Partial Oxidation of Thin Film Ruthenium in MOS Structure-Chemical, Compositional and Electrical Properties

Emil V. Jelenkovic and Suet To

ECS Solid State Lett. 2013, Volume 2, Issue 5, Pages P42-P43.
doi: 10.1149/2.008305ssl

ECS Solid State Letters, **2** (5) P42-P43 (2013)
2162-8742/2013/2(5)/P42/2/$31.00 © The Electrochemical Society

Partial Oxidation of Thin Film Ruthenium in MOS Structure-Chemical, Compositional and Electrical Properties

Emil V. Jelenković[z] **and Suet To**

State Key Laboratory of Ultra-precision Machining Technology, Department of Industrial and System Engineering, The Hong Kong Polytechnic University, Hong Kong, China

Partially oxidized Ru film in MOS structure is investigated from compositional, chemical and electrical point of view with a purpose of revealing the role of oxygen on flatband voltage. The oxidation causes film roughening and non-uniform RuO_2 growth front. Presence of RuO_2 close to the interface and at the interface is confirmed by X-ray photoelectron spectroscopy and Z-contrast imaging. This is related to flatband voltage shift, equivalent to the work function of RuO_2. Oxidation of Ru increases the interface states density.
 [DOI: 10.1149/2.008305ssl]

Manuscript submitted February 4, 2013; revised manuscript received February 21, 2013. Published March 6, 2013.

Scaling down of CMOS silicon technology demands gate electrodes with the work function ∼4.2 eV and ∼5.2 eV suitable for NMOS and PMOS transistors.[1] In searching for appropriate metal electrodes, MOS structures with ruthenium and RuO_2 were extensively studied.[1–6] Reported work function of Ru and RuO2 are in the wide range of 4.6–4.81 eV and 5.0–5.8 eV, respectively.[1,3–6] Dealing with ruthenium and ruthenium oxide is a significant technological challenge. The work function of ruthenium can mimic the value of RuO_2 if MOS structure with ruthenium is exposed to minute amounts of oxygen at elevated temperature without obvious or significant ruthenium oxide growth.[1,5,6] This change can be reversed after exposure to hydrogen gas annealing.[5] Choi et al. demonstrated that effective work function of Ru can be tuned by controlling oxygen content.[2] Also, work function of RuO_2 metal electrode is prone to degradation in hydrogen atmosphere[3,5] or at high annealing temperatures.[5] Usually, ruthenium based electrodes are deposited[1–5] but thermally grown RuO_2 electrodes were introduced as well[6] and this approach can be useful in understanding the role of oxygen in MOS structure with Ru-RuO_2 gate electrode. Therefore, in this report chemical and compositional properties of thermally oxidized Ru incorporated in MOS capacitor are related to the capacitor's electrical characteristics.

To fabricate pMOS capacitors with Ru based electrodes, ruthenium was deposited on dry oxide. Ru electrodes were patterned by lift-off technique and oxidized at 600°C for 30 minutes in oxygen/nitrogen ambient. The grown films were investigated by RBS (Rutherford Backscattering), XPS (X-ray photoelectron spectroscopy), TEM (transmission electron microscopy) and high frequency C-V (capacitance-voltage) measurement.

Fig. 1 shows the effect of ruthenium oxidation on RBS. After fitting the experimental curve, the thickness as of deposited Ru film was found to be about 42 nm, without any top RuO_2 layer. The simulated RBS curve for 600°C oxidized film is fitted with the top layer of RuO_2 of 27.1 nm and total film thickness of about 64.4 nm. The incomplete oxidation of Ru film was observed by X-ray diffraction measurement as well, while the presence of RuO_2 is confirmed by Raman spectroscopy. Both measurements are not shown but are similar to previously published data.[6]

Chemical status of investigated films was obtained by XPS depth profiling analysis. The depth profile spectra of O 1s core level for oxidized Ru film is given in Fig. 2. Oxygen presence in the grown film can be traced down close to the interface with silicon dioxide. The position of the oxygen peak at 529.7 eV is assigned to oxygen in RuO_2 and falls in the range reported in the literature.[7,8] This value remains the same throughout the film thickness with decreased intensity toward the interface with SiO_2.

On the high energy side of oxygen spectra (Fig. 2) shoulders are seen, while the depth profile no. 14 shows a distinctly new peak at even higher binding energy. The experimental data of 14th depth profile are fitted with three peaks 529.7, 531.2 and 532.4 eV and are linked to

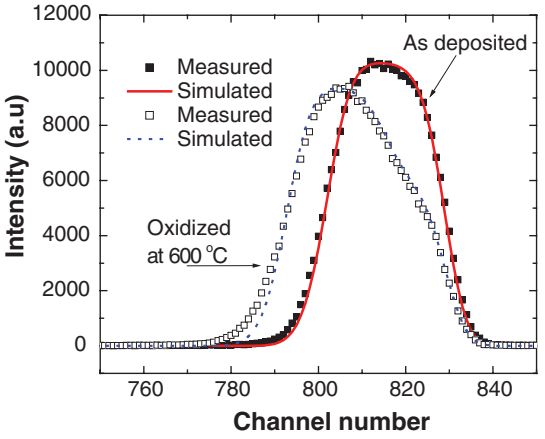

Figure 1. RBS of as deposited Ru film and oxidized at 600°C.

Ru-oxide ion, atomic oxygen and SiO_2 oxygen,[7,8] respectively. In the 14th XPS depth profile, Si 2p core level was recorded for the first time. Its binding energy value was 103.15 eV, pointing the vicinity of the underlying SiO_2 film. This confirms the correctness of above interpretation of O 1s with the highest binding energy in Fig. 2.[9]

Based on the experimental conditions, the calculated inelastic mean scattering path of the excited electron in ruthenium under experimental conditions was about 1.8 nm.[10] Assuming that there was a continuous Ru layer in contact with SiO_2, the first XPS depth profile scan that can register silicon dioxide is at Ru thickness of no more than 4.5 nm. However, observation of Si 2p peak at the 14th scan may be also an indication of pocketed RuO_2 at the interface, which will be verified by Z-contrast imaging.

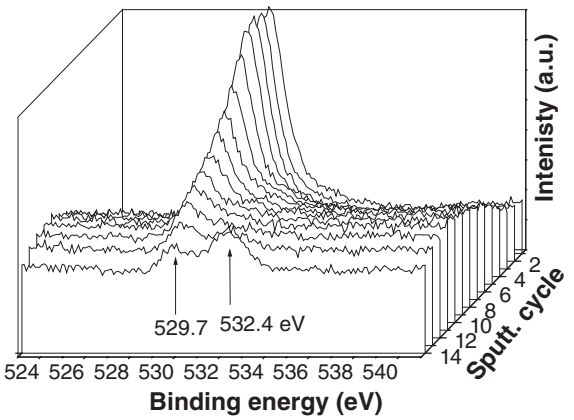

Figure 2. O 1s XPS spectra-depth profile of oxidized Ru film.

[z]E-mail: enemil@inet.polyu.edu.hk

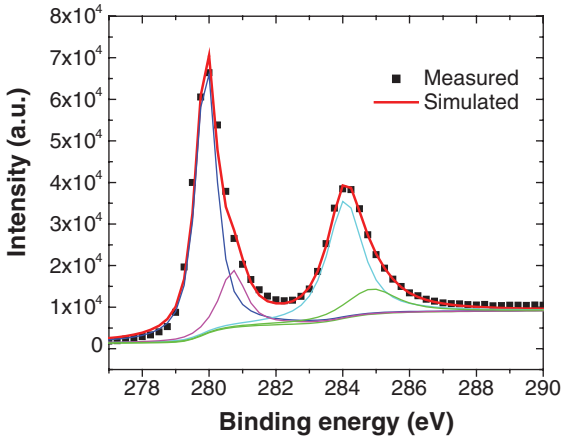

Figure 3. Ru 3d XPS spectrum close to the interface oxidized Ru film/SiO_2.

The Ru 3d core level spectrum of the oxidized film is illustrated for the 14th XPS scan (Fig. 3). The measured data are fitted with two sets of doublets, one set for metallic Ru and the other for RuO_2. At this depth profile level, Ru $3d_{5/2}$ peak is dominated by metal Ru at 280 eV, while the shoulder at high energy is fitted with a peak at 280.7 eV, which is related to oxidized ruthenium metal.[9,10] Therefore, the observation in Fig. 3, regarding the lattice oxygen, is along the finding in Fig. 2.

To complement the picture of the oxidized ruthenium film, cross-sectional TEM analysis was performed. Since we are looking for the critical role of oxygen, a Z-contrast image of the oxidized film is presented in this article (Fig. 4). The film appears rough at the surface and the total film thickness is about 60–65 nm, in a good agreement with RBS finding. The brighter areas of the film are related to the higher average atomic number and are associated with the grains of metallic Ru. The less bright regions are RuO_2 grains. Oxygen mapping (not shown) of the sample region, as in Fig. 4, overlaps with less bright areas of the grown film in the same figure. There are pockets of RuO_2 at the interface with SiO_2 and it may be speculated that they contribute to the oxygen XPS spectra close to the interface (Fig. 2).

The work function of Ru was found to be about 4.6 eV[6] and was obtained from C-V shift difference for MOS capacitors with Ru and Al electrodes. For this purpose, Al electrodes were formed near the Ru electrodes after Al film evaporation and patterning by wet etching. In this evaluation the work function of Al was taken to be 4.1 eV.[11] The oxidation of ruthenium has electrical consequence in shifting flatband voltage to higher value (inset in Fig. 5), providing the effective work function of the oxidized film of about 5.3 eV. This can be associated with work function of RuO_2.[5,6] While for the previous reported investigations of MOS structure with Ru electrode the role of

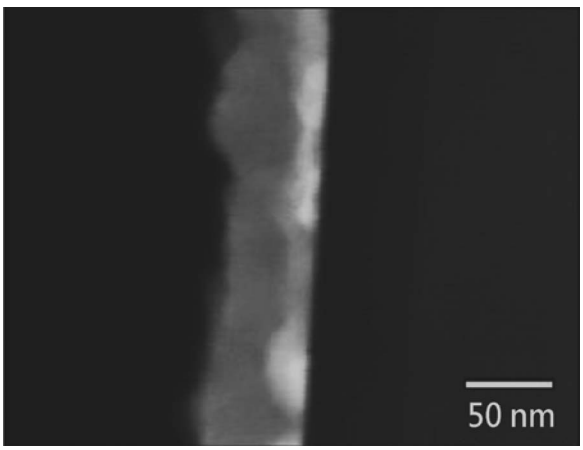

Figure 4. Z-contrast image of oxidized Ru film on SiO_2.

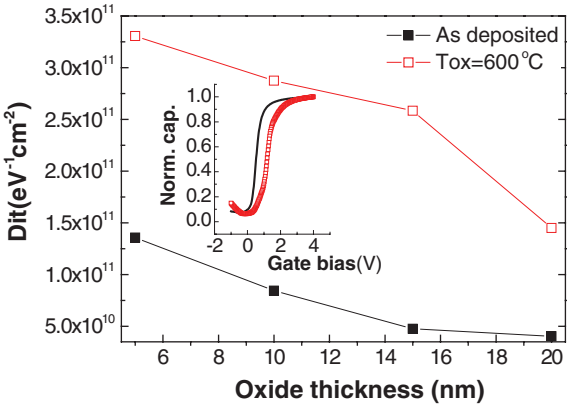

Figure 5. Interface states of MOS capacitor with as deposited Ru and oxidized Ru vs. gate oxide thickness; inset - normalized capacitance, from left to right, as deposited Ru and oxidized Ru gate electrode.

oxygen in MOS was clearly recognized to contribute to the instability of flatband voltage,[1,2,5,6] the nature of its chemical state was largely speculative. However, with this investigation it is proven that oxygen incorporated in RuO_2 at the very interface, together with the diffused oxygen contribute to the change in flatband voltage.

The processing impact on interface states was largely ignored in the previous works due to the problem of flatband instability of Ru based MOS structures exposed to oxygen/hydrogen environment.[1–6] Therefore, in this publication we address the influence of oxidation and gate oxide thickness on interface states. The interface states were extracted using the conductance method (Fig. 5). From Fig. 5, oxidation of Ru electrode gives a rise to the interface states. The interface states appear to be gate oxide thickness dependant. Wen et al.[12] also found a similar trend but could not provide an explanation for it.

In summary, different analytical tools were applied to investigate chemical, compositional and electrical properties of MOS structure with thermally oxidized thin film ruthenium. Ru film was partially oxidized. Diffused oxygen close to oxidized Ru/SiO_2 interface and pockets of RuO_2 in contact with the gate oxide were recorded, giving the effective work function of gate electrode of ~5.3 eV. It was also found that thermal oxidation of ruthenium increases the density of interface states in MOS structure.

Acknowledgments

The work described in this paper was partially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (PolyU 5316/09E) and the Research Committee of The Hong Kong Polytechnic University.

References

1. M. Hasan, H. Park, J.-M. Lee, and H. Hwang, *Appl. Phys. Lett.*, **91**, 033512 (2007).
2. C. Choi, T. Ando, and V. Narayanan, *Appl. Phys. Lett.*, **98**, 083506 (2011).
3. M. Ťapajna, K. Hušeková, J. P. Espinos, L. Harmatha, and K. Fröhlich, *Mater. Sci. Semicond. Proc.*, **9**, 969 (2006).
4. C. S. Park, G. Bersuker, P. Y. Hung, P. D. Kirsch, and R. Jammy, *Electrochem. Solid-State Lett.*, **13**, H105 (2010).
5. L. Pantisano, T. Schram, Z. Li, J. Lisoni, G. Pourtois, S. De Gendt, D. P. Brunco, A. Akheyar, V. V. Afans'ev, S. Sahmuilia, and A. Stesmans, *Appl. Phys. Lett.*, **88**, 243514 (2006).
6. E. V. Jelenkovic and K. Y. Tong, *J. Vac. Sci. Technol. B*, **22**, 2319 (2004).
7. H. Y. H. Chan, C. G. Takoudis, and M. J. Weaver, *J. Catalysis*, **172**, 336 (1997).
8. Lj. Atanasoska, W. E. O'Grady, R. T. Atanasoski, and F. H. Polak, *Surf. Sci.*, **202**, 142 (1988).
9. G. Hollinger, Y. Jugnet, P. Pertosa, and T. M. Duc, *Chem. Phys. Lett.*, **36**, 441 (1975).
10. S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.*, **43**, 689 (2011).
11. S. M. Sze, *Physics of Semiconductor Devices*, 1981, John Wiley & Sons, NY, p. 396.
12. H. C. Wen, P. Lysaght, H. N. Alshareef, C. Huffman, H. R. Harris, K. Choi, Y. Senzaki, H. Luan, P. Majhi, B. H. Lee, M. J. Campin, B. Foran, G. D. Lian, and D.-L. Kwong, *J. Appl. Phys.*, **98**, 043520 (2005).