Resistance switching of copper doped MoO_x films for nonvolatile memory applications

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Nonvolatile and reversible resistance switching of copper doped MoO_x film was studied. Hysteretic-type resistive switching was observed under dc. Reproducible resistance switching over 10^6 cycles was observed under alternative voltage pulses. Two resistance states can be maintained for 25 h at 85 °C. The authors proved that resistance switching might be strongly related with the rupture and generation of multifilaments confirmed by spreading resistance images of a conducting atomic force microscope as well as filamentary conduction by double logarithmic plots. Based on the x-ray photoelectron spectroscopy analysis, local conducting filaments could be formed by thermally diffused copper into MoO_x film from the bottom electrode. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2715002]

Since the first observation of the bistable resistance states in the 1960s,[1] extensive research has been performed to understand the switching mechanism involved and to improve electrical characteristics for memory applications. Recently, numerous new materials, such as TiO_2,[2] NiO,[3] ZrO_x,[4] $Pr_{1-x}Ca_xMnO_3$,[5] Cr doped $SrTiO_3$, (STO_3),[6] Nb:STO_3,[7] Ag doped GeSe,[8] CuS,[9] and single crystalline STO_3,[10] exhibit resistive switching behavior. Although various switching models, such as Schottky barriers with interface states,[7] electrochemical migration at the interface,[11] broadband of localized states,[12] and a phenomenological approach,[13] have been proposed to explain the resistive switching, the exact switching mechanisms based on physical analysis of various materials have not yet been reported. Based on the proposed switching models, the resistive switching can be explained by the motion of oxygen vacancies[10,11] in the crystalline matrix or mobile ions[8] in the insulating glassy matrix. It has been reported that MoO_3 is a good solid-state electrolyte for electrochromic devices.

In this letter, we report on the resistive switching behavior of Cu doped MoO_x for nonvolatile memory applications.[14–16]

400-nm-thick Cu doped MoO_x films were deposited on a Cu substrate at 500 °C via a sputtering system using a 0.5% Cu doped MoO_3 target. During the deposition, Cu diffusion from the Cu substrate increased Cu concentration in the MoO_x thin films. Using conventional photolithography, Pt top electrodes were formed. To analyze the binding energy and composition of each element, x-ray photoelectron spectroscopy (XPS) depth profiling was performed. The crystal structure of the films was also analyzed by x-ray diffraction (XRD). The microscopic nature of the resistive switching was confirmed by a conducting atomic force microscope (C-AFM) tool.

Figure 1(a) shows typical *I-V* characteristics of the Pt/Cu doped MoO_x/Cu device. The *I-V* curves exhibit hysteretic behaviors in both voltage regions. The switching from the high resistance state to the low resistance state can be achieved by applying positive voltage above a critical value at a top gate electrode. By applying a negative gate voltage, we can switch back to the original high resistance state.

Figures 1(b) and 1(c) show the logarithmic plots of the *I-V* curve for the positive- and negative-voltage regions, respectively. For both high resistance states and low resistance states, the slope is approximately 0.99–1.02, which can be explained by Ohm's law.[17,18]

To consider nonvolatile memory applications, endurance and retention tests of the devices were performed. Figure 2(a) shows the resistive switching behavior under a voltage pulse of 2 V for 1 μs. Two stable resistance states can be maintained under a cycle stress of up to 10^6 cycles. In addition, the retention characteristics of two resistance states were monitored at room temperature (RT) and 85 °C. We have confirmed that data retention at 85 °C is sufficiently longer than 25 h, as shown in Fig. 2(b).

To understand the origin of switching behavior, we performed physical analyses of the films. Figure 3 shows the XPS depth profile of each element of the films. Although 0.5% copper doped MoO_3 target was used, the atomic concentration of copper in the films was more than 5%. The high Cu concentration in the bulk MoO_x can be explained by thermal diffusion from the bottom Cu electrode during sputtering at 500 °C. Based on the XRD study, we found various peaks, such as Cu, cupric oxide (CuO), and copper complex $(Cu_4Mo_8O_{17})$.

To observe the microscopic behaviors involved in resistive switching,[9,19–21] spreading resistance images of the film surface were investigated by a conducting AFM. A C-AFM monitors the local conductance with a sufficient spatial resolution, as shown in Fig. 4. After forming a low resistance state, C-AFM analysis was performed at a read voltage of 0.5 V. The multiple peaks in Fig. 4(a) indicate localized high conductance spots. After forming a high resistance state, the experimental results from Fig. 4(b)

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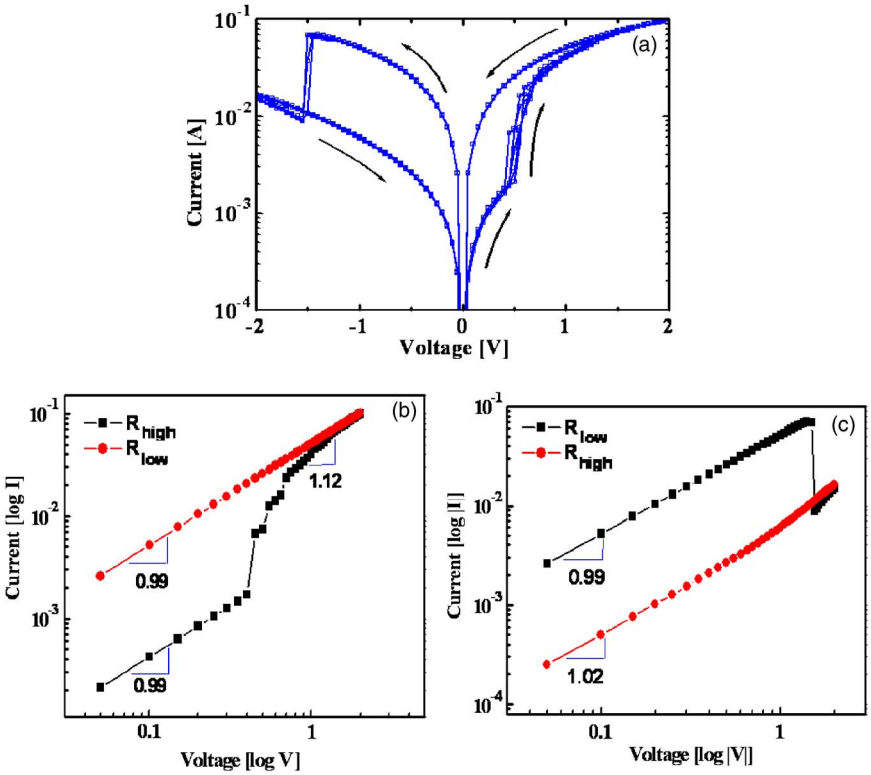

FIG. 1. (a) Hysteretic-type switching behaviors in the memory window from critical positive set voltage to negative reset voltage. *I-V* characteristics at RT in double logarithmic plots in the positive-voltage region (b) and in the negative-voltage region (c). Note that the absolute values of current and voltage are obtained from both origins.

show the numerousconductance peaks but their intensity is lower in comparison with those in the low resistance state. This observation is consistent with the area dependence of Cu doped MoO_x film at both states. As the area of the top electrodes was scaled down, the current levels were also reduced at high resistance states. However, the low resistance states were independent of the area due to the filamentary conduction.

Based on the experimental data, we explain resistive switching behaviors of heavily copper doped molybdenum oxide as follows. After a forming process, we observed the reversible resistance switching behavior, which might be explained by stable filament formation. A high current can flow through conducting filaments at the on state. However, by applying the opposite bias, the conducting filaments can be disconnected near the anode side by the electrochemical reaction. The neutral copper in the matrix can be anodized into copper ions near the anode, which in turn disconnects the filaments.

In summary, we investigated the resistive switching of copper doped MoO_x thin film. We have proposed that resistive switching in the copper doped MoO_x film is due to the formation and rupture of multifilaments, and

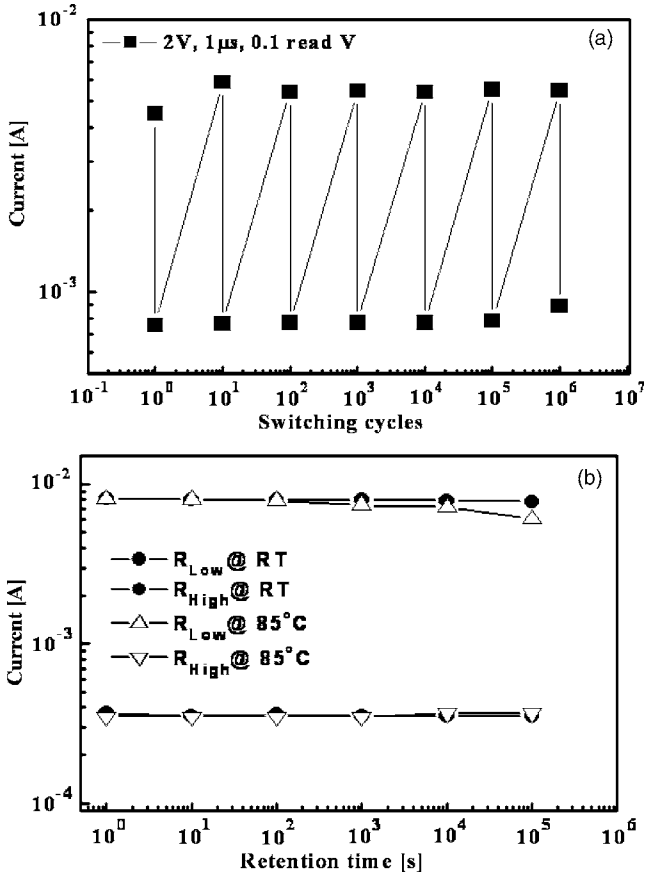

FIG. 2. 10^6 times of endurance test of Cu:MoO_x by voltage pulses. (b) Retention properties of R_{on} and R_{off} at RT and 85 °C.

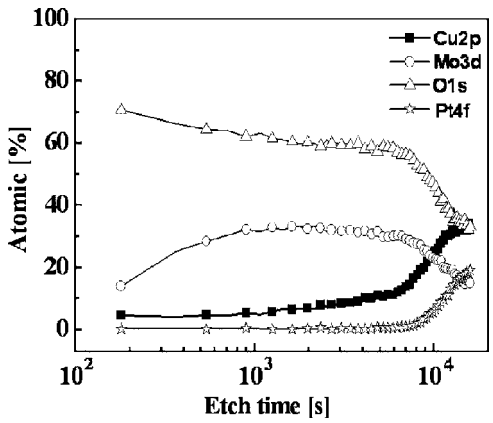

FIG. 3. XPS depth profiling of Cu:MoO_x film. More than 5% copper is diffused into film from the copper substrate.

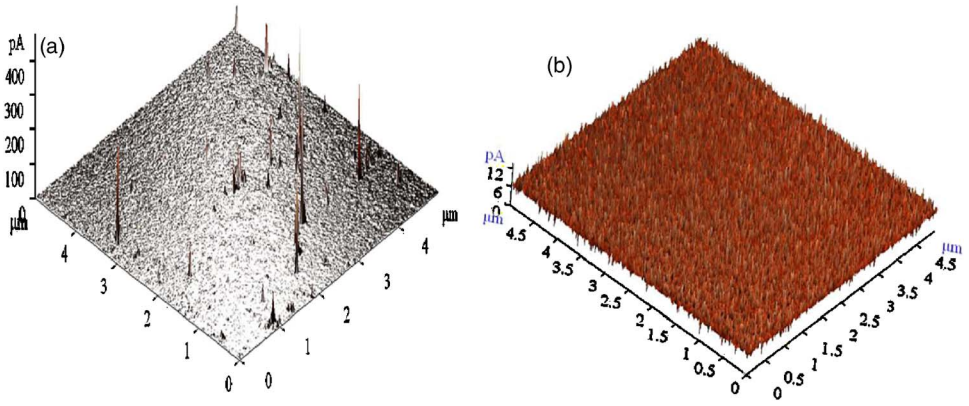

FIG. 4. (a) Spreading resistance image measured by the conducting AFM at low resistance state. (b) Spreading resistance image at high resistance state.

this description was confirmed by conducting AFM. In addition, double logarithmic plots also strongly support filamentary conduction. Considering bistable resistive switching and device uniformity, Cu doped MoO_x film shows promise for future nonvolatile memory applications.

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[1]W. R. Hiatt and T. W. Hickmott, Appl. Phys. Lett. **6**, 106 (1965).
[2]C. C. Rohde, B. J. Choi, D. S. Jeong, S. Choi, J.-S. Zhao, and C. S. Hwang, Appl. Phys. Lett. **86**, 262907 (2005).
[3]S. Seo, M. J. Lee, D. H. Seo, E. J. Jeoung, D.-S. Suh, Y. S. Joung, I. K. Yoo, I. R. Hwang, S. H. Kim, I. S. Byun, J.-S. Kim, J. S. Choi, and B. H. Park, Appl. Phys. Lett. **85**, 5655 (2004).
[4]D. Lee, H. Choi, H. Sim, D. Choi, H. Hwang, M.-J. Lee, S.-A. Seo, and I. K. Yoo, IEEE Electron Device Lett. **26**, 719 (2005).
[5]X. Chen, N. J. Wu, J. Strozier, and A. Ignatiev, Appl. Phys. Lett. **87**, 233506 (2005).
[6]Y. Watanabe, J. G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck, and S. J. Wind, Appl. Phys. Lett. **78**, 3738 (2001).
[7]T. Fujii, M. Kawasaki, A. Sawa, H. Akoh, Y. Kawazoe, and Y. Tokura, Appl. Phys. Lett. **86**, 012107 (2005).
[8]M. Mitkova, Yu Wang, and P. Boolchand, Phys. Rev. Lett. **83**, 3848 (1999).
[9]T. Sakamoto, H. Sunamura, H. Kawaura, T. Hasegawa, T. Nakayama, and M. Aono, Appl. Phys. Lett. **82**, 3032 (2003).
[10]K. Szot, W. Speier, G. Bihlmayer, and R. Waser, Nat. Mater. **5**, 312 (2006).
[11]A. Baikalov, Y. Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, Appl. Phys. Lett. **83**, 957 (2003).
[12]J. G. Simmons and R. R. Verderber, Proc. R. Soc. London, Ser. A **301**, 77 (1967).
[13]M. J. Rojenberg, I. H. Inoue, and M. J. Sanchez, Phys. Rev. Lett. **93**, 178302 (2004).
[14]P. M. S. Monk, R. J. Mortimer, and D. R. Rosseinsky, *Electro-chromism: Fundamentals and Applications* (VCH, Weinheim, 1995).
[15]P. R. Somani and S. Radhakrishnan, Mater. Chem. Phys. **77**, 117 (2002).
[16]T. S. Sian, G. B. Reddy, and S. M. Shivaprasad, Jpn. J. Appl. Phys., Part 1 **43**, 6248 (2004).
[17]G. A. Niklasson and K. Brantervik, J. Appl. Phys. **59**, 980 (1986).
[18]S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley, New York, 1981), pp. 402–407.
[19]L. A. Bottomley, Anal. Chem. **70**, 425R (1998).
[20]S. V. Kalinin, J. Am. Ceram. Soc. **88**, 1077 (2005).
[21]St. J. Dixon Warren, R. P. Ru, S. Ingrey, D. Macquistan, T. Bryskiewicz, G. Smith, and B. Bryskiewicz, J. Vac. Sci. Technol. A **19**, 1752 (2001).