Size-Dependent Phase Transition of VO₂ Nanostructures Induced by Light Excitation

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Abstract

In nanocrystalline VO₂ films the light-induced insulator-to-metal phase transition (I-M PT) dynamics was investigated by femtosecond optical pump-probe technique. The size of VO₂ nanoparticles and the film morphology were found to be critical for the ultrafast light-induced PT dynamics as well as for thermal hysteresis. The I-M PT within subnanosecond scale demonstrates a nearly linear dependence of characteristic transition time on VO₂ particles size. Such a behavior can indicate the importance of phonon interactions with optically-excited electronic states.

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Keywords: Vanadium dioxide; Nanoparticles; Metal-insulator transition; Transient optical properties; Ultrafast optics

1. Introduction

Nonlinear optical materials based on VO₂ are promising for ultrafast optoelectronics due to the phase transition (PT) nature of VO₂. The first-order insulator-to-metal (I-M) PT of VO₂ can be induced either thermally at a temperature of T_c=340 K or by light excitation [1, 2]. Potential technological applications of VO₂ in high-speed optical switches, in laser intracavity mirrors with optically controlled reflectivity, thermochromic windows and diffractive elements [3,4] can be significantly extended by implementation of nanocrystalline VO₂ (nc-VO₂) films due to size-dependent properties of VO₂ nanoparticles (NPs). As shown in Refs.5-7, spectral properties and hysteresis become tunable by controlling VO₂ NP size. An ultrafast control of surface-plasmon resonance is possible within less than 150 fs [8].

In this paper, we report the observation of the light-induced I-M PT in nc-VO₂ films by pump-probe transient grating technique. Excited state dynamics of VO₂ NPs was found to be dependent on optical excitation energy and size of NPs, indicating a complex relaxation behavior of VO₂ in a metastable state. On subnanosecond time scale the structural PT rate increases with decreasing particle size due to confinement effect. These results constitute the...
direct experimental observation of size-dependent PT transient dynamics in VO$_2$ NPs on the 10$^{-13}$-10$^{-10}$ sec time scale.

2. Experimental

Ultrathin nanocrystalline VO$_2$ films were prepared on fused quartz glass substrates by reactive pulsed laser deposition (PLD). Laser pulses from a Lambda Physik Compex 110 laser (KrF excimer, wavelength $\lambda$=248 nm), with ~20 ns duration and 25 Hz repetition rate were focused onto a metallic vanadium target at ~ 4 J/cm$^2$ fluence. Amorphous VO$_2$ films were grown at 20 mTorr pressure in a O$_2$ and Ar gas mixture. Annealing treatment was performed in situ during 40 min at a total pressure of 0.3 Torr and temperatures $T$=590-673 K. After annealing, the films were nanocrystalline, as verified by atomic force microscopy (AFM) and x-ray diffraction (XRD) scans. The XRD results showed only M$_1$ phase with substantially broadened (011) diffraction peak, as expected for NPs with sizes of a few tens of nanometer [6]. AFM analysis of nc-VO$_2$ surface topography has shown an uniform distribution of VO$_2$ spherical nanoparticles with mean radius in the range from 14 nm to 50 nm.

Thermally induced PT of nc-VO$_2$ films was monitored by transmission technique using semiconductor laser with $\lambda$=1310 nm. Samples were placed on Peltier heater, and the transmission signal was measured at normal incidence by silicon photodiode as a function of sample temperature.

The light-induced PT dynamics in VO$_2$ was studied by pump-probe transient grating technique. The experimental configuration was described elsewhere [9]. A Ti:Sapphire Spectra-Physics femtosecond laser system was used as a light source. Laser pulses of 130 fs duration and $\lambda$=400 nm were generated at a 50 Hz repetition rate. An interference pattern in the nc-VO$_2$ film was formed by two equally divided pump pulses, crossed at the angle $\theta=9.0^\circ$. The light-induced I-M PT was realized within maxima of the interference pattern forming the metal/insulator diffraction grating. The intensity of the transmitted diffracted probe pulse was measured as a function of time-delay between pump and probe pulses controlled by an electromechanical optical delay line.

3. Results and Discussion

The information about thermally induced PT of nc-VO$_2$ is important in order to clarify structural and optical properties of the samples. Transmission measurements show that the thermal hysteresis is strongly dependent on the mean radius $R$ of VO$_2$ NPs (Fig.1). The hysteresis loop becomes broader, with steeper edges as VO$_2$ NP size increases. The observed difference in hysteresis has been attributed to different statistical properties of nc-VO$_2$ films, various concentrations of oxygen vacancies, dislocations and mechanical stresses in VO$_2$ NPs of different size [5-7, 10, 11]. The annealing process and NP growth result in modification of nc-VO$_2$ microrelief, making the size distribution of VO$_2$ particles more uniform. As shown in Ref.10, VO$_2$ grains with comparable sizes have similar PT temperatures. Therefore a growth of isolated NPs with preferred characteristic size reduces the dispersion of PT temperatures for different particles in the same film. As a result, the edges of the hysteresis loop become steeper.

Along with thermally induced PT the light-induced PT dynamics is sensitive to the film structure as well [9]. In this work the pump-probe transient grating technique was applied to monitor the PT dynamics in nc-VO$_2$ films with equal thicknesses of 30 nm. Representative evolution of the diffraction signal $\eta(t)$ on a 2.5 ns time scale is shown in Fig.2 for a single film which contains NPs with average radius $R=24$ nm. Here the signal $\eta(t)$ is normalized to its maximal value at pump fluence $w_p$=1.43 mJ/cm$^2$. Diffraction signal is associated with the formation of the spatial metal/insulator diffraction grating, and it demonstrates complex behavior, depending on laser pumping. Thus, the most pronounced qualitative difference appears at highest and lowest excitations. Nevertheless the entire transient behavior of nc-VO$_2$ structure at any optical pump is similar and can be divided into three main processes [12]: (i) I-M ultrafast phase transition (UPT) during several tens to hundreds of femtoseconds, (ii) slower I-M PT on ~0.3 ns time scale, and (iii) the VO$_2$ recovery, metal-to-insulator (M-I) PT on the time scale up to hundreds of nanoseconds.
UPT can be resolved in Fig. 2 as a sharp signal rise at zero delay between pump and probe pulses. Since in transient grating experiment the distribution of light intensity on the surface is alternating, the UPT is initiated in the areas of interference pattern with maximal intensity. Within adjacent areas with lower light intensity the I-M PT becomes slower and occurs up to 0.3 ns. On this time scale the signal grows at lower optical pump (below 1.5 mJ/cm² fluence), but at higher fluence it decreases. Nevertheless, in spite of such a different qualitative behavior, the transient grating signal indicates a growing metallic phase in the film at any optical pumping [12]. As it will be discussed below, the signal behavior depends mostly on geometrical size of metallic VO₂ strips which constitute expanding light-induced diffraction grating in the film. As this PT is completed, the M-I recovery process starts after ~0.3 ns, and it has significant dependence on the pump level. At sufficiently high excitation the M-I PT is defined by thermal effects, while at lower excitation this recovery is nonthermal and occurs due to decay of photoexcited electronic states in metallic VO₂ [12].
Fig. 2. Normalized transient grating diffraction signal versus probe-pulse delay at different pump fluence for \( nc-VO_2 \) film; average radius of VO\(_2\) NPs is \( R=24 \) nm. Inset: AFM image (500×500 nm\(^2\) scan) shows isolated VO\(_2\) nanoparticles.

The UPT dynamics probed by 130 fs pulses for different \( nc-VO_2 \) films demonstrates similar behavior (Fig.3). As shown in Ref 9,13, it is most likely that this transition is driven by the charge-transfer (CT) mechanism which occurs within subpicosecond time domain. The characteristic time for UPT was estimated to be close to autocorrelation width of the laser pulse. Therefore the UPT time is apparently less or close to the pulse duration used in the experiment. A common sharp peak at zero probe delay is associated with the nonlinear contribution to dielectric susceptibility caused by electronic excitations during phase transition. The difference in the intensity of diffraction signal for different films appears to be due to different optical constants, morphologies and different UPT threshold levels of the films. Thus a PLD process with posterior annealing results in gradual modification of amorphous VO\(_2\) film to \( nc-VO_2 \) structure. The concentration of structural defects decreases with increasing NP size [6], and the UPT threshold level is supposed to be changed as well. All these factors consecutively change the \( nc-VO_2 \) optical properties and transient grating signal in Fig.3.

Fig. 3. Transient grating signal upon ultrafast light-induced insulator-to-metal phase transition.

The slower I-M PT during \(-0.3\) ns occurs within areas of the sample where the light intensity is lower as compared to the case of UPT [12]. Only two limiting cases of this transition are shown in Fig.4: for sufficiently high (Fig.4a) and low (Fig.4b) laser excitation with average pump fluence \( w_p=5\) mJ/cm\(^2\) and \( w_p=1\) mJ/cm\(^2\), respectively. Here the signal \( \eta(t) \) is normalized to its maximal value for the film with largest NPs \( (R=37\) nm\) at fluence \( w_p=5\) mJ/cm\(^2\). Note, the sequence in the signal intensity \( \eta(t) \) for different films at lower excitation is in the reverse order as compared to the higher excitation. It occurs because of specific formation of metallic VO\(_2\) grating in ultrathin film, where the metallic trips are wider at higher pump fluence. The structural density and thicknesses of the films were almost the same, and the width of the metallic strips was the main factor which defined the measured signal. Diffraction efficiency is maximal when the size of metallic and insulating VO\(_2\) strips in the induced diffraction grating is the same, since the transparency modulation ratio for such a grating is maximal. Thus, as a concentration of metallic phase grows until 50\%, the signal \( \eta(t) \) increases. However further growth of the metallic phase above 50\% results in the decrease of the signal. In the present experiment the concentration of the metallic phase at lower excitation is less than 50\%, but it is above this value at higher excitation for each film. Therefore the data in Fig.4a and Fig.4b indicates that the amount of metallic phase produced at any fixed optical pumping is maximal for the film with smallest NPs \( (R=14\) nm\) and minimal for the film with largest NPs \( (R=37\) nm\). The transient diffraction signal can be described here by a function \( \eta(t) \equiv H(t) [A \exp(-2t/\tau) + B] \), where \( H(t) \) is the Heaviside function, \( A \) and \( B \) are constants and \( \tau \) is characteristic transition time [12, 14]. The numerical approximation of the
experimental data gives the time $\tau$ with a nearly linear increase with particle size at constant excitation energy (Fig.4c). A slight difference in the PT time was also observed at higher and lower pump fluence for each film.

The I-M PT on $\sim$0.3 ns scale occurs within VO$_2$ areas excited into a certain metastable state [12] which can be attributed to photogenerated vibronic excitons, polarons and electron-hole plasma, while the thermal contribution to the PT on this time scale is expected to be negligibly small. As shown in Ref.13, the first-order I-M PT has vibronic origin during the (V$^{4+}$→V$^{5+}$ + $e_{\text{free}}$) reaction. In this process the deformation field induced by interaction of the 3d$_{z^2}$ state with lattice vibrations in the insulator phase disappears, resulting in structural I-M PT. In femtosecond excitation regime the thermal strain is expected to be negligible, compared to the electronic strain [15]. Photoexcited electrons emit phonons and relax to the band edge during $\sim$1 ps. Apparently, the I-M PT occurs as phonons propagate through the volume of the VO$_2$ particle, interacting with the excited electronic states. Since the phonon propagation length is confined by the size of VO$_2$ particle, the characteristic time of the PT increases with particle size. This assumption is supported by observed nearly-linear dependence of the time $\tau$ on NP size. Moreover, there is not too big difference between $\tau$ obtained from the experiment and estimated sound propagation time through the particle $\tau_s$=2R/$v_s$ (Fig.4c), where $v_s$=4100 m/s is the averaged velocity of surface acoustic waves in crystalline VO$_2$ [16]. Thus, according to obtained data, it is very likely that the phonon interaction with optically-excited electronic
states gives significant contribution to the I-M PT, producing a decay of the metastable state. A slight difference in \( \tau \) at higher and lower pumping for each film can be due to higher concentration of metallic nuclei and higher probability of the resonance PT at higher pumping.

A cooperative behavior of photogenerated vibronic excitons and formation of excitonic clusters can result in additional contribution to the PT dynamics [9, 13]. At a critical concentration of excitons in the clusters, the resonant tunneling occurs to an excited metallic state [13]. Since the diffusion length for carriers is confined by the size of the VO\(_2\) nanoparticle, the characteristic time of the PT should gradually increase with particle size.

4. Conclusion

The time-resolved measurements of excited state dynamics in VO\(_2\) elucidate the size-dependent I-M PT in VO\(_2\) nanoparticles on subnanosecond time scale. At sufficiently high laser excitation the PT in nanoparticles is ultrafast with characteristic time close to 130 fs or less. Moreover, the transient grating signal intensity is strongly dependent on the film morphology due to different optical properties of the films. At lower excitation the PT becomes much slower and occurs within subnanosecond time scale. It is shown that such I-M PT can occur due to phonon interactions with optically-excited electronic states, as phonons propagate through the particle volume. Thus, the characteristic time of the transition increases with VO\(_2\) particle size. Finally, obtained results show a possibility to control the PT time by sizing of VO\(_2\) nanoparticles which is promising for a variety of optoelectronic applications.

References