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Use of EELS STEM technique to estimate the depth profile of tungsten oxide reduction under proton irradiation

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Binary transition metal oxides system (TMOs), such as NiO, TiO_2, ZrO_2, Cu_xO, TaO_x, WO_x and HfO_2 [1] are attract attention for use in constructing a non-volatile resistive-random access memory (RERAM). TMOs are more promising class of materials for creating switching devices in comparison with $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO), $La_{0.7}Ca_{0.3}MnO_3$ (LCMO), Cr-doped $SrZrO_3$. It is because of not only TMOs simpler structure and manufacturing but also possibility of compliance with complementary metal oxide (semiconductor (CMOS) [2]. The operation principle of such unipolar memory devices is to change the resistance level from high resistance state (HRS) to low resistance state (LRS) due to the migration of oxygen atoms when an electric field is applied.

In this paper, it is proposed to create a multilayer structure based on W with different oxygen content from tungsten oxide WO_3. Layers depleted by oxygen atoms will be sink for O+ migrating atoms and conversely when the polarity of the applied field is changed Radiation technique of selective removal of oxygen atoms (SRA) under low-energy proton irradiation was used to create such a structure [3,4].

The WO_3 film was fabricated using cathode sputtering technique at room temperature, from metallic W target in oxygen atmosphere on SiO_2/Si substrates. Irradiation of WO_3 thin films with 1 keV protons at doses of $2.8\cdot10^{18}$, $6.75\cdot10^{18}$ and $11.25\cdot10^{18}$ ions/cm^2 were carried out on a special system with a high-frequency source of oxygen plasma and pulse high voltage bias.

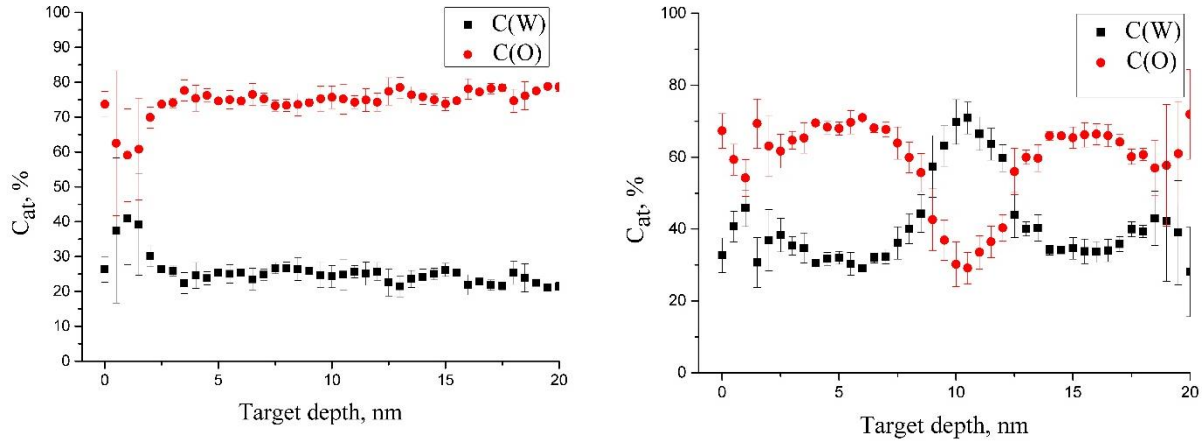
Chemical composition of irradiated WO_3 samples were studied using “Titan 80-300ST” electron microscope in STEM mode, equipped with a GIF-2001 energy loss spectrometer. The EEL spectra were obtained with an energy dispersion 0.5 eV/ch, collection angle, as defined by the GIF aperture and camera length was 14.82 mrad, and convergence angle α=10 mrad. A cross sections samples WO_3/SiO2/Si were prepared by FIB “Helios Nanolab 650”.

Quantitative analysis was carried out with equation:

$$\frac{N_A}{N_B} = \frac{I_A(\beta,\Delta)}{I_B(\beta,\Delta)} \cdot \frac{\sigma_B(\beta,\Delta)}{\sigma_A(\beta,\Delta)}, \quad (1)$$

where I_A, I_B - integrated intensities of the peaks after background subtracting, and σ_A and σ_B - ionization cross section [5].

Figure 1 shows elements depth distribution profiles calculated from EELS data of WO_3 film irradiated with low fluence $2.8\cdot10^{18}$ and high fluence $11.25\cdot10^{18}$ ions/cm^2. It can be seen (Fig. 1a) that at small irradiation dose, the process of selective removal of oxygen atoms occurs in the 2.5 nm depth near-surface layer. Remaining volume of the film retains the stoichiometric composition of the original WO_3 film. A significant increase in the irradiation dose (Fig. 1b) leads to oxygen concentration level decrease and composition of the regions at depths from 2 to 8 nm and from 12 to 20 nm corresponds to WO_2 stoichiometric composition. Also from Figure 1b is clearly visible that at about 10 nm depth that corresponding to the maximum damage depth under proton irradiation, a significant tungsten oxide reduction occurs. At the same time, substantially higher doses are required for complete removal of the remaining impurity oxygen, as is known from the results of previous studies [6]. Experimentally obtained tungsten oxide recovery depth distribution under proton irradiation is nonmonotonic and recovery depth-profile corresponds to the distribution of the dose in depth, which confirms the radiation nature of the selective removal of atoms process.



(a) (b)

Figure 1. Elements depth distribution profiles of the WO3 film irradiated with 1 keV protons (calculated from EELS data) for different doses:
(a) $2.8 \cdot 10^{18}$ ions/cm^2; (b) $11.25 \cdot 10^{18}$ ions/cm^2

1. R.G. Elliman, T.-H. Kim et al, *Nuclear Instruments and Methods in Physics Research B* **307**, 98 (2013).
2. M.K. Yang, J.-W. Park et al, *Applied Physics Letters* **95**, 042105 (2009).
3. B.A. Gurovich, A.G. Domantovski et al, *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques* **5**, 25 (2008).
4. B.A. Gurovich, K.E. Prikhodko et al, *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques* **1**, 35 (2011).
5. D. Williams, A. Carter. *Electron microscopy*. (New York: Springer), 760 (2009).
6. B.A. Gurovich, K.E. Prikhodko, *Phys.Usp.* **52**, 165 (2009).