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Sublimation of GeTe Nanowires and Evidence of Its Size Effect Studied by in Situ TEM

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Abstract: We report sublimation of crystalline GeTe nanowires at elevated temperatures in vacuum imaged by in situ transmission electron microscopy. The GeTe nanowires exhibit significant melting point suppression in the presence of Au contamination. A nanosized effusion cell is formed by coating the GeTe core with a SiO_2 shell, where the core can be evaporated or sublimated from the open end of the shell at high temperatures. By measuring the speed of the moving interface between the condensed and vapor phases, we determined the vaporization coefficient of these nanowires to be greater than or equal to $\sim 10^{-3}$ over a wide range of temperatures. At the final stage of the nanowire vaporization, the material loss occurs at a higher rate, which is evidence of a higher vaporization coefficient for nanosized GeTe. This in situ technique offers a quantitative method of investigating phase transition dynamics and kinetics of nanomaterials, an important topic for designing nanoscale devices to be operated at high temperatures such as phase change memory.

Introduction

Phase-change memory has emerged as a strong contender for replacing flash memory for nonvolatile memory technology. Phase-change material (PCM), commonly chalcogenides and most popularly $Ge_2Sb_2Te_5$ (GST), exhibiting an amorphous—crystalline transition under an applied electrical or optical impulse, can be probed for the existing bit state using either reflectivity or resistivity.[1] The change in optical reflectivity is exploited in rewritable CD and DVD technology. Electrically interrogated PCM devices sandwich the PCM between an electrode and a resistive heating element. To drive the system to crystallize or amorphize, a large current pulse is applied to locally heat the PCM. Devices in excess of 8MB have been assembled with excellent data retention and cycle life;[2] however, upon repeated cycling memory elements ultimately fail due to phase separation and loss of electrical contact integrity with electrodes.[3] While the active PCM is routinely encapsulated, the intense local heating required for switching introduces thermal stress which can damage the encapsulant and allow the PCM to evaporate.[4] To prevent failure and optimize the design of high density data storage, it is important to understand the dynamic transition behavior of PCM from a condensed to vapor phase at the nanoscale.

Single crystalline nanowires of many PCMs have been grown, including GeTe,[5–7] GST,[8] Sb_2Te_3,[5] and In_2Se_3.[9] High density memory arrays constructed from GST nanowires have been shown to withstand $>10^5$ write/rewrite cycles.[8] Reducing the active PCM volume can increase the crystallization speed and lower the power consumption.[10] In addition, nanowires present a convenient test-bed for investigating nanoscale phenomena, especially for in situ techniques. In situ transmission electron microscopy (TEM) heating experiments on metal nanoparticles have identified surface melting and particle coalescence at temperatures much lower than in the bulk.[11,12] Previous in situ TEM heating experiments on encapsulated Ge nanowires have shown a significant depression of the melting point correlated with nanowire diameter.[13] Similarly, for GeTe nanowires without encapsulation, the PCM was observed to melt and subsequently evaporate at temperatures lower than the bulk melting point.[14] With regard to device failure analysis, the development of a void in the active material volume during in

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(1) Lacaita, A. L.; Wouters, D. J. *Phys. Status Solidi A* **2008**, *205* (10), 2281–2297.
(2) Pirovano, A.; Redaelli, A.; Pellizzer, F.; Ottogalli, F.; Tosi, M.; Ielmini, D.; Lacaita, A. L.; Bez, R. *IEEE Trans. Device Mater. Reliab.* **2004**, *4* (3), 422–427.
(3) Nam, S.-W.; Kim, C.; Kwon, M.-H.; Lee, H.-S.; Wi, J.-S.; Lee, D.; Lee, T.-Y.; Khang, Y.; Kim, K.-B. *Appl. Phys. Lett.* **2008**, *92* (11), 111913–3.
(4) Yin, Y.; Miyachi, A.; Niida, D.; Sone, H.; Hosaka, S. *Jpn. J. Appl. Phys., Part 2* **2006**, *45* (28), L726–L726.

(5) Meister, S.; Peng, H.; McIlwrath, K.; Jarausch, K.; Zhang, X. F.; Cui, Y. *Nano Lett.* **2006**, *6* (7), 1514–1517.
(6) Yu, D.; Wu, J.; Gu, Q.; Park, H. *J. Am. Chem. Soc.* **2006**, *128* (25), 8148–8149.
(7) Jennings, A. T.; Jung, Y.; Engel, J.; Agarwal, R *J. Phys. Chem. C* **2009**, *113* (17), 6898–6901.
(8) Lee, S.-H.; Jung, Y.; Agarwal, R. *Nat. Nanotechnol.* **2007**, *2* (10), 626–630.
(9) Sun, X.; Yu, B.; Ng, G.; Nguyen, T. D.; Meyyappan, M. *Appl. Phys. Lett.* **2006**, *89* (23), 233121–3.
(10) Milliron, D. J.; Raoux, S.; Shelby, R. M.; Jordan-Sweet, J. *Nat. Mater.* **2007**, *6* (5), 352–356.
(11) Mohamed, M. B.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. A* **1999**, *103* (49), 10255–10259.
(12) Wang, Z. L.; Petroski, J. M.; Green, T. C.; El-Sayed, M. A *J. Phys. Chem. B* **1998**, *102* (32), 6145–6151.
(13) Wu, Y.; Yang, P. *Adv. Mater.* **2001**, *13* (7), 520–523.
(14) Sun, X.; Yu, B.; Ng, G.; Meyyappan, M. *J. Phys. Chem. C* **2007**, *111* (6), 2421–2425.
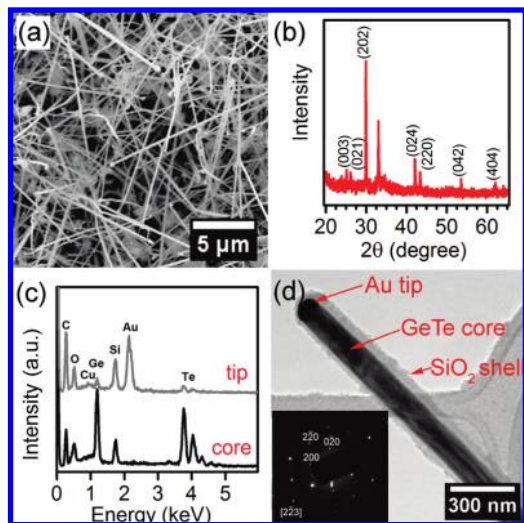
Figure 1. (a) SEM image of as-grown GeTe nanowires. (b) XRD pattern obtained from the as-grown chip, indexed to the rhombohedral structure. (c) EDX spectra of the tip and the body of a nanowire shown in (d). (d) TEM image of a crystalline GeTe nanowire coated with an amorphous SiO_2 shell. Inset: Electron diffraction pattern indexed to the rhombohedral structure.

situ electrical biasing highlights the importance of understanding and preventing PCM loss during cycling.[15] Here we report on a method utilizing in situ microscopy to evaluate the speed of evaporation and sublimation of nanomaterials.

Experimental Section

The GeTe nanowires were grown using the standard Au-catalyzed vapor−liquid−solid (VLS) method.[6] GeTe source powder (Alfa Aesar 99.999%) sublimated at the center of a 1 in. tube furnace was transported by 120 sccm Ar downstream to a SiO_2 substrate covered with 40 nm diameter Au colloids (Ted Pella). A vacuum pump was run continuously to set the furnace pressure at ∼10 Torr. The source was held at 400 °C and the receiving substrates at ∼350 °C for 5 h and then allowed to cool naturally. The nanowires were manually transferred to a molybdenum TEM grid with a lacey carbon film, and the entire grid was coated with an amorphous SiO_2 shell using low temperature plasma enhanced chemical vapor deposition (PECVD). The SiO_2 coating was typically nonconformal at the nanowire ends; this is due possibly to the sharp edges of nanowire there, leading to pores or openings in the SiO_2 at the ends. The SiO_2 shell served to restrict the possible sites for GeTe loss during in situ heating experiments to the nanowire ends only. This creates a well-defined front for quantification of the sublimation dynamics.

The as-grown GeTe nanowires were imaged with scanning electron microscopy (SEM) and TEM and characterized with X-ray diffraction (XRD), electron diffraction, and energy dispersive X-ray spectroscopy (EDX). Representative images and spectra are shown in Figure 1. The GeTe nanowires have diameters ranging from 50 to 150 nm and lengths from a few micrometers to tens of micrometers. The nanowires are crystalline and have a rhombohedral crystal structure, corresponding to the room temperature GeTe phase (JCDPS 47-1079). Figure 1c shows a TEM image of a typical SiO_2-coated GeTe nanowire. Electron diffraction shows a rhombohedral structure with a growth plane of (220). The isothermal in situ heating experiments were performed in a JEOL 3010 TEM using a Gatan 652 Double-tilt Heating Holder. At any temperature set point, we typically waited at least one minute before recording data to allow for the temperature stabilization. For a thermionic

(15) Meister, S.; Schoen, D. T.; Topinka, M. A.; Minor, A. M.; Cui, Y. *Nano Lett.* **2008**, *8* (12), 4562–4567.
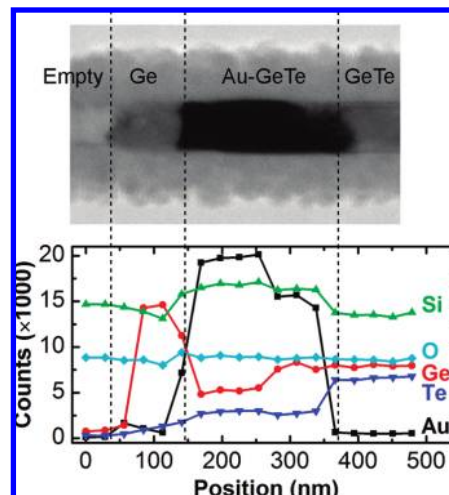
Figure 2. EDX-determined composition of a GeTe nanowire on cooling to room temperature, after it had partially evaporated at ∼500 °C.

emission gun,[16] beam heating is expected to induce only up to 15 K in local temperature increases in GeTe, which has a thermal conductivity as low as 2.5 W m^{-1} K^{-1} in amorphous form and up to 10.9 W m^{-1} K^{-1} in crystalline form.[17]

Results and Discussion

Two distinct cases of phase transformations were observed: melting-evaporation and sublimation. In the first type, the nanowire is still attached to its Au catalyst. The nanowire first melts at that tip (as identified by the disappearance of electron diffraction spots) at relatively low temperatures and then evaporates from the liquid phase through pores in the SiO_2 shell. As the molten front retracts, the GeTe-Au eutectic liquid is preserved at the front and moves as the core evaporates. This process is exactly the reverse of the Au-catalyzed VLS growth. We observed strong depression of the melting point from that of the bulk (724 °C) to ∼500 °C, but only near the tip where Au is present. For the body of the GeTe core where Au is absent, the melting point does not show strong suppression, remaining crystalline at 500 °C. This result indicates that contamination can play a significant role in the observed melting point depression in nanomaterials. The reduced melting point with Au present is expected, given the Au-GeTe eutectic at 480 °C.[18] When the evaporation is interrupted and the system is cooled to room temperature, a GeTe-Au solid solution is formed at the front, as shown in Figure 2. The existence of a small pure Ge segment on the front indicates that the evaporation is slightly noncongruent, with Te evaporating at a higher rate than Ge.[19] Given sufficient time, the nanowire completely evaporates, but with an Au droplet remaining owing to the much lower vapor pressure of Au at the experimental temperatures. Melting below the GeTe bulk melting point as well as subsequent evaporation has been observed previously in uncoated GeTe nanowires at temperatures as low as 390 °C by Sun et al.[14] Au was not

(16) Williams, D. B.; Carter, C. B *Transmission electron microscopy: a textbook for materials science*; Plenum Press: New York, 1996; p 4 v. (xxvii, 729).

(17) Nath, P.; Chopra, K. L. *Phys. Rev. B* **1974**, *10* (8), 3412–3412.

(18) Prince, A. *Au-Ge-Te Phase Diagram, ASM Alloy Phase Diagrams Center*; Villars, P., Okamoto, H., Cenzual, K., Eds.; ASM International: Materials Park, OH, 2006 (http://www.asminternational.org/asmenterprise/APD).

(19) Molchanov, M. V.; Alikhanyan, A. S.; Zlomanov, V. P.; Yashina, L. V. *Inorg. Mater.* **2002**, *38* (6), 559–563.
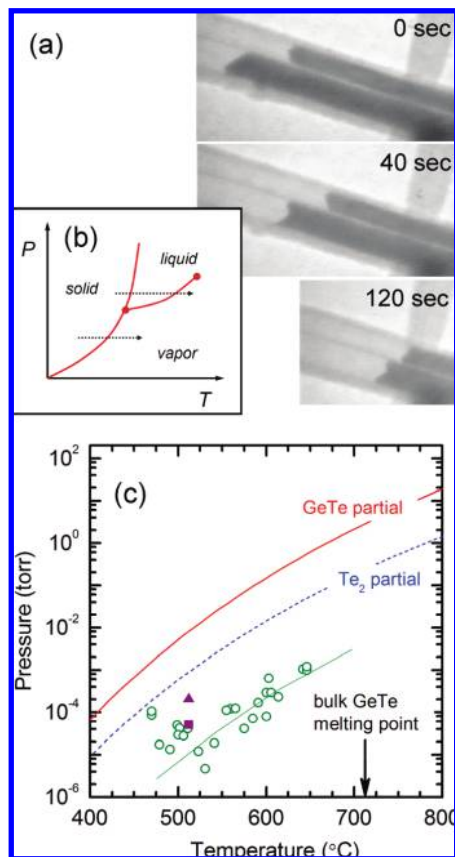
Figure 3. (a) TEM video frames of two GeTe/SiO$_2$ nanowires undergoing sublimation at 469 °C. The inner diameters of the upper and lower wires are 100 and 130 nm, respectively. The sublimation fronts are distinctly faceted. A video of this process is included in the Supporting Information. (b) Schematic phase diagram showing the GeTe nanowire sublimation or melting-evaporation process, (upper and lower, respectively, pictured as dashed arrows). (c) Measured $\alpha \cdot P_v$ of GeTe nanowires (open circles) plotted as a function of temperature together with partial vapor pressures of bulk GeTe [Molchanov et al.]. Also shown are the $\alpha \cdot P_v$ at early stage (solid square) and final stage (solid triangle) estimated for the nanoparticle sublimation in Figure 4. The TEM chamber base pressure was ~10^{-8} torr.

indicated as a significant player in those experiments. The correlation of low melting point to Au-presence in our work does not preclude the suppression of the melting point by other means; however in our experiments on nanowires with diameters ranging from 90 to 200 nm, the Au eutectic completely dominated low temperature melting dynamics.

A different type of behavior was observed when the activated part of nanowire does not contain Au (the Au tip was on the other end or lost during nanowire transfer). The nanowire starts sublimating at relatively low temperatures, and distinct facets of the solid−vapor interface can be seen (see below). Given sufficient time, the GeTe core sublimates away and vanishes completely with no particles remaining. The following discussion focuses on this second type of behavior: sublimation of pure GeTe.

As the GeTe core sublimates isothermally, an empty SiO$_2$ tube remains due to the much lower vapor pressure of the oxide. This process can be seen from Figure 3a and a video included in the Supporting Information. The GeTe core sublimates continuously and the vapor-phase molecules are transported along the oxide tube and escape from the end. The mean free path of the evaporated molecules/atoms can be estimated using
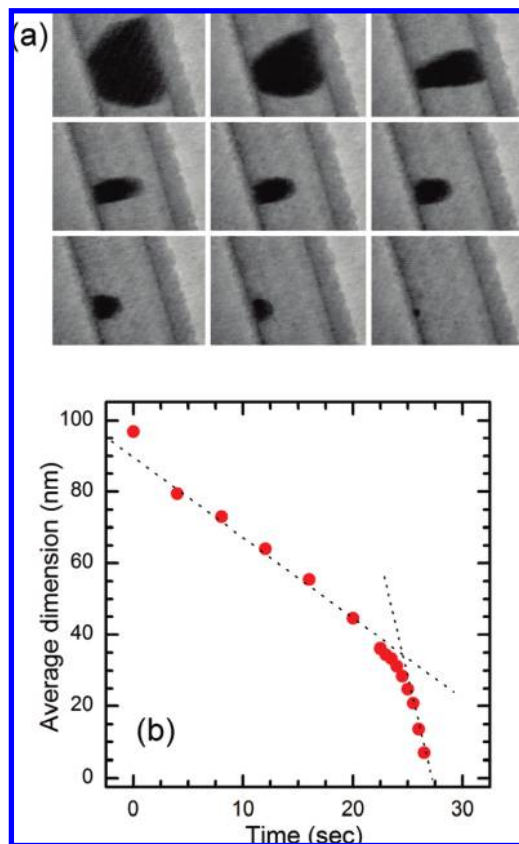
Figure 4. (a) Sequential snapshots of a GeTe nanoparticle sublimating isothermally (at 512 °C) from an oxide shell. The inner diameter of the shell is 90 nm. A video of this process is included in the Supporting Information. (b) Average dimension of the GeTe nanoparticle shown in (a) as a function of time, showing two distinct linear regions, the second of which kicks in at sub-30 nm dimensions.

$l \sim k_BT/[d^2 \cdot P_v(T)]$, where d is the effective diameter of the molecules/atoms and $P_v(T)$ is the equilibrium vapor pressure. l is calculated to be >10 μm for our experimental conditions, which is much larger than the diameter ($D \sim 100$ nm) but comparable to the length ($L \sim 10$ μm) of the nanowires investigated.

This system mimics thermal effusion cells used in deposition of thin films. In the widely used Knudsen cell,[20] the orifice is sufficiently small such that the pressure inside the cell can reach the equilibrium vapor pressure of the condensed phase without being significantly reduced by effusion. At equilibrium, on the interface between the condensed and the vapor phases, the net flux of molecules leaving the condensed phase is equal to the flux joining it from the vapor. This is given by the impingement flux in the ideal gas law

$$J_0 = \frac{P_v(T)A}{\sqrt{2\pi m k_B T}} \tag{1}$$

where $A = \pi(D/2)^2$ is the exposed surface area and m is the molecular mass. In the present nanoscale "cell", however, the vapor is transported following different kinetics as such balance is broken, and thus cannot be treated with the equilibrium model. The opposite of Knudsen-type is Langmuir-type, that is, direct sublimation into vacuum from the surface of the condensed

(20) Smith, D. L. *Thin-film deposition: principles and practice*; McGraw-Hill: New York, 1995.

phase.[21,22] In this case, there is no flux from the vapor recondensing, and the material sublimates with a flux of

$$J_v = \frac{\alpha \cdot P_v(T)A}{\sqrt{2\pi m k_B T}} = \alpha \cdot J_0 \qquad (2)$$

where α is the vaporization coefficient. In an attempt to quantify the sublimation process, we treat the nanowire sublimation in the Langmuir-type kinetics. In this approximation, the sublimation flux must be related to the material loss rate through

$$J_v = \rho \cdot A \cdot \frac{dx}{dt} \qquad (3)$$

where $x(t)$ is the remaining nanowire core length and ρ is the molecular density (molecules/volume). Therefore, the GeTe core length decreases according to

$$x(t) = \frac{\alpha \cdot P_v(T)}{\rho\sqrt{2\pi m k_B T}} \cdot (t_0 - t) \qquad (4)$$

Thus the GeTe core should vanish at a constant, temperature-dependent rate. It was shown, using mass spectrometry, that bulk GeTe evaporates approximately congruently, with GeTe molecules as the main vapor species and Te_2 molecules the next abundant composition at $\sim 1/10$ the concentration of the GeTe molecules.[19] The reported partial vapor pressure of GeTe and Te_2 are plotted in Figure 3c, showing an Arrhenius dependence on temperature with an evaporation enthalpy of ~ 188 kJ/mol.[19] Assuming predominantly congruent sublimation, $\alpha \cdot P_v(T)$ of GeTe can be determined using eq 4. It is clear from Figure 3c that $\alpha \cdot P_v(T)$ of the GeTe nanowires is about 3 orders of magnitude lower than $P_v(T)$ of bulk GeTe. However, they follow approximately the same Arrhenius dependence on temperature. These results indicate that the enthalpy is approximately the same as for the bulk, and the vaporization coefficient of the GeTe nanowires is $\alpha \approx 10^{-3}$ assuming the same $P_v(T)$ as that of the bulk. As a Langmuir-type sublimation has been assumed, this value sets the lower limit for the real vaporization coefficient.

Sublimation of bulk crystals was studied extensively for metals and compounds in the 1950s–1970s. At equilibrium, the molecule flux impinging on the crystal surface, J_i, is equal to J_0 given by eq 1. However, the sublimation flux J_v is smaller than J_0 by a factor of α according to eq 2. Surface atoms sublimate predominantly from active spots (mainly atomic ledges and crystal edges) where the desorption energy is the lowest.[21] Surface atoms at other locations must either thermally diffuse to the ledges, or wait for a ledge to move by. In Knudsen-type sublimation (equilibrium), J_i and J_v are balanced through a third term, the reflection flux, that describes a sticking coefficient of impinging atoms lower than unity. In Langmuir-type sublimation (into vacuum) where $J_i = 0$, J_v can be experimentally measured by thermogravimetric methods and used to determine α. For nanosized materials, however, thermogravimetric analysis is difficult. In this case, in situ imaging of the vaporization process provides an alternative way to quantify α. For most materials with clean surfaces, α was

measured to be equal or close to unity. α much lower than unity could be caused by various effects, such as limited surface atomic diffusion, ledge motion kinetics, entropy restraints in sublimation, and surface contamination.[21] Using the surface diffusion limited scenario, one expects[23]

$$\alpha \sim \frac{\tanh(\bar{\lambda}/\bar{X})}{\bar{\lambda}/\bar{X}} \qquad (5)$$

which is $\approx \bar{X}/\bar{\lambda}$ at small α. Here $\bar{\lambda}$ and $\bar{X}$ are the average spacing between active spots and mean diffusion length of surface atoms, respectively. $\alpha \approx 10^{-3}$ in the GeTe nanowire sublimation implies that $\bar{X}/\bar{\lambda} \sim 10^{-3}$; that is, active sites are extremely widely spaced relative to the atom diffusion lengths. Given the low sublimation temperature, $\bar{X}$ is estimated to be on the order of the interatomic distance, ~ 3 Å, giving rise to $\bar{\lambda} \sim 300$ nm. Considering that the total exposed dimension of the GeTe nanowires is the diameter (<300 nm), this indicates that (i) the atoms mostly sublimate from a small number of active spots, presumably atomic ledges initiated at the edge of the exposed nanowire cross section, and (ii) other effects may also play an important role in limiting the sublimation. For example, a high activation energy for dissociation at the active spots was suggested to explain $\alpha \approx 10^{-7}$ for red phosphorus and NH_4Cl by Hirth et al.[21] and Spingler,[24] respectively. Alternatively, minute surface contamination was used to explain a reduction of α from 1 to 10^{-3} in evaporation of Hg by Knudsen.[25] This mechanism cannot be ruled out in the present work. The low value of α quantified in this work indicates a relatively low material loss rate from GeTe nanowires. This result is useful for designing and operating GeTe-based nanoscale memory devices, as these devices are typically operated at high local temperatures.

As a result of the narrow range of nanowire diameters studied in the in situ heating experiments (90–200 nm), we did not observe a systematic dependence on the nanowire diameter in α. However, the final stage of the sublimation of GeTe nanowires without Au tips can provide a glimpse of the phase transition dynamics at reduced dimensions. At the final stage of sublimation, the remaining GeTe can be treated as a nanoparticle with size smaller than the diameter of the nanowire (~ 100 nm). Tracking the GeTe particle as it vanishes allows us to study the effect of size on sublimation. A typical vanishing process is shown in Figure 4a, and a video is in the Supporting Information. The GeTe particle has a nonspherical shape throughout the process, indicating that it is subliming from the solid phase. To quantify the sublimation dynamics, we approximate the volume of the GeTe particle by $\sim S^{3/2}$ where S is the projected area of the particle in the TEM image. The surface area of the particle is $\sim S$ and an average dimension of the particle can be defined as $L \sim S^{1/2}$. We can analyze these dynamics using eqs 2 and 3 by replacing A with S and x with L, which again yields eq 4 giving $L(t)$ as a linear function. Figure 4b shows L as a function of time, where two distinct linear slopes can be discerned. The values of α determined using the slopes for the early and final stages are plotted in Figure 3. Compared with $\alpha \approx 10^{-3}$ of nanowires, it can be seen that the nanoparticle has higher values of α, ranging from 5×10^{-3} at the early stage to 2×10^{-2} at the final stage. Although this

(21) Hirth, J. P.; Pound, G. M. *Condensation and evaporation: nucleation and growth kinetics*, Macmillan: New York, 1963.
(22) Surek, T.; Pound, G. M.; Hirth, J. P. *J. Chem. Phys.* **1971**, *55* (11), 5157–5163.
(23) Hirth, J. P.; Pound, G. M. *J. Phys. Chem.* **1960**, *64* (5), 619–626.
(24) Spingler, H *Z. Phys. Chem* **1942**, *52B*, 90.
(25) Knudsen, M. *Ann. Phys.* **1915**, *352* (13), 697–708.

conclusion is only semiquantitative due to scattering in experimental data and errors in estimation of the particle geometry, we believe that this shows evidence of increased α for truly nanosized GeTe. This is consistent with eq 5, because as the GeTe particle shrinks in size, the surface is expected to develop a higher density of ledges and high-index facets, resulting an increased $\bar{\lambda}$ and consequently higher α. A full quantification of this size effect requires a systematic investigation of nanosized particle sublimation.

Conclusions

In summary, we have demonstrated that nanoscale sublimation and evaporation can be quantified for a well-defined material geometry using in situ TEM. Melting and sublimation of GeTe nanowires at temperatures below the bulk melting point have been observed. The vaporization coefficient of GeTe nanowires was evaluated to be approximately 10^{-3}. At sufficiently small dimensions, the sublimation rate increases as predicted from classical sublimation theory. With the intense local temperatures required to set/reset the PCM, control of sublimation and evaporation is of critical importance in determining the viability of nanoscale PCM devices.

Supporting Information Available: Videos of nanowire and nanoparticle sublimation captured during in situ TEM and associated captions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Supporting Information for

Sublimation of GeTe nanowires and evidence of its size effect studied by in situ TEM

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Video 1. Video of two GeTe/SiO$_2$ nanowires undergoing sublimation at 469$^{\text{o}}$C. The inner diameters of the upper and lower wires are 100 and 130 nm, respectively. The sublimation fronts are clearly faceted.

Video 2. Video of a GeTe nanoparticle sublimating isothermally (at 512$^{\text{o}}$C) from an oxide shell. The inner diameter of the shell is 90nm.