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Nucleation controlled hysteresis in unstrained hydrothermal VO₂ particles

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While nucleation-limited transformation mechanisms are widely implicated in unstrained, undoped VO₂ nanoparticles, a direct link between nucleation barriers and hysteresis widths has not yet been established. Here, we investigate microscopic transformation of structural domains optically in hydrothermally grown VO₂ particles $\sim$ (0.5 to 46) μm in length, which are not elastically clamped to the substrate. We observe abrupt and generally complete transformation in individual particles, consistent with a nucleation-limited transformation mechanism. The forward and reverse transformation temperatures are not correlated, suggesting a range of potency of nucleation sites for both forward and reverse transformation in undoped particles, resulting in a hysteresis of 2.9 to 46.3 °C. Thus, the macroscopic hysteresis width in bulk VO₂ powders and dispersed particulate films is primarily attributable to a distribution of critical nucleation temperatures between different particles. These findings suggest that as VO₂ volume elements are scaled down for microelectronic applications, manipulation of nucleation sites via defect engineering may be required to control the degree of the VO₂ element reversibility.

I. INTRODUCTION

The metal-insulator transition in VO₂ has been extensively studied due to both fundamental interests in the nature of coupled structural-electronic phase transitions, as well as practical interest in the large changes in electronic resistivity, optical transmittance, reflectivity, and thermal conductivity that accompany this phase transition. These changes in properties accompany a martensitic-like structural phase transition from the low-temperature monoclinic phase (M1) to a high temperature rutile phase (R) near 67 °C [1]. Understanding of specific microscopic phase transformation mechanisms is a critical step along the path of controlling various aspects of the phase transition, including transformation temperatures, transformation widths, and hysteresis widths. In particular, the hysteresis of a phase transition could result from kinetic undercooling or superheating required to overcome nucleation energy barriers of a daughter phase, or could be associated with internal friction accompanied by the growth of a new domain and concurrent motion of a heterophase boundary. Engineering of hysteresis widths could be especially advantageous as it offers an additional, path dependent route to control phase

fraction at a given temperature intermediate between the final transition temperatures, and therefore can control the degree of reversibility (or volatility) of macroscopic properties (resistivity, reflectivity, transmissivity).

Variation of transformation width and the extent of phase coexistence has been controlled by application of external strain in undoped VO₂. Undoped VO₂ particles, elastically clamped to the substrate by high temperature CVD growth (900 – 1100 °C) [2] demonstrate a rich variety of microscopic phase coexistence of M1, M2, and R phases [3-12]. These microstructures result from the balance of external strain energy from elastic clamping to the substrate and the interfacial energy added by domain wall formation [4]. At the particle level, these observations have shown that phase coexistence regimes in individual strained particles lead to broad phase transitions via modifications to thermodynamic driving forces which change T_{cr} [3,4,6,13,14]. In contrast, phase transitions in free-standing VO₂ studied simultaneously in these experiments [3,4,9] are sharp, and no microscopic domains have been observed. The lack of phase coexistence suggests that free-standing, undoped VO₂ particles may represent the ideal setting for studies of intrinsic nucleation in VO₂.

Previous kinetic studies in individual un-doped free-standing VO₂ particles suggest that nucleation of M1 (R) embryos upon cooling (heating) is rate-limiting, while the growth of M1 or R phases is too fast to be observed by most techniques [15]. Heterogeneous nucleation is also posited, as calculations using classical nucleation theory yield a homogeneous nucleation barrier of $\sim 10^4$ kT, ruling out homogeneous nucleation as a mechanism at experimentally observed transition temperatures [16]. Furthermore, a few studies have sought to identify heterogeneous nucleation sites in nano-scaled systems. Oxygen vacancies located at grain boundaries are implicated by plasmonic resonance spectroscopy as heterogeneous nucleation sites [17]. By contrast, in elastically clamped individual VO₂ particles, nucleation sites have been associated with twin walls during the heating transition, and with point defects introduced by α -particle irradiation during the cooling transition [18]. In strained (due to substrate-film lattice mismatch) epitaxial thin films, nucleation has also been statistically linked to domain boundary sites [7,8]. Therefore, in both free-standing and elastically clamped individual particles, heterogeneous nucleation is rate-limiting and associated with crystallographic defects which serve to lower the energy barrier for phase transition.

In contrast to the well characterized heterogeneous nucleation in metallic martensitic systems [19,20], the statistics of nucleation of the martensitic transformation in VO₂ is not well established, and the hysteresis width dependence on particle size as well as the width of transformation peak are not completely explained. In studies on bulk ensembles of particles, a dependence of hysteresis width on availability of nucleation sites has been explained by developing phenomenological models correlating ΔT_{cr} with particle width [15], particle volume [16,21], thin film grain size [22], and thin film defect density [17,22]. However, there remains a lack of direct observations quantifying the statistics of nucleation on an individual particle basis for oxides synthesized by different growth techniques. To address this deficit, it is necessary to

relate the distribution between particles both on heating and cooling to the macroscopically observed transition widths and to identify any particle size dependence within the statistical distributions. Clarifying changes in phase transformation mechanisms requires microscopic investigation of domain nucleation and growth, beginning with the simplest case - undoped, unstrained VO₂. Resolving these questions can expose important underlying clues in understanding transformation mechanisms in both undoped and chemically doped systems, and can reveal new approaches to engineering metal-insulator transitions with desired transformation behavior.

In this work, we observe nucleation limited M1 to R and R to M1 phase transitions in free-standing, hydrothermally grown VO₂ on the individual particle basis by optical microscopy. Furthermore, we identify a distribution of transformation hysteresis across a population of particles, which directly correlates to bulk powder observations of T_c and ΔT_{cr} . Here, we show that a distribution in the potency of nucleation sites between individual particles, both on heating and cooling, is responsible for the observed macroscopic hysteresis width in this phase transition. These findings have strong implications for future scaling of micro or nano-electronic VO₂ devices, which must maximize a number of sufficiently low activation barrier nucleation sites to achieve low hysteresis widths and minimize power dissipations.

II. METHODS

Single crystal particles of VO₂ were synthesized hydrothermally from bulk V₂O₅ powder (Beantown Chemicals) using a reducing agent of high purity isopropanol. Samples were prepared with 1.63 g V₂O₅, 10 mL of isopropanol, and 65 mL of deionized water ($\rho = 18.2 \text{ M}\Omega \text{ cm}^{-1}$, Barnstead International NANOpure Diamond ultrapure water system). The mixtures were placed in 125 mL polytetrafluoroethylene cups and heated in a high pressure autoclave reactor at 210 °C for 72 hours. Samples were recovered by vacuum filtration and washed three times with deionized water and acetone. To relieve any strain from synthesis, samples were annealed under Ar (g) at 550°C for 5 hours. Only M1 and R phases are observed in samples synthesized by this approach [23]. Resulting morphology of VO₂ particles included wire-like structures consisting of a majority single stranded wires, and a few twinned “wishbone” particles (Fig. 1). Length of studied particles ranged from 0.5 to 46.1 μm in length and 0.2 to 1.1 μm in width. Out of plane thickness of the wires was not determined in optical experiments. However, atomic force microscopic (AFM) images of several particles ($N = 35$) show a thickness ranging from 0.1 μm – 0.7 μm . Particle length and width are uncorrelated, however a weak correlation between particle height and width could be calculated [$R^2 = 0.4$; (Fig. S1), [24]]. Individual particle volume is approximated by multiplying the particle area measured in calibrated optical microscopy images by the predicted height from the AFM derived regression function (height = 0.7·width). Differential scanning calorimetry (DSC) of bulk VO₂ samples was conducted on a TA Q2000 using a scan rate of 1 °C and calibrated using an Indium melting point standard.

For optical microscopy studies, samples are dispersed by sonication in high purity ethanol. A drop of suspended VO₂ particles is placed on a glass coverslip, and the solvent is

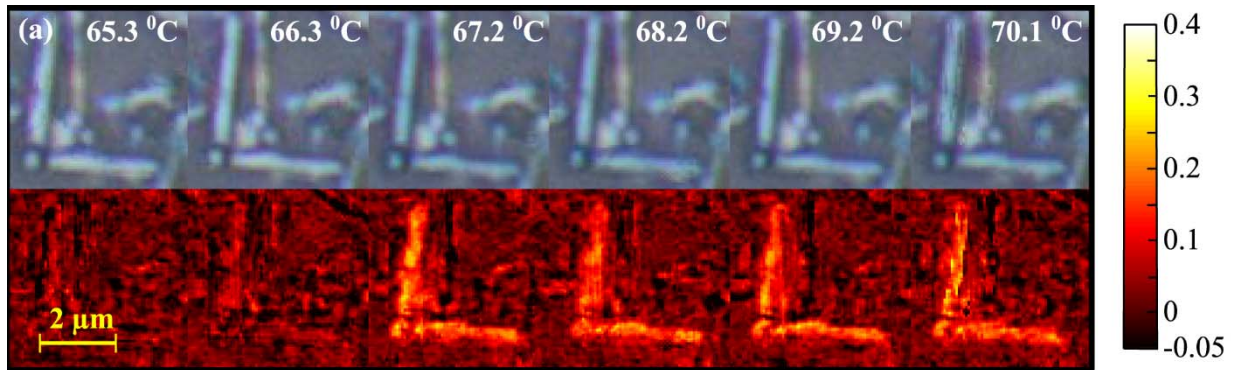
allowed to evaporate, dispersing particles on the underlying glass slide. Resulting particles loosely adhere to the glass substrate, held by relatively weak Van der Waals interactions between particles and the substrate. Thus, unlike CVD-grown VO₂ particles, which evidence substantial elastic clamping with the underlying substrate, hydrothermally-grown VO₂ particles are free to deform during nucleation and growth of secondary solid phases.

Optical microscopy was performed using an Olympus BX-53 polarized light microscope, and images were captured on an Olympus UC30 color CCD camera. Images reported in this work were all collected under bright-field reflected un-polarized white light. Under these conditions, light reflected off high temperature rutile (R) domains is visibly blue-shifted with respect to light reflected off low-temperature monoclinic (M1) phase, due to a subtle decrease in reflectivity between 600-800 nm in the R phase [25]. In all cases, exposure was manually selected and held constant through the image series. Sample temperature was controlled with a Linkham LTS120 Peltier temperature stage, which permits control within ± 0.1 °C from -25 to 120 °C.

III. RESULTS & DISCUSSION

A. Local transformation in VO₂ particles

Optical observations of phase transformation in individual undoped VO₂ particles are consistent with nucleation-limited transformation, followed by rapid propagation of a heterophase (M1/R) boundary through a particle volume. Reflected light microscopy shows abrupt transformation within easily distinguishable particles in response to small temperature changes (Fig. 1). Regions experience a subtle blue-shift upon transformation to the higher temperature R phase, consistent with UV-Vis spectroscopy which indicates stronger reflection in the red region from the low-temperature M1 phase, providing a convenient method with which to readily distinguish M1 and R phases [25]. At temperatures below or above the critical transformation temperatures, T_{cr} , there are no observable changes in the reflected visible spectrum of a specific volume (Fig. 1; Fig. S3-S5, [24]). Thus, phase transformation within domains of undoped VO₂ particles are limited to a relatively narrow temperature difference (< 0.5 °C), limited only by the temperature resolution of the temperature control stage. Similar abrupt transformation behavior is illustrated both on heating and on cooling.



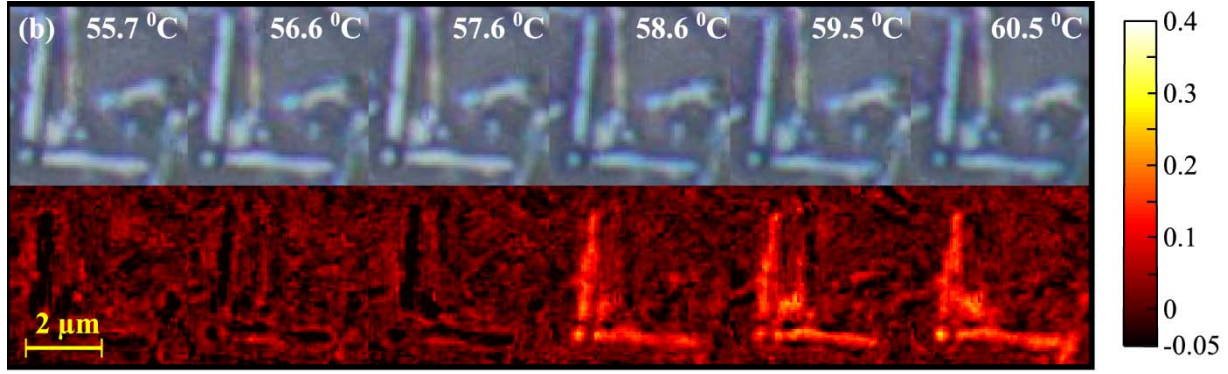


FIG. 1. Abrupt blue-shift in single VO_2 particles under unpolarized reflected white light and the associated red-difference plots during (a) a heating cycle performed at 1 °C increments (b) the subsequent cooling cycle at 1 °C increments. Difference plots were created by extracting normalized red pixel values, and calculating the difference between a low temperature reference image and high temperature image at each pixel. Reference temperatures were 39.3 °C during heating, and 54.7 °C during cooling.

Both forward and reverse transformations in undoped VO_2 particles are consistent with rapid progression from a single, or a very small number of individual nucleation events. In the majority of cases, phase transformation occurs uniformly throughout the entire volume of the particle within one discrete temperature interval (Fig. 1, Fig. S3, [24]). In the few cases which evidence phase coexistence, discrete domains of the sample transform abruptly, leading to two readily identifiable critical transformation temperatures within a single particle (observed in 6% of particles). The length scale of individual domains is on the orders of microns in length (Fig. 2, Fig. S4, [24]). In those cases which evidence phase coexistence within a single particle, heterophase boundaries separating domains that transform at different T_{cr} are spatially fixed from one cycle to the next (Fig. 2, Fig. S4, [24]), suggesting that phase transformation is impeded by some static defect in the particle, which may correspond with either an internal defect (dislocations, twin plane, etc.) or with some external defect (abrupt crystal facet edge). Thus, the occurrence of discrete transformation of two domains may indicate multiple nucleation events within a single particle, or temporary pinning of a grain boundary, which becomes mobile at a higher temperature. As with all nucleation processes, the stochastic nature of the transformation is evident. For a given region, T_{cr} appears fairly repeatable over multiple cycles, albeit with some degree of stochastic behavior (± 1 °C; Fig. 2).

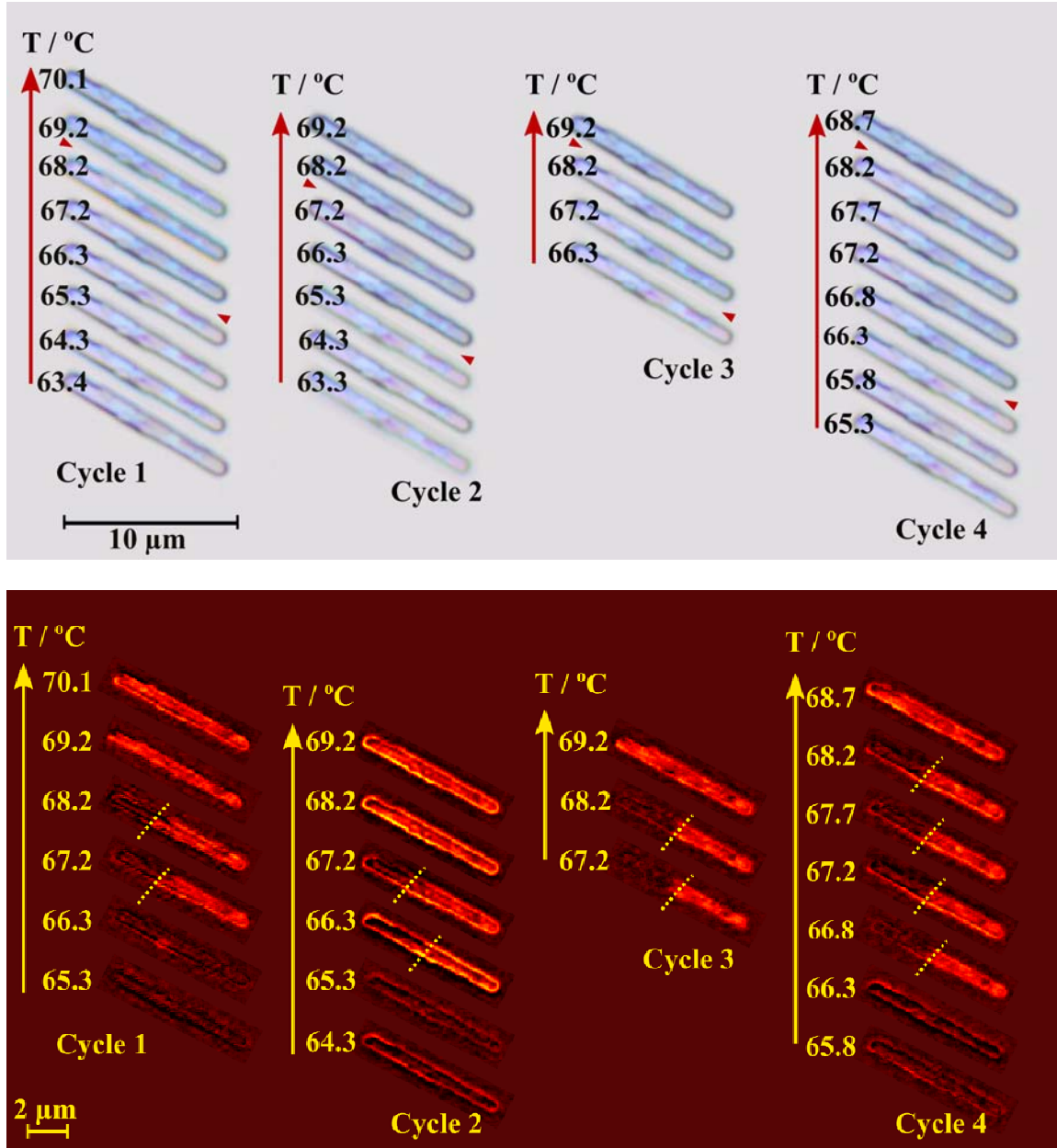


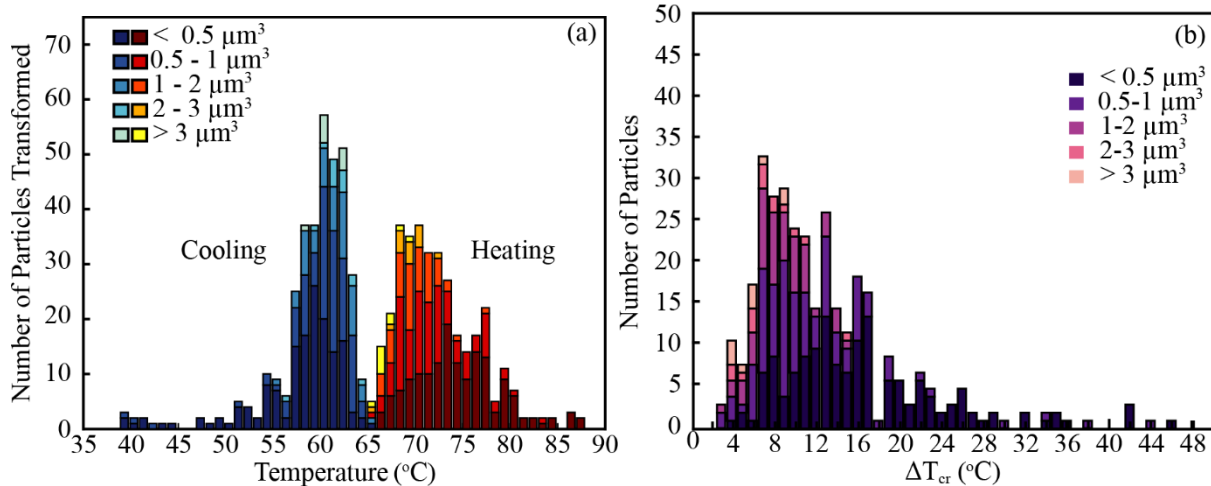
FIG. 2. A single VO₂ particle showing a two-step pinned transition over the course of 2 °C for four cycles in (a) original bright-field images, and (b) difference plots of the red component between the temperature given and 64.3 °C (cycle 1), 63.3 °C (cycle 2), 66.3 °C (cycle 3) and 65.3 °C (cycle 4).

Abrupt phase transformation in undoped VO₂ suggests that the phase transition is kinetically limited by nucleation of new structural domains within an existing solid phase, rather than by limited mobility of a heterophase interface. Classical heterogeneous nucleation is associated with an energy barrier due to the creation of a heterophase interface with some associated interfacial energy. After such domains are nucleated, growth proceeds spontaneously, driven by the volumetric free energy difference between the two phases. Motion of heterophase

boundaries is not observable on the time scales used in optical experiments, suggesting that heterophase boundary motion is very rapid, consistent with thermally driven transitions previously observed in individual particles below nanosecond timescales [26].

B. Transformation of particle ensembles

Transformation of a collection of undoped VO₂ particles is tracked to understand statistical variations observed within that population. Five areas $\sim 140 \times 105 \mu\text{m}$ containing a large ensemble of VO₂ particles ($N = 347$) were imaged during heating and cooling by 1°C increments, and transformation temperatures were tracked for individual particles (Fig. S4, S5). See Supplemental Information for image series [24]. Particles evidence a distribution of both forward ($T_{\text{mean}} = 72.2^\circ\text{C}$, $\sigma \sim 4.4^\circ\text{C}$) and reverse ($T_{\text{mean}} = 59.4^\circ\text{C}$, $\sigma \sim 4.4^\circ\text{C}$) transformation temperatures (Fig. 3). This distribution is dependent on particle volume during both the heating transition and cooling transitions [Fig. 3(a)] within the range of particles sampled in this study ($0.1 - 28.0 \mu\text{m}^3$, Fig. S2). Importantly, forward and reverse temperatures are only weakly correlated [Fig. 3(c)], as would be anticipated if the distribution in transformation temperature was due to a difference in local thermodynamic equilibrium between each particle (e.g., due to variable external strain imposed on an ensemble of particles or variation in oxidation state). Furthermore, it is evident that there is no history effect of the heating transformation which impacts the cooling transition temperature. This distribution of transformation temperatures is consistent with a distribution of potency of nucleation sites for both the forward and the reverse transformations, where the potency of forward and reverse nucleation sites are independent. The range of transformation temperatures between different particles, and between domains within an individual particle (e.g., T_2 , T_3 , Fig. 4) result from differences in the potency of nucleation sites between different domains, each of which require different volumetric free energy driving force (e.g., ΔG_2 , ΔG_3) to overcome the barrier to nucleation (Fig. 4).



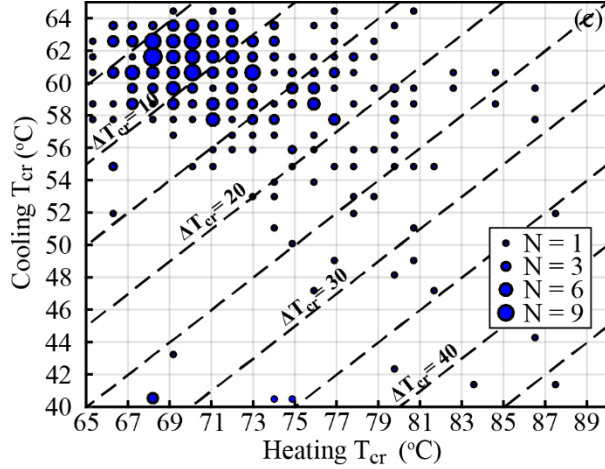


FIG. 3. (a) Histogram of the transition temperature (heating and cooling) of 347 individual particles observed in optical microscopy, and the calculated (b) histogram of the hysteresis in the same 347 individual particles showing extreme variations in hysteresis width between 2.9 and 46.8 °C. Notably, large hysteresis particles are composed exclusively of small particles ($< 2 \mu\text{m}^3$). (c) A scatter plot of the individual particle heating and cooling transition temperatures shows little correlation between heating and cooling transitions.

Integrated transformation on a particle basis shows general agreement on cooling and heating with the aggregate phase transformation as measured by differential scanning calorimetry [Fig. S6, [24]]. The midpoint of the transition on cooling obtained from DSC and particle counts are 61.0 °C and 59.3 °C, respectively, while the midpoints on heating are 71.4 °C and 71.3 °C. Therefore, the hysteresis obtained from the two data sources are also similar (DSC $\Delta T_{\text{cr}} = 10.4$ °C and optical $\Delta T_{\text{cr}} = 12.0$ °C). Deviation of integrated heating transformation signal between DSC and optical counts is most pronounced at higher and lower temperatures, which may indicate a selection bias against smaller particles which occurred during preparation of samples for imaging. Regardless of these small discrepancies, the macroscopic transformation behavior (ΔT_{cr} , heating T_{cr} , and cooling T_{cr}) can be nearly reproduced by the aggregation of microscopic observations in individual particles.

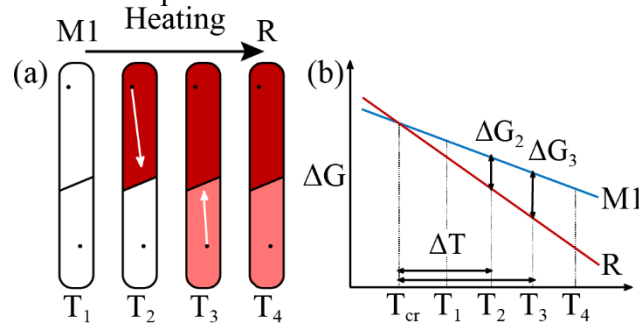


FIG. 4. a) Phase transformation from the M1 to R phase upon heating in undoped VO_2 occurs abruptly after nucleation of a domain from a potent site (black dot), where (b) nucleation in different domains is triggered at different transformation temperatures (T_2 , T_3), depending on the potency of nucleation sites within that domain, and therefore, the thermodynamic driving force (ΔG_2 , ΔG_3) necessary to overcome energetic barriers to nucleation. In general, the facile

interface passes through the particle leading to complete transformation. In ~4 % of particles, this interface is hindered by some crystal defect, leading to transformation of the particle in 2 to 3 distinct domains.

C. Statistics of heterogeneous nucleation in undoped VO₂

In order to quantify the densities of active nucleation sites at a given temperature, size-dependent transformation observations in individual particles (Fig. 3) are interpreted as the probability of observing at least one active site within a particular particle volume at some thermodynamic driving force, ΔG (MJ m⁻³). Here, ΔG represents the excess driving force at some temperature above (below) the bulk transformation temperature ($T_c = 65.3$ °C) for both heating and cooling transformations. Near equilibrium, ΔG is proportional to the temperature difference between T_c (equilibrium) and sample temperature [$\Delta G = \Delta S \cdot (T_c - T)$], with an entropy change of $69.2 \text{ kJ m}^{-3} \text{ °C}^{-1}$ [27].

The cumulative probability, P , of finding at least one active site within a particle volume, V (m³), is given by:

$$P = 1 - \exp(-N) = 1 - \exp[-V \cdot \rho(\Delta G)], \quad (1)$$

in which N is the mean number of potent sites, ρ is the density of active nucleation sites (sites·m⁻³) in a given volume at a given thermodynamic driving force. To relate the activity of nucleation sites to the thermodynamic driving force, the density of nucleation sites is assumed to adopt a power-law relationship [16,28], in which

$$\rho = \alpha \cdot (\Delta G)^\beta. \quad (2)$$

Constants α [sites·(m·J⁻¹) ^{β}] and β (unit-less) provide acceptable empirical agreement with calculated nucleation densities. From extreme value statistical theory, Eq. 1 and Eq. 2 together take the form of a Weibull distribution approaching T_c (65.3 °C) as an upper/lower limit temperature. Thus, α and β derive from a parent distribution of the number of active nucleation sites over a given driving force range, and control the scaling and density of the tails, respectively, of this distribution. The shape and scale of this population of intrinsic defects can be understood to be synthesis and processing dependent. Furthermore, for intrinsic nucleation sites, since the mean number of active sites, N , within a particular volume is $V \cdot \rho$, the cumulative probability of a particle having transformed, P , is a function both of driving force and of particle volume [Fig. 5(d)]. Because both modeled and experimentally calculated nucleation densities are dependent on particle volume, the majority of the rather large uncertainty comes from estimated particle volume, and some portion from the estimated population transformation fraction at each temperature.

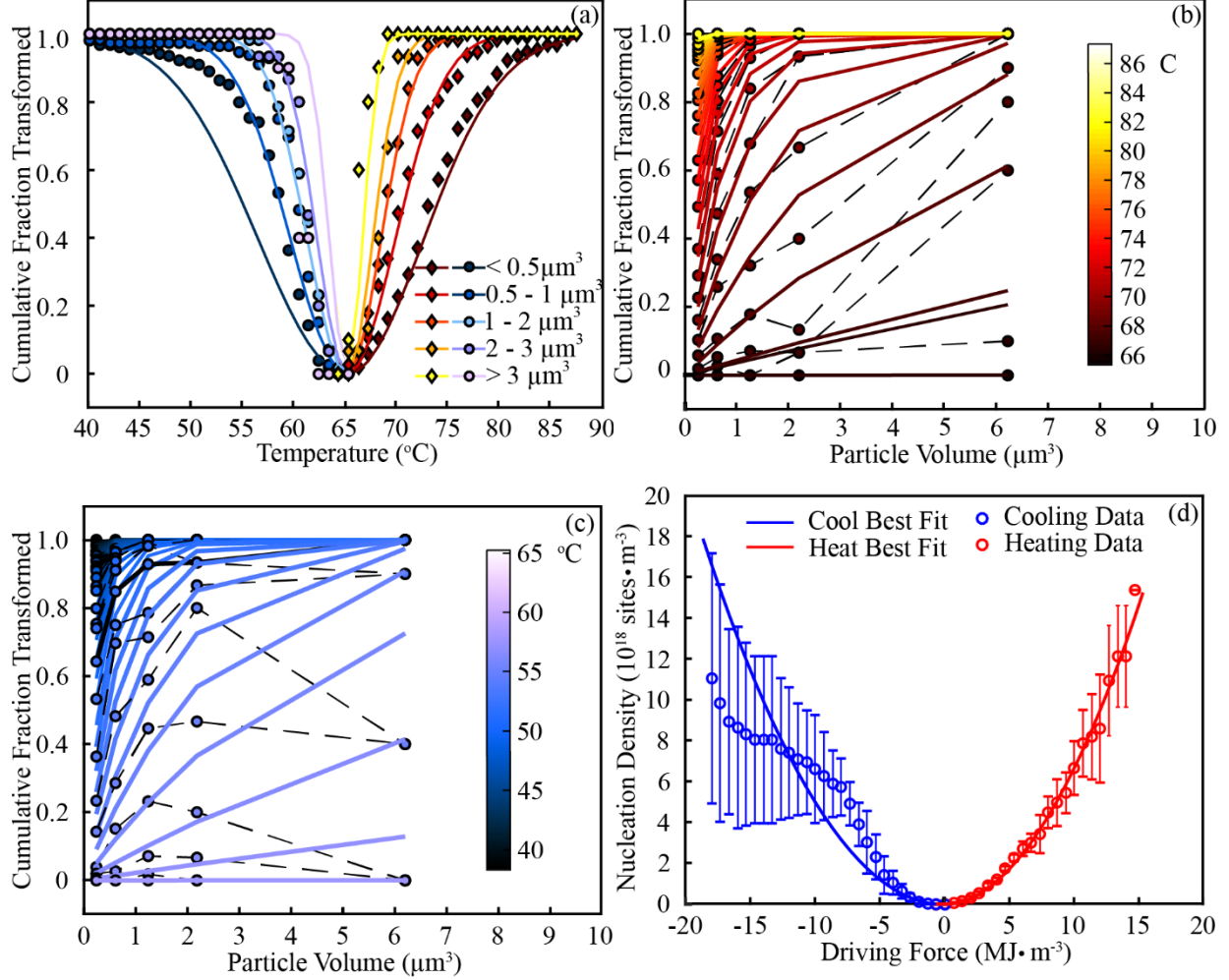


FIG. 5. (a) Cumulative fraction of particles that have transformed for each volume bin as a function of temperature. (b) The opposite transect showing the dependence of the fraction of particles that have transformed at each given temperature on particle volume during the heating experiment, and (c) during the cooling experiment. In (a) – (c) solid lines represent the best fit of Eqn. 1 on heating (warm colors) or cooling (cool colors), and filled circles or diamonds represent experimentally obtained fractions of particles that have transformed. (d) The calculated potent nucleation site density as a function of driving force according to Eqn. 2. Solid lines represent the best fit to Eqn. 2 on heating (red) and cooling (blue). Open circles represent the solution to Eqn. 1 for ρ using experimentally obtained cumulative transformation fractions (F) and volumes (V). Error bars are calculated from error introduced from particle volume and transformation fractions in experimental data.

Fitting parameters are obtained from a least-squares linear regression fit of the entire population, and show little difference between heating and cooling transformations. The α and β parameters, respectively, for heating are $(1.4 \times 10^6 \pm 5.6 \times 10^5, 1.9 \pm 0.2)$, and for cooling transitions are $(1.7 \times 10^4 \pm 5.6 \times 10^5, 2.0 \pm 0.2)$ with 99% confidence intervals reported. A formal hypothesis test shows that there is no statistically significant difference between β on heating and

β on cooling ($p = 0.036$, $\alpha = 0.01$). Any difference between obtained fitting parameters on heating and cooling could be interpreted as (1) a difference in both identity and density of the potent sites for each transition or (2) as a difference in potency activation rate with driving force due to the asymmetry of the activation energy barrier between heating and cooling reactions. The slight difference in fitting parameters (α , β) obtained on heating and cooling cannot conclusively distinguish between these scenarios.

Despite these similarities, a deviation between fitted results and experimentally calculated nucleation density values on cooling is observed (Fig. 5d), with only a small number of particles ($N = 35$) transforming below $-10 \text{ MJ}\cdot\text{m}^{-3}$ (i.e., at larger undercoolings; SFig. 8c). Fitting a separate function to this subpopulation could indicate two distinct populations of defects operating in different driving force regimes during cooling. However, given the poor counting statistics and large uncertainty on the calculated nucleation density, it seems questionable to interpret the findings of this study beyond an identification of a population of intrinsic defects operating in VO₂ particles, whose potency increases with driving force. Here, intrinsic nucleation sites are differentiated from extrinsic sites based upon the presence of particle volume dependence of transformation events, following conclusions of previous observations of martensitic transformations in small particle alloys and ceramics (FeNi [19], ZrO₂ [29], HfO₂ [28]). For both heating and cooling transitions, the volume dependence and scaling with driving force of the transformation fraction, F , indicates a population of intrinsic defects sites, such as point defects or dislocations, which are assumed to be sparsely distributed through the particle volume, and whose absolute number therefore increases as the particle size increases.

The β parameters obtained on heating and on cooling are surprisingly similar to the results of Lopez et al for a similar study on ion implantation deposited VO₂ nano-particles [16]. In surface dominated nano-particles, it would be expected that the potent sites would be physically different than those in hydrothermally synthesized micro-particles, with a different rate of potency increase with driving force. In this study, the resulting calculated defect densities are on the order of $\sim 1 \times 10^{13} \text{ potent sites}\cdot\text{cm}^{-3}$ in comparison to the $\sim 1 \times 10^{15} \text{ sites}\cdot\text{cm}^{-3}$ obtained by Lopez et al for a given driving force. This result indicates that the hydrothermal particles used in this study have a much lower defect density than the nano-particles deposited by ion implantation, and could explain why volume dependence of hysteresis is observed far beyond the volume range that this behavior is predicted by studies on VO₂ nano-particles (Fig. 6).

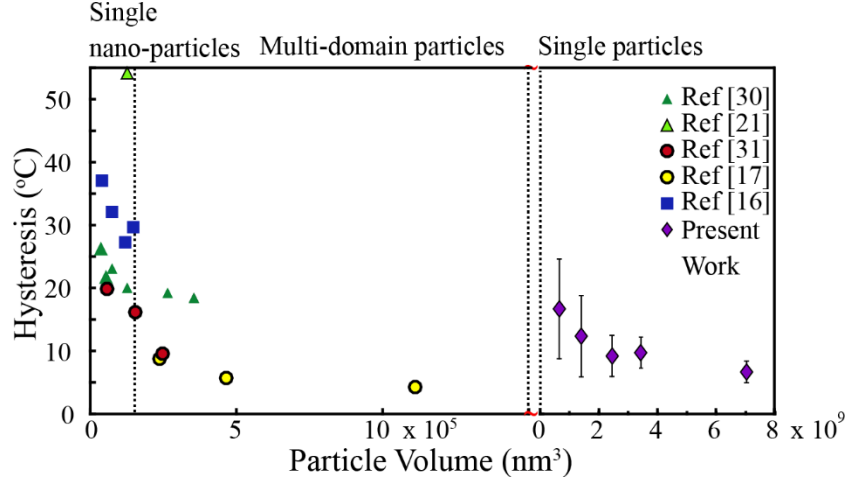


FIG. 6. Dependence of hysteresis width on particle volume of present work as compared with studies in significantly smaller VO₂ volumes [16,17,21,30,31].

D. Broader implications for phase transformation in VO₂

Undoped VO₂ particles that are elastically coupled to the substrate (e.g., grown by a chemical vapor deposition process) demonstrate significant phase coexistence and a rich diversity of microstructures due to the existence of transformation-induced local strain in those systems [3-6,9-11,13]. In contrast, the spontaneous, rapid, and complete transformations observed in most undoped VO₂ particles in this study occur because 1) particles are free to distort as they transform from one crystal structure to another, and 2) particles are small and have low defect densities, enabling a heterophase boundary to travel through a particle unimpeded. As particles grow in size, the likelihood that heterophase boundaries are impeded by internal defects or by some external defect will increase. In these cases, complete descriptions of transformation kinetics require consideration of energetic barriers limiting both nucleation and motion of heterophase boundaries past defects of varying barrier height. However, for the particle sizes investigated here, or within smaller volumes envisioned as the basis for two terminal electronic devices [32], temperature-induced phase transformations can be well-described by a stochastic nucleation process caused by local fluctuations overcoming some energy barrier to transformation [16].

The hysteresis (or degree of volatility) of the phase transformation has implications for the ability to store some metastable state within the material, or to transform between two states while dissipating relatively small amounts of energy[32]. The entire assemblage of undoped VO₂ particles evidences an extraordinary variation of hysteresis widths (2.9 to 46.3 °C). It is reasonable to expect that this variation of hysteresis widths would increase as VO₂ volumes are scaled down to relevant length for microelectronics due to a similar probability of finding a potent nucleation site within a particular volume. This would be anticipated even in VO₂ synthesized by different approaches containing different overall densities of nucleation sites.

The implication for hysteresis engineering of coupled electronic-structural phase transformations in VO₂ is clear. To reduce the magnitude of hysteresis observed within a given volume requires introducing potent nucleation sites for both the M1 to R and R to M1 transformations. Defect (vacancies or interstitials) introduction, aside from by applying external stress, might occur up to a certain limit by α -particle bombardment [18], chemical-doping [23,33], or electron-beam irradiation [29]. Thus, required temperatures or switching voltages might be reduced, and hysteresis widths systematically engineered.

V. CONCLUSIONS

In summary, we have directly shown that hysteresis width of the M1/R phase transition in un-doped, unstrained hydrothermally synthesized VO₂ particles is primarily controlled by the availability of nucleation sites in individual particles. Growth of daughter phases observed by optical microscopy is much faster than can be observed at experimental time-scales, and are not kinetically limiting. Instead, a distribution of nucleation sites with variable nucleation barrier heights between individual particles, or domains separated by internal defects, reproduces the macroscopically observed transformation hysteresis width. Moreover, the transformation temperatures upon heating and cooling are not correlated, indicating separate distributions of nucleation sites upon heating and cooling, rather than any local thermodynamic variability. The implications for VO₂ based device engineering are that introduction of potent nucleation sites is necessary for ΔT_{cr} reduction, especially at high-density, scaled-down dimensions.

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