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Ultrafast Hot Electron Induced Phase Transitions in Vanadium Dioxide

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Abstract. The Au/Cr/VO_2/Si system was investigated in pump–probe experiments. Hot-electrons generated in the Au were found to penetrate into the underlying VO_2 and couple with its lattice inducing a semiconductor-to-metal phase transition in ~2 picoseconds.

1 Introduction

The semiconductor-to-metal transition (SMT) in vanadium dioxide (VO_2) is a canonical example of strongly correlated systems[1]. The first order SMT occurs at a Tc of ~340 K and has been discussed as the basis for potential applications ranging from photoactive filters to ultrafast optical switching. The SMT in VO_2 manifested by large changes in resistivity and optical properties[2,3] accompanied by a simultaneous structural changes[4,5] from the low-temperature monoclinic with band gap of ~0.7 eV[6] to high temperature rutile phase. It is generally agreed that SMT arises from the combination of Peierls and Mott mechanisms. It was recently reported that in VO_2, the SMT can be assisted by scattering due to the surface plasmon resonance in a nanocomposite comprising an array of Au nanoparticles covered by a thin film of VO_2[7]. Here, we report that for an Au layer on top of VO_2, it is possible with femtosecond pulses at proper wavelengths to directly dope the hot electrons from Au into VO_2 layer and to observe the SMT phenomena without direct excitation of VO_2, this approach provides a new means for inducing structural transitions – especially important along the ground state surface.

2 Sample Preparation and experimental setup

A polycrystalline 125 nm-thick VO_2 layer was grown on a Si (100) substrate by electron beam deposition, and the VO_2 films were coated with Cr (1 nm thickness) and Au (20 nm thickness) films by thermal deposition. Switching behavior was verified by measuring the white light (tungsten filament) reflection intensity using an InGaAs photodetector while the sample temperature cycled from 25 °C to 100 °C. Normal switching temperature, contrast and hysteresis were observed. The Au/Cr/VO_2/Si samples were characterized by optical pump–probe experiments in reflection mode with a femtosecond regenerative laser amplifier. The 800-nm optical pump was focused on the sample at an incident angle of 4.3° from the surface normal, while a 400-nm p-polarized probe pulse

was focused on the pump spot at an incident angle of 60° from the surface normal. The reflectivity from the samples was detected using standard lock-in methods.

3 Results and Discussion

The (*1/e*) penetration depth of the 800-nm light in VO_2 is ~150 nm, while penetration depth of the 400-nm probe in VO_2 is ~30 nm, which means that the probing area was uniformly excited by the optical pump pulses for the VO_2/Si sample. However, the penetration depth of 800-nm light in Au is 13 nm and the fluence reaching the VO_2 film would be lower than the critical threshold needed to induce the phase transition. Figure 1 shows the changes in reflectivity as a function of delay time for Au/Cr/VO_2/Si and Au/Cr/Si. Below the threshold absorbed fluence of 2.8 mJ/cm^2, there was a short-term decrease in reflectivity of the Au/Cr/VO_2/Si film (Fig. 1a) (τ: 0.8 ps, it recovered in ~5 ps), which was also observed for the Au/Cr/Si film (Fig. 1b), where τ is the characteristic time constant. This change was attributed to the hot electrons excitation or electron temperature changes in the gold layer[8]. Above the threshold fluence (>3.0 mJ/cm^2), a decrease in the relative contribution from the short-time component and appearance of longlived term reduction in the reflectivity were observed for the Au/Cr/VO_2/Si film. The subtraction of the time-resolved reflectivity of Au/Cr/Si film from Au/Cr/VO_2/Si film with same laser absorbed fluence shows the time-scale of this phase transition phenomena in Au/Cr/VO_2/Si film (Fig. 1c); this phase transition occurred within about ~2 ps.

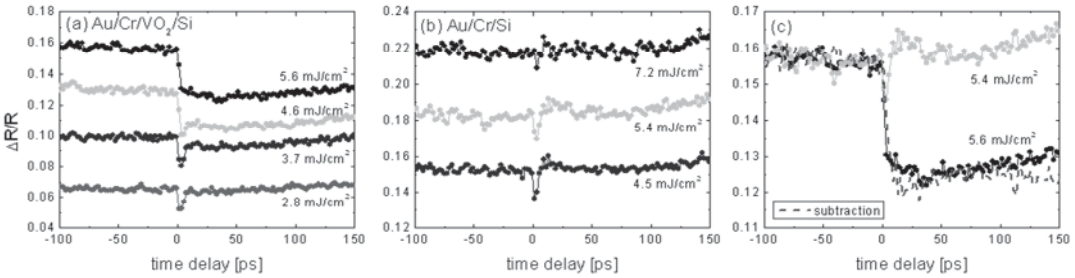

Fig. 1. Changes in reflectivity with delay time for Au/Cr/VO_2/Si (a) and Au/Cr/Si (b) at the laser-absorbed fluence values of 2.8–7.2 mJ/cm^2, as indicated. In (c), the dush line represents the subtracted change in the reflectivity of Au/Cr/Si from that of Au/Cr/VO_2/Si at the incident fluence of 5.6 mJ/cm^2.

Because of the top Au film, only 10% of the optical pulse could reach the VO_2 surface, far below less the threshold fluence required for photo-induction of the SMT in VO_2. Given the probe-penetration depth of ~30 nm and the thermal diffusion coefficient of 0.02 cm^2/s[9], it would take more than 100 ps to excite the probed area with thermal lattice diffusion. Because the sound speed in VO_2 is 4×10^3 m/s[10], acoustic relaxation into shear components will occur within around 10 ps for a length scale of tens of nanometer. SMT observed in VO_2 in this experiment occurred much faster than the rate of these thermal processes and the reflectivity change in the time scale of ~2 ps cannot be explained by either optical or thermal processes. The optical pulses produced a significant amount of hot electrons in the Au layer, which can induce the SMT in the underlying VO_2. The contact between Au/Cr and VO_2 and the band-gap of VO_2 in semiconductor phase makes ohmic junction[11,12]. The temperature of the hot electrons (T_e) produced in the Au layer can be calculated with the laser absorbed fluence (P) and heat capacity (C_e) as:

$$P = \int_{T_0}^{T_e} C_e t dt = \frac{1}{2} C_e \left(T_e^{\,2} - T_0^{\,2} \right), \tag{1}$$

where T_0 is room temperature (293 K) (Ref. 13). The hot electrons generated on the Au surface would be transported ballistically through the 20 nm-layer by the ballistic electron motion within 100 fs. According to equation (1), the temperature of the hot electrons at a laser fluence of 5 mJ/cm^2 would be 7000 K (0.6 eV). In case of the photo-induced phase transition, it is required ~5% of excited electron from valence band to conduction band for the phase transition. From the Fermi-Dirac distribution with the electron temperature of 7000 K, the electron numbers of ~5% corresponds to the electron energy of 1–2 eV. The penetration depth of the 1–2 eV electrons in VO_2 is around a few nanometers; therefore, the direct injection and primary scattering of electrons will transfer the energy to the cold VO_2 lattice, which could trigger SMT.

4 Conclusion

This work illustrates that it is possible to exploit hot electrons to induce structural phase transitions and provides a new approach for stimulating structural transitions along ground state surface. This method could greatly extend the range of atomically resolved structural dynamics as well as provide a general means for inducing structural transitions in otherwise transparent materials.

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