Dynamical tuning of the concentration of defects in oxides provides a route to controlling new functionalities.\textsuperscript{[1]} The chemical potential to capture the functionalities driven by mobile ions and defects can be one of the key control parameters (as well as electric field, magnetic field, and stress) for tuning the functionality of complex oxides.\textsuperscript{[3]} Interesting signatures related to oxygen vacancies have been explicitly observed in widespread physical applications, including solid oxide fuel cells,\textsuperscript{[12]} catalysts,\textsuperscript{[3]} optoelectronics,\textsuperscript{[4]} and electronics.\textsuperscript{[5–14]}

In the virgin state of most single-phase oxides (either binary or ternary oxides), the concentration of oxygen vacancies ($V_\text{o}^-$) in the notation of Kröger and Vink\textsuperscript{[8]} is probably not enough to give ‘ionotronic’ (ionic + electronic) behavior. Depending on the device structures and applications, different approaches have been proposed to increase the $V_\text{o}^-$ concentration of oxides in virgin samples. For example, irreversible electroforming is usually required to generate percolating oxygen deficient phases with application of a high electrical stimulus to single-phase oxides (Figure 1a).\textsuperscript{[15,16]} Since this electroforming is random and uncontrollable, the variation of device performance across the chip and from-chip-to-chip has been a formidable technical challenge.\textsuperscript{[12]} In addition, since electroforming is destructive, it frequently damages or even kills the devices\textsuperscript{[16]} and presents very serious obstacles for practical devices. Another method to increase $V_\text{o}^-$ in single-phase oxide materials is partial substitution (Figure 1b) with dopants (e.g. Y-doped ZrO$_2$ and Gd-doped CeO$_2$).\textsuperscript{[9]} This method has been mainly used in oxide electrolytes working at very high temperature for solid oxide fuel cells and oxygen sensors. Higher mobility $V_\text{o}^-$ has been reported in lateral multilayers (Figure 1c).\textsuperscript{[7]} Oxygen disorder is observed at the lateral semicoherent heterointerfaces of dissimilar structures, thus providing large concentrations of $V_\text{o}^-$ distributed throughout lateral interfaces. However, it is difficult to adapt the lateral multilayers to circuit elements because the current flows in lateral directions, which results in inherently poor integration density. The artificial engineering of $V_\text{o}^-$ in ionotronic devices working at room temperature is still in the early stages.

Here, in very simple, self-assembled nanoscaffold films containing nanocolumns with ~10-nm-radius and ~10-nm-intercolumn-spacing, we demonstrate electroforming-free reversible electroresistance at room temperature. The nanoscaffold films (Figure 1d) are very easy-to-grow, since they self-assemble to give vertical heterointerfaces with $V_\text{o}^-$ channels along the interfaces. The structure has a clear advantage over conventional multilayers in multifunctional device nanoengineering.\textsuperscript{[7,18–21]} Our strategy is to design vertical interfaces using two structurally incompatible oxides, which are likely to generate a high concentration $V_\text{o}^-$. The resistance variations exceeded two orders of magnitude, with excellent uniformity and tunability. Using electron energy loss spectroscopy, we find oxygen deficiency at the vertical heterointerfaces of nanocolumns and matrix, arising from structural incompatibility. Using conductive atomic force microscopy, we find that high conductivity is confined at vertical heterointerfaces, potentially leading to terabit integration density. Using numerical simulations, we explain the electroresistance in nanoscaffold films by the Joule-heating-accelerated drift of oxygen vacancies localized at vertical heterointerfaces.

We grew nanoscaffold films of SrTiO$_3$-Sm$_2$O$_3$, BaTiO$_3$-Sm$_2$O$_3$, and Ba$_{0.9}$Sr$_{0.1}$TiO$_3$-Sm$_2$O$_3$ onto (001) Nb-doped SrTiO$_3$ substrates using a simple one-step process of pulsed laser deposition. The cubic bixbyte Sm$_2$O$_3$ is an ideal material because it substitutes only minimally into alkaline earth titanate perovskites.\textsuperscript{[19–23]} Figure 2a shows the nonvolatile resistance ($R$) switching as a function of voltage (V) in nanoscaffold SrTiO$_3$-Sm$_2$O$_3$ films, whose electrodes are circular Pt with 50-µm-radius. For all the electrical measurements, we grounded the Nb-doped SrTiO$_3$ substrate and applied the voltage to the Pt electrodes. The films were highly resistive (~10 MΩ) in their virgin state. To switch

Shinbuhm Lee, Abhijeet Sangle, Ping Lu, Aiping Chen, Wenrui Zhang, Jae Sung Lee, Haiyan Wang, Quanxi Jia, and Judith L. MacManus-Driscoll*
the resistance value, we applied sequential voltage pulses, with amplitude increasing or decreasing with time. To read the resistance value between each voltage pulse, +0.1 V was applied and the current was measured. When we applied a small positive voltage, the virgin state was switched into low-resistance state (LRS). When we applied a small negative voltage, the device in the LRS could be switched back into the high-resistance state (HRS). Similar $R-V$ curves were also observed in other nanoscaffold Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-Sm$_2$O$_3$ and BaTiO$_3$-Sm$_2$O$_3$ films (Figure S1).

It should be noted that we could obtain a broad range of intermediate resistance states since the resistance switching occurs gradually. The inner concentric loops in Figure 2a (black to blue curves) show that the ratio of high and low resistances can be finely tuned, depending on the amplitude of applied voltage. For example, resistance ratios of LRS and HRS were ~100 (black curve) and ~10 (green curve) when we applied $|V|$ of 10 V and 5 V, respectively. The phenomenon has recently been attracted great attentions to realize multilevel data storage memory (so-called memristor)\[8–13\].

Interestingly, the nonlinear electroresistance occurs without destructive electroforming in the nanoscaffold devices. Indeed, the resistance of HRS ($\sim$10 M$\Omega$) is very similar to that of the virgin state even after many repeated electrical cycles (Figure S2). The resistance values of both LRS and HRS scaled inversely with the electrode area, indicating that the conduction pathways are uniformly distributed. On the contrary, electro-forming was present in single SrTiO$_3$ and Sm$_2$O$_3$ films, since the current increased suddenly when we applied a voltage in their virgin state (Figure S3).

The electroresistance in the electroforming-free nanoscaffold films was superior to electroforming single-phase oxides in following aspects. First, the resistance variation with repeated electrical cycles (i.e., endurance) is very uniform in our nanoscaffold films. We applied sequential voltage pulses of $+10$ V and $-10$ V to switch the resistance state and $+0.1$ V between each voltage pulse to read the resistance. The excellent uniform resistance variations last for over $10^3$-cycles, as shown by a black line in Figure 2b. After one month, we found that the device had retained the original resistance state without obvious degradation (long retention, Figure S4). As shown by the grey line, the device still reveals excellent uniform resistance variations over $10^6$ cycles with a similar resistance ratio. In addition, the uniform endurance and the nonvolatile $R-V$ curves are reproducible from device to device (Figure S5). Second, the resistances of HRS and LRS are tunable by varying deposition conditions. Figure 2c and d show large variations of resistance with orders of magnitude change when we varied either the film thickness or the laser repetition rate during film deposition, respectively. We can easily obtain a resistance corresponding to an optimum current level (e.g., $\sim$1 $\mu$A) for both low power consumption and reliable information sensing. As pointed out in other reports,\[12,22\]
the simultaneous realization of the above-mentioned properties in the same device was the most difficult problem in single-phase oxide films due to the requirement of electroforming. To the best of our knowledge, our nanoscaffold devices are the first to give electroforming-free behavior in a simple device along nano-engineered ionic channels.

To explore the possible origin of the intriguing, new non-linear electroresistance phenomenon we have observed in the nanoscaffold films, we investigated the atomic structure at the vertical interfaces. Figure 3 is a scanning transmission electron microscopy (STEM) high-angle annular dark-field (HAADF) image of nanoscaffold SrTiO₃-Sm₂O₃ films in cross-sectional-view, showing spontaneous phase ordering. The 100-nm-long bright nanocolumns are very straight. The dark and bright contrast regions of ~10-nm-width are alternatively separated like a “nano-comb”. Due to atomic number Z-contrast nature of HAADF imaging, the dark and bright areas in the image correspond to the SrTiO₃ and Sm₂O₃, respectively. The result was further confirmed by energy-dispersive x-ray spectroscopy (EDS) (Figure S6). The epitaxial Sm₂O₃ phase grows on the Nb-doped SrTiO₃ substrate with a 45° in-plane rotation to minimize their lattice mismatch, which was also proven by an x-ray diffraction phi-scan (Figure S7). The reciprocal space maps also reveal that the (012) Sm₂O₃ peak of SrTiO₃-Sm₂O₃ nanoscaffold films is much narrower than that of single Sm₂O₃ films (Figure S8). This indicates that, in the nanoscaffold film, both Sm₂O₃ and SrTiO₃ are well crystallized and their lattice constants are uniform through the thickness of the film.

Now, we consider structural incompatibility at the vertical interfaces of SrTiO₃ and Sm₂O₃. According to schematic crystallographic modeling in Figure 3c, every 11th Sm atomic plane can match with the SrO layer of every 8th SrTiO₃ unit cell because 10 \times a_{Sm \text{O}_2} \approx 7 \times a_{Sr \text{TiO}_3} (\approx 27 \text{ Å}), where a_{Sm \text{O}_2} (\approx 2.7 \text{ Å}) and a_{Sr \text{TiO}_3} (\approx 3.9 \text{ Å}) correspond to interplanar spacing of the Sm₂O₃ (004) and SrTiO₃ (001) planes, respectively. This partial lattice matching is energetically favorable because the residual strain could be significantly reduced. However, between matching planes, the vertical interfaces should be structurally incompatible due to large lattice misfit and different atomic patterns of SrTiO₃ (perovskite, Pm\text{m}3\text{m}) and Sm₂O₃ (bixbyite, Ia\text{3}3). Hence, misfit dislocations should exist at the vertical interfaces, leading to higher density V_{o\text{r}}. Considering the structural incompatibility at the vertical interface of the SrTiO₃ matrix and the Sm₂O₃ nanocolumns, we propose that a large concentration of V_{o\text{r}} can readily form there. To check this hypothesis, we measured the concentration profile of atomic elements across the vertical interface by EELS. Shown in red circles is the calculated EELS signal of O element.

Figure 3. Formation of V_{o\text{r}} at vertical heterointerfaces due to the structural discontinuity of SrTiO₃ matrix and Sm₂O₃ nanocolumn. a) “Nano-comb”-like spontaneous phase ordering in cross-sectional-view of nanoscaffold SrTiO₃-Sm₂O₃, as revealed by cross-sectional STEM HAADF image. b) High-resolution HAADF image of vertical interface of SrTiO₃ matrix and Sm₂O₃ nanocolumn in cross-sectional-view. c) Crystallographic modelling of vertical interface between SrTiO₃ and Sm₂O₃. d) STEM HAADF plan-view image of SrTiO₃ matrix and Sm₂O₃ nanocolumn. e) Measured concentration profile of Sm (green line), Ti (grey line) and O (blue circles) elements across the vertical interface using EELS. Shown in red circles is the calculated EELS signal of O element.
of \( \tau \) was determined to be 1.1 ± 0.1 eV, based on an Arrhenius plot of 1/\( \tau \). The value of 1.1 eV agrees well with the activation energy of \( V_o^- \)[8,26,27] suggesting that the drift of \( V_o^- \) dominates the high-to-low resistance switching in our nanoscaffold devices.

We found that \( \tau \) decreased by more than seven orders of magnitude, when we increased \( V_p \) linearly within 10 V, as shown in Figure 4e. Different from the planar structure of FLASH memory, the writing/erasing and reading can take place in the same direction due to the vertical geometry of the devices, possibly disturbing the data storage by the reading operation. However, this so-called voltage-time dilemma can be overcome when their operating times behave nonlinearly to the operating stimuli.[27] The nanoscaffold device represents this case due to the significant nonlinearity of the \( V_p-\tau \) relationship. Interestingly, the nonlinearity of the \( V_p-\tau \) relationship becomes much steeper with just a slight decrease of film thickness. From the measured data of the 8-nm-thick device, we found that \( \tau \) decreases by nine orders of magnitude within 6 V.

To understand this dependence quantitatively, we calculated \( \tau \) by considering the joule-heating-accelerated drift of \( V_o^- \) (see Supporting Information for details). As displayed by the solid lines, the calculated \( \tau \) values are in good agreement with the measured ones. These results clearly show a significant role of drift of \( V_o^- \) on the electroresistance in the nanoscaffold devices.

Overall, the observed electroresistance in nanoscaffold film can be explained by the modulation of the interfacial electronic barrier due to the migration of \( V_o^- \). Due to the high concentration of oxygen vacancies, the SrTiO\(_3\)-Sm\(_2\)O\(_3\) vertical interface regions belong to the class of n-type semiconducting oxides.[8,10] The contact of Pt and n-type semiconducting oxide typically forms Schottky-like barrier due to high-work-function of the Pt metals. The asymmetric \( I-V \) curves in Figure S2 supports this Schottky-barrier formation. Since the bottom interface with Nb-doped SrTiO\(_3\) substrate in an Ohmic contact, the major contribution for the electroresistance will come from the upper interface. When \( V_o^- \) produced at the SrTiO\(_3\)-Sm\(_2\)O\(_3\) vertical interfaces, are attracted toward the upper interface with application of a negative voltage and are concentrated near the upper interface, the remaining region becomes \( V_o^- \)-deficient.[28,29] As the \( V_o^- \)-deficient region becomes wider, the interfacial electronic barrier is widened, causing the device to go into the HRS. When \( V_o^- \) move away from the upper interface with application of a positive voltage, the width of the \( V_o^- \)-deficient region is narrowed and the interfacial electronic barrier is narrowed, causing the device to go into the LRS.

In conclusion, we have developed easy-to-grow nanoscaffold devices showing extraordinary field-dependent electroresistance at room temperature, using \( V_o^- \) localized at vertical heterogeneous interfaces. The resistance variations exceed two orders of magnitude with very high uniformity and tunability. Using EELS, we found that oxygen deficient regions are readily confined at the vertical interface of the nanocolonn and the matrix, due to the structural incompatibility of dissimilar oxides. Regularly distributed and spatially confined \( V_o^- \) present in our films minimize the stray conduction channels, which are responsible for non-uniformity and non-reproducibility in single-phase oxides. The \( V_o^- \) engineering at the nanoscale by means of nanoscaffold structures spatially confines the conduction channels at vertical interfaces and gives better control over the device performance with high
uniformity and reproducibility. Our experimental and theoretical approaches provide the fundamental basis for understanding the electroresistance in nanoscaffold devices. These capabilities for exploring and controlling ionically active functionality should lay the basis for ionotronic technologies, e.g. ionic transport, electrochemical phenomena and magneto-electric coupling, in vertical oxide heterointerfaces which may find wide applications in universal devices and clean energy.
Experimental Section
We deposited insulating SrTiO$_3$-Sm$_2$O$_3$ nanoscaffold films onto 1 at.% Nb-doped SrTiO$_3$ (001) substrates by a simple one-step process of pulsed laser deposition. Although we used a polycrystalline target containing SrTiO$_3$ and Sm$_2$O$_3$ of 50:50 weight ratio, the self-assembled growth of SrTiO$_3$ and Sm$_2$O$_3$ is expected, as schematically shown in Figure 1d. The growth of SrTiO$_3$-Sm$_2$O$_3$ nanoscaffold films can be modeled as a diffusion process.[9] The multicomponent species come to the film surface and phase-separate into nanoscaffold films. We used a KrF laser (λ = 248 nm) with a fluence of 1.5 J/cm$^2$ and a repetition rate of 1–10 Hz. The films were grown at a substrate temperature of 800 °C and an oxygen pressure of 0.2 mbar. Film thicknesses were in the range of 1–10 nm. The films were grown at a substrate temperature of 800 °C and an oxygen pressure of 0.2 mbar. Film thicknesses were in the range of 1–10 nm.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by the European Research Council (ERC) (Advanced Investigator grant ERC-2009-AdG-247276-NOVOX), the UK Engineering and Physical Sciences Research Council (EPSRC) and the US National Science Foundation (grant no. NSF-1007969). The work at Los Alamos National Laboratory was supported by an LDRD program and performed, in part, at the Centre for Integrated Nanotechnologies, a U.S. Department of Energy and Office of Basic Energy Sciences user facility.

Received: April 28, 2014
Revised: June 28, 2014
Published online: July 28, 2014

[1] S. V. Kalinin, A. N. Spaldin, Science 2013, 341, 858.
[2] E. D. Wachsman, K. T. Lee, Science 2004, 303, 334.
[3] H. Jee, W. S. Choi, M. D. Biegalski, C. M. Folkman, I-C. Tung, D. D. Fong, J. W. Freeland, D. Shin, H. Ohta, M. F. Chisholm, H. N. Lee, Nat. Mater. 2013, 12, 1057.
[4] D. Kani, T. Terasima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, H. Kan, A. Ishizumi, Y. Kanemitsu, Y. Shimakawa, M. Takano, Nat. Mater. 2005, 4, 816.
[5] C.-H. Yang, J. Seidel, S. Y. Kim, P. B. Rossen, P. Yu, M. Gajek, Y. H. Chu, L. W. Martin, M. B. Holcomb, Q. He, P. Maksymovych, N. Balke, S. V. Kalinin, A. P. Baddorf, S. R. Basu, M. L. Scullin, R. Ramesh, Nat. Mater. 2009, 8, 483.
[6] J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, S. S. P. Parkin, Science 2013, 339, 1402.
[7] T. Fix, E.-M. Choi, J. W. A. Robinson, S. Lee, A. P. Chen, B. Prasad, H. Wang, M. G. Blamire, J. L. MacManus-Driscoll, Nano Lett. 2013, 13, 5886.
[8] R. Waser, R. Dittmann, G. Staikov, K. Szot, Adv. Mater. 2009, 21, 2632.
[9] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, Nature 2008, 453, 80.
[10] J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart, R. S. Williams, Nat. Nanotechnol. 2008, 3, 429.
[11] M.-J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, U-I. Chung, I.-K. Yoo, K. Kim, Nat. Mater. 2011, 10, 625.
[12] J. J. Yang, D. B. Strukov, D. R. Stewart, Nat. Nanotechnol. 2013, 8, 13.
[13] J. Borghetti, G. S. Snider, P. J. Kuekes, J. J. Yang, D. R. Stewart, R. S. Williams, Adv. Mater. 2013, 25, 1114.
[14] J. P. Strachan, M. D. Pickett, J. J. Yang, S. Aloni, A. L. D. Kilcoyne, G. Medeiro-Ribeiro, R. S. Williams, Adv. Mater. 2010, 22, 3573.
[15] J. J. Yang, F. Miao, M. D. Pickett, D. A. A. Ohlberg, D. R. Stewart, C. N. Lau, R. S. Williams, Nanotechnology 2009, 20, 215201.
[16] J. Garcia-Barriocanal, A. Rivera-Calzada, M. Varela, Z. Sefrioui, E. Iborra, C. Leon, S. J. Pennycook, J. Santamaria, Science 2008, 321, 676.
[17] H. Zheng, J. G. W. S. Lofland, Z. Ma, M. Mohades-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlom, M. Wuttig, A. Royburd, R. Ramesh, Science 2004, 303, 661.
[18] J. L. Macmanus-Driscoll, P. Zerrer, H. Wang, H. Yang, J. Yoon, A. Fouchet, R. Yu, M. G. Blamire, Q. X. Jia, Nat. Mater. 2008, 7, 314.
[19] S. A. Harrington, J. Zhai, S. Denev, V. C. Gopal, H. Wang, Z. Bi, S. A. T. Redfern, S.-H. Baek, C. W. Bark, C.-B. Eom, Q. X. Jia, M. E. Vickers, J. L. Macmanus-Driscoll, Nat. Nanotechnol. 2011, 6, 491.
[20] O. J. Lee, S. A. Harrington, A. Kursunovic, E. Defay, H. Wang, Z. Bi, C.-F. Tsai, L. Yan, Q. X. Jia, J. L. Macmanus-Driscoll, Nano Lett. 2012, 12, 4311.
[21] International Technology Roadmap for Semiconductors (ITRS). Emerging Research Devices. ITRS technical report 2012, http://www.itrs.net, accessed: September, 2013.
[22] C. Korte, A. Peters, J. Janek, D. Hesse, N. Zakharov, Phys. Chem. Chem. Phys. 2008, 10, 4623.
[23] M. M. McGibbon, N. D. Browning, M. F. Chisholm, A. J. McGibbon, S. J. Pennycook, V. Ravikumar, V. P. Dravid, Science 1994, 266, 102.
[24] Y.-H. Hsieh, J.-M. Liou, B.-C. Huang, C.-W. Liang, Q. He, Q. Zhan, Y.-P. Chiu, Y.-C. Chen, Y.-H. Chu, Adv. Mater. 2012, 24, 4564.
[25] F. Miao, J. J. Yang, J. Borghetti, G. Medeiro-Ribeiro, R. S. Williams, Nanotechnology 2011, 22, 254007.
[26] S. Menzel, M. Waters, A. Marchewka, U. Böttger, R. Dittmann, R. Waser, Adv. Funct. Mater. 2011, 21, 4487.
[27] R. Muenstermann, T. Menke, R. Dittmann, R. Waser, Adv. Mater. 2010, 22, 4819.
[28] J. S. Lee, S. Lee, B. Kahng, T. W. Noh, Appl. Phys. Lett. 2013, 102, 253503.
[29] H. Zheng, F. Straub, Q. Zhan, P.-L. Yang, W.-K. Hsieh, F. Zavaliche, Y.-H. Chu, U. Dahmen, R. Ramesh, Adv. Mater. 2006, 18, 2747.