at 250 mTorr for 40 minutes) to render VO_2 stoichiometric and crystalline. Thereafter, gold was deposited using electron beam

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evaporation while the thickness was monitored by a quartz crystal microbalance. Because the Au overlayer is too thin to form a continuous film and does not wet the VO_2, the process creates a network or nanomesh of Au nanoparticles covering the VO_2 nanoislands, as shown in Fig. 1(a). As control, a similar sample of VO_2 nanoislands without the gold coating was also fabricated on a glass substrate. This allowed comparison of the response of the two samples when switched thermally, that is, in a steady-state fashion as shown in Fig. 1(b). The ultrafast non-equilibrium dynamics of the two samples were also compared when the hybrid nanomaterial was switched with a laser pulse.

We used non-degenerate pump-probe spectroscopy to characterize the ultrafast optical response of the hybrid metal/VO_2 nanostructures. The samples were pumped at 790 nm (above band gap) at fluences ranging from 0.28 mJ/cm^2 to 6.16 mJ/cm^2, and probed by a time-delayed 3100 nm probe generated in an optical parametric amplifier. The pulse duration was 50 fs, as measured using an autocorrelation setup.

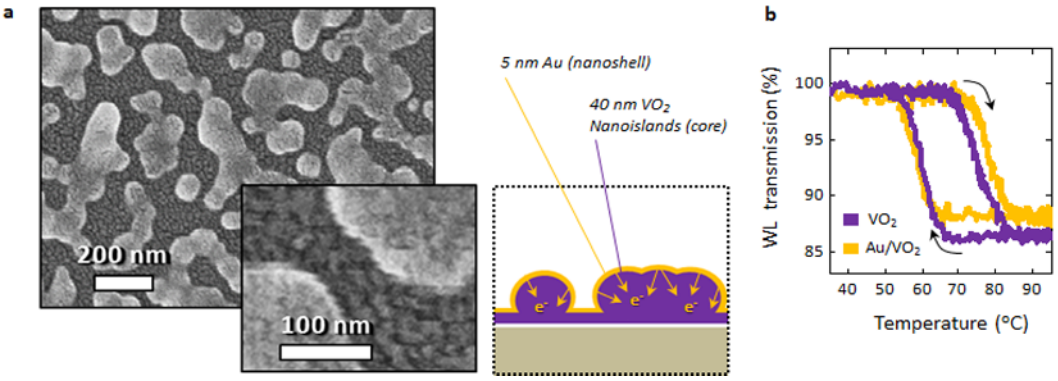

Fig. 1. (a) Scanning electron micrograph of gold-capped VO_2 nanoislands. The figure on the right depicts electrons from the gold nanoislands being injected into the vanadium dioxide following pulse excitation (b) White-light transmission hysteresis measurements comparing the pristine VO_2 nanoislands versus the hybrid gold/VO_2 nanomaterial. Note that the change in T_c is negligible, but there is a small change in contrast.

3 Results and discussion

Figure 2(a) shows the measured differential transmission at the lowest pump fluence of 0.28 mJ/cm^2 for both the pristine VO_2 and Au/VO_2 samples. From the pristine VO_2 data, we see that only the electronic component of the transition is excited with its characteristic fast relaxation. Due to the below-threshold pump fluence — found to be ~1.2 mJ/cm^2 for this sample — the structural phase transition has not been triggered yet. However, in the Au/VO_2 nanomaterial case, the structural signature is already visible and marked by a growing decrease in the transmission during the concurrent electronic relaxation occurring between 1-2 ps. By fitting the optical response with a two-component recovery rate dynamics associated with the electronic and structural relaxation lifetimes, we found that for all pump fluences, relaxation lifetimes of both components from the hybrid nanomaterial were always longer than the pristine case. Moreover, in the hybrid nanomaterial case, no fluence threshold dependence was observed, suggesting than even for the below-threshold pump-pulse interaction with the gold nanoislands, ballistic or "hot" electrons are created and injected into the VO_2. This has the effect of assisting the ultrafast switching by directly populating the conduction band of the VO_2, as shown in figure 2(b). Consequently, this explains the triggering of the structural phase transition for the hybrid system even at the lowest measured fluences.

We conclude that initiation of the phase transition in the VO_2 is assisted by electron injection from the Au nanoparticles. Hole injection is here excluded as holes from the VO_2 *d*-bands cannot be created through a single-photon absorption at 800 nm. Thus, hot electrons from intraband excitations of the conduction bands assist this phase-changing process. Such an electron-injection effect can

potentially be isolated from the optically triggered phase-transition in the VO_2 by monitoring this process on epitaxially films of VO_2, thus facilitating interfacial injection along particular crystallographic directions of the VO_2. More importantly, since VO_2 was used as a model material, ultrafast electron injection could be a novel *independent* way to induce phase-transition phenomena in other materials that have strongly correlated electronic systems.

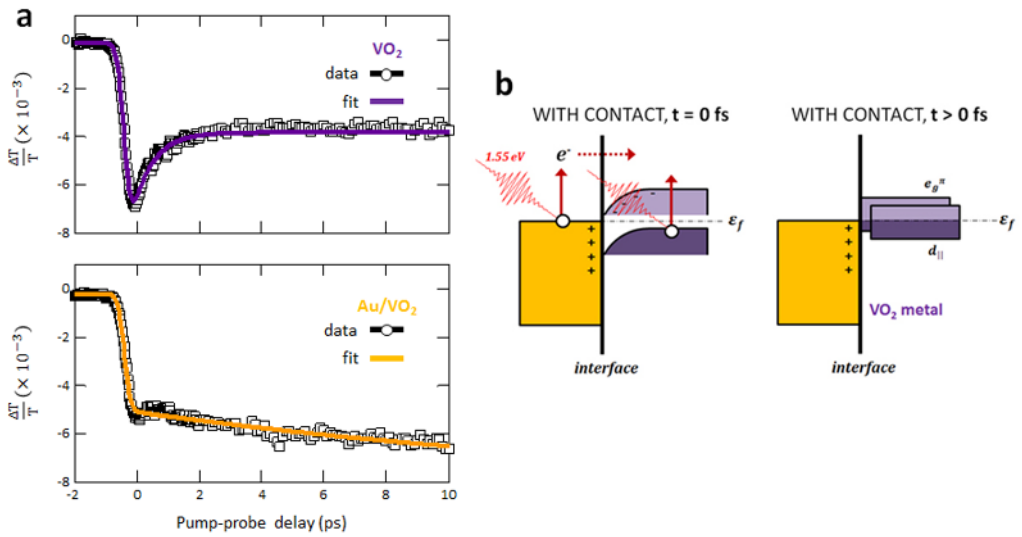

Fig. 2: (a) Ultrafast optical response of the pristine (top) VO_2 film (40 nm) compared to the gold nanoislands (5nm)/VO_2 (40 nm) hybrid nanomaterial (bottom) at the lowest pump fluence only. Fits are shown as the dashed lines. (b) Schematics of the Au/VO_2 band diagram during and after excitation. Hot electrons injected across the interface from the Au nanoparticles to the VO_2 are depicted by the dashed arrow.

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