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COMMUNICATIONS

RUTHENIUM OXIDE FILMS PREPARED BY REACTIVE UNBALANCED MAGNETRON SPUTTERING

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We prepared RuO_2 thin films on Si substrates by reactive unbalanced magnetron sputtering in $Ar+O_2$ gas mixture using a planar round ruthenium target of 50 mm in diameter. Films were sputtered in the constant voltage mode at a power of 10 W, total pressures in the range from 0.2 to 10 Pa and partial pressure of O_2 from 0 to 80 % at temperatures up to 600 °C and negative substrate dc bias voltage. The crystallographic nature of films was investigated by x-ray diffraction. RBS measurements revealed changes of composition with the bias voltage. It was found that there were changes of structure, electrical and mechanical properties with the oxygen flow ratio, substrate temperature and bias voltage. Nanoindentation measurements were used to evaluate the hardness and reduced modulus of films.

K e y w o r d s: ruthenium oxide, reactive magnetron sputtering

1 INTRODUCTION

A new class of superhard materials with hardness higher than 40 GPa has been suggested with the transition-metal dioxides of Zr, Ru and Hf [1, 2]. Permanently there is a high need to have superhard film material with hardness close to diamond based on the different nature (oxides, nitrides) for use as cutting tools with high resistance to abrasion and oxidation. Under ambient conditions RuO_2 possesses the rutile structure, and undergoes to pressure induced phase transitions, first to an orthorhombic distortion phase at 8 GPa and second to the cubic fluorite type phase at 12 GPa. The cubic fluorite phase is metastable at ambient conditions with a bulk modulus of 399 GPa [3]. Phase transitions of rutile crystallographic TiO_2 structure were recently provided in anvil cell at high pressure (60 GPa) and temperatures over 1000 K [4]. Such a transition gives a new polymorph of TiO_2 with a cotunnite (PbC12) structure with modulus of elasticity of 431 GPa and microhardness of 38 GPa, which is one of the least compressible and hardest polycrystalline materials comparable to diamond and c-BN. These experiments show that there is a possible way to obtain predicted hard phase of ruthenium oxide and questions are open for accomplishment of such a transformation in a wider range, both in volume and as a film material. To realize the mentioned phase transitions meant to define the initial structure properties of RuO_2. The aim of this work was to understand the deposition process of ruthenium oxide films and so to lay a ground of rutile-fluorite phase transition experiments. Among other interesting properties of RuO_2 is the low electrical resistivity at room temperature resulting from the partially filled Ru4d states and high chemical and thermodynamic stability. These properties are convenient for bottom contact electrode in gigabit-scale DRAMs and ferroelectric films prepared using high temperature deposition methods. Excellent diffusion properties of RuO_2 interlayer were improved in the diffusion system of $Al/RuO_2/Si$ for annealing temperature as high as 600 °C [5, 6]. Thin films of RuO_2 were prepared by different deposition techniques such a MOCVD [7], spray pyrolysis and sputtering [8, 9]. Reactive magnetron sputtering is very promising method because the stoichiometry of the deposited films can be controlled and metallic targets can be used.

2 EXPERIMENTS AND MEASUREMENTS

RuO_2 thin films were prepared on Si substrates by reactive unbalanced magnetron sputtering in $Ar+O_2$ mixture using a planar round ruthenium target of 50 mm in diameter in on axis target-substrate geometry. The target to substrate spacing was 60 mm. Films were sputtered in the constant voltage mode at a power of 100 W at different total pressures in the range from 0.2 to 10 Pa and O_2 flow ratio between 0 to 80 % on Si substrates. Substrate temperatures were up to 560 °C and a negative dc bias voltage was applied. Substrates were externally heated and electrically biased to defined values. Ar (3N7) and O_2 (3N) were introduced into sputtering chamber through a mass-flow controlling system to desired pressure as measured by capacitance manometer. Prior to deposition the target was sputter precleaned at 0.7 Pa in Ar for 10 min. After that the desired flow O_2 gas was introduced to the chamber and total pressure of $Ar+O_2$ mixture was set up and deposition started. We could remind that in deposition of RuO_2 an advan-

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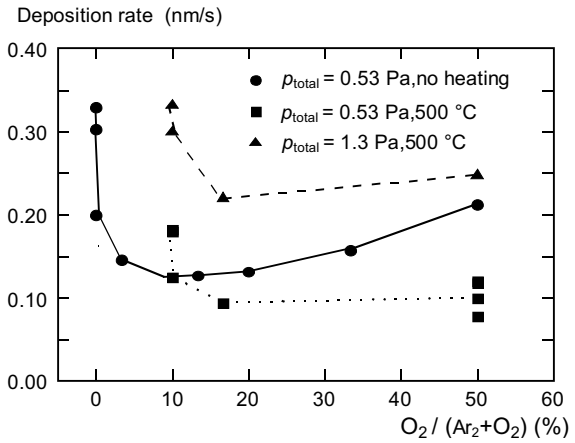

Fig. 1. Deposition rate of the RuO_2 films prepared at different growth conditions vs oxygen flow ratio (OFR).

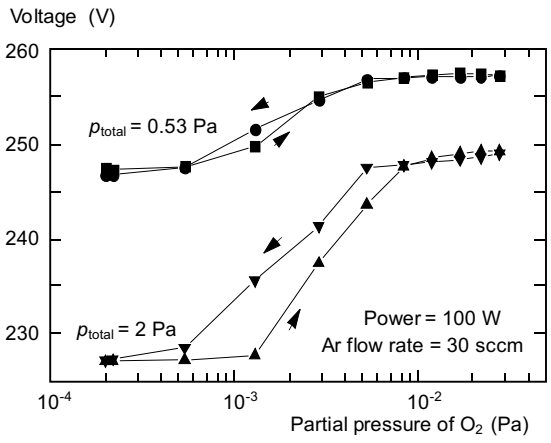

Fig. 2. Hysteresis dependence of sputtering voltage V_s as a function of partial pressure of oxygen pO_2.

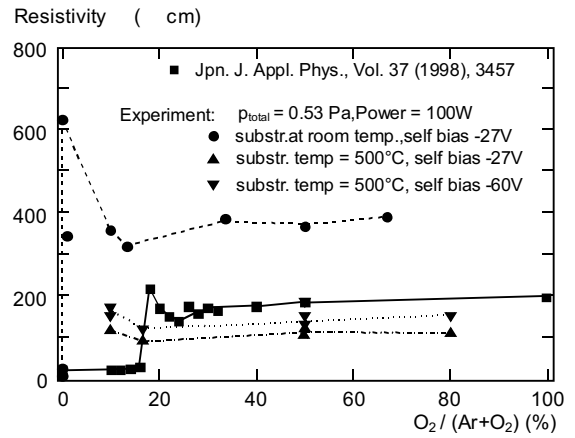

Fig. 3. Changes of resistivity of RuO_2 films versus oxygen flow ratio (OFR) for different deposition conditions.

tage is that oxide that is created on the target surface in reactive sputtering process is a high conductive material (tens of $\mu\cdot$ohm$\cdot$cm) and so there is no problem with arcing, which is common for non-conductive oxides reactive sputtering [10]. A series of films were grown with different total thickness ranging from 100 to 1000 nm, depending on deposition conditions and time. The deposition rates were calculated from the final coating thickness and corresponding deposition time. The thickness of films was measured using a Dektak profilometer. The crystal structure was identified by X-ray diffraction $\Theta/2\Theta$ scans with a PW 1820 powder diffractometer with an accuracy of 0.015° in 2Θ. The films grown on C and Si substrates were used for composition analysis by Rutheford backscattering spectroscopy (RBS). For this purpose the $^4He^+$ ion beam with 1.8 MeV energy from Van de Graaf accelerator at NIRIN (Nagoya, Japan) was applied. The sheet resistance and resistivity of films were evaluated by 4-point probe measurements.

Figure 1 shows the changes of the deposition rate of RuO_2 films versus oxygen flow ratio (OFR). We can observe an abrupt decrease of the deposition rate at a certain oxygen flow ratio also as a dependence of different deposition conditions (substrate temperature, partial pressure). The edge of decrease of the deposition rate of films grown without heating at the oxygen flow ratio 3 % is lower than 30 % which was specified by [11] and also is in good correlation with hysteresis dependence of the measured sputtering voltage V_s versus partial pressure of oxygen pO_2, Fig. 2. When the substrate was heated, the edge of decreasing of the deposition rate is shifted to about 15 % of OFR and is increasing towards higher values in dependence of the total pressure. The shift could be explained by lowering of sticking coefficient of oxygen on ruthenium with rise of substrate temperature, behaviour known from other metal oxide systems. When the oxygen flow ratio is higher than 20 % the deposition rate slightly increases because of more oxygen atoms arrival from plasma to the film surface, which take part in the growth process. This result correlate with an electrical resistivity rise and stoichiometry changes towards the excess of oxygen in the deposited layer, which was confirmed by RBS measurements. It has been shown on the dependence of the substrate voltage V_s versus pO_2 that the memory effect of oxide on the target is relatively lower in comparison with targets with a higher difference between the resistivity of metal and its oxide, *eg*, Al and Al_2O_3 [12, 13, 14]. We can observe some kind of shallow minima of this dependence for which we have no explanation up to now. Such behaviour was also neglected in [11]. We can conclude that small amount of oxygen in the deposition chamber is sufficient for complete oxidation of Ru target, which is expressed by a lowering of the deposition rate and settling of V_s versus pO_2 dependence. RBS measurements have shown that when the amount of oxygen increases to the value of OFR = 50 % the composition of films is slightly over-stoichiometric with O : Ru ratio equal to 2.4.

We have measured the dependence of the deposition rate versus substrate negative bias voltage and we found that it is falling down monotonically for different oxygen flow ratio from 10 to 50 %. Within the region of higher negative voltage an etching effect of ion bombardment

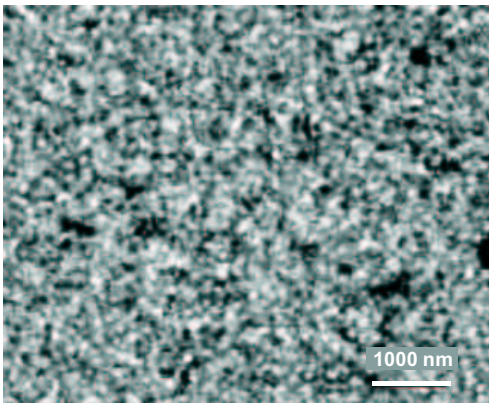

Fig. 4. SEM micrograph of the surface of RuO_2 films deposited at 500 °C.

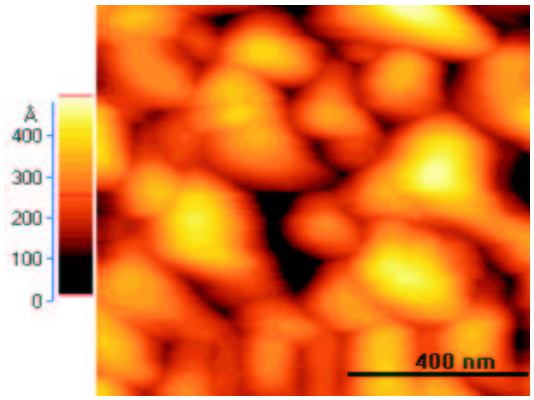

Fig. 5. AFM image showing the surface of the sample of RuO_2 film on silicon substrate deposited at 500 °C.

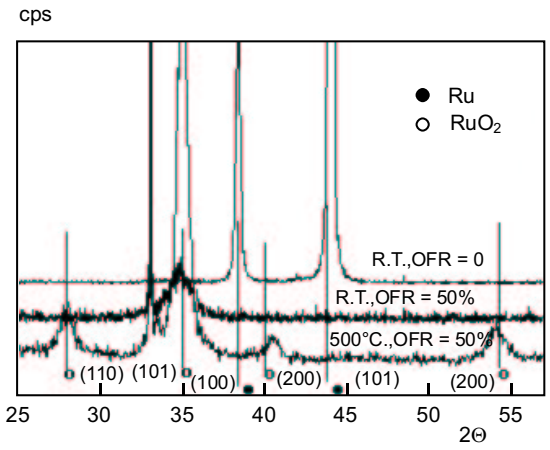

Fig. 6. XRD spectra from deposited RuO_2 film prepared at different deposition conditions (substrate temperature, Oxygen Flow Ratio – OFR).

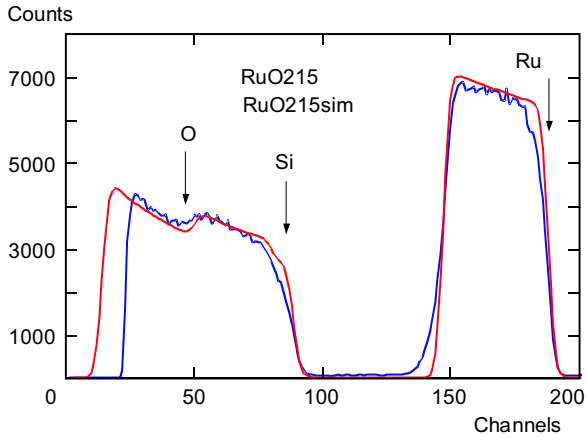

Fig. 7. Measured and simulated RBS spectra of ruthenium oxide film deposited on silicon substrate for 1.8 MeV alpha particles from the film grown at 0.53 Pa, OFR = 10 % and 540 °C substrate temperature, bias voltage 60 V and thickness of film 350 nm. The substrate was silicon.

was observed and a zero growth rate can be reached at negative voltages higher than 130 V.

Figure 3 shows the measured changes of electrical resistivity of the films as a function of the oxygen flow ratio in comparison with results from [11]. We can see the shift of resistivity jump to the minimal value when the oxygen flow ratio was at about 3 % in the case without heating the substrate. This jump was noticed at the values of OFR where the fall in deposition rate occurred, Fig. 1. Besides this we can observe that resistivity of RuO_2 films decreases with increasing the substrate temperature and negative bias voltage, which is in good agreement with previous published results [11]. The minimum of resistivity about 90 $\mu\Omega$cm was reached when OFR was in the region from 15 to 20 %. This is about 2.5 times higher value in comparison with the bulk resistivity of RuO_2 crystal.

Optical microscopy, SEM and AFM observations of the film surface recorded surface morphology properties of RuO_2 films. SEM micrograph on the Fig. 4 shows the smooth surface of RuO_2 films after deposition at 500 °C. AFM image shows the surface of the sample of RuO_2 film on silicon substrates with grains diameter from 150 to 250 nm deposited at the same temperature, Fig. 5.

Figure 6 presents diffraction patterns of samples prepared at different deposition conditions. When the oxygen flow ratio was lower than 3 % and deposition was run without substrate heating, a single phase Ru is formed which is expressed by Ru(100) and Ru(101) intensive peaks. With increasing the oxygen flow ratio up to 50 % RuO_2 films were grown at room temperature conditions with different stoichiometricity.

Typical RBS spectrum of ruthenium oxide films is shown on Fig. 7. For the RBS experimental data analysis the software program RUMP was used to simulate the composition depth profile. We found a good agreement of measured and simulated RBS spectra at different deposition conditions. RBS measurements have shown that films were more stoichiometric when the substrate dc bias voltage in the range from self-bias (−27 V) up to −60 V was increased, Table 1. We could explain this result that more stoichiometric films are obtained when higher bombardment by Ar flux from plasma towards to the surface is responsible for removal of weak atoms of oxygen from

Table 1. Reduced modulus B_r, hardness H and stoichiometry calculated from RBS measurements of ruthenium oxide films prepared at different sputtering conditions.

Sample	Oxygen Flow Ratio-OFR (%)	Substrate Temperature (°C)	Substrate Bias (V)	Dep. Rate ; Thickness (nm/s);(nm)	RBS Analysis	Reduced Modulus B_r *(GPa)	Hardness H (GPa)
Ru	0	No heating	−27 (selfb)	0.33 ; 420	Ru	210.7 ± 21.8	10.6 ± 2.2
RuO_2	50	540	−27 (selfb)	0.12 ; 230	$RuO_{2.5}$	155.2 ± 31.7	9.4 ± 1.7
RuO_2	50	540	−60	0.10 ; 190	$RuO_{2.4}$	163.1 ± 22.7	10.5 ± 1.0

the surface of the growing film. In this case XRD patterns have shown a preferential growth of crystals in direction (101) of RuO_2 rutile structure. We have observed the high influence of the substrate temperature on the growth of structured polycrystalline films.

In Fig. 6 we can compare the strong difference between XRD spectra of two films prepared at the same deposition conditions differing only in substrate temperature. When the substrate temperature was 500 °C and OFR 50 %, we can observe the single-phase RuO_2 peaks. The strong peak intensity indicates good crystallinity of films. Preferential orientation change between (110) to (101) of the planes was measured by [11] with the medium values of oxygen flow ratio at 30 %, while for when oxygen flow ratio was higher than 32 % the main peak was broad and small. Opposite to this our films show good crystallinity even at higher values of oxygen flow ratio, see Fig. 6. It is generally accepted that energetic ion bombardment of growing films on substrate by ions having origin in plasma plays a crucial role in the formation of sputtered films. We tried to exploit such an influence of ion bombardment for creating of deposition conditions, which could be proper to develop possible tensile stress or expected phase transitions in the growing films. We can observe the peak shifts of the plane (101), (110) and (200) of the rutile phase markedly at the higher substrate temperatures recorded on Fig. 6. These shifts refer to a tensile strain in films material.

Nanoindentation measurement was used to evaluate the mechanical properties of the films. We have measured a reduced modulus B_r and hardness H of the RuO_2 films prepared at different deposition conditions using Hysitron nanoindenter with the aimed penetration depth below 20 % of the film thickness to avoid the substrate influence. Results are summarized in Table 1. The reduced modulus B_r (reduced with the properties of the cube corner diamond tip) is much more reliable than the hardness values since the hardness is dependent on the drift rate and the reduced modulus describes a real physical property *ie* the strength of chemical bond. It is surprising that our Ru films had similar or slightly higher values of reduced modulus B_r in comparison with RuO_2 films. There was no large difference between the measured hardness of Ru metal and RuO_2 oxide films.

3 CONCLUSIONS

We have demonstrated that using unbalanced magnetron sputtering we can prepare rutile RuO_2 films of good quality and, by changing the deposition conditions, to control their composition, structure, mechanical and electrical properties. This step in our research is a good ground for next experiments with a possible transition of rutile phase or direct deposition of orthorhombic or fluorite structure of RuO_2. For the next work it will be necessary to find proper deposition conditions for the growth of superhard orthorhombic or fluorite phase and/or to deposit Ru02 film in severely inhomogeneous conditions of growth (substrate temperature, high ion bombardment, different dopants) cause high stress in film material which we believe that it could be the basis for easier pressure phase transitions accomplished at lower external pressures and temperatures. Direct measurement of the strain in RuO_2 films using some standard method could be proper for the correlation of the strain in films with XRD measurements.

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