XPS analysis of surface modification of Cu-Ru composites for interconnect applications

R Sule[1], **JKO Asante**[2], [1], **PA Olubambi**[1], **WD Roos**[3]

[1]Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa
[2]Department of Physics, Tshwane University of Technology175 Nelson Mandela Drive,Arcadia Pretoria, South Africa
3 Department of Physics, University of Free State, Blomfontein, South Africa

E-mail: rasidis@tut.ac.za, richysule@yahoo.com Tel: +27(0)12382 4976

Abstract. Sub-micron sized ruthenium reinforced copper composites as suitable material for electronic interconnection applications was synthesized using powder metallurgy technique. High purity sub-micron starting powders were blended in a turbula mixer and sintered. Oxidation test was conducted at temperature ranging from 20 °C-800 °C with the heating rate of 10 °C/min inside the furnace. The X-ray photoelectron spectroscopy was used to examine the surface composition of the sintered Cu, Cu+2.5vol%Ru and 5vol%Ru samples. The RuO_2 $3p_{5/2}$ (280.33 eV) was observed at the surface of Cu-Ru composites sample. Measured intensity ratio of Cu to CuO decrease linearly with increasing Ru addition and indicate the reduction in Cu oxidation rate.

Key works: Copper interconnects; Powder metallurgy; XPS analysis

1. Introduction

Electronic packaging in a variety of microelectronic applications however, involves interconnecting, powering, protecting, and cooling of semiconductor circuits [1]. Interconnect material purpose is to join two electrical terminals with low parasitics such as electrical resistance, inductance and capacitor to be reliable in field used [2]. Copper based interconnect are manufactured into various products especially consumer electronic product such as electronic toys, cell phone, microprocessor, fast static RAM and home appliances. However, application of copper has been limited by the oxidation of copper at elevated temperature and humidity [3]. When copper is heated in air at low temperature around 200 °C it formed Cu_2O film on the surface [3]. Further increase in temperature will result in formation of cupric oxide (CuO) over the copper surface. The resultant effects of Cu oxidation are cracks, decrease in the interfacial shear strength and poor bonding between the component and the substrate which causes device failure. Therefore, it is essential to understand and modify their surface properties in other to improved the performance of copper interconnect materials.

Copper and copper composites interconnect materials has been synthesis by several techniques such as electrodeposition, bottom up growth and electrochemical deposition, selective laser sintering and powder metallurgy. Powder metallurgy techniques have been used to synthesize copper and copper composite for different electronics applications [4]. Besides, there is virtually no reported studies on the effects of ruthenium on the oxidation properties of copper composites for interconnect materials. Studied on similar copper based composites synthesized by powder metallurgy route is also very limited. This study presents an investigation of oxidation properties of Cu-Ru composites synthesized by powder metallurgy route using X-ray photoelectron spectroscopy.

2. Experimental procedure

The specimens were produced by blended the powders using turbula T2F mixer for 5 hours. After the mixing, the mixed powder was characterized using SEM/EDS to check the homogeneity and the elemental composition of mixed powder. The mixed powders were consolidated using high temperature high pressure technique. Approximately 8 g of blended powders was poured into a graphite pot and place inside the graphite die. Argon gas was then allowed to flow through the furnace during the furnace temperature cycle to prevent oxidation. The consolidated samples measured 18mm in diameter and 3 mm thickness. Figure 1 showed the sintering profile of the specimens. The oxidation test was conducted at temperature ranging from 20 °C-800 °C with the heating rate of 10 °C/min inside the furnace.

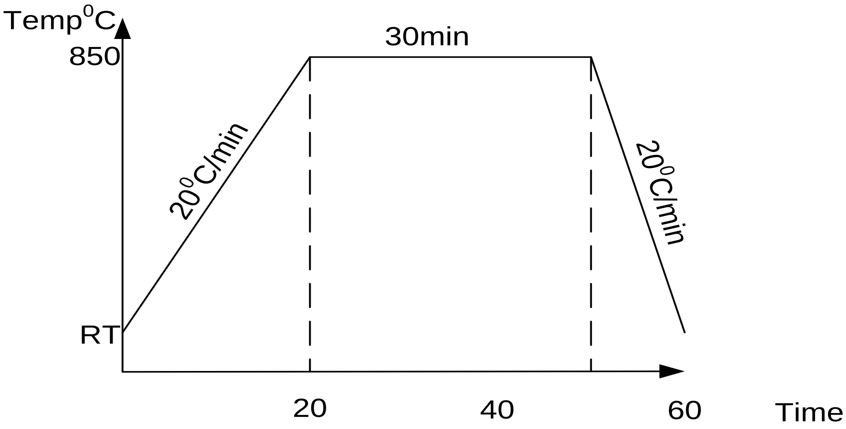

Figure1: The sintering profile for the specimens (a) Cu, Cu+2.5vol%Ru at 850°C (b) Cu+5vol%Ru at 900°C

2.1 X-Ray Photoelectron Spectroscopy

The X-Ray Photoelectron Spectroscopy (XPS) spectra measurements were carried out in a PHI 80-360 electron energy analyzer using Al Kα photons (1486.6 eV) in an ultrahigh vacuum chamber with a base pressure better than 10^{-9} Torr. The anode type x-ray source run at 15 kV, 300 W power. The scan survey for full spectrum was collected at pass energies of 175.5 eV. The measurements were performed on sample surface at a takeoff angle of 45^0 between the direction of the analyzer and specimen plane. The binding energy scale was calibrated using sputter clean, pure copper foil. Spectral analysis was performed using the peak fitting software (XPSPEAK version 4.1) after a Shirley background subtraction [5]. Peak fitting solutions were obtained for $\varkappa^2 < 2$, where $\varkappa^2$ is the standard deviation. In order to investigate the oxidation behavior of sintered samples and also collect information on surface absorption, the sintered samples were not sputtered before XPS analysis. The XPS spectra were least curve fitted using standard Lorentzian-Gaussian lines. A broad scan survey spectrum was first obtained to identify the elements present in the samples. After the elemental composition has been determined, narrow detailed scans of selected peaks was carried out for more detailed analysis of the chemical composition.

3 Results and discussion

The as sintered samples were analyzed using XRD. The XRD results showed that the processing sequence used in fabricating the sample did not encourage oxidation of copper and composites samples [6]. The surface chemical states of heated Cu, Cu+2.5 vol%Ru and Cu+5 vol%Ru samples were characterized using XPS. Wide scan spectra in the range of 0-1000 eV was done to identify the surface elemental composition of the samples. Generally, XPS and XAES can be used to distinguish between Cu metal, Cu_2O and CuO. The CuO was usually characterized by high- intensity shake-up satellites at ~9 eV higher binding energy than main Cu $2p_{3/2}$ peak [7].

3.1 Heated pure copper sample

Detailed scan was carried out on the heated pure copper sample from 928.0 eV to 939 eV region. The results from curve fitting revealed two peaks at binding energy position of 932.44 eV and 934.27which correspond to pure Cu [5] and CuO $2p_{3/2}$ (when examined from the XPS database spectra line). See figure 2a.The results indicated that copper undergo oxidation significantly after heat treatment. This result is consistent with the previous report [3]. Furthermore, scan survey was carried on the oxygen peaks observed in pure heated Cu sample as shown in figure 2b. The O1s XPS spectrum was observed at 530.97 eV binding energy position. After detailed analysis, four peaks were fitted with binding energy of 530.51 eV, 531.42 eV, 532.66 eV and 533.86 eV respectively. Judging from the XPS standard spectra line, binding energy corresponding to 533.8 eV was found to be O_2/Cu. The atomic species with O1s binding energy of 533.8 eV showed characteristic feature of molecular oxygen on copper surface [8]. In addition, a unique O1s feature which could be O^{1-} species is found at 531.42 eV. This is reasonably consistent with report on Ni surface [8].

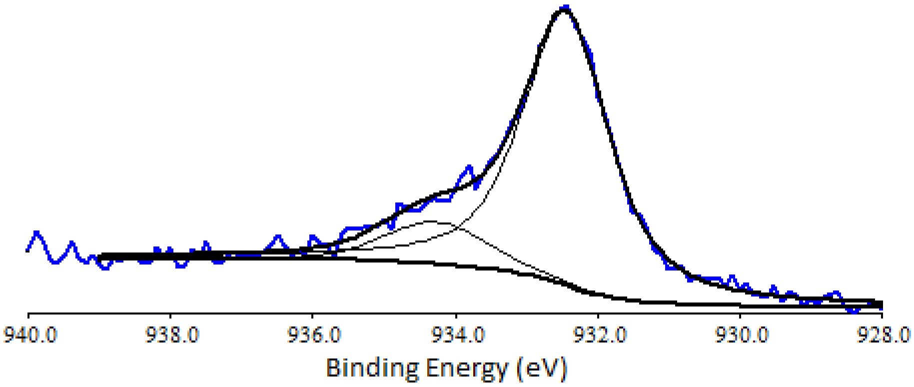

Figure 2a: XPS Cu $2p_{3/2}$ peaks spectra for after heat treatment

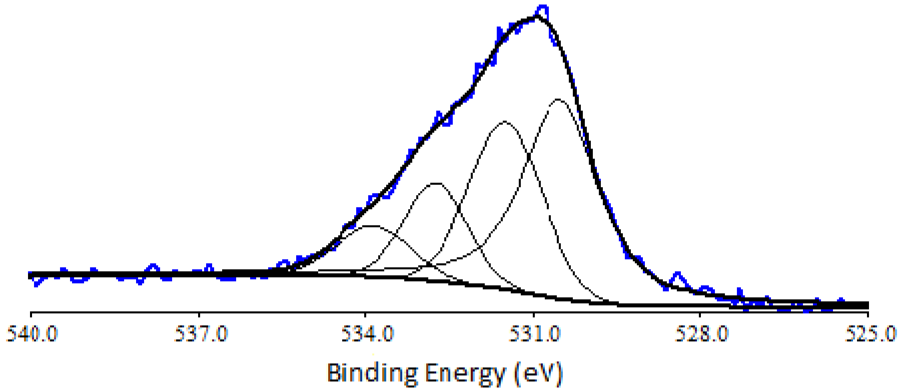

Figure 2b: XPS O1s spectra for oxygen peaks on pure Cu after heat treatment

Table 1 summarizes the measured energy position of heated copper and copper-ruthenium composites samples. In the same table, the full width at half maximum (FWHM) and the intensity value of the constituent elements were reported.

3.2 Heated Cu with 2.5vol%Ru

Ruthenium has been widely used as diffusion barrier for metallization. In examining the influence of 2.5 vol% Ru on Cu composites samples, the XPS results revealed two peaks at binding energy positions of 932.4 eV and 934.02 eV. The results from curve fitting indicate that, the major peak at 932.4 eV with FWHM of 1.45 corresponds to pure Cu $2p_{3/2}$ according to [5] and the minor peak at 934.02 eV with FWHM of 1.45 corresponds to CuO [7] as showed in figure 3. Figure 4 showed the binding energy spectra of O1s observed in Cu+2.5 vol% Ru sample. The O1s peak was observed at energy position 530.79 eV. The fitted peak values for O1s were 532.95 eV, 530.70 eV, 532.05 eV and 533.57 eV. The peak values for O1s binding energy 532.95 and 530.70 fall in H_2O and OH domain according to [9]. Furthermore, binding energy corresponding to 533.8 eV was found to be O_2/Cu [8]. However, O1s at binding energy position 532.05 eV could not be identify due to the major shift in binding energy position. On the other hand, two peaks were observed at energy position of 280.33 eV and 284.66 eV in which the binding energy corresponds to RuO_2 and Ru respectively [11,12,14]. The results showed that 2.5 Ru volume percent resulted in the formation of RuO_2 as shown in figure 5**.**

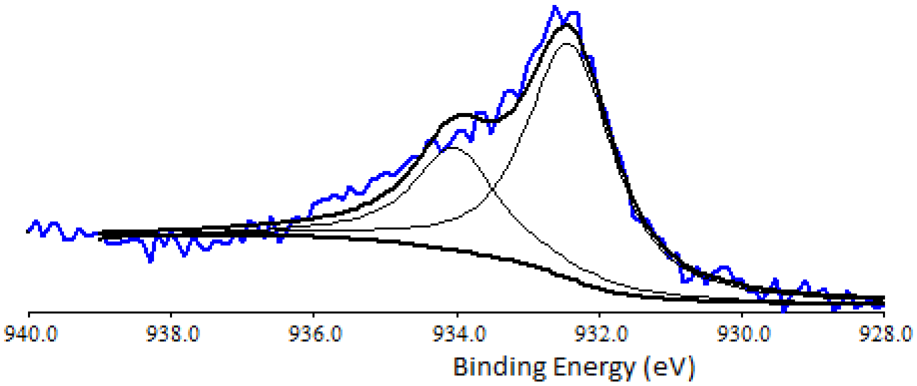

Figure 3: XPS spectra for Cu $2p_{3/2}$ in Cu+2.5 vol%Ru

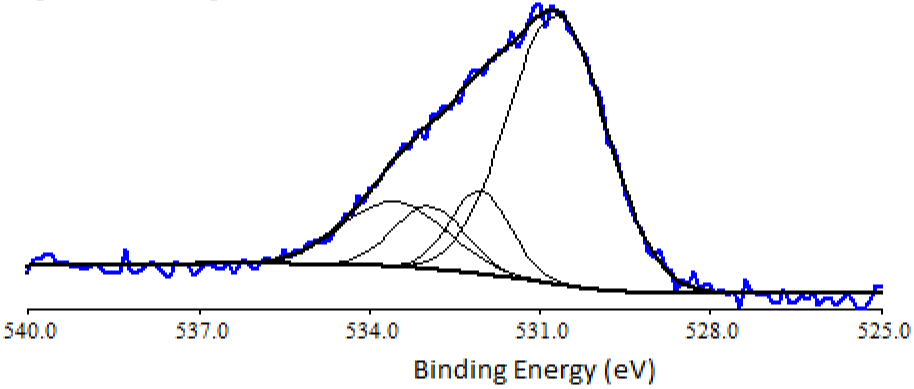

Figure 4: XPS spectra for O1s in Cu+2.5 vol%Ru

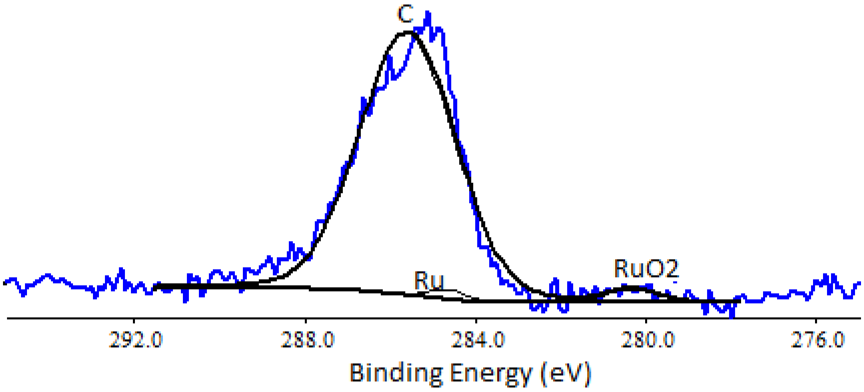

Figure 5: XPS spectra for RuO_2 $2p_{5/2}$ at BE of 280.34 eV in Cu+2.5 vol%Ru

3.3 Heated Cu with 5 vol%Ru

The results from curve fitting of Cu+5 vol%Ru sample revealed two peaks at energy positions of 932.72 eV and 934.14 eV which correspond to pure Cu and CuO 2p3/2 (when examined from XPS database spectra line) respectively [8], as shown in figure 6. Figure 7 showed the binding energy spectra of O1s observed in Cu+5 vol% Ru sample. The O1s main peak was observed at energy position 530.94 eV. The fitted peak values for O1s were 530.51 eV, 532.66 eV, 533.86 eV and 531.42 eV. These energies are reasonably consistent with previously observed O1s XPS binding energy of H_2O and OH [5] and [10].

On the other hand, the peak of RuO_2 $3d_{5/2}$ was observed at energy position of 280.34 eV as shown in figure 8. The observed energy position was reasonably consistent with previous results [11,15]. Furthermore, Over, cited by Ernst & Sloof [13] reported that RuO_2 was the only known stable oxide of Ru at room temperature up to 900 K and became volatile RuO_4 above this temperature. In addition, another small peak was observed at energy position of 284.66 eV. The binding energy position for this peak was found between $5d_{3/2}RuO_3$ (283.3 eV) [7] and $3d_{3/2}C_2H_4/Ru$ (284.20 eV) [14]. However, analyzing the Ru 3d peak is always a challenging task due to the presence of C 1s peak overlapping with Ru $3d_{3/2}$ peak [12,14]. The binding energy position 284.66 eV was considered as Ru since volatile RuO_3 and RuO_4 could only form at a temperature above 900K [13].

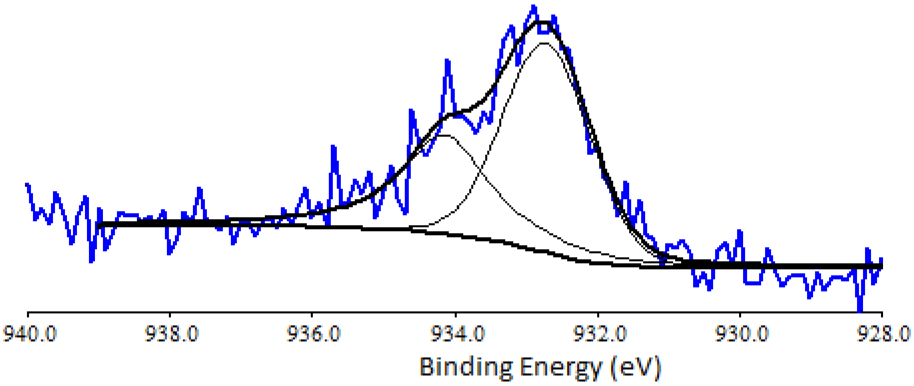

Figure 6: XPS spectra for Cu $2p_{3/2}$ in Cu+5 Ru vol%

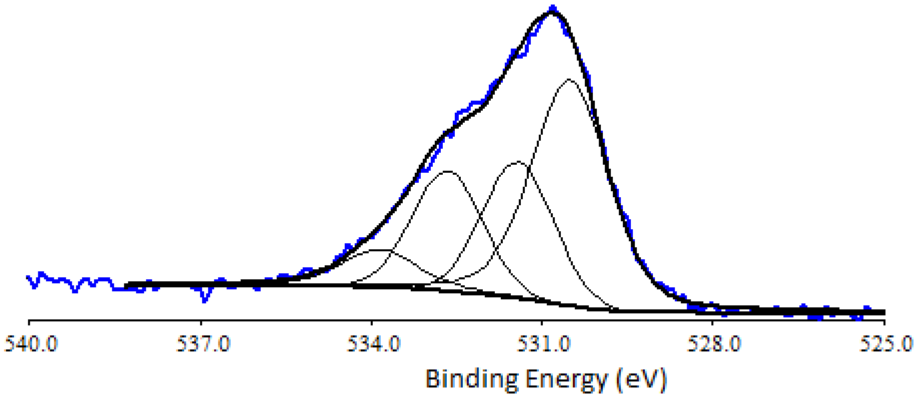

Figure 7: XPS spectra for O1s in Cu+5 Ru vol%

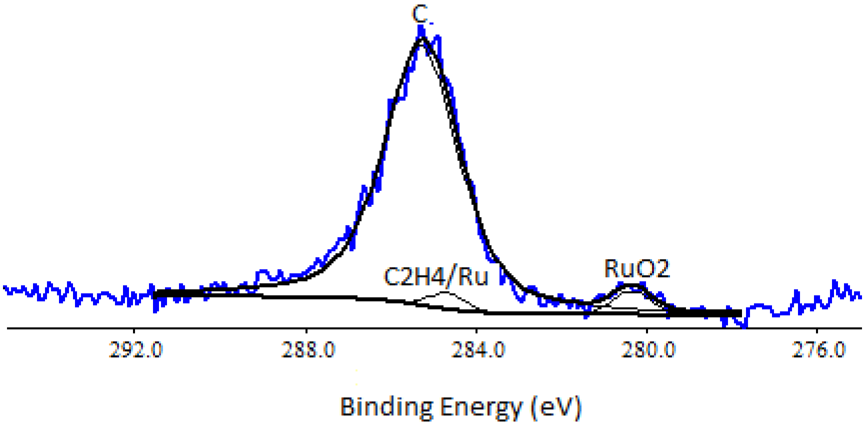

Figure 8: XPS spectra for RuO_2 $2p_{5/2}$ at BE of 280.34 eV in Cu+5vol%Ru

In order to obtained quantitative insight into the effect of ruthenium on copper, the intensity value of the Cu/CuO peaks were obtained. Although, it is difficult to estimate the degree of reduction in CuO in each sample but this approach give evaluation of the effect of ruthenium in copper. The intensity ratio of Cu to CuO reduced linear with Ru addition and this could be attributed to the reduction in Cu oxidation rate. Platzman [5] reported that the change in the intensity ratio of Cu to Cu_2O after 1hr of exposure to ambient air give an indication that native oxidation was fast. The reduction in oxidation rate of copper could be attributed to an impurity segregated layer that formed on the surface of copper [4]. The present results further confirm the statement from [5] that the oxidation properties of Cu based alloys are highly dependent upon the alloying elements and concentration

Table 1: Elemental surface composition of oxidized samples

Material	$Cu2P_{3/2}$ (eV)	$RuO_2 3d_{5/2}$	$Ru3d_{3/2}$	Intensity (a.u)	Int ratio Cu/CuO
Cu					
Cu	932.44 (1.45)			11700.51	1.37
CuO	934.27 (1.45)			8560.25	
Cu+2.5 vol%Ru					
Cu	932.40 (1.45)			9100.71	1.14
CuO	934.02 (1.45)			7973.14	
RuO_2		280.33 (1.45)		525.33	
Ru			284.66 (1.45)	515.02	
Cu+5 vol%Ru					
Cu	932.75 (1.45)			5334.45	1.07
CuO	934.14 (1.45)			4982.58	
RuO_2		280.34 (1.45)		244.12	
Ru			284.66 (1.45)	239.77	

Full width at half maximum (FWHM) of peaks were given in parentheses

4 Conclusion

In this paper, the study of the oxidation behavior of Cu and Cu-based composites of ruthenium (Ru) using XPS has been done. The information obtained from the peak fitting of oxidized Cu and Cu-Ru composite samples revealed that Cu and CuO form at binding energy position of 932.44 eV and 934.27 eV respectively. The intensity ratio of Cu to CuO in pure specimen was 1.37. The addition of 2.5 vol% ruthenium revealed RuO_2 and CuO. The intensity ratios of Cu to CuO in the 2.5 vol% Ru and the 5 vol% were 1.14 and 1.07 respectively.

References

[1] Schubert T, Trindade B, Weißg¨arber T, Kieback B. Interfacial design of Cu-based composites prepared by powder metallurgy for heat sink applications. Mater Sci Eng A 2008; 475:39-44.

[2] Pan MY, Guptal M, Tay AAO, Vandyanathan K. Development of bulk nanostructured copper with superior hardness for use as interconnect material in electronic packaging. Microelectron Reliab 2006; 46:763-767.

[3] Chuang CL Aoh, JN, Din, RF. Oxidation of copper pads and its influence on the quality of Au/Cu bonds during thermosonic wire bonding process. Microelectronics and reliability 2006; 46(2-4):449-458

[4] Gupta M, Tay AAO, Vaidyanathan K, Srivatsan TS. An investigation of the synthesis andcharacterization of copper sample for use in interconnect application. Mater Sci A 2007;454–455:690–4.

[5] Platzman I, Brener R, Haick H, Tannenbaum R. Oxidation of polycrystalline copper thin films at ambient conditions. The Journal of Physical Chemistry C. 2008;112(4):1101-8.

[6] Sule R, Olubambi PA, Abe BT, Johnson OT. Synthesis and characterization of sub-micron sized copper–ruthenium–tantalum composites for interconnection application. Microelectron Reliab (2012)

[7] Kim K, Winograd N. X-ray photoelectron spectroscopic studies of ruthenium-oxygen surfaces. Journal of Catalysis. 1974;35(1):66-72.

[8] Rajumon M, Prabhakaran K, Rao C. Adsorption of oxygen on (100),(110) and (111) surfaces of Ag, Cu and Ni: an electron spectroscopic study. Surface Science. 1990;233(1-2):L237-L42.

[9] Nefedov VI, Firsov MN, Shaplygian IS. Copper (II) Oxide. J. Electron Spectrosc. Relat. Phenom. 1982; 26:65

[10] Yamamoto S, Bluhm H, Andersson K, Ketteler G, Ogasawara H, Salmeron M & Nilsson A. In-situ X-ray photoelectron spectroscopy studies of water on metals and oxides at ambient conditions. Peer Reviewed 2008; 1-27

[11] Riga J, Tenret-Noel C, Pireaux J J, Caudano R verbist J J. Electronic Structure of Rutile Oxides TiO_2, RuO_2 and IrO_2 Studied by X-ray Photoelectron Spectroscopy. Physica Scripta. 1977;16:351-354

[12] Al-Ajlonya, A., Kanjilala, A. Catalfanoa, M. Harilala, S.S. Hassaneina A. & Rice B. Low energy electron bombardment induced surface contamination of Ru mirrors doi: 10.1117/12.916114

[13] Ernst M, Sloof W. Unraveling the oxidation of Ru using XPS. Surface and Interface Analysis. 2008;40(3-4):334-7.

[14] Hrberk,J. J. Vac. Sci. Technol1986; A 4: 86

[15] Chen, C. C., Chen, R .S., Tsai, T.Y., Huang, Y .S. Tsai, D.S& Tiong,K.K. The growth and characterization of well aligned RuO2 nanorods on sapphire substrates. J Phys Condens Matter 2004;16: 8475–8484