Nanomechanical actuation from phase transitions in individual VO_2 micro-beams

Hua Guo,[1,2] Kevin Wang,[1] Yu Deng,[3] Y. Oh,[4] S. A. Syed Asif,[4] O. L. Warren,[4] Z. W. Shan,[4,5] J. Wu,[1] and A. M. Minor[1,2,a)]

[1]*Department of Materials Science and Engineering, University of California, Berkeley, California 94720, USA*
[2]*National Center for Electron Microscopy, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[3]*National Laboratory of Solid State Microstructures and Center for Materials Analysis, Nanjing University, Nanjing 210093, China*
[4]*Hysitron, Incorporated, 9625 West 76th Street, Minneapolis, Minnesota 55344, USA*
[5]*Center for Advancing Materials Performance from the Nanoscale (CAMP-Nano), State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China*

(Received 2 April 2013; accepted 19 May 2013; published online 12 June 2013)

The mechanical response due to structural phase transitions in individual VO_2 nanowires was quantitatively investigated *in situ* in a transmission electron microscope. The electron beam was employed to locally heat the nanowire, and stress-strain was measured *in situ* using a microfabricated push-to-pull device. Tensile loading was found to increase the metal-insulator transition temperature and decrease the insulator-insulator transition temperature, consistent with the phase diagram of VO_2. These phase transitions resulted in an axial mechanical response of the VO_2 nanowires, an effect that can potentially be used to actuate nanostructures or gauge the local temperature change induced by electron beam irradiation. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4810872]

The phase transition behavior of vanadium dioxide (VO_2) at 68 °C has been extensively investigated for decades.[1–3] The distinct difference in physical properties between the monoclinic (M) insulating phases at lower temperatures and the rutile (R) metallic phase at higher temperatures makes VO_2 an interesting functional material for applications in sensing, smart coatings, and electromechanical switches. The actual mechanical response of these phase transitions in VO_2 has not been widely studied, compared to its electrical and optical properties. The mechanical response of VO_2 across the phase transition is important not only for assessing fatigue and reliability of VO_2-based electronic and optical devices but also a key property in the recently developed VO_2-based microactuation.[4] Limited by the brittleness and polycrystallinity of thin film specimens of VO_2, mechanical investigation has been difficult to assess in VO_2 thin films. This limitation was recently alleviated by the successful synthesis of single-crystal VO_2 nanowires,[5] in which large elastic strain exceeding 2% can be obtained before mechanical failure.[6–8] In this work, we investigate and quantify the mechanical response of individual VO_2 nanowires across the phase transition *in situ* in a transmission electron microscope (TEM). This analysis leads to a discussion of potential applications for VO_2.

According to the phase diagram as shown schematically in Figure 1(a),[9] three structures, i.e., M1, M2, and R, are involved in the insulator-insulator transition (IIT: M1-M2) and metal-insulator transition (MIT: R-M1 or R-M2). For clarity, the recently reported[10] triclinic structure (T phase) was not considered in our analysis since the triclinic phase is just a continuously distorted variant of the M1 phase. Because of this, the mechanical response from the phase transition between M1 and T phases is continuous. To simplify the analysis, the T phase was not distinguished especially from the M1 phase. The IIT and MIT can be driven thermally or mechanically along the horizontal or vertical axes of the phase diagram. Single-crystal VO_2 nanowires are always grown along their R-phase c-axis.[5,11] Accompanying the IIT or MIT, the nanowire develops a spontaneous strain, resulting in a change in the nanowire length. For example, the d-spacing of the planes perpendicular to the nanowire axis, the (-201) plane in the M1 phase, the (020) plane in the M2 phase, and the (001) in the R phase are 2.88, 2.90, and 2.85 Å, respectively. Therefore, the nanowire length will shrink (or elongate) by $\sim$1% when going from M1 to R (or from M1 to M2) phase. Considering the Young's modulus of 140 GPa in VO_2,[3] a large force will accumulate in individual nanowires if the nanowire is clamped with a fixed length. The force is expected to be proportional to the fraction of the nanowire that undergoes the phase transition, which can depend on the axial temperature distribution if the nanowire is heated non-uniformly.

In a TEM, the electron beam can serve as the local heating source. A recently developed *in situ* TEM mechanical testing device can readily provide a way to stretch/compress an individual nanowire while quantifying its stress and strain, electron diffraction pattern (DP), and domain evolution in response to the phase transition.[8] The phase transition temperature of VO_2 is just slightly above room temperature and can be further lowered by doping with tungsten.[12,13] In this regard, VO_2 nanowires are a good model system to probe *in situ* a nanoscale solid-solid phase transition.

The VO_2 nanowires were prepared using a variant of the vapor transport method.[6,9,14] To apply a load and measure the mechanical response of individual nanowires, a push-to-pull (PTP) device developed by Hysitron[8,15] was employed with a PI 95 nanoindentation instrument[16–19] in a JEOL 3010

[a)]Author to whom correspondence should be addressed. Electronic mail: aminor@berkeley.edu

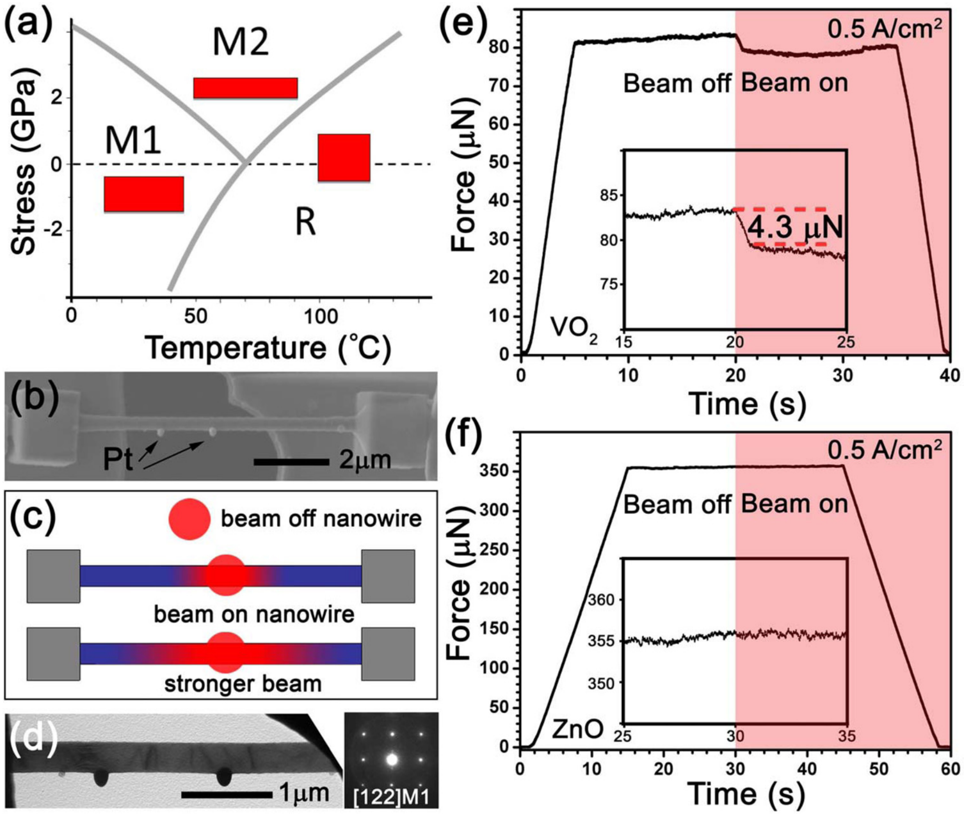

FIG. 1. (a) Schematic stress-temperature phase diagram of VO_2. The stress is along the rutile c-axis, which is the nanowire axial direction. The relative shape of each phase is shown schematically in the diagram for a horizontally oriented structure the three phases. (b) SEM image of a VO_2 nanowire, which was bonded to a PTP device by depositing Pt on both ends. Pt markers were also added to the sample as indicated. (c) Schematic of the specimen in a TEM. Higher electron beam intensity was used to heat the sample to higher temperatures. (d) TEM BF image of a VO_2 nanowire, on which two Pt markers were deposited for true strain measurement. (e) Force-time curve acquired from a VO_2 nanowire. A force drop of about 4.3 μN was detected when the e-beam was moved onto the VO_2 nanowire. (f) Force-time curve acquired from a ZnO nanowire, for which no force change was observed under similar test conditions to (e).

TEM. As shown in Figure 1(b), a 7.4 μm long VO_2 nanowire with a cross-sectional area of 0.11 μm^2 was bonded onto the PTP device using electron beam (e-beam) induced Pt deposition in a dual-beam focused ion beam (FIB) system. In addition to the Pt welds on both ends of the nanowire, two tiny Pt mounds were deposited near the middle of the nanowire to calibrate the true strain measurement, where details of the procedure and device preparation can be found in the Refs. 8 and 20.

The electron beam was focused onto the center of the nanowire to induce local heating. The electron beam was moved rapidly onto or away from the nanowire, while the nanowire was held under tensile loads in the displacement-controlled mode. For a given electron accelerating voltage, increasing the beam intensity introduces more energy into the focal spot.[21] In this way, various temperatures profiles could be achieved as schematically shown in Figure 1(c).

Figure 1(d) is a TEM bright field (BF) image of the nanowire on the PTP device. The DP indicates that the VO_2 nanowire starts in the M1 structure, and its loading axis is along the $[100]_{M1}$ direction. The force-time curve in Figure 1(e) shows the nanowire mechanical response due to the phase transition in response to an electron beam intensity of 0.5 A/cm^2 at a preloading of 82.0 μN. The recorded force dropped suddenly by 4.3 μN when the electron beam was moved onto the center of the nanowire. For comparison, a ZnO nanowire of similar dimension was tested in the same condition. No such force change could be found from the ZnO nanowire, as shown in the curve in Figure 1(f), which is consistent with the fact that ZnO does not undergo a structural phase transition under these conditions.[22] Any temperature rise at this low beam intensity did not induce a detectable thermal expansion in the ZnO nanowire. This is consistent with the expectation that thermal expansion is insignificant as compared to expansion due to a phase transition in the nanowire. Considering that during a fixed-displacement mode an extension in nanowire length relaxes the nanowire and lowers the total stress, the observed force decrement in Figure 1(e) is understood to result from the IIT (M1 to M2 phase transition), consistent with the phase diagram in Figure 1(a).

It should be pointed out that due to the axial temperature distribution, it is expected that only the portion of the nanowire around the electron beam (spot size ~100 nm) transitioned to the M2 phase, as opposed to the entire nanowire. Otherwise, the force change would be much higher than the recorded value. Given the $Y = 140$ GPa modulus[3] of the M phases and the 1% spontaneous strain, the force change should be about 2.1 μN for every 100 nm long segment of nanowire undergoing the IIT. The 4.3 μN of force change indicated that the M2 domain length in the IIT extends beyond the physical size of the electron beam. We also note that during routine TEM imaging of the entire nanowire with a beam current of 0.1 A/cm^2, no obvious change in force was detected from the VO_2 nanowire. This demonstrates that e-beam heating in routine TEM imaging (parallel beam with relatively large field of view) does not cause a phase transition in our quantitative mechanical test.

Further mechanical tests were conducted on a different VO_2 nanowire (21.0 μm long and cross-sectional area of 0.28 μm^2) at different force levels and various beam intensities. Figure 2(a) shows a force-time curve for a tensile preloading of 70.0 μN, during which the IIT occurred. A force drop of 13.2 μN was detected from an electron beam intensity of 13.4 A/cm^2. Once the beam was moved away from the sample, the force returned to the original level, reflecting

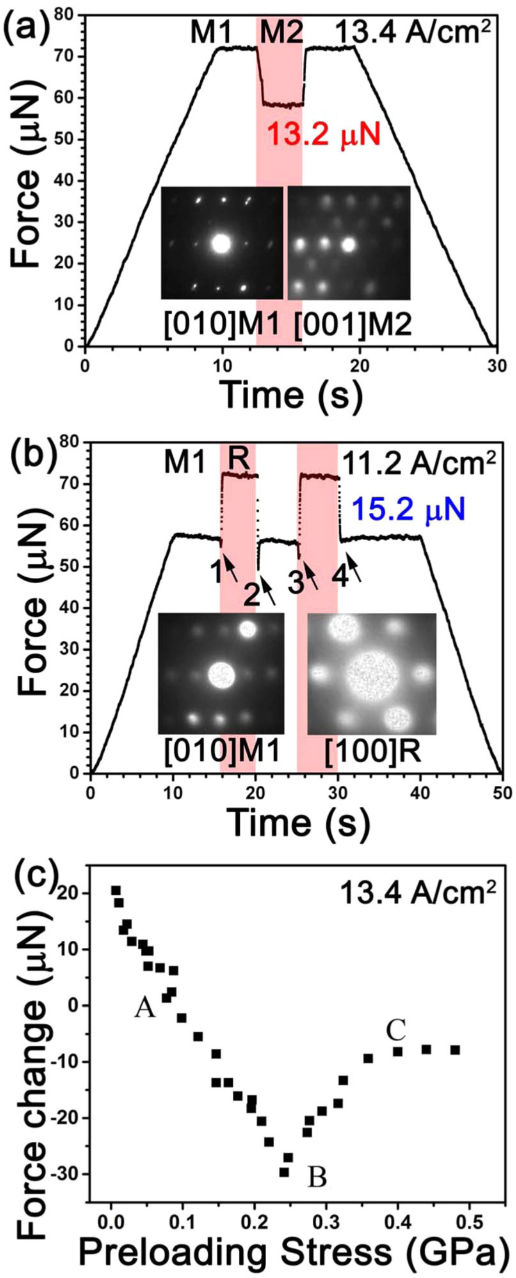

FIG. 2. (a) Force-time curve acquired from a VO_2 nanowire during which the IIT occurred under an e-beam intensity of 13.4 A/cm^2. DPs of the M1 and M2 phases are shown inset. (b) Force-time curve acquired from a VO_2 nanowire during which the MIT occurred under a beam intensity of 11.2 A/cm^2. DPs of M1 and R phases are shown inset. (c) Mechanical response of the MIT and IIT as a function of the preloading stress. At point A, the elongation of the VO_2 nanowire from M1 to M2 phase transition and thermal expansion was almost cancelled by its contraction from M1 to R phase transition, resulting in a net mechanical response as zero. At point B, strain-induced M1 to M2 phase occurred, which decreased the elongation of the VO_2 nanowire and the force drop value from that point, when the electron beam was on. After point C, only thermal expansion occurred.

the complete reversibility of the phase transition. The IIT is further confirmed by the DPs of the original M1 phase and the electron-beam induced M2 phase, as shown in the inset in Figure 2(a). From the phase diagram in Figure 1(a), when fixed at the natural length of the nanowire (zero initial tensile stress), sufficient heating would drive the MIT in VO_2 (from M1 to R); consequently, the nanowire would respond with an increase in tensile force. In contrast, when fixed at a large length (high initial tensile stress), sufficient heating would drive the IIT in VO_2 (from M1 to M2); consequently, the nanowire would respond with a decrease in tensile force. Under an intermediate initial stress, the MIT and IIT would coexist along the nanowire with non-uniform heating.

To observe the MIT a smaller preload was applied with a similar spot size. As shown in Figure 2(b), the MIT occurred, for a preloading of 55.0 μN. The DPs of the original sample and the sample experiencing beam heating clearly show the M1 phase in the former and the R phase in the latter. In contrast to the force drop in the IIT (M1 to M2 phase transition), here the force increased by 15.2 μN in the MIT (M1 to R phase transition). Such a force increment is clearly due to the nanowire length contraction, causing the instrument to increase the force applied to maintain a constant nominal strain along the nanowire. It should be noted that even when the temperature is quite high at the beam spot, the two ends of the nanowire remain at a lower temperature. Therefore, in addition to the MIT, the IIT always happens along the nanowire. The recorded force change is the net of the force decrease from the IIT and the force increase from the MIT.

According to the phase diagram of VO_2 in Figure 1(a),[9] under tensile loading the M2 phase is an intermediate phase between M1 and R phases at elevated temperatures. In our tests, the IIT always accompanied the M1 to R phase transition, as has been reported before in Raman studies.[23,24] In our experiments, the transient force decrease associated with the IIT (M1-M2) was always clearly seen right before the MIT (M1-R), as pointed to by arrows 1 and 3 in the force curve in Figure 2(b). In contrast, the M2 phase could also appear right before the MIT during cooling (R-M1), although this was not always detected. In the first cooling process in Figure 2(b), a force bounce of ~8.0 μN (arrow 2) from the lowest force measured during the R to M1 phase transition signifies the emergence of M2 as the intermediate phase. In the next R to M1 phase transition (arrow 4), such a force bounce was absent.

The phase diagram in Figure 1(a)[9] also shows that a tensile stress raises the critical temperature of the MIT and lowers the temperature of IIT.[6,25] Consequently, under a constant electron beam intensity, the force change should be a function of the preloading stress. Figure 2(c) shows results from a series of tests similar to that shown in Figures 2(a) and 2(b) at varying preloads. In this case, the preloading amount changes which phase transitions are triggered by the electron beam. Figure 2(c) plots the change in force (μN) for a given stress state (GPa) of a nanowire, showing that the force change starts out positive, similar to that seen in Figure 2(b). Besides an effect from thermal expansion, this behavior is a result of both the IIT and MIT phase transitions happening concurrently (the MIT occurring in the location of highest beam intensity, and the IIT occurring in a lower temperature area). At a preloading of ~0.1 GPa, the force changes caused by IIT and MIT essentially cancel each other out, leading to a zero net mechanical response (point A in Figure 2(c)). After this point, the IIT starts to dominate the mechanical response, resulting in a negative force change, similar to that seen in Figure 2(a). Beyond a certain initial strain level (point B in Figure 2(c)), the initial preloading tensile stress is so high that it already induces a high fraction of M2 phase in the nanowire even without the electron-beam

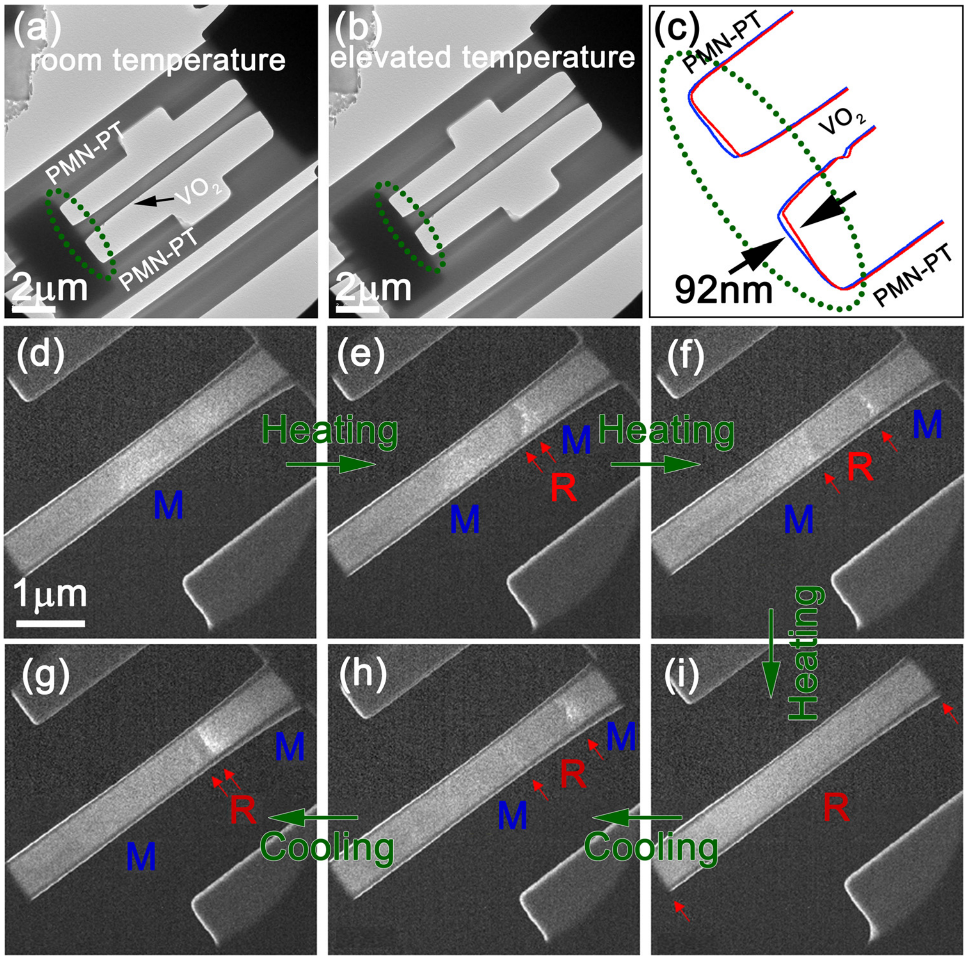

FIG. 3. *In situ* TEM heating experiment of a VO_2 nanowire actuated piezoelectric device. (a) TEM BF image of a piezoelectric PMN-PT frame fabricated by FIB within which a VO_2 nanowire is loaded along the middle. (b) TEM BF image of the PMN-PT frame at 100 °C. Elongation of the frame was measured at the left side as indicated by the dashed circle. (c) Contours of the frames at room temperature in blue and at elevated temperature in red. A length change of 92 nm was found, reflecting a strain of about 0.9% in the VO_2 nanowire. (d)-(i) *In situ* heating process of the device, showing the R phase propagation as the temperature increases gradually. (h)-(g) Cooling process of the device, showing that the R phase converts to M phase continuously as temperature decreases.

heating; thus, the amount of IIT trigged by the electron beam starts to decrease. At a very high tensile preload of ~0.40 GPa (Point C in Figure 2(c)), the force change plateaus. The entire nanowire should turn completely into the M2 phase at such high preloading tensile stress before the electron-beam heating. Therefore, the plateau beyond Point C in Figure 2(c) is attributed to the wire being completely transformed to M2 by the preload, and the force change due to the thermal expansion of the M2-phase only.

All of the various mechanical responses observed here occur rapidly in less than one second. Presumably, this actuation could be sped up with a faster and more powerful heating source. On the other hand, a slow, linear, and controllable response can be useful for certain microactuation applications. In order to investigate this behavior, an *in situ* TEM heating holder (Gatan) was used to provide slow uniform heating of a single nanowire. Here we attempt to use the spontaneous strain of the VO_2 phase transition to output electricity via a piezoelectric frame. In this case, a single 10.0 μm long VO_2 nanowire was fixed onto a FIB-fabricated frame of single crystalline piezoelectric $Pb(Mg_{1/2}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT),[26] as shown in the TEM BF image in Figure 3(a). Comparing the TEM BF images of the sample between room temperature and 100 °C, the PMN-PT frame was compressed by the VO_2 nanowire by about 92 nm (here the temperature sensor is mounted at the TEM holder, and therefore only gives an estimate of the actual sample temperature). The contour difference of the frame at these two temperatures clearly shows the 0.9% spontaneous strain in the VO_2 nanowire. Although electrical measurement capability was inaccessible in this setup, a voltage output would be expected from the deformed PMN-PT frame, providing a proof of concept for VO_2 nanowire-driven piezoelectrics. Figures 3(d)–3(i) show how the R phase domain evolves along the nanowire under global heating and cooling.

In summary, the mechanical response of individual single-crystal VO_2 nanowires resulting from the IIT and MIT were quantitatively investigated by carrying out *in situ* tests in a TEM. The sign and magnitude of the mechanical response can be tuned by controlling either the temperature or preloading stress. The nanomechanical behavior observed can be fully understood from the phase diagram of VO_2. These experiments indicate that the phase transition induced elongation or contraction in VO_2 nanowires could potentially be used to sense local temperature, gauge electron beam irradiation, or actuate microstructures.

The authors acknowledge that the research was supported in part by a US Department of Energy SBIR grant (DE-FG02-07ER84813) awarded to Hysitron, which does not constitute an endorsement by DOE of the views expressed in the article. The *in situ* experiments were performed at the National Center for Electron Microscopy, which is supported by the Office of Science, Office of Basic Energy Sciences, Scientific User Facilities Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Z. W. Shan was supported by NSFC (50925104) and the 973 program of China (2010CB631003).

Materials synthesis and data analysis were supported by an NSF CAREER Award under Grant No. DMR-1055938.

[1]F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[2]N. F. Mott, Rev. Mod. Phys. **40**, 677 (1968).
[3]V. Eyert, Ann. Phys. (Berlin, Ger.) **11**, 650 (2002).
[4]K. Liu, C. Cheng, Z. Cheng, K. Wang, R. Ramesh, and J. Wu, Nano Lett. **12**, 6302 (2012).
[5]B. S. Guiton, Q. Gu, A. L. Prieto, M. S. Gudiksen, and H. Park, J. Am. Chem. Soc. **127**, 498 (2005).
[6]J. Cao, E. Ertekin, V. Srinivasan, W. Fan, S. Huang, H. Zheng, J. W. L. Yim, D. R. Khanal, D. F. Ogletree, J. C. Grossman, and J. Wu, Nat. Nanotechnol. **4**, 732 (2009).
[7]W. Fan, J. Cao, J. Seidel, Y. Gu, J. W. Yim, C. Barrett, K. M. Yu, J. Ji, R. Ramesh, L. Q. Chen, and J. Wu, Phys. Rev. B **83**, 235102 (2011).
[8]H. Guo, K. Chen, Y. Oh, K. Wang, C. Dejoie, S. A. S. Asif, O. L. Warren, Z. W. Shan, J. Wu, and A. M. Minor, Nano Lett. **11**, 3207 (2011).
[9]J. Cao, Y. Gu, W. Fan, L. Q. Chen, D. F. Ogletree, K. Chen, N. Tamura, M. Kunz, C. Barrett, J. Seidel, and J. Wu, Nano Lett. **10**, 2667 (2010).
[10]J. M. Atkin, S. Berweger, E. K. Chavez, M. B. Raschke, J. Cao, W. Fan, and J. Wu, Phys. Rev. B **85**, 020101 (2012).
[11]J. Wu, Q. Gu, B. S. Guiton, N. P. de Leon, L. Ouyang, and H. Park, Nano Lett. **6**, 2313 (2006).
[12]J. P. Pouget, H. Launois, J. P. D'Haenens, P. Merenda, and T. M. Rice, Phys. Rev. Lett. **35**, 873 (1975).
[13]Q. Gu, A. Falk, J. Wu, L. Ouyang, and H. Park, Nano Lett. **7**, 363 (2007).
[14]C. Cheng, K. Liu, B. Xiang, J. Suh, and J. Wu, Appl. Phys. Lett. **100**, 103111 (2012).
[15]Y. Oh, E. Cyrankowski, Z. W. Shan, and S. A. S. Asif, "Micro/nanomechanical test system employing tensile test holder with push-to-pull transformer," U.S. patent application 20100095780 (2010).
[16]A. M. Minor, S. A. S. Asif, Z. W. Shan, E. A. Stach, E. Cyrankowski, T. J. Wyrobek, and O. L. Warren, Nat. Mater. **5**, 697 (2006).
[17]O. L. Warren, Z. W. Shan, S. A. S. Asif, E. A. Stach, J. W. Morris, Jr., and A. M. Minor, Mater. Today **10**, 59 (2007).
[18]Z. W. Shan, R. K. Mishra, S. A. S. Asif, O. L. Warren, and A. M. Minor, Nat. Mater. **7**, 115 (2008).
[19]Z. W. Shan, G. Adesso, A. Cabot, M. P. Sherburne, S. A. S. Asif, O. L. Warren, D. C. Chrzan, A. M. Minor, and A. P. Alivisatos, Nat. Mater. **7**, 947 (2008).
[20]C. Chisholm, H. Bei, M. Lowry, J. Oh, S. A. S. Asif, O. L. Warren, Z. W. Shan, E. P. George, and A. M. Minor, Acta Mater. **60**, 2258 (2012).
[21]L. W. Hobbs, *Introduction to Analytical Electron Microscopy* (Plenum, New York, 1979), Chap. 17.
[22]R. Agrawal, B. Peng, and H. D. Espinosa, Nano Lett. **9**, 4177 (2009).
[23]A. C. Jones, S. Berweger, J. Wei, D. Cobden, and M. B. Raschke, Nano Lett. **10**, 1574 (2010).
[24]B. Hu, Y. Ding, W. Chen, D. Kulkarni, Y. Shen, V. V. Tsukruk, and Z. L. Wang, Adv. Mater. **22**, 5134 (2010).
[25]M. Marezio, D. B. McWhan, J. P. Remeika, and P. D. Dernier, Phys. Rev. B **5**, 2541 (1972).
[26]Z. W. Yin, H. S. Luo, P. C. Wang, and G. S. Xu, Ferroelectrics **229**, 207 (1999).