Ruthenium Oxide Films Prepared by Reactive Biased Target Sputtering

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1. Background

RuO2 in both crystalline and amorphous forms is of crucial importance for theoretical as well as practical purposes, due to the unique combination of characteristics, such as metallic conductivity, high chemical and thermal stability, catalytic activities, and high work function. Due to such properties, RuO2 finds great promise in various applications, for example, in electronic applications, in integrated circuit development, thick or thin film resistors, ferroelectric films and a buffer layer for the high-temperature superconducting thin films. The well-known application of RuO2 is as an electrode in energy storage electrochemical supercapacitors that possess high power density, exhibit excellent pulse charge–discharge property and very long cycle life. In recent years, the use of ruthenium oxide as an electrode material was extensively investigated. It was found that amorphous and hydrous ruthenium oxide formed various methods was a promising for MEMS devices as electrodes, etc.

RuO2 Thin films have been prepared using many methods, including reactive sputtering, chemical vapor deposition (CVD), atomic layer deposition (ALD). Bias target Sputtering (BTS) patented by 4Wave is a hybrid technology that incorporates advantages of both Ion Beam Sputtering (IBS) and Magnetron Sputtering to provide superior film properties, with high deposition rates and scalability. The advantages of Bias Target Sputtering (BTS) compared with other techniques include low process temperature, relatively low equipment cost, and easy operation, less maintenance and control capability of composition and morphology to prepare large area thin films.

In the present report, RuO2 films have been obtained using BTS method and preliminary results of surface roughness, resistivity and thermal stability have been presented.

2. Results

Table 1 presents the electrical resistivity, surface roughness and growth parameters of RuO_2 films with varying oxygen deposition percentages and applied negative target bias by BTS. The RuO_2 has a resistivity value of below 20μΩ.cm below 3% of oxygen concentration in processing chamber during growth, this indicates that films are composed of a mixture of Ru and RuO_x, and have a lower resistivity of 17 μΩ.cm at 3%. As expected, the resistivity of RuO_2 films increased up to 200 μΩ.cm as the percent oxygen increased in processing chamber during growth, which indicates the films are fully stoichiometric and no pure Ru metal in bulk. The resistivity gets to the relatively stable state when the O_2 concentration at 10% (fig. 1). Additionally, the significant change of Resistivity value at 25% O2 probably results from the uncertainty of thickness measurement. On the other hand, the resistivity of RuO_2 films reduced by around 10% after annealing at 400^0C for 10min. in air, which is well consisted with the literature values. Resistivity changes may be attributed to crystallinity improvement after the annealing process. It is suspected that the crystallinity improvement reduces charge-carrier tapping so that conductivity of RuO_2 film could increase.

Table 1. measured results of deposited RuO_2 films by BTS

$O_2/(O_2+Ar)$ (%)	Thickness (nm)	G/R (Å/s)	Rs (Ω/Sq)	Anneal (Rs) 400^0C	Resistivity (μΩ.cm)
10	168	0.9	8.5	7.5	143
20	55	0.3	25.64		141
15	145	0.8	10.06		145
5	175	0.97	7.88		138
3	78	0.65	2.2		17
25	86	0.23	22.7		195
0	40	0.66	3.01		12

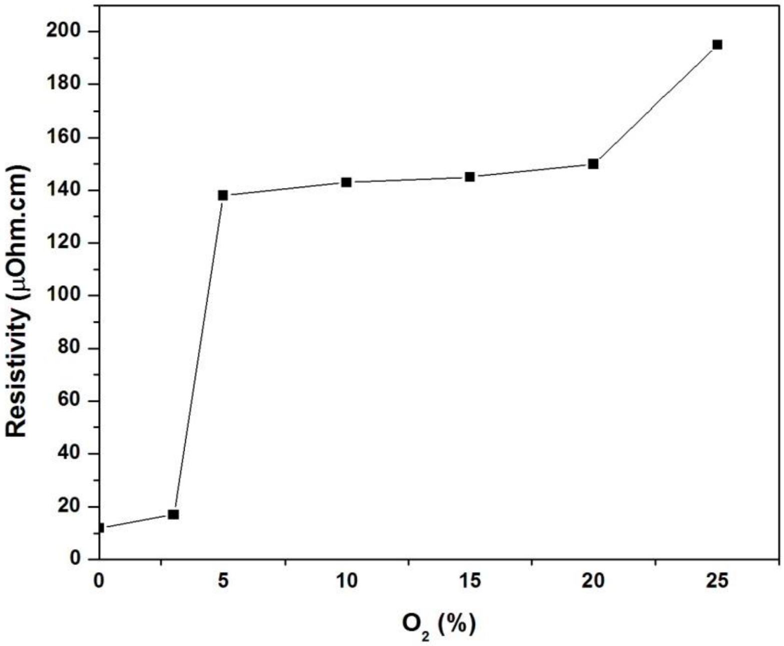
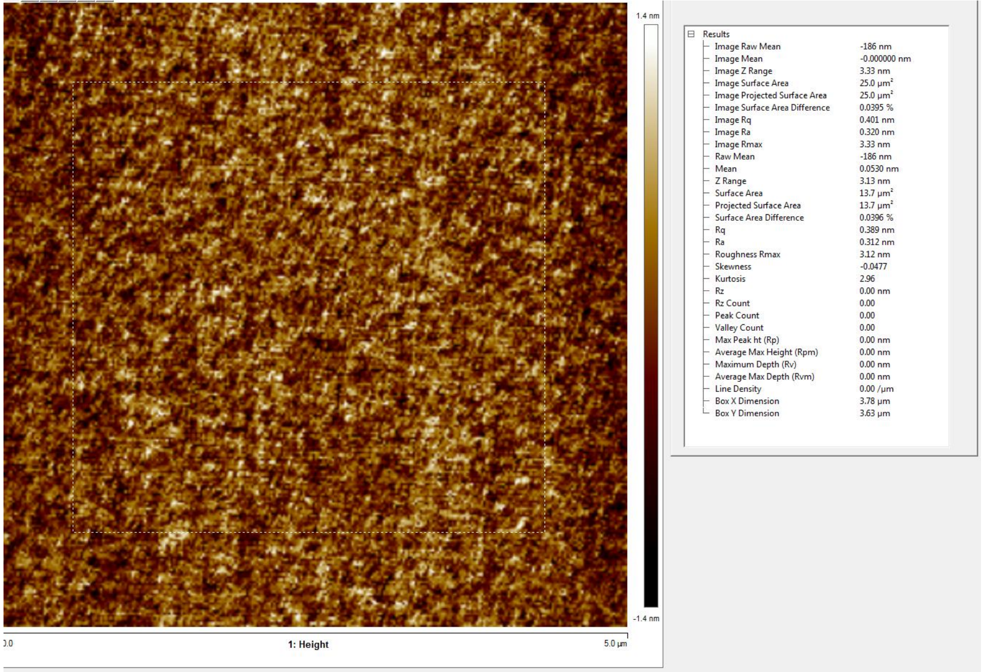


Fig.1. Resistivity of as-deposited RuO_2 film with various O_2 in processing chamber

Figure 2 shows the AFM of the surface of as-deposited films and annealed films in air. The as-deposited film and the films annealed at 400^0C exhibited smooth surface morphology. The thickness of RuO_2 film is about 55nm measured by Progiler. It is seen that surface roughness of as-deposited Ruo2 films has a range of about 0.3 to 0.5nm. However, Annealing has a significant effect on the surface roughness which increases by one time before and after annealing. Both values are much smaller than that of previously published value presented in table 2.

Fig. 3 presents the XRD spectra of the as-deposited and annealed RuO_2 films at 400^0C in air for 15min. the as-deposited films prepared at room temperature is amorphous with less crystals and shows very weak intensity of (101) and (211) peaks. However, the annealed films are showing a clear increase in crystallinity. After annealing of samples, the film shows a strong preferred orientation along (101) direction.



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⊟ Results
   Image Raw Mean                    -186 nm
   Image Mean                        -0.000000 nm
   Image Z Range                     3.33 nm
   Image Surface Area                25.0 µm²
   Image Projected Surface Area      25.0 µm²
   Image Surface Area Difference     0.0395 %
   Image Rq                          0.401 nm
   Image Ra                          0.320 nm
   Image Rmax                        3.33 nm
   Raw Mean                          -186 nm
   Mean                              0.0530 nm
   Z Range                           3.13 nm
   Surface Area                      13.7 µm²
   Projected Surface Area            13.7 µm²
   Surface Area Difference           0.0396 %
   Rq                                0.389 nm
   Ra                                0.312 nm
   Roughness Rmax                    3.12 nm
   Skewness                          -0.0477
   Kurtosis                          2.96
   Rz                                0.00 nm
   Rz Count                          0.00
   Peak Count                        0.00
   Valley Count                      0.00
   Max Peak ht (Rp)                  0.00 nm
   Average Max Height (Rpm)          0.00 nm
   Maximum Depth (Rv)                0.00 nm
   Average Max Depth (Rvm)           0.00 nm
   Line Density                      0.00 /µm
   Box X Dimension                   3.78 µm
   Box Y Dimension                   3.63 µm
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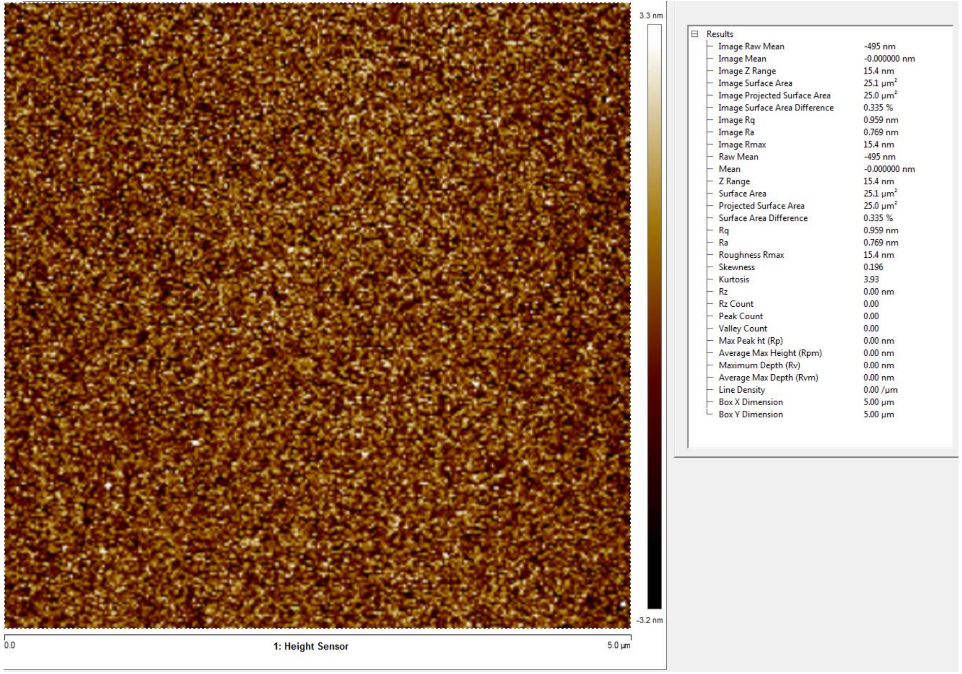
(a) As-deposited



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⊟ Results
   Image Raw Mean                    -495 nm
   Image Mean                        -0.000000 nm
   Image Z Range                     15.4 nm
   Image Surface Area                25.1 µm²
   Image Projected Surface Area      25.0 µm²
   Image Surface Area Difference     0.335 %
   Image Rq                          0.959 nm
   Image Ra                          0.769 nm
   Image Rmax                        15.4 nm
   Raw Mean                          -495 nm
   Mean                              -0.000000 nm
   Z Range                           15.4 nm
   Surface Area                      25.1 µm²
   Projected Surface Area            25.0 µm²
   Surface Area Difference           0.335 %
   Rq                                0.959 nm
   Ra                                0.769 nm
   Roughness Rmax                    15.4 nm
   Skewness                          0.196
   Kurtosis                          3.93
   Rz                                0.00 nm
   Rz Count                          0.00
   Peak Count                        0.00
   Valley Count                      0.00
   Max Peak ht (Rp)                  0.00 nm
   Average Max Height (Rpm)          0.00 nm
   Maximum Depth (Rv)                0.00 nm
   Average Max Depth (Rvm)           0.00 nm
   Line Density                      0.00 /µm
   Box X Dimension                   5.00 µm
   Box Y Dimension                   5.00 µm
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(b) Annealed at 400^0C for 20min.

Fig.2. typical AFM surface morphology of RuO2 thin films on thermal oxidized Si wafers

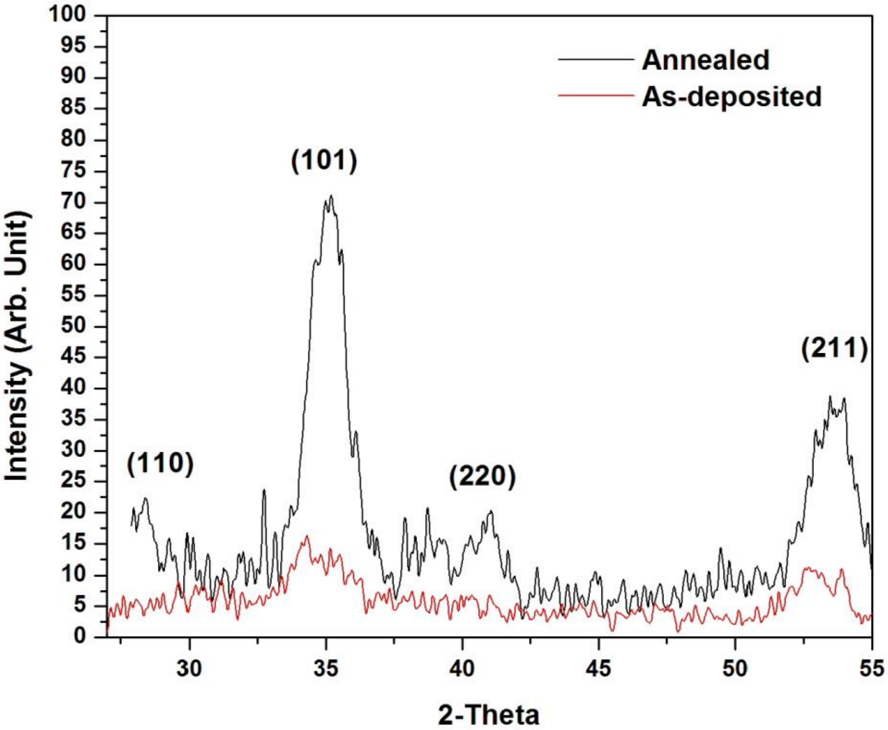

Fig. 3. X-ray diffraction of RuO2 films before and after annealed at 400^0C I n air

Table 2 presents the previously published data in other groups. It is observed that resistivity of ruthenium oxide films is greater than 200 μΩcm at room temperature which were mostly fabricated by magnetron sputtering. Overall, our preliminary results including resistivity, surface roughness are superior to those listed in table 2 which is a great indicator that BTS is a promising technique for RuO2 growth.

Table2. A summary of different deposition techniques for the growth of RuO2 with the process temperature and the reported values.

Resitivity (μΩcm)	Growth Method	Surf. Roughness	Sub. Tem.	Source
350 150	Magnetron sputtering		RT 500	J. Electrical Engineering, Vol.55, No.1-2, 2004, 39-42
180	Magnetron sputtering			Jpn. J. Appl. Phys. Vol37 (1998)3457
350	Magnetron sputtering	1.2~1.8nm	RT	ACS Appl. Mater. Interfaces, 2012, 4, 4588-4594
270	Magnetron sputtering		RT	J. Mater. Res. 1996, 11(11)
280	Sol-gel		300	ABS. 87 206th Meeting

270	Sol-gel		400	J. Phys. IV France, o8(1998)
120	ALD		225	J. Alloys and Componds Vol.625, 2015, 120-124
	Magnetron sputtering	1.4~2.8nm	RT	J. Korean Phys. Soc. Vol. 39 2001 S382-384

2. Conclusion and plan

Recent work at 4Wave demonstrated the capability of BTS to deposit low resistive (150 μΩcm), very smooth (0.5nm) RuO_2 films at room temperature. Further efforts to test the feasibility of volume production of RuO2 films should be made in short term, with high deposition rates and scalability on 4wave prototype platform.