# Critical behavior and size effects in light-induced transition of nanostructured VO<sub>2</sub> films

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The light-induced insulator-to-metal phase transition was investigated by femtosecond pump-probe techniques in nanocrystalline VO<sub>2</sub> films. The size of VO<sub>2</sub> nanoparticles and the VO<sub>2</sub> film morphology were found to be critical for the ultrafast light-induced phase-transition dynamics. Experimental measurements of the third-order nonlinear susceptibility  $\chi^{(3)}$  for the insulating phase at different excitation levels and transient grating experiments show a size-dependent threshold behavior which is related to the light-induced transition process. Optical properties of VO<sub>2</sub> nanoparticles,  $|\chi^{(3)}|$  data, and transition dynamics at subnanosecond time scale also demonstrate a pronounced size dependence. The rate of structural phase transition increases due to confinement effect as particle size decreases. Nucleation of the metallic phase shows a critical behavior with formation of a metastable state in VO<sub>2</sub>. A kinetic model for the metallic phase growth and transient grating signal evolution upon ultrafast laser excitation is developed for VO<sub>2</sub> thin film.

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## I. INTRODUCTION

The extraordinary optical properties of nanomaterials have attracted much attention in recent years due to their dependence on size and geometrical shape of nanostructures.<sup>1</sup> Among the wide range of such materials, nanostructured vanadium dioxide is promising for modern optoelectronic applications due to its photorefractive properties originating from a metal-to-insulator phase transition (M-I PT). At room temperature VO<sub>2</sub> is an insulator with semiconducting properties. Nondestructive 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.<sup>2-6</sup> The light-induced PT of VO<sub>2</sub> makes this material attractive for potential technological applications in highspeed optical switches, laser intracavity mirrors with optically controlled reflectivity, thermochromic windows, diffractive elements, and actuators.<sup>7-12</sup> The range of such applications can be significantly extended by fabrication of nanocrystalline VO<sub>2</sub>(nc-VO<sub>2</sub>) films. Recent considerable efforts in the development of VO2-based nanostructures show their outstanding properties.<sup>13–19</sup> As shown in Refs. 13 and 19-23, nonlinearity, spectral properties and hysteresis become tunable by sizing of VO<sub>2</sub> nanoparticles (NPs), and ultrafast control of surface-plasmon resonance is possible within less than 150 fs.<sup>17</sup>

The M-I PT phenomenon in VO<sub>2</sub> was discovered a half century ago.<sup>2</sup> Nevertheless, the nature of electronic states involved as well as the driving force of the PT in this correlated metal oxide is still not entirely clear. Different theoretical approaches employ Mott-Hubbard<sup>24–26</sup> or Peierls<sup>27–33</sup> conceptions to describe the PT and band structure of VO<sub>2</sub>. Many experiments show the important role of electronelectron correlations which stabilize the insulator phase of VO<sub>2</sub>.<sup>34–45</sup> At the same time, x-ray and ultrafast optical studies reveal structurally driven properties of the PT.<sup>46,47</sup> Upon light-induced PT the vibrational spectrum is modified by photoexcited electrons, resulting in structural instability. Ultrafast terahertz spectroscopy elucidates the coherent structural dynamics and transient electronic conductivity of  $VO_2$  on femtosecond<sup>38</sup> and picosecond<sup>48,49</sup> time scales.

Experimental studies show that along with ordinary optical excitations of free carriers in VO<sub>2</sub>, it is possible to form bound electronic states (e.g., excitons or polarons).<sup>38,40,50-54</sup> The formation of these states could play an important role in the PT mechanism. The existence of small polarons in VO<sub>2</sub> was suggested by Mott.<sup>55</sup> Later investigations have shown that the large polaron intermediate-coupling could be more appropriate for VO<sub>2</sub> systems.<sup>50</sup> The x-ray-absorption study of  $(Ti, V)O_2$  solutions has revealed a core excitons in pure monoclinic VO<sub>2</sub>.<sup>51</sup> A recent optical studies show signatures of exciton self-trapping on femtosecond time scale<sup>38</sup> as well as possible presence of charge-transfer (CT) excitons.<sup>40</sup> Charge-transfer and exciton models can explain the main features of the light-induced PT on different time scales.<sup>54,56</sup> In terms of the exciton model the I-M PT occurs due to formation of specific intermediate states related to Frenkel excitons and vibronic Wannier-Mott excitons. Further development of these models can bring deeper understanding of the PT phenomenon in VO<sub>2</sub> complexes.

There has been a significant research effort aimed at understanding the influence of structural characteristics onto PT properties (i.e., hysteresis, conductivity, temperature threshold of M-I PT, and dynamics of the light-induced PT).<sup>17–23,56–61</sup> Since physical characteristics of semiconductors depend on particle size, the reduction in VO<sub>2</sub> particles down to several nanometers considerably changes electronic and optical properties of the samples. Variation in VO<sub>2</sub> particle size within the nanoscale region alters the confinement of electrons, affects the VO<sub>2</sub> electronic structure, and thus PT properties. In this connection, a study of size-dependent light-induced PT dynamics is of special interest.

In this paper the experimental results elucidate the phase transition dynamics in nanocrystalline  $VO_2$  films upon ultrafast laser excitation. We report on metallic phase nucleation on the femtosecond time scale and nucleus growth on subnanosecond time scale in metastable  $VO_2$  at different levels of optical excitation. The systematic studies of the third-order nonlinear susceptibility, transient optical properties,

and relaxation times manifest size-dependent phase transition in VO<sub>2</sub> nanoparticles. The formation of an exited electronic state is crucial for the PT threshold and for nucleus growth dynamics. Generally, excited state dynamics is dependent on optical excitation energy and size of VO<sub>2</sub> NPs, indicating the complex relaxation character of VO<sub>2</sub> which is optically switched to a metastable state. This work also proposes model for the nucleus growth kinetics demonstrating agreement with experimental data.

#### **II. EXPERIMENTAL**

Ultrathin VO<sub>2</sub> nanocrystalline films were prepared by reactive pulsed laser deposition (PLD) technique combined with *in situ* thermal treatment of the sample in the vacuum chamber. A Lambda Physik Compex 110 KrF excimer laser was used for the ablation process. Laser pulses of  $\sim 20$  ns duration and wavelength  $\lambda = 248$  nm at a 25 Hz repetition rate were focused onto a metallic vanadium target at  $\sim 4 \text{ J/cm}^2$  fluence. Amorphous VO<sub>2</sub> films were grown on quartz glass substrates at room temperature and a 20 mTorr chamber pressure in a O<sub>2</sub> and Ar gas mixture. Each deposition lasted 7 min and the film was immediately annealed in situ for 40 min at a total pressure of 0.3 Torr. Annealing temperatures were varied in the range T=590-673 K. The resulting films had nearly the same thickness of 30 nm, as measured with a stylus profilometer. The annealed films were nanocrystalline, as verified by atomic force microscopy (AFM) and by x-ray diffraction (XRD) scans. At a constant annealing time, the temperature increase resulted in larger VO<sub>2</sub> NP size. Thus, each nc-VO<sub>2</sub> film was synthesized as a layer of randomly distributed VO<sub>2</sub> nanoparticles. Here we assume that a single VO<sub>2</sub> NP consists of a single nanocrystal. Crystalline VO<sub>2</sub> films without NPs have been also prepared by PLD and are described elsewhere.<sup>56</sup>

The morphology of the samples was characterized by XRD and AFM methods. The XRD measurements were performed in a Bruker AXS D8 Discover diffractometer. The surface topography data were acquired on a Park Scientific Instruments Autoprobe CP AFM. The surface scans are performed in contact mode, using a silicon-nitride cantilever. To improve measurement accuracy, several different randomly selected sites were analyzed for each film.

To obtain information about optical properties of the samples, reflectance and transmission measurements were performed using two different lasers with wavelengths  $\lambda = 527$  nm and  $\lambda = 1310$  nm as light sources. Angular dependence of the reflection coefficient was measured with a goniometer stage and amplified photodiode. Transmission measurements were conducted at normal incidence and at different temperatures of the *nc*-VO<sub>2</sub> films. Temperature was maintained by a computer-controlled Peltier heater.

The light-induced PT in nc-VO<sub>2</sub> films was studied by pump-probe transient grating (TG) technique. The same experimental configuration was used in degenerate-four-wavemixing (DFWM) experiments in order to find the third-order nonlinear susceptibility of the samples.<sup>56,62</sup> There is only a slight difference between DFWM and TG procedures. DFWM measurements were conducted at simultaneous interaction of pump and probe pulses with the sample while the TG measurements employed a variable delay between pump and probe. A Ti:Sapphire spectra-physics femtosecond laser system was used as a light source. Laser pulses of 130 fs duration with central wavelength  $\lambda$ =400 nm and Gaussian beam shape were generated at a 50 Hz repetition rate. Laser radiation delivered from the laser system was split into pump and probe beams. An interference pattern was formed on the nc-VO<sub>2</sub> film by two equally divided pump pulses with crossing angle  $\theta = 9^{\circ}$ . As a result the light-induced PT was realized within maxima of the interference pattern forming a metal/ insulator diffraction grating with period of 2.5  $\mu$ m. The probe pulse was focused to a 100  $\mu$ m spot within the central area of the interference pattern. Its intensity was reduced by neutral density filters to avoid nonlinear interaction with the sample. Time-resolved transient grating experiments were conducted in forward geometry. 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.

#### **III. RESULTS AND DISCUSSION**

### A. Structure and optical properties of nanocrystalline VO<sub>2</sub> films

The structure of VO<sub>2</sub> films was studied by x-ray diffraction and by atomic force microscopy. The morphology of nc-VO<sub>2</sub> films and average size of the VO<sub>2</sub> NPs was found to be dependent on the film growth rate, gas pressure in the chamber, annealing time and temperature. The PLD film was amorphous for unannealed test samples. Here XRD scans did not show any diffraction signal attributable to VO<sub>2</sub> and distinguishable from the broad  $SiO_2$  substrate peak [Fig. 1(a)]. For the annealed samples a single XRD peak is found at the angle  $2\theta = 28^{\circ}$ , attributed to monoclinic  $M_1$  phase with preferred orientation of VO<sub>2</sub> crystallites with (011) planes parallel to the substrate surface. The diffraction peaks were substantially broadened in comparison with those of standard  $VO_2(M_1)$  powder samples, as expected for nanocrystals with sizes of a few tens of nanometers.<sup>19</sup> These results indicate the reorganization of the amorphous film to a nanocrystalline structure through the annealing process.

To determine the surface parameters, such as root-meansquare (rms) roughness, power spectral density (PSD) function of the surface, and average size of VO<sub>2</sub> nanoparticles, the AFM measurements were performed. Figure 1(b) shows representative AFM image of a nc-VO<sub>2</sub> film with randomly distributed isolated particles. Average size of VO<sub>2</sub> NPs was calculated for each film by graphical and statistical analysis of AFM images. It was found that the samples contain NPs with characteristic radii *R* varying from 14 to 37 nm.

Statistical analysis of the surface height profiles gives information about rms roughness  $\delta_{\rm rms}$  and the PSD function. The rms roughness describes the irregularity of the surface height and is an integral characteristic of the surface.<sup>63</sup> Thus, as could be expected for *nc*-VO<sub>2</sub> films,  $\delta_{\rm rms}$  increases with particle size from 0.6 to 1.6 nm [see inset in Fig. 1(c)]. More detailed information about roughness was obtained from the PSD. A PSD function is proportional to the magnitude of the



FIG. 1. (a) XRD patterns of amorphous VO<sub>2</sub> film before annealing and nc-VO<sub>2</sub> film after annealing. (b) AFM image of a nc-VO<sub>2</sub> film with isolated nanoparticles. (c) Power spectral density function of the nc-VO<sub>2</sub> film surfaces as a function of the spatial frequency. The insert shows the rms roughness of the films versus the average radius of VO<sub>2</sub> nanoparticles.

rms roughness components versus spatial frequency of the surface relief decomposition.<sup>63,64</sup> Since the nc-VO<sub>2</sub> films are isotropic and uniform, PSD data were averaged for all azimuthal directions. Characteristic parameters of the surfaces can be determined from the shape of the PSD functions shown in Fig. 1(c). Thus, similar slopes of PSD curves indicate similar statistical characteristics of different surfaces. A noticeable difference in PSD appears for spatial frequencies below f=1/(2R). Within this frequency range the amplitude of PSD functions correlates with the characteristic size of VO<sub>2</sub> NPs, showing gradual increase of the surface inhomogeneity with particle size. As spatial frequency exceeds f=1/(2R), such a correlation disappears. At higher frequencies the PSD amplitude does not depend strictly on NP size. This could be due to additional presence of multiscale  $VO_2$ nanocrystallites with sizes much smaller than the average NP size. Moreover, a low frequency component of PSD function increases significantly as particles grow while higher frequency component undergo a relatively small change. This fact indicates a growth of nanoparticles with a preferred size, as was also observed directly in the AFM images.

It is well known that the optical properties of materials significantly depend on the material morphology. Therefore quantitative analysis of reflection and transmission data can give information about material optical constants and structure. Results of reflectance measurements versus angle of incidence at  $\lambda$ =527 nm are presented in Fig. 2 for a 30-nm-thick unannealed amorphous VO<sub>2</sub> film and for the nanocrystalline film with largest NPs. The figure shows the reflect



FIG. 2. (Color online) Angular dependence of the reflectance in two polarizations for amorphous and nanocrystalline VO<sub>2</sub> films at  $\lambda$ =527 nm. Symbols are experimental data, lines are calculated reflectance. The inset shows the Brewster angle versus particle size.

tance for two orthogonal polarizations, perpendicular ( $R_s$ ) and parallel ( $R_p$ ) to the incidence plane. The angular dependences of  $R_s$  and  $R_p$  are typical for semiconductor films with a Brewster angle located between 67° and 76° (see inset in Fig. 2).

A good agreement was obtained between experimental data and theoretical curves calculated with the Fresnel relations applied for thin films according to Ref. 65. By fitting of the experimental data, the index of refraction at  $\lambda$ =527 nm was found to be n=2.6+i0.6 for the amorphous VO<sub>2</sub> film and n=3.0+i0.8 for the nc-VO<sub>2</sub> film with largest NPs. Thus, annealing produces noticeable changes in the film morphology and optical constants. As annealing time and NP size increases, the concentration of structural defects and oxygen nonstoichiometry decreases, <sup>19</sup> resulting in the increase of the real and imaginary parts of the complex refractive index and, as a consequence, in the gradual change of the Brewster angle.

To gain knowledge about the relation between optical properties and structure of nc-VO<sub>2</sub> films upon thermally induced PT, optical transmission measurements were conducted. Spectral measurements (not presented here) within the visible optical range have shown that the relative change of the transmittance during PT does not depend strictly on the VO<sub>2</sub> particle size. Nevertheless the shape and slope of each hysteresis loop for transmittance measured at  $\lambda = 1310$  nm are strongly dependent on the film structure and mean radius of nanoparticles (Fig. 3). The hysteresis loop becomes broader with steeper edges as VO<sub>2</sub> NP size increases.

The observed differences in hysteresis have been attributed to different statistical properties of nc-VO<sub>2</sub> films, various concentrations of oxygen vacancies, dislocations and mechanical stresses in VO<sub>2</sub> NPs of different size.<sup>13,19,20,57</sup> The annealing process and NP growth result in higher crystalline perfection of the VO<sub>2</sub> structure and modification of microrelief, making the size distribution of VO<sub>2</sub> particles more uniform. According to Ref. 57, VO<sub>2</sub> grains with comparable sizes have similar PT temperatures. Therefore a



FIG. 3. (Color online) Transmittance of nc-VO<sub>2</sub> films versus temperature at  $\lambda = 1310$  nm.

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. At the same time, the whole temperature range of the hysteresis loop is a function of structural defects of VO<sub>2</sub> structure.<sup>20,57</sup>

Vanadium dioxide has a relatively large third-order non-linear susceptibility  $\chi^{(3)}$ .<sup>62,66</sup> For ultrathin VO<sub>2</sub> solid films in the insulating phase the  $|\chi^{(3)}|$  is around  $(5-8) \times 10^{-9}$  esu at  $\lambda = 400$  nm and drops to  $5 \times 10^{-10}$  esu for the metallic phase. Experimental measurements of  $\chi^{(3)}$  for the insulating phase are difficult because the light interaction with VO<sub>2</sub> induces the first-order phase transition, giving an additional contribution to the optical response. To accomplish correct measurements of  $\chi^{(3)}$  by DFWM technique it is important to separate diffraction signals related to  $C_{2h}^5 \rightarrow D_{4h}^{14}$  lattice transformation and to excitation of the population density grating. In this study, in order to detect only the signal from the population density grating, the optical pump was adjusted at different levels near and below the threshold for the lightinduced I-M PT. Since below a threshold point the lattice transformation is not initiated, the DFWM signal is due to excitation of the electronic subsystem only. The third-order susceptibility for each sample was measured in a series of experiments at different pump levels versus peak intensity of electromagnetic field in the film, as shown in Fig. 4(a). We note that these intensities are four times larger than those of a single pump beam  $I_0$  due to interference effect. The  $|\chi^{(3)}|$ values were calculated from experimental DFWM data in accordance with the relation for diffraction signal from Refs. 67 and 68.

For each individual sample the Fig. 4(a) shows a nearly constant  $|\chi^{(3)}|$  value, as peak field intensity increases up to  $\sim 3 \times 10^{10}$  W/cm<sup>2</sup> and up to  $\sim 1 \times 10^{10}$  W/cm<sup>2</sup> for a crystalline VO<sub>2</sub> film without NPs and for the *nc*-VO<sub>2</sub> film with smallest NPs, respectively. Above these threshold levels the  $|\chi^{(3)}|$  values decrease significantly. Generally, the third-order nonlinear susceptibility does not depend on incident light intensity. Therefore the set of  $|\chi^{(3)}|$  measurements at different pump levels should give the same result. However this is valid only for material in the same phase. If the material undergoes a PT, its nonlinear susceptibility changes as well. Hence, in accordance with the data obtained, the third-order



FIG. 4. (Color online) The third-order nonlinear susceptibility of VO<sub>2</sub> films in insulating phase. (a)  $|\chi^{(3)}|$  as a function of peak intensity of the interference field in the film. The experimental data are taken at laser pump level below (filled symbols) and above (open symbols) I-M PT threshold. (b)  $|\chi^{(3)}|$  as a function of particle radius.

nonlinear susceptibility for insulating VO<sub>2</sub> can be assigned to  $|\chi^{(3)}|$  measured at lower optical pumping below the PT threshold level. This threshold is associated with pump intensity when the  $|\chi^{(3)}|$  starts to change. In Fig. 4(a) the corresponding region is depicted by a solid line. As can be seen, the I-M PT threshold level is larger for crystalline film and decreases with NP size from  $3 \times 10^{10}$  W/cm<sup>2</sup> to  $1 \times 10^{10}$  W/cm<sup>2</sup>.

Below the threshold for each sample the  $|\chi^{(3)}|$  data are slightly dispersed near a constant level which can be considered as the averaged third-order nonlinear susceptibility. To define the size dependence of nonlinear susceptibility more precisely, the  $|\chi^{(3)}|$  measurements were conducted for different samples at the same experimental conditions and at peak pump intensity of  $I_0 = 1 \times 10^9$  W/cm<sup>2</sup> which is significantly below the I-M PT threshold. The data obtained are shown in Fig. 4(b). The third-order susceptibility demonstrates a gradual increase with NP size. Such behavior can originate both from excitonic enhancement of  $\chi^{(3),69}$  and from size dependence of the VO<sub>2</sub> morphology, crystallinity and number of structural defects. However it is difficult to estimate here the individual contributions of these two factors. Films with larger particles have higher crystallinity, lower concentration of defects and, as a consequence, higher  $\chi^{(3)}$ . On the other hand, the excitonic enhancement can be also signifi-



FIG. 5. (Color online) Normalized diffraction efficiency versus probe-pulse delay at different pump fluence for single nc-VO<sub>2</sub> film; average radius of nanoparticles is R=24 nm.

cant. It is important to note that the excitonic enhancement of the third-order susceptibility occurs in small semiconductor particles with radii *R* much larger than the exciton Bohr radius but smaller than the excitation wavelength  $\lambda$ ,<sup>69–71</sup> and such particles are under consideration in the present study. It is also possible to expect an excitonic enhancement of  $\chi^{(3)}$  in ultrathin crystalline film without NPs but with thickness  $d \ll \lambda$ .

# B. Transient grating dynamics upon light-induced phase transition

### 1. Time evolution of the diffracted signal

The light-induced phase transition in VO2 is ultrafast and can occur faster than 150 fs.<sup>17,21,38,47,56</sup> However if light intensity is not sufficiently high, the I-M PT process takes tens or hundreds of picoseconds.<sup>72</sup> Such a longer PT also occurs for relatively thick VO<sub>2</sub> films (d > 50 nm) because of strong light absorption in the film.<sup>73–75</sup> Films used in our experiments have nearly equal thicknesses which correspond to the light penetration depth in VO<sub>2</sub> at  $\lambda$ =400 nm ( $\simeq$ 30 nm). Therefore laser excitation produces an almost uniform distribution of metallic nuclei across the film, perpendicularly to the surface. However in the lateral direction the nucleation occurs only within areas where the laser pump intensity exceeds a PT threshold. Such experimental conditions facilitate the data analysis and allow development of a model for metallic phase evolution in the system. The growth of the new phase during and after light illumination is highly nonlinear and depends on light intensity, pulse duration, wavelength, density, and type of excited electronic states in VO<sub>2</sub>.

A representative evolution of the TG diffraction signal  $\eta(t)$  for one *nc*-VO<sub>2</sub> film on a 2.5 ns time scale at different excitation levels is shown in Fig. 5. Here  $\eta(t)$  is normalized to its maximal value at pump fluence of 1.43 mJ/cm<sup>2</sup>. The signal is associated with the formation of the spatial metal/insulator diffraction grating and demonstrates complex be-





FIG. 6. (a) Distribution of the light intensity on the film surface in transient grating experiment and photoinduced change in the real and imaginary parts of the complex dielectric constant for ultrathin VO<sub>2</sub> film at  $\lambda$ =400 nm. The range of  $\varepsilon(x)$  variation is taken from Ref. 76. The ultrafast I-M PT occurs when the intensity of resultant electromagnetic field in the film I(x) exceeds a PT threshold  $I_{\text{PT}}$ . (b) Optically exited carrier density grating. (c) TG diffraction signal versus volume fraction of metallic phase.

havior depending on average pump fluence. Generally, the structural dynamics of VO<sub>2</sub> at any optical excitation can be separated into three main components: (i) ultrafast phase transition (UPT) with characteristic time less than 500 fs, (ii) extended phase transition (EPT) during  $\sim 0.1-0.3$  ns, and (iii) the VO<sub>2</sub> recovery (metal-to-insulator transition) on the time scale up to hundreds of nanoseconds.<sup>6,56,72</sup>

The UPT can be resolved in Fig. 5 as a sharp signal rise at zero time delay. Since the distribution of light intensity on the film surface is alternative, the UPT is initiated in the areas of the interference pattern where field intensity is maximal [see Fig. 6(a)]. Within adjacent areas with lower light intensity the PT becomes to be slower (EPT) and occurs during  $\sim 0.1-0.3$  ns. The M-I recovery process stars after this period of time.

It has to be noted that the evolution of TG signal for thin nc-VO<sub>2</sub> film significantly different as compared to other materials and, therefore, it requires special consideration. Since the experiment is performed for ultrathin films, the intensity distribution across the film is uniform at each point but has a periodical modulation along the film surface. The ultrafast optical pump excites a population density grating  $\Delta n$  [Fig. 6(b)] and also produces the I-M PT within areas where the field intensity is higher than the PT threshold level  $I_{\rm PT}$  [Fig. 6(a)]. The diffraction signal intensity  $\eta(t)$  depends on both these factors. However, as shown in Refs. 56 and 75, at sufficiently high optical pump the change of VO<sub>2</sub> optical properties on the picosecond time scale is determined mostly by growth of new metallic phase during PT and the contribution of excited electronic states is small. Therefore, as a good approximation in the light-induced I-M PT experiment, the transient signal  $\eta(t)$  is determined mostly by evolution of metallic phase in the film. In ultrathin VO<sub>2</sub> films the boundary between insulator and metallic phases is quite sharp. This happens because the insulating phase changes to the metallic one abruptly in the area where the pump intensity exceeds the I-M PT threshold  $I_{\text{PT}}$  [Fig. 6(a)]. Thus, the spatial distribution of  $\varepsilon(x)$  for the thin VO<sub>2</sub> film can be approximated by a Heaviside-type function

$$\varepsilon(x) \simeq \varepsilon_I + \frac{(\varepsilon_M - \varepsilon_I)}{1 + \exp(-\gamma [2I_0 + 2I_0 \cos(q_x x) - I_{\rm PT}])}, \quad (1)$$

where  $\varepsilon_M$  and  $\varepsilon_I$  are dielectric constants of metallic and insulating VO<sub>2</sub>, correspondingly,  $q_x = 2\pi/\Lambda$  is the grating vector, and  $\Lambda = \lambda/2 \sin(\theta/2)$  is the diffraction grating period,  $I_0$ is the peak intensity of each incident pump beam,  $\gamma$  is a constant which defines the steepness of the  $\varepsilon(x)$  function at the metal-insulator boundary. Therefore, in spite of the sinusoidal distribution of pump intensity in the film, the VO<sub>2</sub> dielectric constant  $\varepsilon(x)$  is modulated by a rectangular function due to the step boundary between metallic and insulating phases.

The spatial inhomogeneity of  $\varepsilon(x)$  is a principal factor which defines the TG diffraction signal intensity. This signal is proportional to the averaged squared value of the dielectric constant variation as  $\eta(t) \sim \langle |\Delta \varepsilon|^2 \rangle$ .<sup>77–79</sup> As shown in the Appendix, taking into account the rectangular modulation of  $\varepsilon(x)$ , the spatial averaging of  $|\Delta \varepsilon|^2$  gives  $\langle |\Delta \varepsilon|^2 \rangle = |\varepsilon_0|^2 [\xi(1 - \xi)]$ , where  $\varepsilon_0 = \varepsilon_M - \varepsilon_I$  and  $\xi$  is the volume fraction of metallic phase in the film. This result allows defining the TG diffraction signal as

$$\eta(\xi) \simeq \eta_0 [4\xi(1-\xi)],\tag{2}$$

where  $\eta_0$  is a maximal diffraction intensity. This relation shows that the diffraction signal is maximal when the metallic and insulating phases have equal volume fractions in the film [Fig. 6(c)].

The TG data in Fig. 5 show significant qualitative difference at highest and lowest pumping. Nevertheless, according to Eq. (2), at different excitation levels the evolution of the TG signal indicates similar structural dynamics in the film. Thus, at higher optical pumping the volume fraction of the metallic phase is  $\xi > 1/2$  and, in agreement with Eq. (2), signal  $\eta(t)$  decreases on ~0.3 ns time scale as the metallic phase grows. At lower pump level the situation is opposite:  $\xi < 1/2$  and  $\eta(t)$  increases, as the metallic phase grows as well. A study of this phase growth in optically excited VO<sub>2</sub> on ~0.3 ns time scale (EPT) is discussed in the next section.

#### 2. Kinetics of metallic phase growth after optical excitation

To obtain information about the EPT in VO<sub>2</sub> nanostructures, EPT dynamics was studied for nc-VO<sub>2</sub> samples at different excitation levels. Figure 7 shows TG diffraction efficiency for highest ( $w_p = 5 \text{ mJ/cm}^2$ ) and lowest ( $w_p$ =1 mJ/cm<sup>2</sup>) laser fluence used in such experiment. Here,  $\eta(t)$  is normalized to its maximal value for the film with R =37 nm at  $w_p = 5 \text{ mJ/cm}^2$ . We note that the sequence in the signal intensity  $\eta(t)$  for different films at higher excitation [Fig. 7(a)] is in the reverse order as compared to the lower



FIG. 7. (Color online) Normalized diffraction efficiency upon EPT in *nc*-VO<sub>2</sub> films at excitation energy (a)  $w_p=5 \text{ mJ/cm}^2$  and (b)  $w_p=1 \text{ mJ/cm}^2$ . Dashed lines are a fit by Eqs. (2) and (9).

excitation [Fig. 7(b)]. Nevertheless the metallic phase growth dynamics is similar in both cases, as discussed in previous section. According to Eq. (2), diffraction efficiency would be maximal if the size of metallic and insulating  $VO_2$  strips in the induced diffraction grating is the same  $(\xi = 1/2)$ , since the transparency modulation ratio for such a grating is maximal. In the present experiment the fraction of the metallic phase at lower excitation is less than 1/2 but it is above this value at higher excitation for each film. At higher pump level [Fig. 7(a) the signal is stronger for samples with larger particle size in accordance with Eq. (2) and Fig. 6(c), because the fraction of metallic phase  $\xi$  is above 1/2 but  $\xi$  is lower for the nc-VO<sub>2</sub> films with larger particles as compared to the films with smaller particles. As optical fluence decreases to  $w_p$ =  $1 \text{ mJ/cm}^2$  the sequence of the curves is reversed [Fig. 7(b) because the  $\xi$  becomes lower than 1/2 for all films but  $\xi$  anyhow is still lower for the films which contain larger particles.

Previous study of VO<sub>2</sub> TG dynamics in ultrathin VO<sub>2</sub> films has shown that the diffusion processes in the film plane do not give noticeable contribution to the I-M PT at least on ~200 ps time scale.<sup>56</sup> It was confirmed by TG measurements with different grating periods,  $\Lambda = 1 \ \mu m$  and  $\Lambda$ =2.5  $\mu m$ , where the relaxation dynamics was found to be identical for different  $\Lambda$ . According to Refs. 78–80, this result indicates that the heat or currier diffusion along the grating vector in the film plane cannot be considered as a primary origin of EPT. Moreover, such diffusion in *nc*-VO<sub>2</sub> films is even weaker in comparison with solid crystalline VO<sub>2</sub> films due to localization of relaxation processes within the volume of single nanoparticles. Hence, the heat or currier diffusion in the lateral direction in ultrathin VO<sub>2</sub> films can be neglected.



FIG. 8. (Color online) Time dependence of normalized transient grating signal  $\eta(t)$  for crystalline VO<sub>2</sub> film without NPs on Al<sub>2</sub>O<sub>3</sub> substrate upon light-induce I-M PT at different excitation energies. Dashed lines are fit by Eq. (2) and (9).

An estimation of the heat flow in VO<sub>2</sub> with thermal diffusion coefficient of 0.02  $\text{ cm}^2/\text{s}$  made in Ref. 6 shows that the thermally induced transition is relatively slow and can be observed on the time scale larger than 1 ns. A study of a thermal contribution to the I-M EPT and M-I recovery dynamics was reported in Ref. 72 for thin VO<sub>2</sub> films. It was shown that this contribution to the EPT on subnanosecond time scale is small but can be dominant on longer scale in the recovery. Figure 8 shows an example of such PT dynamics in the crystalline  $VO_2/Al_2O_3$  film. Thus, if the pump energy is sufficiently high  $(w_p > 2 \text{ mJ/cm}^2)$ , the temperature of VO<sub>2</sub> film can exceed the PT point  $T_c$  after interband electron-hole recombination and electron-phonon relaxation. In this case the M-I recovery process is thermal and occurs due to heat sink from the film to the substrate. As a result, it strongly depends on substrate thermal conductivity  $K_s$  and takes from tens of nanoseconds to microseconds.<sup>62,72</sup> The difference in recovery time for VO2 films deposited on single-crystal  $Al_2O_3$  ( $K_s$ =42 W m<sup>-1</sup> K<sup>-1</sup>) and glass substrate with lower  $K_{\rm s}(K_{\rm s}=1.38~{\rm W~m^{-1}~K^{-1}})$  is around two orders of magnitude. However, the thermal processes in PT dynamics can be suppressed by reducing the laser excitation energy down to relatively low level ( $w_p \leq 2 \text{ mJ/cm}^2$ ), when it is still possible to induce the I-M PT but without increase of the film temperature above the critical point  $T_{c}$ . Then the thermal influence onto PT becomes negligibly small and the heat sink into the substrate does not control the M-I recovery. The recovery occurs almost simultaneously for VO2 films deposited onto substrates with different thermal conductivities and takes only  $\sim 2.5$  ns.<sup>62,72</sup> Thus, at sufficiently low laser excitation the total VO<sub>2</sub> structural dynamics, including EPT, cannot be assigned to thermal processes in the film. It is also important to note that the characteristic time of EPT in Ref. 72 was found nearly independent on the laser pump energy and was the same for different VO2 films deposited on glass and Al<sub>2</sub>O<sub>3</sub> substrates. The EPT time  $\tau$  in Fig. 8 also shows only a slight dependence on optical excitation, as it will be shown below. These results indicate that the thermal contribution to EPT on subnanosecond time scale is rather small at any optical pumping. Therefore EPT dynamics could be assigned to an interaction of lattice vibrations with excited electronic states.

Since the PT of VO<sub>2</sub> is a first-order transition, the EPT should be considered in terms of a decay of some metastable state into metallic phase. Thus, after laser excitation whole film is switched to a metastable state, except areas where the I-M transition is already done. As noted above, the thermal contribution to EPT is unlikely. Therefore the VO<sub>2</sub> metastability can be associated with single or cooperative optically excited electronic states. In this scenario the EPT occurs as a growth of metallic nuclei within metastable zones of the film. Here we assume that the metallic nuclei are formed during UPT, the size of single nucleus is less than the size of VO<sub>2</sub> NP and the nucleus growth process is confined by NP volume. In TG experiment the concentration and sizes of nuclei are nonuniform in the film plane and have a periodical distribution.

The evolution of VO<sub>2</sub> metallic phase after optical excitation can be described in terms of a phenomenological model of the new phase boundary migration. After ultrafast light excitation and formation of metallic nuclei, the nucleus growth occurs on a 100–300 ps time scale. This relatively slow transition (EPT) can be associated with motion of a nucleus boundary in the metastable zone of VO<sub>2</sub> with a velocity  $v_M$  in response to the net pressure P(t) on the boundary. Here we can assume that the 'pressure' is a generalized function of the I-M PT driving force, which depends on the optical excitation level and on the nature of excited electronic states in VO<sub>2</sub>. From the recrystallization theory of solids,<sup>81</sup> the velocity  $v_M$  is taken to be directly proportional to the pressure as

$$v_M(t) = M(t)P(t), \tag{3}$$

where M(t) is the mobility of the nucleus boundary. Since the EPT occurs in a highly nonequilibrium environment, the mobility M(t) and pressure P(t) both depend on optical pump fluence  $w_p$  and time t. Evidently, at temperatures below the PT point  $T_c$  and without optical excitation the nucleus boundary mobility and PT driving force are zero and PT does not occur. However, laser excitation considerably changes the PT conditions. Optical pumping generates numerous excited electronic states which form a metastable state of VO<sub>2</sub> and reduce the activation energy  $\Delta G_{cr}$  for nucleus boundary migration. As a result, the metallic phase grows in the metastable zone of the film. In order to analyze the nucleus growth dynamics, we apply the approximation where the mobility M(t) is independent of the PT driving force and independent of the details of the mechanism of boundary migration, and is an exponential function<sup>81</sup> which can be expressed as

$$M = M_0 \exp\left(-\frac{\Delta G_{cr}}{k_B T}\right),\tag{4}$$

where  $M_0$  is the maximal mobility, T is the lattice temperature, and  $k_B$  is the Boltzmann constant. Here we neglect thermal effects in I-M transition dynamics and assume that at room temperature the activation energy  $\Delta G_{cr}$  depends only on the energy of excited electronic states including cooperative effects. In terms of this model, an optically excited single electronic state reduces the activation energy to some level  $G_{ex}^0$ . Additional contribution of cooperative interactions between excited states can provide further reduction in this energy. Since the energy of a cooperative excited state has quadratic dependence on concentration  $n_{ex}$  of active quasiparticles in the cluster (for instance, excitons or polarons),<sup>82</sup> the activation energy can be approximated as

$$\Delta G_{cr} = G_{ex}^0 - G_{ex}^1 n_{ex}^2, \tag{5}$$

where the second term corresponds to the contribution of cooperative interactions and  $G_{ex}^1$  is a constant.

In this model we do not emphasize the nature of the excited electronic states. It can be an excitation in VO<sub>2</sub> due to charge transfer and lattice distortion. In our previous studies<sup>54</sup> we have developed models of I-M PT which are based on exciton interaction with the VO<sub>2</sub> lattice. The main idea involves the creation of a cooperative potential well due to interaction between excited states which facilitate the PT process. The depth of this well depends on the concentration of photoexcited electrons per VO<sub>2</sub> cluster. Assuming an exponential decay of excited states in the cluster, their concentration can be expressed as  $n_{ex}=n_0e^{-t/\tau_{ex}}$ , where  $n_0$  is a maximal concentration and  $\tau_{ex}$  is a characteristic lifetime. As a result, the activation energy is

$$\Delta G_{cr} = G_{ex}^0 - G_{ex}^1 n_0^2 e^{-2t/\tau_{ex}}.$$
 (6)

In this approximation the time dependence of the boundary mobility is caused by decay of cooperative states only. Here we assume that the activation energy  $G_{ex}^0$  has a constant value on the monitored time scale.

The EPT occurs in the metastable zone of the film and the PT driving force has to be controlled by a level of metastability. Therefore the temporal behavior of the PT driving force will be proportional to the decay of the metastable state. Assuming an exponential decay pattern, the pressure on the metallic phase boundary can be expressed as  $P(t) = P_0 e^{-t/\tau_m}$ , where  $P_0$  is the maximal pressure, and  $\tau_m$  is the characteristic decay time of the VO<sub>2</sub> metastable state. This characteristic time describes decay of all exited electronic states, including hot free electrons and cooperative states. Time  $\tau_{ex}$  is expected to be close or equal to  $\tau_m$ , however the relation between these times can be found only after the exact nature of excited electronic states in VO<sub>2</sub> is revealed. The nucleus boundary velocity is then

$$v_M(t) = v_0 \exp\left(\frac{G_{ex}^1 n_0^2 e^{-2t/\tau_{ex}}}{k_B T} - \frac{t}{\tau_m}\right),$$
(7)

where  $v_0 = M_0 P_0 \exp(-G_{ex}^0/k_B T)$ . Equation (7) allows one to calculate the volume fraction of metallic phase in the film upon EPT and to determine the TG signal (2). However, since in TG experiment the light pulse can produce many metallic nuclei with nonuniform distribution, the growth speed of the metallic phase within grating period has to be described by an averaged value  $\langle v_M \rangle$ . Here  $\langle \dots \rangle$  denotes a spatial averaging.

The total volume fraction of metallic phase  $\xi$  can be presented as a sum of the metallic phase fraction  $\xi_0$  produced during UPT and the fraction  $\xi_M$  which is related to the incipient metallic phase in the metastable area of the film during EPT. Taking into account that some fraction  $\xi_I$  of VO<sub>2</sub> metallic nanoparticles undergo also a recovery process (i.e., M-I PT), the net volume fraction of metallic phase can be written as  $\xi = \xi_0 + \xi_M - \xi_I$ . For thin film this relation can be expressed by using the boundary velocity  $\langle v_M \rangle$  for metallic phase and  $\langle v_I \rangle$  for incipient insulating phase during M-I recovery as

$$\xi(t) \approx \xi_0 + \frac{1}{\Lambda} \int_0^t \langle v_M(t') \rangle dt' - \frac{1}{\Lambda} \int_0^t (1 - e^{-t'/\tau_m}) \langle v_I \rangle dt',$$
(8)

where the recovery starts right after decay of the metastable state. Assuming that the recovery process is much slower than EPT and has a nearly constant velocity  $\langle v_I \rangle$  on the monitored 2.5 ns time scale, the metallic phase fraction in the film can be modeled by

$$\xi(t) \approx \xi_0 + \frac{\langle v_0 \rangle}{\Lambda} \int_0^t \exp\left(\frac{\langle G_{ex}^1 n_0^2 \rangle e^{-2t'/\tau_{ex}}}{k_B T} - \frac{t'}{\tau_m}\right) dt' - \frac{\langle v_I \rangle}{\Lambda} \int_0^t (1 - e^{-t'/\tau_m}) dt'.$$
(9)

On the picosecond scale, when the recovery process is not started yet, the third term in the Eqs. (8) and (9) can be neglected. The approximation of experimental data by Eqs. (2) and (9) shows good coincidence for the crystalline  $VO_2$  film without NPs (Fig. 8) as well as for *nc*-VO<sub>2</sub> films [Fig. 7 and 11(b)]. Thus, this model can be applied for different structures and can give quantitative information about evolution of a new phase in the system.

Previous study of EPT in thin solid VO<sub>2</sub> films did not show significant differences in characteristic times for EPT at various levels of optical excitation.<sup>72</sup> Nevertheless, in this work we found that the transition time  $\tau$  for crystalline VO<sub>2</sub> film is slightly decreasing from 0.24 ns to 0.20 ns as excitation level increases (Fig. 8). Here the time  $\tau$  was derived by fitting Eqs. (2) and (9) to TG experimental data, and good agreement was obtained when times  $\tau_m$  and  $\tau_{ex}$  were chosen to be equal  $(\tau = \tau_m = \tau_{ex})$ . In *nc*-VO<sub>2</sub> structures additional influence on time  $\tau$  can be produced by spatial confinement of optical excitations within volume of single NPs. Figure 9 shows the EPT time derived from the data in Fig. 7, where it demonstrates a nearly linear increase with particle size at constant excitation energy. This size-dependent EPT in VO<sub>2</sub> NPs can be due to lower activation energy  $\Delta G_{cr}$  in smaller NPs and due to different propagation time of optical excitations in different NPs. Also, a slight difference in time  $\tau$  was observed at higher and lower pumping for each film. Perhaps, such a dependence of  $\tau$  on laser excitation level is related to the higher probability of the transition at higher pumping due to some processes of phonon coupling with photoexcited states which are not considered in the phenomenological model discussed above.

Recently Baum *et al.*<sup>6</sup> reported on the ultrafast electron diffraction study of light-induced I-M PT of VO<sub>2</sub> and have shown that the PT within  $\sim 300$  ps occurs as a shear motion of atoms, and the speed of this motion is close to the aver-



FIG. 9. EPT time versus particle size (symbols). Solid lines are a linear fit. The dotted line shows the ballistic propagation time in  $VO_2$  crystalline particle.

aged speed of acoustic waves in crystalline VO<sub>2</sub>,  $v_s \approx 4000 \text{ m/s.}^{83}$  In the present work, the characteristic time  $\tau$  of EPT was found longer but comparable with propagation time of ballistic phonons through the nanoparticle  $t_R$  $=2R/v_s$  (Fig. 9). These results indicate that the EPT is rather a phonon-assisted transition. An estimation of phonon scattering in VO<sub>2</sub> shows that a resonant and nonresonant phonon scattering on V-V dimers is noticeable while the elastic scattering by defects should be neglected because the mean free path of this scattering is substantially above the size of  $VO_2$ particles, film thickness and TG period. We also note that the elastic phonon scattering by NP's surface and excitation of breathing acoustic modes in NPs could provide additional contribution to the PT dynamics. However in the present study we did not observe any signature of coherent acoustic oscillations.

Since the femtosecond optical pulse generates  $\simeq 6$  THz coherent V-V oscillations,<sup>38,47</sup> the resonant phonon scattering should occur on V-V dimers. According to Ref. 84 the cross section of this scattering is  $\sigma = \lambda_0^2 / \pi$ , where  $\lambda_0$  is the phonon wavelength. Taking into account the concentration of vanadium ions in VO<sub>2</sub>  $(3 \times 10^{22} \text{ cm}^{-3})$ ,<sup>50</sup> we derive a mean-free path  $\ell \simeq 5 \times 10^{-8^{\circ}}$  cm. This length has order of VO<sub>2</sub> lattice period and, therefore, initially generated optical phonons are confined to a few lattice periods. The phonon propagation on distances longer than  $\ell$  occurs due to nonresonant scattering, where initial phonon of frequency  $\nu_0$  decays to lower energy phonons with  $\nu_1 \simeq \nu_0/2, \nu_2 \simeq \nu_1/4, ..., \nu_i \simeq \nu_1/2^{i.84}$  It is also interesting to note that the estimated characteristic time of the resonant phonon scattering is  $\tau^* \simeq 120$  fs which is around UPT time of VO<sub>2</sub>. Hence, it is possible that this scattering could be significant during UPT.

The nonresonant scattering with cross section<sup>84</sup>  $\sigma = (\lambda_0^2/\pi)(\Gamma/\nu_0)^2(\nu/\nu_0)^4$  occurs due to anharmonic phonon interactions with V-V pairs. Assuming that the width of phonon state  $\Gamma$  at  $\nu_0 \approx 6$  THz is quite broad under high-intensity optical excitation,<sup>38</sup>  $\Gamma = 1.5$  THz, the estimation of the meanfree path gives  $\ell_1 \approx 120$  nm for  $\nu_1$  phonons. The magnitude of this length is comparable with the size of VO<sub>2</sub> nanoparticles and *nc*-VO<sub>2</sub> film thickness. For  $\nu_1$  phonons we find the characteristic scattering time approximately 30 ps which is within the order of measured EPT time  $\tau$  (Fig. 9). Hence, the



FIG. 10. (Color online) Normalized transient grating signals upon ultrafast light-induced insulator-to-metal phase transition of nc-VO<sub>2</sub> films.

contribution of nonresonant scattering to EPT could be noticeable. This scattering leads to quasidiffusional phonon propagation, where the propagation time linearly depends on distance traveled but is longer than the ballistic propagation time  $t_{B}$ .<sup>84,85</sup>

As shown above the thermal, in the ordinary sense, contribution to the light-induced transition is unlikely during the time period up to hundreds of picoseconds. Nevertheless the contribution of nonequilibrium phonons to the EPT dynamics should to be crucial. VO<sub>2</sub> can undergo the EPT as phonons propagate through the volume of the VO<sub>2</sub> particle, producing a decay of the optically excited metastable state (e.g., state produced by excitons, polarons, or dense electronhole plasma) via phonon scattering. The first-order I-M PT has vibronic origin during the  $(V^{4+} \rightarrow V^{5+} + e_{free})$  reaction with *percolation behavior*.<sup>54</sup> In this process the deformation field induced by interaction of the  $3d_{\parallel}$  state with lattice vibrations in the insulator phase vanishes, resulting in structural I-M PT.

#### 3. Ultrafast transition and nucleation of metallic phase

The I-M UPT dynamics was studied at a constant pump level  $w_p=5$  mJ/cm<sup>2</sup>. Figure 10 shows the sharp signal rise associated with UPT within the subpicosecond time domain. The characteristic time for UPT was estimated to be close to the autocorrelation width of the excitation laser pulse. Therefore, the UPT time for VO<sub>2</sub> nanoparticles is apparently less or close to the pulse duration used in the experiment. A common sharp peak at zero delay is associated with the nonlinear contribution to the dielectric susceptibility caused by electronic excitations upon laser pulse interaction with the sample. It was also found that the TG signal amplitude during UPT depends on the size of the nanoparticles.

The amplitude of the signal at constant pump level is gradually larger for the samples with larger NPs (Fig. 10). However, this result shows some ambiguity compared with the relative change in the transmittance during PT, which did not show an evident correlation with VO<sub>2</sub> NP size either at  $\lambda$ =1310 nm (Fig. 3) or within the broad visible spectral range. Therefore, a gradual increase of the TG signal with particle size within the picosecond time scale is difficult to assign to a different relative change of the transmittance and/or optical constants upon PT. Most likely it is a consequence of different I-M PT threshold levels in different films.

Taking into account that the boundaries between insulator and metallic phases in a light-induced grating are sharp, the phase change along the VO<sub>2</sub> film can be approximated by Heaviside-type function, as discussed in Sec. III B 1. Thus, the metallic phase fraction  $\xi_0$  produced during ultrafast transition is defined by

$$\xi_0 \simeq \frac{1}{m\Lambda} \int_0^{m\Lambda} \frac{dx}{1 + \exp(-\gamma [2I_0 + 2I_0 \cos(q_x x) - I_{\rm PT}])},$$
(10)

where *m* is an integer number. This relation shows that  $\xi_0$  depends on the PT threshold level  $I_{\text{PT}}$ . Since the metallic grating induced during UPT produces the diffraction signal  $\eta(\xi_0) \cong \eta_0[4\xi_0(1-\xi_0)]$ , [see Eq. (2)], then at constant pump level  $I_0$  the TG signal  $\eta(t)$  is strictly proportional to the threshold  $I_{\text{PT}}$ .

At a pump fluence  $w_p = 5 \text{ mJ/cm}^2$  the induced fraction of metallic phase  $\xi_0$  in the film exceeds 1/2. Therefore in accordance with Eq. (2) and Fig. 6(c), a higher signal in Fig. 10 corresponds to the lower  $\xi_0$ . Moreover, taking into account Eq. (10), the observed decrease in diffraction signal with NP radius indicates that the threshold level  $I_{\text{PT}}$  of I-M PT also decreases with the radius of VO<sub>2</sub> particles. We note that this result is in good agreement with the conclusion about the PT threshold obtained from analysis of the third-order nonlinear susceptibility in Sec. III A [Fig. 4(a)].

In contrast to bulk VO<sub>2</sub>, it is likely that the influence of the NP's interface on the threshold level  $I_{PT}$  is dominant. In VO<sub>2</sub> NPs the low frequency order-disorder soft mode can be modified due to size effect. Since the experimental results indicate that the threshold  $I_{PT}$  is reduced for small NPs, the interaction strength between interface soft mode and optically excited electronic states has to be increased as the NP's size decreases, resulting in a higher probability of I-M PT.

It has to be also noted that the decrease of the pump fluence down to  $w_p = 1 \text{ mJ/cm}^2$  results in a reduction of  $\xi_0$ below 1/2 and, as a consequence, in opposite behavior of the diffraction signal  $\eta(t)$ : the signal increases as the particle size decreases, as was shown in Fig. 7(b). Further decrease in excitation energy will lead to significant reduction in size and concentration of metallic nuclei in the film.

A monitoring of excited states dynamics at low concentration of metallic nuclei can give important information about nucleation and subsequent nucleus growth in VO<sub>2</sub> NPs during EPT. To study the metallic phase nucleation in nc-VO<sub>2</sub> film the laser pump was reduced to the minimal level of 300  $\mu$ J/cm<sup>2</sup>, as low as the TG signal was still measurable. We note that this amount of energy is substantially below minimum value required to produce thermally induced PT in thin film. Therefore a thermal contribution to the PT dynamics in VO<sub>2</sub> can be neglected.

Figure 11 shows the absolute diffraction efficiency for nc-VO<sub>2</sub> films with equal thicknesses but NPs of different radii. Compared to the data in Fig. 10, the TG signal at lower pump level demonstrates significant differences on the time scale of a few picoseconds [Fig. 11(a)], where it yields a



FIG. 11. (Color online) Time dependence of absolute diffraction efficiency  $\eta(t)$  for nc-VO<sub>2</sub> films at the excitation energy  $w_p$ = 300  $\mu$ J/cm<sup>2</sup>. (a) TG signal on a 3 ps time scale. (b) Evolution of the signal  $\eta(t)$  demonstrates I-M EPT (signal growth on a ~0.1–0.3 ns scale) and M-I PT (recovery process on a longer time scale). Dashed lines are approximations by Eq. (2) and (9). Inset shows a start of I-M EPT.

sharp peak at zero delay time. Furthermore, as the pump pulse ends, the diffraction signal level for different samples becomes the same after 0.5 ps.

As noted above, the TG signal at sufficiently high pump is mostly due to light-induced metallic phase in the film (see Figs. 5, 7, 8, and 10). However, the considerable qualitative difference between the TG signal  $\eta(t)$  on picosecond time scale in the case of lower [Fig. 11(a)] and higher optical excitation (Fig. 10) indicates that the contribution of metallic phase to the signal at lower pumping is significantly reduced. Moreover, at low excitation the signal  $\eta(t)$  has the same level for all films on the 0.5-2.0 ps time scale. This result indicates that the diffraction signal in Fig. 11(a) originates rather from the population density grating but not from metallic phase, as it was also shown for  $|\chi^{(3)}|$  data in Sec. III A (Fig. 4). The same level of TG signal on this time scale is due to the same level of electronic excitations in different films produced by 300  $\mu$ J/cm<sup>2</sup> pulse. Thus, the excited state dynamics on the 0.5-2.0 ps time scale could be considered as the formation of a metastable state which is responsible for the growth of metallic nuclei. Here we assume that the nucleation of the metallic phase occurs as a UPT process but the contribution of metallic nuclei to the diffraction signal becomes to be noticeable on the time scale longer than 2.0 ps. Nucleus growth starts only after formation of a metastable state. As seen from the inset in Fig. 11(b), this occurs on a time scale above 2.0 ps for *nc*-VO<sub>2</sub> films with *R*=14, 21, and 24 nm, where the growth of metallic phase results in a signal rise with separation for different films. For the film with *R*=25 the signal rise is not distinguishable on 16 ps time scale, but it appears on a longer time scale [Fig. 11(b)]. Growth of nuclei during  $\sim 0.1-0.3$  ns causes a significant difference for different films. The signal rise is noticeable for the films with smaller NPs due to intense nucleus growth, while neither the *nc*-VO<sub>2</sub> film with largest NPs (*R*=37 nm) nor the crystalline VO<sub>2</sub> film without NPs show any increase of the signal [Fig. 11(b)]. For the latter films the TG signal just decreases after laser excitation.

Growth dynamics of the nuclei can be treated in terms of the EPT model discussed above, where Eqs. (9) and (2) give a good approximation to the experimental data [Fig. 11(b)]. Thus, the nucleation of metallic phase occurs rather as a UPT process in VO<sub>2</sub> and the EPT is a growth of metallic nuclei with radii larger than a critical value  $r_c$ . Since the TG data were obtained at quite low optical excitation level, some nuclei have radii smaller than a critical value  $r_c$  and, therefore, cannot grow. Perhaps this takes place distinctly in the crystalline film without NPs and in the nc-VO<sub>2</sub> film with R=37 nm. Here all metallic nuclei recover back to the insulating phase without growing, and the metastable state decays to the initial nonexcited state within a few nanoseconds.

As shown in Refs. 13, 19, 20, and 57 and also in Sec. III A, the number of defects is increased for films with smaller VO<sub>2</sub> particle size. Since the probability of nucleation is higher within areas with structural defects,<sup>81</sup> the concentration of nuclei in nc-VO<sub>2</sub> films with smaller NPs has to be higher. Moreover, at sufficiently high concentration, some nuclei can run into a single nucleus with overcritical radius  $r > r_c$ , even if initial radii were  $r < r_c$ . Thus, in nc-VO<sub>2</sub> films with smaller NPs optical pumping produces more metallic nuclei, and many of them are merged and grow up, giving the most pronounced rise in TG signal, as can be seen in Fig. 11(b). The recovery process back to the initial insulating  $M_1$  state starts after EPT and appears as signal decay in Fig. 11(b) within only a few nanoseconds.

Data obtained in this work along with previous results<sup>56,86</sup> suggest that the CT accompanied by electron-phonon interactions is a primary order parameter in light-induced firstorder PT of VO<sub>2</sub>. Optical pumping produces such a CT followed by symmetry change from monoclinic  $C_{2h}^5$  to tetragonal  $D_{4h}^{14}$  space group. Vanadium ions in VO<sub>2</sub> exist in different charge states. The insulating phase contains mainly  $V^{4+}$  ions and, upon optical excitation, light induces the  $V^{4+}$  $\rightarrow V^{4+}$  CT via intermediary oxygen ion, forming a recharged state for the V-O-V triad as  $(V^{4+} \rightarrow O \rightarrow V^{4+}) \Rightarrow (V^{5+} - O - V^{3+})$ . Here the  $V^{5+}$  ion is a basic ion for ionic core formation in the metallic state. The  $V^{3+}$  ion is unstable due to resonance conditions fulfillment because  $3d^2$  shell states are immersed into the 3*d*-conduction band. As a result, the  $V^{3+}$  state decays due to resonance transition from  $3d^2$  electrons to the VO<sub>2</sub> conduction band as  $(V^{5+}-O-V^{3+}) \Rightarrow (V^{5+}-O-V^{4+}+e_{free})$ . The free electron belongs to the conduction electron band of the metallic state. Thus, the subsequent percolation behavior of  $(V^{5+}-O-V^{4+}+e_{free})$  clusters leads to final insulator-to-metal phase transition with  $VO_2$  symmetry change. This is a general model of the light-induced PT in  $VO_2$ . Here the mechanism and dynamics of the CT can be considered in terms of direct CT by high-intensity light and in terms of photoexcited electronic states, including cooperative effects.<sup>54</sup>

#### **IV. CONCLUSION**

This paper demonstrates the studies on the light-induced phase transition and optical properties of nanostructured VO<sub>2</sub> films. The heat treatment of the *nc*-VO<sub>2</sub> films results in crystallization of initially amorphous VO<sub>2</sub> film and growth of isolated crystalline nanoparticles of preferential size, depending on annealing temperature. Optical properties of *nc*-VO<sub>2</sub> undergo gradual changes as the characteristic size of nanoparticles increases, demonstrating an increase of refractive index, and third-order nonlinear susceptibility  $\chi^{(3)}$ . For different films in insulating phase the  $|\chi^{(3)}|$  values were found in the range  $6.8 \times 10^{-9} - 9.0 \times 10^{-9}$  esu at  $\lambda = 400$  nm. The growth of  $\chi^{(3)}$  with nanoparticle size can be derived from the gradual change in the film morphology, crystallinity, and number of structural defects. Moreover, the obtained data indicates possible excitonic enhancement of  $\chi^{(3)}$  in nanocrystals.

The third-order nonlinear susceptibility and phase transition threshold level both demonstrate higher values for crystalline film without nanoparticles as compared to nc-VO<sub>2</sub>. The analysis of  $|\chi^{(3)}|$  data obtained at different pump power and transient grating study of the ultrafast phase transition of nc-VO<sub>2</sub> show a decrease in the transition threshold level with VO<sub>2</sub> particle size. Such a decrease for smaller particles can occur due to interaction between optically excited electronic states and an order-disorder mode at the interface.

We show that the ultrafast phase transition of nanocrystalline VO<sub>2</sub> films occurs within 130 fs at sufficiently high laser excitation while at lower excitation the insulator-tometal transition becomes much slower and extended up to hundreds of picoseconds. Such extended phase transition occurs when optical excitation produces a metastable state in VO<sub>2</sub> which is necessary for the growth of metallic nuclei. Thus, metallic nuclei grow in a highly nonequilibrium state of VO<sub>2</sub> where the contribution of cooperative effects to the growth process can be significant.

The metallic phase growth kinetics after laser excitation has been modeled in terms of recrystallization theory of solids. The proposed model demonstrates a good agreement with experimental data and can be appropriate for VO<sub>2</sub> thin films as well as for bulk VO<sub>2</sub>. A fitting procedure applied to the experimental data reveals a diminution of the characteristic transition time as the size of VO<sub>2</sub> nanoparticles decreases. A largest time was observed for crystalline film without particles. It is shown that such size-dependent behavior of the transition time for nc-VO<sub>2</sub> can originate from phonon propagation through the volume of the VO<sub>2</sub> particle accompanied by interactions with photoexcited states.

Photoexcited state dynamics monitored at a relatively low laser excitation regime indicates formation of a metastable state of the VO<sub>2</sub> system on a time scale of  $\sim 10^{-12}$  s, and the growth process of the metallic nuclei starts right after forma-

tion of this state. The critical radius of nuclei diminishes as the optical excitation increases and the nucleation in the films with higher concentration of structural defects can form relatively large nuclei with overcritical size due to coalescence of smaller nuclei. Finally, it is pointed out that correct understanding of the exact nature and dynamics of photoexcited electronic states and of their role in the phase transition processes is of significant importance for the development of VO<sub>2</sub>-based optical materials

# APPENDIX

The averaged value  $\langle |\Delta \varepsilon|^2 \rangle$  can be calculated by spatial averaging of  $|\Delta \varepsilon(x)|^2 = |\overline{\varepsilon} - \varepsilon(x)|^2$  along the light-induced me-

tallic grating. Here the average dielectric constant  $\overline{\varepsilon}$  depends on the concentration of metallic phase in the film, and for the case of rectangular modulation of  $\varepsilon(x)$  [see Fig. 6(a)] it is defined as  $\overline{\varepsilon} = \zeta_I \varepsilon_I + \zeta_M \varepsilon_M = \varepsilon_I + \zeta_M \varepsilon_0$ , where  $\varepsilon_0 = \varepsilon_M - \varepsilon_I$ ,  $\zeta_M$ and  $\zeta_I$  are the volume fractions of metallic and insulator phase in the film, respectively, and  $\zeta_M + \zeta_I = 1$ . The spatial averaging gives then

$$\begin{split} \langle |\Delta \varepsilon|^2 \rangle &= \frac{1}{m\Lambda} \int_0^{m\Lambda} |\overline{\varepsilon} - \varepsilon(x)|^2 dx = |\overline{\varepsilon} - \varepsilon_M|^2 \zeta_M + |\overline{\varepsilon} - \varepsilon_I|^2 \zeta_I \\ &= |\varepsilon_0|^2 \zeta_M (1 - \zeta_M). \end{split}$$

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