

Size-dependent phase transitions and morphological control over phase change properties using colloidal nanoparticle building blocks

Marissa A. Caldwell¹, H. S. Philip Wong¹, Simone Raoux², Ravisubhash Tangirala³, Robert Y. Wang³, and Delia J. Milliron^{3*}

¹Departments of Chemistry and Electrical Engineering, Stanford University, Stanford, California, 94305; ²IBM T. J. Watson Research Center, Yorktown Heights, New York, 10598; ³The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California, 94720. *E-mail: dmilliron@lbl.gov

Colloidal nanocrystals have long been used to study the dependence of phase stability and transitions on size. Structural phase stability, in particular, can change dramatically in the few nanometer regime where the surface plays a significant role in determining the overall energy of the system. Implications include the well known depression of melting temperature with decreasing size and changes to the kinetics and thermodynamics of crystal-crystal phase transitions sometimes leading to extremely hysteretic behavior and metastable structures. Polytropy and crystalline phases not found in the bulk have likewise been observed in nanocrystals. We are studying the size-dependent phase stability of colloidal GeTe nanoparticles, synthesized alternatively in crystalline or amorphous form. GeTe is a representative phase change memory material, exhibiting bistability. It is also the simplest ferroelectric material, undergoing a displacive transition from the high symmetry rock salt phase to a distorted, rhombohedral phase around 325 °C. Hence, the scaling behavior of the amorphous-crystalline and rhombohedral-cubic transitions at small sizes has direct bearing on understanding materials limits to scaling of phase change and ferroelectric random access memories. Using in-situ x-ray diffraction while heating, we observe the crystallization of our amorphous nanoparticles and the reversible rhombohedral-cubic phase transition of our nanocrystals. Remarkably, the amorphous phase is maintained above 300 °C, finally crystallizing at more than 150 °C above the bulk film crystallization temperature. At the same time, the resistivity of a film of these nanoparticles drops by orders of magnitude upon heating, demonstrating that such solution-processed films retain the high resistivity contrast required for memory applications. By preparing films from nanoparticles of different sizes, from 2.2 to 4.5 nm in diameter, we show that the crystallization temperature depends strongly on size, reaching 400 °C for the smallest particles studied. Our long term goal is to utilize such size effects to tune the properties of phase change memory materials by manipulating nanostructured morphology as well as more conventional composition parameters.

Key words: nanoparticles, scaling, x-ray diffraction, GeTe

1. INTRODUCTION

Germanium telluride (GeTe) is simultaneously the phase change memory material and the ferroelectric material with the simplest composition. It's ferroelectricity is defined by a symmetry-breaking displacive transition from the rock salt structure at high temperature, to a crystalline phase with rhombohedral symmetry stable below ~325 °C. In addition, the amorphous phase of GeTe is sufficiently stable under ambient conditions that non-volatile phase change memory devices can be operated based on the reversible amorphous-crystalline transition. For optical discs as well as electronic memories, the large contrast in electronic properties between these two states makes readout straightforward.

However, GeTe is not considered promising for practical memory applications and more complex chemical compositions have been investigated in order to achieve favorable phase switching characteristics. In particular, the small band gap of GeTe results in a high carrier concentration which screens the displacive field, effectively preventing electronic switching of the polarization direction[1]. Meanwhile, the crystallization and melting temperatures[2] are not competitive with ternary or quaternary phase change memory compounds, such as those along the GeTe-Sb₂Te₃ tie-line or Ag, In-doped Sb₂Te[3]. However, phase transitions, including melting[4,5] and ferroelectric displacive transitions[6,7], have been shown to change systematically with size, particularly at the

nanometer-scale of interest for future electronic memory devices. For example, at ~ 20 nm or less, the melting temperature, which determines the operating power of a phase change memory device, is expected to change significantly. In general, the relative stability of condensed phases differs at small sizes from the bulk. These changing relative stabilities are expected to directly influence switching characteristics of ferroelectric and phase change devices.

The relevance to device applications and the general interest in nanoscale phase stability have prompted recent reports on the properties of GeTe thin films[8] and nanowires[9,10]. In addition, the properties of patterned arrays of phase change nanodots on the order of 20 nm in diameter have been investigated[11], but the properties of nanoparticles of GeTe, or any phase change material, below 20 nm have been elusive. Colloidal nanoparticles have been used to study melting and crystal-crystal phase transitions in this size regime, resulting in scaling laws that describe size-dependent phase stability[12]. However, while there has been extensive work in developing colloidal routes to metal chalcogenide nanocrystals, including those in the II-VI family[13-15], as well as the lead chalcogenides[16] and tin telluride[17], a direct colloidal route to germanium chalcogenide nanoparticles has not been reported. Also, there is little published work on the colloidal synthesis of amorphous nanoparticles which are needed to study the size-dependence of crystallization. Here, we report the synthesis of colloidal amorphous GeTe nanoparticles, their size-dependent crystallization properties and electrical characterization relevant to memory applications.

2. EXPERIMENTS

2.1 GeTe Nanoparticle Synthesis and Size Selection

Germanium telluride nanoparticles were synthesized through a hot injection route from GeI_2 and tellurium, both initially stabilized by trioctylphosphine (TOP). These precursors were reacted at 250°C in a trioctylphosphine oxide (TOPO) solution in the presence of dodecanethiol to form a brown colloid. The reaction is held at 250°C for 8 minutes, allowing the nanoparticles to grow. The resulting nanoparticles can be dispersed in non-polar solvents such as toluene and chloroform.

To generate nanoparticles of different sizes, the synthesis reaction was allowed to proceed for 15 minutes, leading to a broad distribution of sizes. Then, size-selected samples were produced by first adding 1:1 v/v of ethanol to a chloroform dispersion of the nanoparticles. Then, ethanol was added in 1 mL increments and the precipitate after each addition was collected by centrifugation.

2.2 Nanoparticle Characterization Techniques

The nanoparticles were characterized by a variety of techniques including: transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), and powder x-ray diffraction (XRD). TEM images and EDS spectra were collected by a JEOL 2100 TEM at 200 kV. Samples were prepared by dropping a dilute dispersion of nanoparticles from toluene on a copper grid spanned by ultrathin carbon on a lacy carbon support film. Powder XRD was collected by a Bruker D8-Advance X-ray diffractometer equipped with a GADDS area detector and operated at 40 kV and 20 mA at the wavelength of $\text{Cu K}\alpha$, 1.54 Å. Samples were prepared by drop casting a thick film of nanoparticles onto a Si wafer.

2.3 In situ XRD

Nanoparticles were deposited from a toluene dispersion onto Si substrates in a nitrogen filled glove box. After deposition, the nanoparticles were capped with a 5 nm thick layer of sputtered silica to prevent evaporation at high temperatures. In-situ XRD patterns were collected while heating at the National Synchrotron Light Source at Brookhaven National Laboratory, beam line X20. The samples were heated at a rate of 1 K/s with simultaneous collection of the XRD by a linear array detector using a photon energy of 6.9 keV (wavelength of 1.797 Å) in a He atmosphere.

2.4 Electrical Resistance Measurements

Samples for electrical characterization were prepared by drop casting a thick film of nanoparticles onto a glass substrate pre-patterned with Au electrodes, separated by a 50 μm gap. Resistance was measured as a function of temperature in a custom built isothermal chamber in a nitrogen filled glove box. The chamber consisted of a hollow copper cylinder encircled by a band heater. Small ports allowed electrical probes to contact the sample. Temperature was measured by a thermocouple embedded in the copper directly beneath the sample. I-V characteristics were taken in a four point probe configuration with the source current ranging from $-1\text{e-}7$ A to $1\text{e-}7$ A using a Keithly 2425 source measure unit.

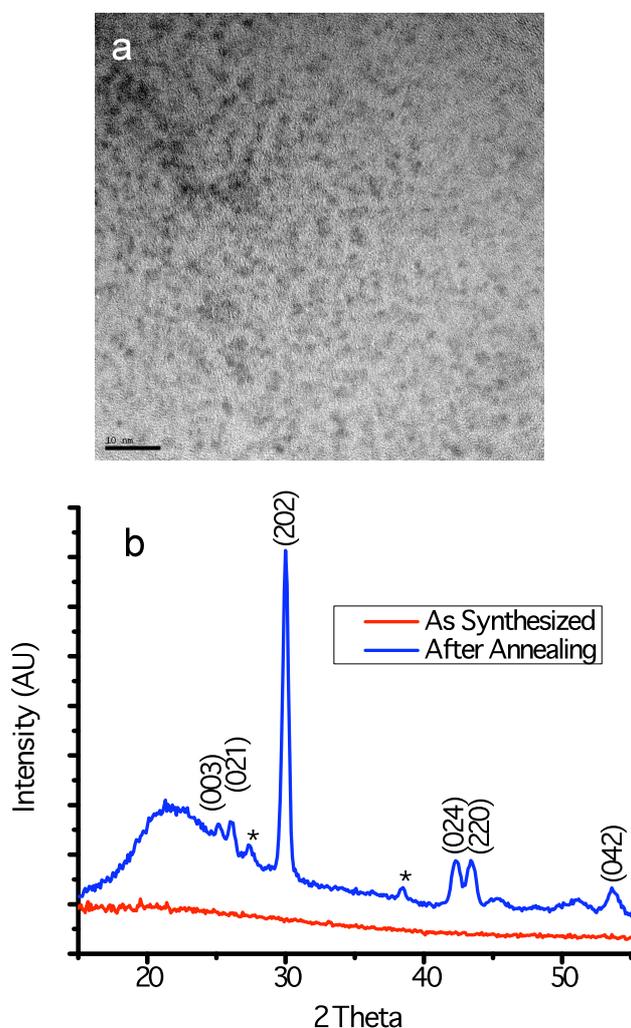


Figure 1. a) Bright field transmission electron microscope (TEM) image of amorphous GeTe nanoparticles. b) Powder x-ray diffraction (XRD) of the nanoparticles as synthesized and after annealing at 400 $^{\circ}\text{C}$.

3. RESULTS & DISCUSSION

3.1 Nanoparticle Characterization

Small, amorphous nanoparticles are particularly challenging to characterize as conventional structural elucidation techniques such as powder XRD are unenlightening and TEM imaging on the nanoparticles is limited by the lack of diffractive contrast. Nonetheless, the average size can be estimated from TEM (Figure 1a) as 3.5 nm in diameter, ranging from ~ 2.5 nm to ~ 4.5 nm and, independent of size, the EDS showed stoichiometric composition of 1:1 Ge:Te within experimental error. The amorphous nature of the nanoparticles is evident by both TEM and XRD. By high resolution TEM, no fringes characteristic of ordered atom columns were observed. Also, XRD of a film of the nanoparticles (Figure 1b) shows no sharp features, but rather broad humps characteristic of an amorphous state. After annealing at 400 $^{\circ}\text{C}$ in an inert atmosphere, the film crystallized to rhombohedral GeTe (JCPDS 00-047-1079), consistent with the composition found by EDS.

3.2 Size Selection and Size-Dependent Crystallization

To investigate the amorphous phase stability of the nanoparticles, in-situ XRD was used to observe thermally induced crystallization on different size ranges of the nanoparticles. The size distribution from the as-synthesized nanoparticles was fractionated into three size ranges. From TEM observations, the average sizes of each fraction were estimated as: 2.2 nm (~ 1.7 -2.8 nm), 3.5 nm (3-4 nm), and 4.5 nm (4-5 nm) in diameter. Initially, all samples were amorphous by XRD (Figure 2) and the only diffraction peaks observed were from a small amount of crystalline Te impurity which commonly appeared at the longer reaction times used to generate a broad range of particle sizes. The Te nanocrystals became concentrated in the smallest fraction collected by size-dependent precipitation. In all samples, as the temperature was increased, new

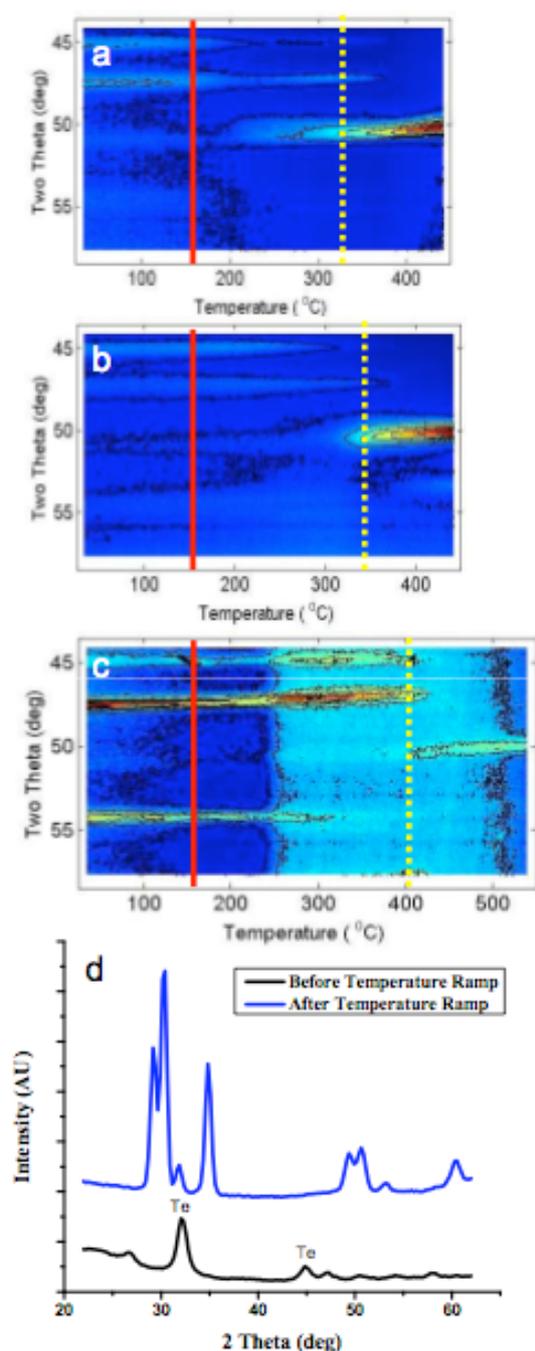


Figure 2. In situ XRD of size fractionated GeTe nanoparticles. a) 4.5 nm average diameter b) 3.5 nm and c) 2.2 nm. Red lines represent the crystallization temperature of a bulk GeTe film, dashed yellow lines show crystallization temperature of the nanoparticles. d) XRD patterns of nanoparticles before and after temperature ramp annealing experiment.

peaks began to appear, which were assigned to crystalline GeTe. This was confirmed with Θ - 2Θ scans over a wide 2Θ region collected after heating which always match rhombohedral GeTe. The region around $2\Theta=50^\circ$ was used to monitor nanoparticle crystallization as the GeTe peaks in this area are well separated from the Te peaks as well as other potential contaminants, such as Ge or GeO_2 . Taking the peak in the differential scattered intensity versus temperature as the crystallization temperature, even the largest (4.5 nm) nanocrystals crystallize at far higher temperature (320 °C) than thick sputtered films of GeTe (which crystallize at 160 °C[8]). And, as the average size of the nanoparticles decrease, the peaks at 50° appear at still higher temperatures, indicating a further increase in the crystallization temperature, to 350 °C for 3.5 nm and to 400 °C for 2.2 nm diameter nanoparticles. The fact that the crystallization temperature increases as the size decreases suggests that the amorphous phase is more stable, relative to the crystalline phase, in small particles. It is important to note that the size-dependence of the crystallization temperature cannot be explained by differences in nanoparticle sintering. Smaller particles always sinter at lower, not higher, temperatures, so a sintering-driven crystallization process would result in a size trend opposite that we observe. This insight allows us to conclude that sintering *follows* crystallization in these temperature ramp annealing experiments.

3.3 Electronic Properties

In order to ascertain the electronic properties of the GeTe nanoparticles, resistance versus temperature measurements were made. As synthesized, the GeTe nanoparticle films had extremely high resistance, out of the range of our source measure unit ($> 3e8 \Omega$). As the temperature was increased, the resistance decreased gradually, consistent with thermally-assisted electronic conduction, e.g. by hopping between adjacent nanoparticles (Figure 3b). Then, a sudden drop in resistance occurs at approximately 340 °C, consistent with the crystallization temperature, observed by in situ XRD (Figure 3a), of a similar sample. The resistance drops approximately five orders of magnitude to a few kilohms. The transition temperature was approximately independent of heating rate between 5 and 30 K/min, the maximum achievable rate in our apparatus. These observations combined lead to the conclusion that the change in resistance is concurrent with crystallization, as is observed for bulk GeTe.

3.4 Relevance to Phase Change Memory Technology

The excitement and investment surrounding phase change memory hinges, in part, on its potential to scale to very small dimensions far into the future. We were motivated to evaluate the properties of phase change nanoparticles by

considering that the most fundamental limitation to device scaling may be the changing properties of the phase change material itself. The material must retain the necessary characteristics for device operation at very small sizes including bistability of the amorphous and crystalline states and high electrical resistance contrast. While a number of previous studies have probed the question of scaling in phase change materials, most have employed thin films, which are scaled in only one dimension. For instance, the demonstration of the smallest switchable volume was done by switching a spot in a continuous film[18]. There are large energetic differences between a small crystalline spot in an amorphous film (or the opposite) and an isolated nanocrystal in a matrix, a situation that more closely resembles an ideal memory device, where in a small column of phase change material is isolated in dielectric material, between two electrical contacts.

The size dependence of the crystallization temperature, observed by XRD, and evident in the resistance versus temperature measurements, demonstrates that the phase change properties of nanoscale GeTe differ from those of bulk films. As shown, the amorphous nanoparticles have increased stability as the size decreases, showing a marked increase in crystallization temperature at small size. This can be compared to previously reported trends for ultrathin GeTe films[19]. For the thinnest films (2 nm) crystallization occurred ~ 150 °C above the bulk film value of 160 °C. Our results trend in the same direction, but the changes are much greater, owing to the high surface to volume ratio of nanoparticles, which exaggerates the effects of surface energy. Previous work has established a correlation between the surface energy of a phase and its relative stability at small sizes. A metastable state with lower surface energy than its thermodynamically stable counterparts is relatively stabilized in small nanoparticles. In fact, stabilization of small particles of amorphous oxides have been explained on this basis[20]. We suggest a similar mechanism may account for the enhanced stability of our small amorphous phase change nanoparticles.

The crystallization temperature is directly related to the non-volatility of a phase change memory device. From this perspective, a higher crystallization temperature at small sizes should improve data retention of the memory bit. Since the smallest particles show the highest amorphous phase stability, as phase change memory scales, the lifetime storage stability should increase. This is in marked contrast to magnetic recording technologies where the storage stability decreases with size scaling since the smaller magnetic domains have limited thermal stability and are more readily randomized.

Our results suggest two approaches to use GeTe nanoparticles in the fabrication of phase change memory devices. First, we have shown that amorphous GeTe nanoparticles can be thermally crystallized into a continuous film with low electrical resistance. In this way, the nanoparticles offer a solution processable route to the programming material of a phase change device. Compared to physical deposition methods such as sputtering or evaporation, solution processing is less expensive and, critically, easily fills high aspect ratio features to facilitate fabrication of the ideal phase change device structures[21]: pillar devices minimize the switching power of the memory device, a crucial parameter that must be reduced for successful commercialization. Second, if the nanoscale morphology can be maintained while cycling the device, e.g. by encapsulating each nanoparticle in a thin shell of silica, then nanoparticle

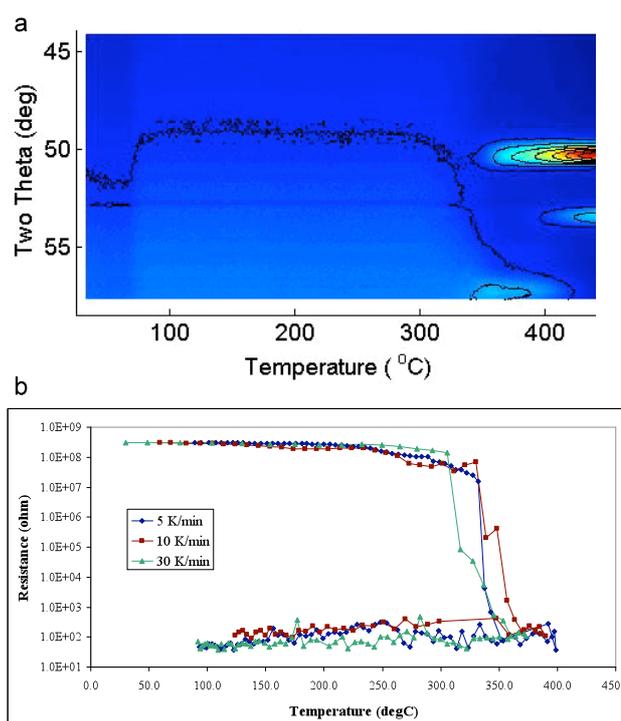


Figure 3. a) In situ XRD of GeTe nanoparticles. b) Resistance versus temperature of nanoparticle films at heating rates from 5 to 30 K/s.

size can be leveraged as a new mechanism for tuning phase stability and the associated memory switching characteristics.

4. CONCLUSION

By synthesizing and characterizing the crystallization of small GeTe nanoparticles, we have demonstrated that size has a profound effect on the amorphous-crystalline transition of this prototypical phase change material. Amorphous GeTe nanoparticles were synthesized, and size selection was used to isolate narrow size ranges within the broader range of 1.7 nm – 5 nm. Nanoparticle films were shown to exhibit the large resistive contrast between phases required for memory applications. Below 5 nm, the crystallization temperature was greatly increased, reaching 240°C above that of bulk films for the smallest (2.2 nm diameter) nanoparticles studied.

Previous work on diverse materials has shown that melting temperatures are markedly depressed in the same size range. In a phase change memory device, the material's melting temperature determines the amount of power needed to reset the device to the amorphous state. For nanoscale phase change memory devices, these trends in phase transition temperatures predict improving data retention and decreasing switching power at small sizes. This predicts a very positive outlook for scaling phase change memory to ever smaller sizes. On the other hand, our results also predict an ultimate scaling limit for phase change devices at which the crystallization temperature and melting temperature coincide. Below this size, the material will never crystallize and will rather transition directly from the amorphous phase to the melt, eliminating the potential to store data in the state of the solid material. While a quantitative estimate of this critical size for GeTe would require measurement of size-dependent melting for this specific material, we can approximate it by considering the size-dependent melting properties known for GeTe thin films in addition to other metal chalcogenide materials. Previous work on thickness dependent melting temperature for crystalline GeTe thin films (2 nm thick) have shown ~150°C depression from the bulk value[19]. In addition, 1.3 nm particles of CdS, which has a bulk melting temperature of 1405°C, significantly higher than that of bulk GeTe (724°C), melt at ~330°C[4]. Given these reference points, we suggest that this ultimate limit for phase change switching in GeTe is not much below the 2.2 nm of our smallest nanoparticles.

REFERENCES

1. E. F. Steigmeier and G. Harbeke, *Solid State Comm.*, 1970, **8**, 1275-1279.
2. M. Chen, K. A. Rubin and R. W. Barton, *Appl. Phys. Lett.*, 1986, **49**, 502-504.
3. N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira and M. Takao, *J. Appl. Phys.*, 1991, **69**, 2849-2856.
4. A. N. Goldstein, C. M. Echer and A. P. Alivisatos, *Science*, 1992, **256**, 1425-1427.
5. H. Jiang, K.-S. Moon, H. Dong, F. Hua and C. P. Wong, *Chem. Phys. Lett.*, 2006, **429**, 492-496.
6. W. S. Yun, J. J. Urban, Q. Gu and H. Park, *Nano Lett.*, 2002, **2**, 447-450.
7. J. E. Spanier, A. M. Kolpak, J. J. Urban, I. Grinberg, L. Ouyang, W. S. Yun, A. M. Rappe and H. Park, *Nano Lett.*, 2006, **6**, 735-739.
8. S. Raoux, J. L. Jordan-Sweet and A. J. Kellock, in *Materials Research Society*, eds. A. H. Edwards, P. Fons, S. Raoux, P. C. Taylor and M. Wuttig, Materials Research Society Symposia Proceedings, San Francisco, CA USA, 2008, pp. 1072-G1005-1002
9. D. Yu, J. Wu, Q. Gu and H. Park, *J. Am. Chem. Soc.*, 2006, **128**, 8148-8149.
10. S. Meister, H. Peng, K. McIlwrath, K. Jarausch, X. F. Zhang and Y. Cui, *Nano Lett.*, 2006, **6**, 1514-1517.

11. Y. Zhang, H. S. P. Wong, S. Raoux, J. N. Cha, C. T. Rettner, L. E. Krupp, T. Topuria, D. J. Milliron, P. M. Rice and J. L. Jordan-Sweet, *Appl. Phys. Lett.*, 2007, **91**, 013104-013103.
12. S. H. Tolbert, A. B. Herhold, L. E. Brus and A. P. Alivisatos, *Phys. Rev. Lett.*, 1996, **76**, 4384.
13. M. L. Steigerwald, A. P. Alivisatos, J. M. Gibson, T. D. Harris, R. Kortan, A. J. Muller, A. M. Thayer, T. M. Duncan, D. C. Douglass and L. E. Brus, *J. Am. Chem. Soc.*, 1988, **110**, 3046-3050.
14. Z. A. Peng and X. Peng, *J. Am. Chem. Soc.*, 2001, **123**, 183-184.
15. C. B. Murray, D. J. Norris and M. G. Bawendi, *J. Am. Chem. Soc.*, 1993, **115**, 8706-8715.
16. J. J. Urban, D. V. Talapin, E. V. Shevchenko and C. B. Murray, *J. Am. Chem. Soc.*, 2006, **128**, 3248-3255.
17. S. Schlecht, M. Budde and L. Kienle, *Inorg. Chem.*, 2002, **41**, 6001-6005.
18. C. D. Wright, M. Armand and M. M. Aziz, *IEEE Trans. Nano.*, 2006, **5**, 50-61.
19. S. Raoux, R. M. Shelby, J. Jordan-Sweet, B. Munoz, M. Salinga, Y.-C. Chen, Y.-H. Shih, E.-K. Lai and M.-H. Lee, *Microelect. Engin.*, 2008, **85**, 2330-2333.
20. A. Navrotsky, *Proc. Natl. Acad. Sci.*, 2004, **101**, 12096-12101.
21. D. J. Milliron, M. A. Caldwell and H.-S. Philip Wong, *Nano Lett.*, 2007, **7**, 3504-3507.

Biographies

Dr. D. J. Milliron is the Director of the Inorganic Nanostructures Facility at The Molecular Foundry, Lawrence Berkeley National Laboratory. Her research involves the synthesis and assembly of molecular and nanoparticle building blocks into electronic materials and devices. Target applications include energy devices, such as batteries and photovoltaic cells, as well as electronic memories, including phase change and electrochemical resistive switching devices. R. Tangirala and R. Y. Wang are postdoctoral researchers in Dr. Milliron's research group. Prof. H. S. P. Wong is a Professor of Electrical Engineering at Stanford University whose research involves nanoelectronic memory and logic devices, spanning new materials development, assembly, and device fabrication. M. A. Caldwell is a doctoral candidate in Prof. Wong's research group. Dr. S. Raoux is a Research Staff Member at IBM's T.J. Watson Research Center where she is involved in exploratory materials science for electronic applications, including phase change memory materials.