CHEMISTRY OF MATERIALS
Communication

Chem. Mater. **2011,** *23,* 123–125 123
DOI:10.1021/cm1020959

Dopant Control by Atomic Layer Deposition in Oxide Films for Memristive Switches

J. Joshua Yang,*,† Nobuhiko P. Kobayashi,‡ John Paul Strachan,† M.-X. Zhang,† Douglas A. A. Ohlberg,† Matthew D. Pickett,† Zhiyong Li,† Gilberto Medeiros-Ribeiro,† and R. Stanley Williams†

†*Hewlett-Packard Laboratories, Palo Alto, California, United States, and* ‡*Electrical Engineering Department, Baskin School of Engineering, University of California, Santa Cruz, California, United States*

Received August 10, 2010
Revised Manuscript Received December 1, 2010

Transition metal oxide thin films play an indispensable role in nanoelectronic and nanoionic devices[1,2] proposed for the next-generation nonvolatile memory,[3−11] neuromorphic computing,[12] stateful logic,[13] and some hybrid circuits.[14] The promise of metal oxide thin films comes from their wide range of electrical properties, ranging from insulating, semiconducting, metallic, to even superconducting behavior[2,15] with exquisite dependence on the doping level. A trace level of compositional change in oxides induces a large amount of defects, which serve as native dopants in the oxide films and dramatically change their conductance.[16] Microscopically in a thin film device, the slight compositional change is in the embodiment of ionic motion, which gives rise to memristive switching under an electric field.[17−19] The drift of oxygen vacancies in titanium oxide thin films under electric field has been demonstrated to be responsible for memristive switching.[20−22] Because an electric field can modulate only the dopant distribution profile within a nanoscale distance,[23,24] the properties and performance of memristive devices are to a large degree dictated by the initial dopant distribution profile formed during the fabrication of the switching oxides.[21] For instance, the initial dopant distribution profile in the oxide film determines the switching polarity even when an electroforming step is involved: an asymmetrical oxygen vacancy profile leads to a certain well-defined switching polarity,[21,22] whereas a symmetrical profile results in an electrically reconfigurable switching polarity.[9]

Among the variety of fabrication techniques, atomic layer deposition (ALD)[25] is likely the most technologically relevant and ALD oxide films have been extensively studied as gate oxides in the metal-oxide-semiconductor field-effect transistor (MOSFET) structure and dielectric media in the DRAM stack capacitors. The focus has been on reducing the leakage current as well as increasing the dielectric constant and the breakdown voltage in the previous work,[25,26] where stoichiometric oxides were desired. However, for memristor applications, the composition of the oxides needs to be tuned within a certain range with process windows different from the above studies. Accordingly, the unusual growth modes, such as the nonself-limited growth, become valuable to explore for memristor engineering, which is demonstrated in this conmmunication.

A series of titanium oxide thin films were deposited under various deposition conditions with an thermal ALD tool made by Cambridge NanoTech Inc. Tetrakis (dimethylamino) titanium ($Ti(NC_2H_6)_4$, TDMAT) from Sigma-Aldrich was used as the Ti precursor and H_2O was used as the oxygen precursor. Depending on the specific reaction system, the exposure time of the oxygen precursor and the substrate temperature are two control parameters that may possibly vary the composition of the ALD film.[25,27−29] In our experiments, we fixed the pulse duration of the Ti

*Corresponding author. E-mail: jianhua@hp.com.

(1) Waser, R.; Dittmann, R.; Staikov, G.; Szot, K. *Adv. Mater.* **2009**, *21*, 2632.
(2) Norton, D. P. *Mater. Sci. Eng., R* **2004**, *43*, 139.
(3) Szot, K.; Speier, W.; Bihlmayer, G.; Waser, R. *Nat. Mater.* **2006**, *5*, 312.
(4) Yang, J. J.; Zhang, M.-X.; Strachan, J. P.; Miao, F.; Pickett, M. D.; Kelley, R. D.; Medeiros-Ribeiro, G.; Williams, R. S. *Appl. Phys. Lett.* **2010**, *97*, 232102.
(5) Kwon, D. H.; Kim, K. M.; Jang, J. H.; Jeon, J. M.; Lee, M. H.; Kim, G. H.; Li, X. S.; Park, G. S.; Lee, B.; Han, S.; Kim, M.; Hwang, C. S. *Nat. Nanotechnol.* **2010**, *5*, 148.
(6) Sanchez, M. J.; Rozenberg, M. J.; Inoue, I. H. *Appl. Phys. Lett.* **2007**, *91*, 252101.
(7) Chae, S. C.; Lee, J. S.; Kim, S.; Lee, S. B.; Chang, S. H.; Liu, C.; Kahng, B.; Shin, H.; Kim, D. W.; Jung, C. U.; Seo, S.; Lee, M. J.; Noh, T. W. *Adv. Mater.* **2008**, *20*, 1154.
(8) Park, C.; Jeon, S. H.; Chae, S. C.; Han, S.; Park, B. H.; Seo, S.; Kim, D. W. *Appl. Phys. Lett.* **2008**, *93*, 042102.
(9) Yang, J. J.; Borghetti, J.; Murphy, D.; Stewart, D. R.; Williams, R. S. *Adv. Mater.* **2009**, *21*, 3754.
(10) Choi, B. J.; Jeong, D. S.; Kim, S. K.; Rohde, C.; Choi, S.; Oh, J. H.; Kim, H. J.; Hwang, C. S.; Szot, K.; Waser, R.; Reichenberg, B.; Tiedke, S. *J. Appl. Phys.* **2005**, *98*, 033715.
(11) Gergel-Hackett, N.; Hamadani, B.; Dunlap, B.; Suehle, J.; Richter, C.; Hacker, C.; Gundlach, D. *IEEE Electron Device Lett.* **2009**, *30*, 706.
(12) Snider, G. S. Spike-timing-dependent learning in memristive nanodevices. In *2008 IEEE International Symposium on Nanoscale Architectures*; IEEE: Piscataway, NJ, 2008; pp 85−92.
(13) Borghetti, J.; Snider, G. S.; Kuekes, P. J.; Yang, J. J.; Stewart, D. R.; Williams, R. S. *Nature* **2010**, *464*, 873.
(14) Xia, Q. F.; Robinett, W.; Cumbie, M. W.; Banerjee, N.; Cardinali, T. J.; Yang, J. J.; Wu, W.; Li, X. M.; Tong, W. M.; Strukov, D. B.; Snider, G. S.; Medeiros-Ribeiro, G.; Williams, R. S. *Nano Lett.* **2009**, *9*, 3640.
(15) Inoue, I. H.; Rozenberg, M. J. *Adv. Funct. Mater.* **2008**, *18*, 2289.
(16) Knauth, P.; Tuller, H. L. *J. Appl. Phys.* **1999**, *85*, 897.
(17) Strukov, D. B.; Snider, G. S.; Stewart, D. R.; Williams, R. S. *Nature* **2008**, *453*, 80.
(18) Chua, L. O. *IEEE Trans. Circuit Theory* **1971**, *CT-18*, 507.
(19) Chua, L. O.; Kang, S. M. *Proc. IEEE* **1976**, *64*, 209.
(20) Janousch, M.; Meijer, G. I.; Staub, U.; Delley, B.; Karg, S. F.; Andreasson, B. P. *Adv. Mater.* **2007**, *19*, 2232.
(21) Yang, J. J.; Pickett, M. D.; Li, X.; Ohlberg, D. A. A.; Stewart, D. R.; Williams, R. S. *Nature Nanotechnol.* **2008**, *3*, 429.
(22) Yang, J. J.; Miao, F.; Pickett, M. D.; Ohlberg, D. A. A.; Stewart, D. R.; Lau, C. N.; Williams, R. S. *Nanotechnology* **2009**, *20*, 215201.
(23) Miao, F.; Yang, J. J.; Strachan, J. P.; Stewart, D.; Williams, R. S.; Lau, C. N. *Appl. Phys. Lett.* **2009**, *95*, 113503.
(24) Pickett, M. D.; Strukov, D. B.; Borghetti, J. L.; Yang, J. J.; Snider, G. S.; Stewart, D. R.; Williams, R. S. *J. Appl. Phys.* **2009**, *106*, 074508.
(25) George, S. M. *Chem. Rev.* **2009**, *110*, 111.
(26) Kim, S. K.; Kim, W. D.; Kim, K. M.; Hwang, C. S.; Jeong, J. *Appl. Phys. Lett.* **2004**, *85*, 4112.

Published on Web 12/29/2010

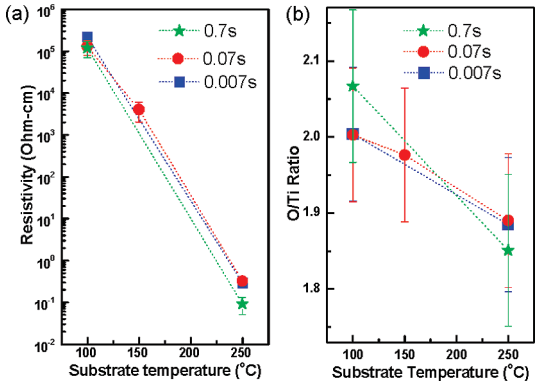

Figure 1. (a) Resistivity and (b) O/Ti ratio of ALD Ti oxide films grown at different temperatures with different H_2O pulse durations.

precursor to be 7s, whereas varying the pulse duration setting of the oxygen precursor (H_2O) to be 0.7 , 0.07, and 0.007 s. The valve response time of our ALD system is about 0.01 s. Even though the absolute values of the resulting H_2O pulse durations observed in the chamber were longer than the corresponding settings, a distinct variation trend was obtained in the water pulse duration (see Figure S1 in the Supporting Information). The Ar purging (3 sccm) time was 2 s after the Ti precursor pulse and 20 s after the water pulse. Two sets of samples were grown at the substrate temperatures of 100 and 250 °C, with each set consisting of three samples made with the above H_2O pulse durations. One additional sample was grown at 150 °C with the H_2O pulse duration of 0.07 s. X-ray diffraction and Raman spectra indicated that the films deposited at both 100 and 150 °C are amorphous, while the films deposited at 250 °C are anatase crystalline phase (see Figures S2 and S3 in the Supporting Information). The bandgaps of the films grown at different temperatures with different H_2O pulse durations were close to each other, at about 3.5 eV (see Figure S4 in the Supporting Information). The electrical resistivity of the oxide films were measured at room temperature using the DC four point probe method with samples grown on Si/SiO_2 (100 nm) substrates.

As shown in Figure 1a, while changing the H_2O pulse duration introduced almost no change in the electrical resistivity, the growth temperature was found to be very effective in changing the electrical resistivity. As can be seen in Figure 1a, the electrical resistivity decreased by over 5 orders of magnitude when increasing the substrate temperature by 150°. The oxide film grown at 100 °C was a good insulator with a resistivity of 1×10^5 ohm cm, whereas the one grown at 250 °C exhibited metallic electrical characteristics with a resistivity lower than 1 ohm cm.

Given in Figure 1b are the oxygen to titanium ratios determined by Rutherford backscattering (RBS). The variance of O/Ti ratios of the films grown at the same substrate temperature but with different water pulse durations was within the uncertainty of the RBS measurement, consistent with resistivity results (i.e., the O/Ti ratio did not change as the H_2O pulse duration varied for a given substrate temperature). In addition, the measured O/Ti ratios showed that the film grown at 100 °C was close to the stoichiometry of 2:1, whereas the film grown at 250 °C was oxygen deficient. The growth per cycle (GPC) decreased with the substrate temperature and increased with the H_2O pulse duration in the sample set studied (see Figure S5 in the Supporting Information). A higher GPC than the saturation growth rate (0.4−0.5 Å/s) at 100 °C suggests that there might be some residual water after purging at low temperature, which may have contributed to the high GPC at low temperature. The decomposition temperature of the Ti precursor is about 180 °C[30] and the film deposition from thermal decomposition is unlikely before 150 °C but possible at 250 °C, which should result in a higher growth rate at high temperature. However, the GPC at 250 °C was in fact close to the value one would expect for a normal saturation growth. This could be a result of the compensation between the precursor decomposition (increasing the GPC) and the desorptions (decreasing the GPC) of precursors and/or interediate products. It has been shown based on density functional theory (DFT) calculation that in the TDMAT and H_2O system the reaction is very fast because of a low reaction energy barrier while the intermediate products are not stable and their desorption is thermodynamically favorable,[31] which may give rise to the observation that the O/Ti ratio was not sensitive to the H_2O pulse duration but fairly sensitive to the substrate temperature in this system.

Oxygen vacancies are accepted to be the dominant defects in oxygen deficient titanium dioxide film at room temperature.[16,32] The agreement between the trends of the O/Ti ratio vs substrate temperature and resistivity vs substrate temperature strongly suggests that oxygen vacancy concentration controlled by substrate temperature is responsible for the observed change in the electrical resistivities. However, other factors that change with substrate temperature, including atomic structure and impurity concentrations, may also contribute to the observed resistance change and need to be carefully examined.

Atomic ordering of the films strongly affects electron mobility, which in turn affects the film electrical resistivity. Therefore, electron mobility needs to be characterized for films with different microstructures. Hall measurements were carried out with the van der Pauw configuration to obtain electron mobility for the amorphous (low substrate temperature) and crystalline films (high substrate temperature). The measured electron mobility in crystalline titanium oxide films is approximately 10 times of that in the amorphous films (see Figure S6 in the Supporting

(27) Puurunen, R. L. *J. Appl. Phys.* **2005**, *97*, 121301.
(28) Nalwa, H. S., *Atomic Layer Deposition*; Academic Press: New York, 2002; Vol. *1*.
(29) Kaupo, K.; Mikko, R.; Markku, L.; Janne, J. *J. Vac. Sci. Technol., A* **1997**, *15*, 2214.
(30) Elam, J. W.; Schuisky, M.; Ferguson, J. D.; George, S. M. *Thin Solid Films* **2003**, *436*, 145.
(31) Xie, Q.; Jiang, Y.; Detavernier, C.; Deduytsche, D.; Van Meirhaeghe, R. L.; Ru, G.; Li, B.; Qu, X. *J. Appl. Phys.* **2007**, *102*, 083521.
(32) Weibel, A.; Bouchet, R.; Knauth, P. *Solid State Ionics* **2006**, *177*, 229.

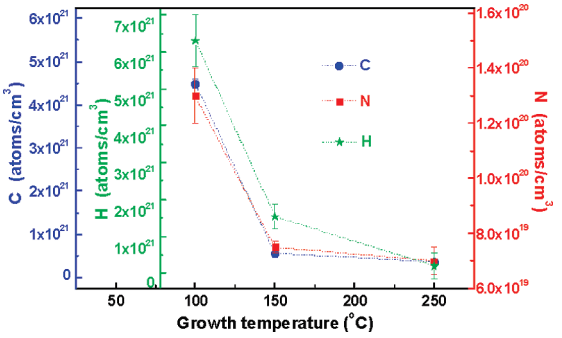

Figure 2. Impurity concentrations of carbon, nitrogen, and hydrogen in ALD Ti oxide films grown at different temperatures with the H_2O pulse duration of 0.07s. The film density was about 7×10^{22} atoms/cm^3.

Information), which can not account for the observed 5 orders of magnitude resistivity change in the titanium oxide films. Carbon and nitrogen are known to serve as acceptors in a TiO_2 film and may compensate the oxygen vacancy donors, resulting in a more resistive film. The concentrations of the impurities in the titanium oxide films grown at different substrate temperatures are given in Figure 2. The carbon and nitrogen concentrations were measured by secondary ion mass spectroscopy (SIMS) and the hydrogen concentration was measured by hydrogen forward scattering (HFS). The concentrations of all of the three impurities decreased with increasing substrate temperature, which is also consistent with the decreasing resistivity with increasing substrate temperature. However, an inconsistency can be seen by comparing the variation trend of impurity concentrations in Figure 2 with the trend of resistivities in Figure 1. Although the resistivity monotonically decreased with the substrate temperature, the concentration of impurities decreased abruptly from 100 to 150 °C and remained almost constant (C and N) or decreased only slightly (H) from 150 to 250 °C. Moreover, samples fabricated with the same substrate temperature but different H_2O pulse durations exhibited a very similar resistvity despite of the different impurity levels detected in these samples (see Figure S7 in the Supporting Information). This indicates that the impurity variation is unlikely to have been the major cause of the observed resistance change in the oxide films grown at different temperatures. The reason could be that these impurities are not activated to be effective dopants or their effects negate each other, for example, hydrogen is also known to be able to "passivate" acceptors. The role of the impurities in the films is not very clear at this moment. On the one hand, different mobile ions inside the system may be desirable for novel device properties.[33] On the other hand, understanding the switching mechanism becomes even more difficult with these impurities. It is also possible that the impurities degrade the performance of the devices.

(33) Strukov, D. B.; Borghetti, J. L.; Williams, R. S. *Small* **2009**, *5*, 1058.

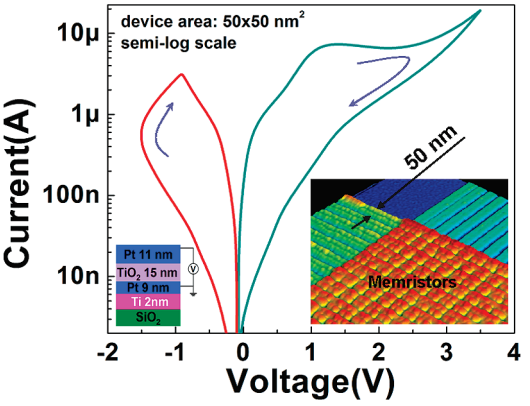

Figure 3. A typical $I-V$ curve of nanodevices with the titanium oxide layer deposited at 150 °C by ALD. Inset is the schematic of the stack and atomic force microscopy image of the devices.

We can see from Figure 2 that for the substrate temperature of 150 °C, the impurity levels are already fairly low and the oxide film is still not too conductive as a switching material. Nanoscale devices have been fabricated utilizing 150 °C as the ALD oxide film growth temperature. The device stack was Si/SiO_2 100 nm/Ti 2 nm/Pt 9 nm/TiO_2 15 nm/Pt 11 nm with the 2 nm Ti layer serving as an adhesion layer.[34] The Pt electrodes were 50 nm wide nanowires fabricated by nanoimprint lithography (NIL). After an initial electroforming step[22] by a voltage sweep up to +8 V on the top electrode, the nanodevice exhibited reversible switching as shown in Figure 3. The ON/OFF conductance ratio was about 100 and the current level of the switching was under 20 μA, making it an attractive device for low-power operation.

In summary, the resistivity of ALD titanium oxide films using TDMAT and H_2O as precursors was found to decrease monotonically by over 5 orders of magnitude with increasing substrate temperature from 100 to 250 °C, which is attributed to the increase in oxygen deficiencies observed in that temperature range. The precursor pulse duration appeared to have negligible influence on the O/Ti ratio as well as the conductance in the material system used here. The oxygen vacancy concentration may be tuned by continuously changing the substrate temperature during film growth to obtain a desired dopant profile in the device, leading to some well-defined device properties.

Acknowledgment. We thank J. Nickel, X. Li, F. Miao, W. Yi, T. Ha, and C. Le for excellent experimental assistance. This work was funded in part by the Defense Advanced Research Projects Agency (DARPA) under Agreement HR0011-09-3-0001.

Supporting Information Available: Figures S1–S7 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(34) Yang, J. J.; Strachan, J. P.; Xia, Q.; Ohlberg, D. A. A.; Kuekes, P. J.; Kelley, R. D.; Stickle, W. F.; Stewart, D. R.; Medeiros-Ribeiro, G.; Williams, R. S. *Adv. Mater.* **2010**, *22*, 4034.