Light scattering by epitaxial VO₂ films near the metal-insulator transition point

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Experimental observation of metal-insulator transition in epitaxial films of vanadium dioxide is reported. Hemispherical angle-resolved light scattering technique is applied for statistical analysis of the phase transition processes on mesoscale. It is shown that the thermal hysteresis strongly depends on spatial frequency of surface irregularities. The transformation of scattering indicatrix depends on sample morphology and is principally different for the thin films with higher internal elastic strain and for the thicker films where this strain is suppressed by introduction of misfit dislocations. The evolution of scattering indicatrix, fractal dimension, surface power spectral density, and surface autocorrelation function demonstrates distinctive behavior which elucidates the influence of structural defects and strain on thermal hysteresis, twinning of microcrystallites, and domain formation during the phase transition. © 2015 AIP Publishing LLC.

INTRODUCTION

Metal-Insulator transition phenomenon in vanadium dioxide receives much attention since Morin’s discovery.¹ VO₂ shows unique transformation of structural, electronic, and optical properties above room temperature, at T₁ ≈ 340 K.¹–⁸ Upon heating, VO₂ undergoes a first-order insulator-to-metal phase transition (PT) with reversible change of monoclinic symmetry to tetragonal one. A number of studies were focused on size-dependent transition in isolated nanoparticles and film grains due to importance of fundamental processes involved in the PT dynamics and prospective technological use of VO₂-based materials.⁹–¹⁵ The observations of spatially resolved PT in VO₂ at the nanoscale level were recently reported in several papers, which demonstrate noticeable size-dependent transition dynamics in nanoparticles and nanocrystalline films.¹⁶–²¹

Despite significant effort in experimental and theoretical study of VO₂, the problem related to the PT mechanism in this material is still far from complete understanding owing to variety of discrepant experimental data. Slight variations in sample morphology and stoichiometry result in considerable change of elastic, electronic, and optical properties near the critical point. While studies of PT in single-crystal nano-beams, nanorods, and nanoplatelets usually provide most reproducible data, the information about PT dynamics in epitaxial and polycrystalline VO₂ films is quite fragmentary. At the same time, the understanding of structural dynamics in thin films is of special interest, since different films represent stochastic or highly ordered model systems with different morphology and concentration of structural defects. It was shown recently²²–²⁴ that the stress and strain in VO₂ film significantly depend on film thickness, grain size, and substrate.

The new information about multi-scale structural PT and domain formation can bring better understanding of different physical processes near the PT point of VO₂.

In this paper, we demonstrate the influence of internal strain and morphology of epitaxial VO₂ films on thermally induced domain formation and PT dynamics at different spatial scales. Angle-resolved measurements of elastic light scattering were performed to obtain the power spectral density (PSD), fractal dimension, and autocorrelation function (ACF) of the surface near T₁. It is shown that the size and shape of hysteresis loop depend on surface spatial frequency due to grain-size-dependent elastic strain and/or concentration of structural defects. The thermal evolution of scattering pattern and surface morphology of strained continuous film is found considerably different as compared to the film with overcritical thickness, where strain is relaxed via misfit dislocations (MDs). We find that the internal elastic strain in thin VO₂ film is the main origin which affects scattering indicatrix, producing twinning of microcrystallites and domain formation during PT.

EXPERIMENTAL

The pulsed laser deposition (PLD) technique was applied to fabricate a set of VO₂ films on single-crystal (012)Al₂O₃ (r-cut) and (001)Al₂O₃ (c-cut) sapphire substrates. The ablation of metallic vanadium target was performed by excimer laser (Lambda Physik Compex 110) with wavelength λ = 248 nm (KrF excimer), 10-ns pulse duration, and 4 J/cm² fluence, and a chamber atmosphere of O₂ and Ar at 30 mTorr pressure. Gases were injected into chamber through separated mass flow controllers with 20:5 (O₂:Ar, cm³/min:cm³/min) flow rate. The X-ray diffraction patterns of all VO₂ films evidenced single monoclinic M₁–phase at room temperature.

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Several laser sources were employed to study the thermally induced PT in VO$_2$. A continuous wave 8 mW semiconductor laser with wavelength $\lambda = 1310$ nm was used in optical transmission measurements, and a 2 mW He-Ne laser with $\lambda = 632.8$ nm was used as a probe light source in the light scattering experiment. The sample temperature was controlled by a Peltier heater.

The observation of light scattering was conducted with a scatterometer described elsewhere.\textsuperscript{25,26} This apparatus provided measurements of bidirectional-scatter-distribution-function

$$BSDF(\theta, \varphi) = \left[ \frac{dI_{\text{scatt}}(\theta, \varphi)}{d\Omega} \right] \frac{1}{I_0 \cos \theta},$$

where $\theta$ and $\varphi$ are the polar and azimuthal scattering angles, respectively. $I_0$ is the intensity of incident light, $dI_{\text{scatt}}$ is the intensity of light scattered into solid angle $d\Omega$.

Angle-resolved elastic light scattering is a powerful technique for statistical analysis of surface irregularities of different sizes.\textsuperscript{27-33} While this technique does not provide real-space imaging of the surface roughness or VO$_2$ domains, it produces direct reciprocal-space imaging with robust statistical information about distribution of the inhomogeneities. Any type of structural ordering on the mesoscale, self-organization, twinning of microcrystals, and domain formation produces sharp diffraction peaks or symmetric features (e.g., lines, rings, squares, rhombs, hexagons, etc.) in the scattering indicatrix. Complex evolution of the structure on different scales can be easily identified and monitored by measuring the scattering signal at certain angles.

In this work, the measured BSDF data were used for calculation of two-dimensional (2D) power spectral density function of the surface as

$$PSD(f) = BSDF(f)/\text{OF},$$

where $\text{OF}$ is an optical factor which depends on dielectric permittivity and scattering angle.\textsuperscript{33} $\text{OF}$ was calculated using equations obtained by Elson in Ref. 34. The optical constants for these calculations were obtained from additional angular measurements of reflection coefficient and data fit for s- and p-polarization of incident light. The PSD($f$) function represents the statistical distribution of surface roughness versus surface spatial frequency $f = \sin \theta/\lambda$ and is the Fourier transform of the surface autocorrelation function $ACF(r)$.

The autocorrelation function defines correlation of surface irregularities versus the translation length $r$ in the surface plane.\textsuperscript{33} At zero translation $ACF(0) = \delta^2$, where $\delta$ is rms roughness. In this work, we use the normalized autocorrelation functions $ACF/\delta^2$, calculated from scattering (ACF$_s$) and atomic-force-microscopy data (ACF$_{AFM}$), where $ACF_s(0) = 1$ and $ACF_{AFM}(0) = 1$.

There are several instrumentation-dependent limitations to observe the structural dynamics by elastic light scattering such as wavelength and light polarization, angle of incidence, aberration of the optical system, and resolution of the charge-coupled device (CCD). The light scattering experiment depends on a significant number of different parameters, and some of them can be unknown. The range of spatial frequencies available for observation is limited by the probe wavelength. In this work, the measurements were performed at normal incidence. The light scattered at $\theta = 90^\circ$ corresponds to the maximal spatial frequency available for observation, $f_{\text{max}} = \sin 90^\circ/\lambda = 1/\lambda$. The central part of the scattering indicatrix is blocked by the sample holder, which prevents measurement of the signal for low spatial frequencies $\leq 0.4$ mm$^{-1}$.

The Raman effect was measured in backscattering configuration from room temperature to 400 K by a Renishaw Raman Microspectrometer RM2000 system. The instrument was equipped with a CCD detector, Leica microscope, and a diode laser with wavelength $\lambda = 532$ nm.

The VO$_2$ film surface was also scanned by atomic-force-microscope (AFM, Park Scientific Instruments, Autoprobe CP). The AFM topography analysis, calculation of spectral density, and autocorrelation function of the surface roughness were performed with WSxM software.\textsuperscript{35}

RESULTS AND DISCUSSION

Surface morphology and domain formation

The distribution and orientation of crystalline domains in thin ferroelastic VO$_2$ film strongly depend on the strain field and correspond to the minimum of elastic energy. Self-organization of VO$_2$ domains is a complex problem related to the misfit strain $\varepsilon_m$ between film and substrate, defects, and interference of strain fields from different crystallites. The influence of the substrate on the net strain is crucial. Thus, the parallel ordering of ferroelastic microcrystals in most cases reduces the long-order strain field,\textsuperscript{36} as observed for nanoplatelets,\textsuperscript{16,21,37,38} nanobeams,\textsuperscript{39} and for epitaxial VO$_2$ films on TiO$_2$\textsuperscript{40} and Al$_2$O$_3$ single-crystal substrates.\textsuperscript{24,41-45} The r-cut sapphire substrate Al$_2$O$_3$ is characterized by a rectangular atomic lattice on the surface, and the VO$_2$ PLD film is strongly oriented on this substrate with directions [010]$_{VO_2}/[100]_{Al_2O_3}$ and [001]$_{VO_2}/[021]_{Al_2O_3}$. Some of these directions can be slightly misoriented within less than 1°.\textsuperscript{25} Such a small misorientation is likely due to elastic interaction between different crystallites, defects and substrate.

The BSDF indicatrices of hemispherical light scattering are shown in Fig. 1(a) for 30-nm-thick VO$_2$/Al$_2$O$_3$(r-cut) film as a function of both polar $\theta$ and azimuthal $\varphi$ angles. A distinctive feature of these indicatrices is a square-like pattern outlined by isophotes in the central area within $0^\circ < \theta \leq 55^\circ$. The isophotes are parallel to [010] ($\beta_m$) and [001] ($\gamma_m$) directions of the epitaxial VO$_2$ film. At larger polar angles, this pattern loses its sharpness. A slight elongation of isophotes along $\varphi = 90^\circ$, $270^\circ$ direction is due to intrinsic polarization anisotropy of the scattering process, since the polarization of incident light was oriented along this azimuthal direction. The power spectral density function PSD$_s$ of the surface calculated from scattering indicatrix eliminates such polarization anisotropy [Fig. 1(b)]. Nevertheless, the square-like pattern remains in the center of the PSD$_s$ map and is a signature of highly ordered domains in the film.

The texture of epitaxial films is highly influenced by the substrate and film thickness. In order to demonstrate this
influence, we show several scattering indicatrices obtained for VO₂ films deposited on c-cut Al₂O₃ (Fig. 2), which are considerably different as compared to indicatrices for VO₂/Al₂O₃(r-cut). In a series of previous XRD studies, it has been shown that the VO₂/Al₂O₃(c-cut) film undergoes 3-fold twinning. These films are highly textured with orientation of [100]VO₂ domain axis along three equivalent crystallographic directions of Al₂O₃(c-cut) substrate. As a result, for uniformly twinned 50-nm-thick VO₂/Al₂O₃(c-cut) film the indicatrices show symmetric directions of scattering with 60° angular separation [Fig. 2(a)]. The local twinning of some films can produce more complex texture with rotation of domains by the angles other than 60°. Thus, the indicatrices for 30-nm-thick VO₂/Al₂O₃(c-cut) show the preferential directions of scattering with 45° and 75° angular separation [Fig. 2(b)]. This indicates the presence of domains rotated by 45° and 75°. The specific domain formation in VO₂/Al₂O₃(c-cut) makes these films optically isotropic, while the films deposited on Al₂O₃(r-cut) retain their optical properties inherent to VO₂ single crystal. The local morphology of VO₂/Al₂O₃(r-cut) was found to be more uniform within the sample, as compared to VO₂/Al₂O₃(c-cut), and further discussion will be focused on optical properties of VO₂/Al₂O₃(r-cut).

The AFM data for 30-nm-thick VO₂/Al₂O₃(r-cut) films yield the rms roughness of the surface as δ = 96 Å. Fig. 3(a)
shows that the lateral shape of VO₂ grains is somewhat rectangular, similar to nanorods studied by Sohn et al.²⁶ and Kim et al.²⁷ The average lateral size of VO₂ grains is \( d_{av} \approx 305 \text{ nm} \), which corresponds to spatial frequency \( f_s = 1/d_{av} = 3.3 \text{ nm}^{-1} \). This range is unattainable in the scattering measurements since the maximal spatial frequency probed by the He-Ne laser is \( f_{\text{max}} = 1/\lambda = 1.58 \text{ nm}^{-1} \). However, the square-like pattern in the scattering indicatrix at \( \theta < 55^\circ \) (\( f < 1.3 \text{ nm}^{-1} \)) indicates that the VO₂ crystallites are organized into highly ordered clusters. Above \( \theta = 55^\circ \), this pattern is distorted and less pronounced owing to increased randomness in orientation of smaller surface irregularities.

The 2D autocorrelation function of surface roughness calculated from AFM topography [Fig. 3(b)] shows a presence of isotropic and weak anisotropic components. The isotropic component of surface roughness contributes only in the central maximum of ACF\(_{AFM} \) with near-exponential decay within \( ~300 \text{ nm} \) [inset in Fig. 3(c)] and, therefore, can be easily separated from the rest of ACF\(_{AFM} \). A periodical anisotropic component results in the oscillation of ACF\(_{AFM} \), showing fringes with period of 0.55 \text{ nm}. This indicates an ordering of microstructure along the fringe direction.

Taking into account AFM data, the observed indicatrices in Fig. 1 can be characterized in terms of fractal surface scattering where the scattered field contains information about subwavelength VO₂ crystallites organized in highly ordered square-like structures due to anisotropic ordering on the single-crystal r-cut sapphire substrate. The structure of epitaxial VO₂/Al₂O₃ films is a classic example of a “supercrystal,” where the groups of nanocrystals are organized in polysynthetic domains.²⁶ In contrast to a single-crystal, the “supercrystal” film is a quite flexible structure with relatively high mechanical mobility of nanocrystals. Thus, a small change in the elastic energy results in splitting of the film into domains of the same or different phases in order to reduce the net elastic energy.²⁶,²⁰ This is an intrinsic property of thin VO₂ films which qualitatively changes the temperature-dependent scattering pattern in Fig. 1(a).

The information about fractal properties of the sample was obtained from the power spectra PSD\(_{AFM} \) and PSD\(_{s} \) calculated from AFM topography and scattering data, respectively. It is noted that the data obtained from AFM and from elastic light scattering cover different ranges of spatial frequencies. Moreover, these experimental techniques are based on different physical processes of interaction between the probe (i.e., light or AFM tip) and the surface. The comparison of PSD\(_{s} \) and PSD\(_{AFM} \) functions shows their overlap [Fig. 3(c)]. Also, the slope of PSD\(_{AFM} \) within \( f = 1.4–3.0 \text{ nm}^{-1} \) coincides with the slope of PSD\(_{s} \) function. This indicates that the AFM and light scattering measurements yield the same information about fractal dimension of the surface. At lower spatial frequencies \( f < 1.3 \text{ nm}^{-1} \), the PSD\(_{AFM} \) function has only few data points, and within this range the accuracy of AFM measurement is slightly lower as compared to higher frequencies. Since the AFM is a conventional and precise tool to characterize surface roughness, the overlap between PSD\(_{s} \) and PSD\(_{AFM} \) data denotes a high precision of scattering measurements.

Both PSD functions show fractal-like behavior and can be characterized by 2D power spectrum²⁸

\[
PSD(f) = \frac{\Gamma[(n+1)/2]}{2\Gamma(1/2)\Gamma(n/2)} \frac{K_n}{f^{n+1}},
\]

where the \( K_n \) and \( n \) are constants. The Hausdorff-Besicovitch dimension is defined as \( D = (5 - n)/2 \) and, along with \( K_n \) and \( n \), is the fractal parameter of surface inhomogeneity.²¹–²³

The PSD\(_{s} \) functions at different azimuthal angles \( \phi \) show the same slope in a \( \log - \log \) graph [Fig. 3(c)], indicating a relatively high isotropic component of surface roughness. Applying the fractal approach for analysis of surface roughness, one can expect the independence of the fractal parameters on experimental bandwidth. However, the fitting of PSD data with Eq. (3) shows some difference. The parameters obtained for PSD\(_{s} \) are \( n = 1 (D = 2) \), while the PSD\(_{AFM} \) shows multifractal behavior and can be described by a sum of PSD functions with \( n = 2.75 (D = 1.13) \) at \( f = 3.3–30 \text{ nm}^{-1} \) and \( n = 1 (D = 2) \) at \( f > 30 \text{ nm}^{-1} \) and \( f = 1.4–3.0 \text{ nm}^{-1} \). It is important to note that the lower limit of the linear part of PSD\(_{AFM} \) with \( n = 2.75 \) coincides with the spatial frequency of VO₂ crystallites \( f_s = 3.3 \text{ nm}^{-1} \). Moreover, the fractal parameters of PSD\(_{s} \) coincide with those of PSD\(_{AFM} \) at \( f > 30 \text{ nm}^{-1} \) and \( f = 1.4–3.0 \text{ nm}^{-1} \).

The PSD data in Fig. 3(c) reveal the multifractal structure of the film. The distribution of small VO₂ irregularities with \( f > 30 \text{ nm}^{-1} \) likely replicates the Al₂O₃ substrate roughness. The obtained fractal dimension \( D = 2 (n = 1) \) corresponds to the extreme fractal and indicates close-packed crystallites of rugged surface.²²,²³ The distribution of larger VO₂ grains with \( f_s < f < 30 \text{ nm}^{-1} \) is organized into another fractal structure with \( D = 1.13 (n = 2.75) \) related to smoother surface. However at \( f < f_s \) the VO₂ irregularities again are organized in domains with \( D = 2 (n = 1) \), at \( f > 30 \text{ nm}^{-1} \).

The averaged power spectra PSD\(_{s} \) calculated for 30-nm-thick film in insulating and metallic state show a noticeable difference in slope (see inset in Fig. 4(a)). The fractal dimension decreases from \( D = 2 (n = 1) \) to \( D = 1.85 (n = 1.3) \) during the PT, indicating a smoothing of surface irregularities in the metallic phase.

In terms of Rayleigh smooth-surface criterion,³³ the epitaxial VO₂ film with \( \delta < \lambda/(4\pi) \) can be considered as optically smooth. For such surface the BSDF(\( \theta \)) is nearly scaled PSD function, as depicted in Fig. 4(a) for the cross-section of the scattering indicatrix at \( \varphi = 0^\circ \), \( T = 296 \text{ K} \). Therefore, correct information about statistical distribution of surface inhomogeneities can be obtained directly from BSDF data. This is “scatter prediction” method that allows reconstructing the evolution of surface irregularities when the system is in nonequilibrium or quasi-equilibrium state, and material optical constants are unknown.

The distinctive feature of BSDF(\( \theta \)), BSDF(\( \phi \)), and PSD\(_{s} \) for VO₂/Al₂O₃ is a presence of sharp peaks, as identified in Figs. 1 and 4. This is the typical signature of strong ordering of crystallites along different directions. The self-organized surface structures scatter light as differently oriented diffraction gratings whose period depends on film temperature. Thus, the BSDF undergoes noticeable change.
an isotropic formation of domains with sizes less than 
region affected by the PT uniformly spreads to 
tering pattern begins well below the critical temperature \(T_c\) 
domain formation process. Moreover, the evolution of scat-
realignment of domains and significantly varies from sample 
This temperature-dependent process corresponds to the 
diffraction peaks uniformly fill up all scattering indicatrix. 
\[
\frac{\varepsilon_s}{2\gamma H} \]
(4)
Since \(f_D \sim \sqrt{\varepsilon_s/\gamma}\), a small change in the internal strain of the film or nucleation of new phase both result in the formation of new domain pattern, affecting the scattering indicatrix.

For 30-nm-thick \(\text{VO}_2/\text{Al}_2\text{O}_3\) (r-cut), the change in scattering indicatrix starts at room temperature, immediately when heating is applied. The arbitrary cross-section of the indicatrix at \(T = 333\) K shows sharp peaks at \(f \approx 0.6\) \(\mu\)m\(^{-1}\) \([f = 0.59\) \(\mu\)m\(^{-1}\) in Fig. 4(a)] which are assigned to strong ordering of \(\text{VO}_2\) domains with a period of \(d = 1.7\) \(\mu\)m. At the PT temperature \(T_c = 341\) K, the structural inhomogeneity of the film becomes highest due to coexistence of different phases. The sharpness of the square-like pattern in the center of scattering indicatrix in Fig. 1 decreases. When the temperature reaches \(T = 365\) K, the \(\text{VO}_2\) has completely switched into its metallic R-phase and the new set of quasi-periodic diffraction peaks appears [starting at \(f = 0.53\) \(\mu\)m\(^{-1}\) in Fig. 4(a)]. This behavior corresponds to self-organization of domains in new periodic structures with minimal elastic energy.

Additional information about evolution of \(\text{VO}_2\) structure was obtained from the autocorrelation function \(ACF_s\) calculated by Fourier transform of PSD\(_s\)(\(f\)) and BSDF\(_s\)(\(f\)) using the Gerchberg-Saxton error reduction (ER) algorithm which significantly reduces numerical error. This algorithm was also applied to restore absent PSD\(_s\)(\(f\)) data at the periphery up to \(f = 2.1\) \(\mu\)m\(^{-1}\) and in the central area of the scattering indicatrix blocked by the sample holder [Fig. 1(b)]. At some temperatures, the calculation of PSD\(_s\) was not performed, because of lack of information about \(\text{VO}_2\) optical constants near the PT point. Therefore, ACF\(_s\) were calculated from BSDF\(_s\) data instead of PSD\(_s\), since BSDF\(_s\)(\(f\)) is practically a scaled PSD\(_s\)(\(f\)) for a smooth surface, as discussed above and shown in Fig. 4(a).

FIG. 4. The evolution of scattering pattern and power spectral density of the surface roughness for 30-nm-thick film \(\text{VO}_2/\text{Al}_2\text{O}_3\) (r-cut). (a) Cross-sections of the BSDF scattering indicatrix and PSD\(_s\) at \(q = 0\). Inset shows the azimuthally averaged PSD\(_s\) function for insulating and metallic phases. Dashed lines are fit by Eq. (3). (b) The relative change \(\Delta\text{BSDF}(T)/\text{BSDF}\(_0\) near the PT point, where BSD\(_{296}\) is obtained for insulating \(\text{VO}_2\) at \(T = 296\) K, and \(\Delta\text{BSD}(T) = \text{BSD}(T) - \text{BSD}\(_0\)\). Arrows mark the region that corresponds to the noticeable emergence of new diffraction peaks.

with temperature (Figs. 1 and 4). During the PT most diffraction peaks are shifting, emerging, or decaying due to twinning of \(\text{VO}_2\) microcrystallites accompanied by “dynamic” domain formation process. Moreover, the evolution of scattering pattern begins well below the critical temperature \(T_c\) and persists well above it.

The emergence of new diffraction peaks can be observed in Fig. 4(b) at higher spatial frequencies above \(f = 1.2\) \(\mu\)m\(^{-1}\) already at \(T = 308\) K. This figure indicates an isotropic formation of domains with sizes less than \(d = 1/f = 0.83\) \(\mu\)m. As the temperature reaches \(T = 328\) K, the region affected by the PT uniformly spreads to \(f = 0.9\) \(\mu\)m\(^{-1}\) \((d = 1/f = 1.1\) \(\mu\)m\). With further temperature increase, new diffraction peaks uniformly fill up all scattering indicatrix. This temperature-dependent process corresponds to the realignment of domains and significantly varies from sample to sample. The self-organized surface structure consists of parallel-sided \(\text{VO}_2\) domains with period \(d_D = \sqrt{2\gamma H/\varepsilon_s}\), where \(\gamma\) is the specific surface energy of the domain boundary, \(H\) is the film thickness, and \(\varepsilon_s\) is the specific surface energy of local deformations at the boundary between film and substrate. The spatial frequency of this structure is 

\[
f_D = \sqrt{\frac{\varepsilon_s}{2\gamma H}} \]
(4)
and related to the uniform isotropic component of roughness and calculated from the central peak of ACF map. The difference in experimental bandwidth results in different values of ACL obtained by different techniques. Thus, the autocorrelation length $ACL_{AFM} = 100 \text{ nm}$ [inset in Fig. 3(c)] derived from AFM measurements is almost five times less than $ACL_{s} = 595 \text{ nm}$ calculated from scattering data at $T = 296 \text{ K}$ [see inset in Fig. 5(b)]. As the temperature increases, the ACL$_{s}$ decreases and reaches a 529 nm minimum at PT critical point $T_c = 341 \text{ K}$. This indicates a gradual increase of disorder in the VO$_2$ film. However, after the PT at $T = 353 \text{ K}$, the order significantly increases and the ACL$_{s}$ recovers to 574 nm. The noded maxima of ACF$_{s}$ [Fig. 5(a)] migrate during the heating process and in the metallic phase they become more pronounced [see inset in Fig. 5(b)]. Their locations at $T = 353 \text{ K}$ are not strictly aligned in a mesh as at $T = 296 \text{ K}$, and in vertical direction [Fig. 5(a)] the average separation between maxima at $T = 353 \text{ K}$ shrinks to 1.8 $\mu$m, indicating noticeable surface reconstruction.

There are two origins for surface scattering: inhomogeneity of the dielectric permittivity $\varepsilon$ and geometrical roughness. Since below the PT point there are no metallic nuclei which could provide significant disorder in dielectric constant, it is difficult to assign the observed significant change of ACF$_{s}$, BSDF, and shift of diffraction peaks in Figs. 1(a) and 4 to scattering from temperature-dependent inhomogeneity of $\varepsilon$. The Raman scattering experiment conducted by Atkin et al. has shown that the intermediate M$_2$-phase can nucleate in strained VO$_2$ at temperatures below $T_c$. However, nucleation of M$_2$-phase during the heating process would not add noticeable disorder in $\varepsilon$ either, since the dielectric constants of M$_1$ and M$_3$ phases are almost indistinguishable within the optical region. On the other hand, new M$_3$-phase at the nanoscale can certainly change the strain field of polydomain VO$_2$ film and, as a result, can introduce further domain formation and new elastic deformations.

In this work, Raman scattering was measured at different temperatures of the film in order to verify the presence of M$_2$-phase. Fig. 6 shows Raman spectra of stoichiometric VO$_2$ at different temperatures. As shown in Refs. 57–59, the distinctive signature of M$_2$ and T-phase in strained sample is splitting and blueshifting of the Ag 613 cm$^{-1}$ phonon mode as well as decay of the low-frequency mode Ag 194 cm$^{-1}$. Nevertheless, the Raman spectra in Fig. 6 do not show such behavior, indicating absence or low concentration of M$_2$-phase at room temperature and near the PT point $T_c$. While even a small concentration of M$_2$-phase can affect the net strain field, another origin of elastic strain in the film is a difference in thermal expansion of VO$_2$ ($5.78 \times 10^{-6} \text{ K}^{-1}$) at 298–334 K and $13.35 \times 10^{-6} \text{ K}^{-1}$ at 339–360 K$^{60}$ and Al$_2$O$_3$ substrate ($8 \times 10^{-6} \text{ K}^{-1}$)$^{61}$ This can produce a noticeable change in the strain field of the epitaxial film when the temperature changes by several degrees.

Taking into account Eq. (4) along with Raman scattering and thermal expansion data, the observed continuous evolution of BSDF within broad temperatures outside the PT range (Figs. 1 and 4) is assigned to domain formation and elastic deformation of the film due to strain effects. It is very likely that in the 30-nm-thick VO$_2$/Al$_2$O$_3$ the elastic strain, particularly misfit strain, is not relaxed via formation of static dislocation network. Instead, the strain relaxation is accompanied by “dynamic” temperature-dependent formation of twins, presumably oriented at $\sim 45^\circ$ angle to the substrate as observed by Zhao et al. for VO$_{2}$/Al$_2$O$_3$(t-cut) epitaxial film.

The conclusion about the presence of significant internal strain in thin VO$_2$ film is in agreement with data obtained in Ref. 22, where the absolute value of residual stress was found to be higher for thinner films. It was shown that the residual stress for the 100-nm-thick VO$_2$ film deposited on Si substrate by radio frequency (RF) sputtering is $-677 \text{ MPa}$.
and it changes to $-73$ MPa as the thickness increases to 440 nm. Moreover, the PT produces additional alteration of the stress. For PLD films grown on single-crystal Al$_2$O$_3$ (r-cut) substrate the absolute value of internal stress is certainly different and is expected to be higher due to epitaxial nature of the film.

The structure of epitaxial film remains continuous on the microscopic level upon full cycle of the PT process due to phase coherency. This coherency is attained by relaxation of structural strain via microdeformations at the grain boundaries and at the boundary which separates different VO$_2$ phases and domains. The strain energy is transferred into energy of structural microdeformations and/or defects. Supressing the long-order macroscopic strain field in the epitaxial film, the microdeformations are non-coherent with the net strain field and are a residual origin of the strain. Therefore, the strain-assisted domain formation in the film starts mostly within the microdeformations. That is, at the boundary of neighboring grains or phases and at structural defects.

The angle-resolved light scattering technique provides direct statistical imaging of multi-scale grain-size-dependent transitions in the film. The thermal hysteresis of scattering signal for structures with different spatial frequencies $f$ is shown in Fig. 7. We note that the smaller structures with higher spatial frequencies scatter light less and their contribution is almost hidden in the total scattering signal $I_{\text{scatt}}/I_0$ integrated within hemisphere. Therefore Fig. 7(a) shows normalized graphs of scattering signal $I_{\text{scatt}}^*$ for different $f$, where $I_{\text{scatt}}^* = 1$ corresponds to insulating and $I_{\text{scatt}}^* = 0$ to metallic phase. In order to define the point of steepest slope of the hysteresis, $dI_{\text{scatt}}^*/dT$ derivatives were calculated. Here, the thermal range between minima of $dI_{\text{scatt}}^*/dT$ curves is defined as a characteristic width $\Delta T$ of the hysteresis. Thus, Fig. 7(b) shows the same $\Delta T = 3.5$ K for structures with different spatial frequencies. Nevertheless, the hysteresis is different for different structures: it noticeably broadens at higher spatial frequencies. This broadening is assigned to stronger misfit strain and higher concentration of structural defects in smaller grains.$^{10,11,63}$

Other important aspects which can be monitored by light scattering are fluctuations of density and entropy due to defects, strains, and coexistence of insulator and metallic phases near the critical point.$^{64}$ These factors increase fluctuation of the dielectric constant $\varepsilon$ as the temperature approaches the PT point and, as a consequence, increase the scattering signal. This appears as a sharp rise of the scattering [dashed portion in Fig. 7(a)], and referenced as “transition opalescence.”$^{65}$ It is remarkable that such a scattering feature is more pronounced and broader for smaller grains. This result proves the heretofore debatable opinion that the smallest VO$_2$ grains are under relatively high and random local elastic strains from the substrate and neighbouring grains, and can contain larger number of oxygen vacancy defects which provide significant system disorder at the critical point.

Influence of the film thickness on structural transformation of the film

It was found that the increase of the film thickness above some critical value results in noticeable changes of scattering and hysteresis properties. Thus, the integrated scattering intensity for 125-nm-thick PLD film is increased by a factor of two with respect to the 30-nm-thick film, indicating increased surface roughness by a factor of $\sim \sqrt{2}$. The distribution of VO$_2$ crystallites in the thicker film has a higher degree of isotropy, resulting in almost complete blurring of the rectangular shape of isophotes in Fig. 8(a), particularly at higher spatial frequencies. Nevertheless, this distribution is not random and forms strongly ordered groups of crystallites.

The cross-section of the scattering indicatrix along an arbitrary direction shows equidistant BSD(f) maxima [Fig. 8(b)]. Thus, separation of BSD(f) peaks for azimuthal directions $\varphi = 47^\circ$ is $\Delta f = 8.7 \times 10^{-2}$ $\mu$m$^{-1}$. The BSD(f) with equidistant maxima is related to corrugated surface relief and can be modeled by superposition of light scattering from a diffraction grating of several lines superimposed onto a stochastic surface relief. The modeling of BSD(f) using the equation for the intensity of light diffraction by periodical structures$^{66,67}$

$$I_{DG} = I_0^p \left( \frac{\sin(N \pi f)}{\sin(\pi f)} \right)^2 \left( \frac{\sin(\pi s f)}{\pi s f} \right)^2,$$

shows good coincidence with experimental data when the diffraction grating consists of $N = 3$ lines with period $d = 12$ $\mu$m, separated by boundaries with width $s = 0.61$ $\mu$m. Here, $I_0^p$ is maximal diffraction intensity. The location of the
equidistant diffraction peaks $I_{DG}$, their separation $\Delta f_{DG} = 8.3 \times 10^{-2} \, \mu m^{-1}$, as well as presence and positions of minor diffraction peaks are very close to those in the experimental BSDF(f) data [Fig. 8(b)]. This model assumes that the VO$_2$ crystallites organize as relatively large ordered 12 $\mu$m domains, separated by a 0.61 $\mu$m boundary formed by one or two crystallites. Moreover, since epitaxial VO$_2$ film can be considered as a “supercrystal,” as discussed above, it is expected that the large 12 $\mu$m domains also contain ordered sub-structures with spatial frequencies $f_i = i \times \Delta f_{DG}$, where $i$ is the number of diffraction order.

The theoretical modeling of light diffraction is shown for single periodical structure with $N = 3$. However, the real surface of epitaxial film is the ensemble of ordered but different in shape VO$_2$ grains. This system has noticeable stochastic component that contributes to the scattering indicatrix, resulting in slight difference between positions of some diffraction peaks obtained experimentally and from theoretical calculation [Fig. 8(b)].

Despite similar scattering indicatrices for 30-nm- and 125-nm-thick films VO$_2$/Al$_2$O$_3$ (r-cut) [Figs. 1(a) and 8(a)], there is considerable difference in their temperature-dependent structural transformation. The BSDF(f) of the thinner film shows significant qualitative change at different temperatures (Figs. 1(a) and 4), but the 125-nm-thick film shows almost uniform decay of diffraction peaks without any significant shift or distortion [Fig. 8(b)]. When VO$_2$ is switched into its metallic phase, the local BSDF(f) maxima are suppressed at $T = 373$ K, but their positions remain the same. This indicates that the domain pattern of the 125-nm-thick film remains also the same, and no additional twinning or “dynamic” temperature-dependent reorganization of domains occurs. It is very likely that the static domain structure is formed during the PLD process via generation of the dislocation network and introduction of new grain boundaries or microcracks.

The VO$_2$ PLD film on r-cut Al$_2$O$_3$ substrate is mismatched, with misfit strain $\varepsilon_m = 4.0\%$ along [010]$_{VO_2}$ and $\varepsilon_m = -5.1\%$ along [001]$_{VO_2}$. If the thickness is smaller than the critical value $h_c$, the film is maximally strained but free of MDs. However, when the thickness exceeds the threshold $h_c$, the MD network abruptly appears to reduce the misfit strain. Data obtained for the 125-nm-thick VO$_2$/Al$_2$O$_3$ (r-cut) film indicate that the thickness of this film is above $h_c$. Thus, the PLD at $T = 825$ K has formed a flat epitaxial film in tetragonal phase with relatively high concentration of MDs. It is also very likely that when the film is cooled down to room temperature after the deposition, different thermal expansion of the film and substrate along with the VO$_2$ volume contraction by $\sim 0.044\%$ (Ref. 60) resulted in additional generation of dislocations, new grain boundaries, or microcracks with self-organization of VO$_2$ domains into periodical structures. Once generated, the network of structural defects then significantly contributes to the PT process. These defects prevent a “dynamic” temperature-dependent twinning of 125-nm-thick film during the PT, as compared to the thinner film. As a result, sharp BSDF(f) peaks in scattering indicatrix do not shift, but decay as temperature increases [Fig. 8(b)].

As shown previously for VO$_2$/Si samples prepared by RF sputtering, the absolute value of residual stress drops by more than nine times, as the film thickness increases from 100 nm to 440 nm. For the epitaxial VO$_2$/Al$_2$O$_3$ (r-cut) PLD films, the strain and stress both are noticeably suppressed already for 125-nm-thick film due to introduction of structural defects, as revealed from the evolution of scattering pattern in Fig. 8(b). The alteration of the stress during the PT is small enough and insufficient to produce the film twinning or formation of new domains.

The relative change of the scattering signal allows to identify spatial frequencies of VO$_2$ domains with different PT properties. Thus, the $\Delta$BSDF(T)/BSDF$_0$ indicatrix in Fig. 9(a)
can be divided into three regions: $\Delta f_1 = 1.15$–1.58 $\mu m^{-1}$ (size range is 0.633–0.870 $\mu m$), $\Delta f_2 = 0.7$–1.15 $\mu m^{-1}$ (size range is 0.870–1.43 $\mu m$), and region with $f < 0.7 $ $\mu m^{-1}$ ($d > 1.43$ $\mu m$). Near the PT point, at $T = 336$ K, the scattering signal drops uniformly within the region $\Delta f_1$ with higher rate. As the temperature approaches $T = 341$ K, the signal continuously decreases, but with noticeably different rate for each region, indicating different PT dynamics for domains of different size.

The VO$_2$/Al$_2$O$_3$ films used in this study are epitaxial and nearly stoichiometric, but their different microstructure significantly affects the thermal hysteresis. The hysteresis loop of optical transmittance and integrated light scattering for the 125-nm-thick film [Figs. 9(b) and 9(c)] is much broader and significantly tilted as compared to the hysteresis of the thinner film [see Fig. 7(a)]. This difference is attributed to the higher concentration of structural defects in the 125-nm-thick film. As was discussed above, the strain field in this film is significantly reduced due to high density of MDs. Therefore, the broad and tilted hysteresis in Figs. 9(b) and 9(c) has no significant relation to the strain but rather to the presence of defects. The structural defects shift the PT temperature. During the PT, some domain walls are pinned by defects, contributing to the distortion of the hysteresis shape and width.

The hysteresis of optical transmittance $I_{TG}/I_0$ does not coincide exactly with that of integrated light scattering $I_{scatt}$ $I_0$ [Figs. 9(b) and 9(c)], since the scattered light is additionally affected by structural and dielectric constant inhomogeneity. Hysteresis loops $I_{scatt}/I_0$ show significant grain-size-dependence. Using the derivatives $dI_{scatt}/dT$ [Fig. 9(d)], the characteristic hysteresis width for $f = 0.62$ $\mu m^{-1}$ is found to be $\Delta T = 19.5$ K. However as soon as spatial frequency exceeds 0.7 $\mu m^{-1}$, the hysteresis width shrinks to $\Delta T = 5$ K and weakly depends on $f$. Along with narrowing of hysteresis, the second principal feature of Fig. 9(c) is a gradual shift of the hysteresis loop with its steeper slope to higher $f$, as the spatial frequency increases. Here, at the higher spatial frequency $f = 1.4$ $\mu m^{-1}$, the hysteresis width and position remarkably approaches those values related to thinner film [see Fig. 7(a)], indicating similar physical properties of the 30-nm-thick film and grains of the 125-nm-thick film with $f = 1.4$ $\mu m^{-1}$.

The observed behavior of hysteresis loops for different spatial frequencies evidences a gradual size-dependent change of structural parameters. The MD network is assumed as the main origin which affects the thermal hysteresis. The broad hysteresis $\Delta T = 19.5$ K for $f < 0.7$ $\mu m^{-1}$ and its abrupt change to $\Delta T \approx 5$ K above $f = 0.7$ $\mu m^{-1}$ [see Fig. 9(d), inset] indicates that the larger structures with $f < 0.7$ $\mu m^{-1}$ contain higher densities of MDs. The pining of domain walls by defects changes the tilt of the hysteresis loop and possibly is the origin of the second minimum [2] in the $dI_{scatt}/dT$ curve for $f = 0.62$ $\mu m^{-1}$. The significant change of the hysteresis width and slope at $f = 0.7$ $\mu m^{-1}$ indicates a possible presence of a “transverse” threshold for the generation of MDs at this spatial frequency. Above $f = 0.7$ $\mu m^{-1}$ the concentration of MDs rapidly drops and continuously decreases for smaller grains. Thus, already at $f = 1.4$ $\mu m^{-1}$, the hysteresis loop of the 125-nm-thick film approaches in shape that of the 30-nm-thick film, which is almost free of MDs.

**CONCLUSION**

In this paper, the influence of strain and structural defects on thermally induced PT of epitaxial VO$_2$/Al$_2$O$_3$ films has been discussed. The angle-resolved light scattering measurements show that the elastic stain significantly affects the thermal transition, resulting in temperature-dependent twinning of microcrystallites and domain formation at temperatures much below the PT point $T_c$. The scattering indicatrix, surface power spectral density, and autocorrelation function demonstrate distinctive qualitative change during the transition. At the critical temperature $T_c$, disorder of the 30-nm-thick film reaches the highest level due to coexistence of insulating and metallic phases. Here, the surface autocorrelation length drops to its minimal value. However, when
VO₃ switches into metallic state, the autocorrelation length recovers back, close to its initial value in the insulating phase. As the film switches from M₁ to R-phase, the fractal dimension of the surface decreases, indicating smoother surface with more uniform optical properties in the metallic phase. It is shown that the hysteresis loop depends on spatial frequency of surface irregularities. Smaller grains of 30-nm-thick film have broader hysteresis and noticeable “transition opalescence” due to higher elastic strain and higher concentrations of point defects.

When the film thickness exceeds the threshold value for the introduction of misfit dislocations, these dislocations noticeably suppress the internal strain in the film. Thus, the strain in relatively thick 125-nm film is substantially reduced, showing considerably different light scattering and structural evolution upon thermally induced PT, as compared to the strained 30-nm-thick film with lower concentration of structural evolution upon thermally induced PT, as compared to the strained 30-nm-thick film with lower concentration of dislocations, since domain walls of a new phase are pinned by defects. In the absence of internal strain, the BSDF scattering pattern does not change qualitatively with temperature, indicating the absence of temperature-dependent film twinning or formation of new domain pattern.

The considerably different evolution of the scattering indicatrix for the films with higher internal elastic strain and for thicker films where this strain is suppressed by misfit dislocations opens new possibilities for selection and classification of these films by angle-resolved light scattering technique.

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