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Effects of Substrate Temperature and the O_2/Ar Ratio on the Characteristics of RF Magnetron Sputtered RuO_2 Thin Films

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RuO_2 thin films deposited directly on Si substrate by RF magnetron sputtering method using RuO_2 target have been investigated. Special interest was focused on the effect of process parameter on the surface roughness of RuO_2 films. Crystallization behavior and electrical properties of the films deposited at 300°C were superior to those deposited at room temperature. Metallic Ru phase was formed in pure Ar and this phase had resulted poor adhesion after post annealing process in oxidizing ambient. Microstructural analysis reveals that the size of the RuO_2 crystallites gets smaller and the surface becomes smoother as the O_2 partial pressure or film thickness decreases. Irrespective of the O_2/Ar ratio, resistivity of RuO_2 films ranged in 50~70 μΩ-cm As the film thickness decreases, there is a thickness where the resistivity rises abruptly Such an onset thickness turned out to be dependent on the O_2/Ar ratio.

Key words : RuO_2, O_2/Ar ratio, Surface roughness, Resistivity

I. Introduction

For thin film ferroelectrics, electrical properties are dominated by microstructure of the films and interfacial state between dielectric layer and bottom electrode. It is becoming increasingly apparent that underlying bottom electrodes play an important role in determining film performance.[1] Therefore there has been many studies on the electrode materials to improve the properties of ferroelectrics on top of those.

General requirements for the electrode materials are low resistivity, thermal stability, surface flatness, and the minimum reaction with ferroelectric films.[2,3] Considering such properties, Pt has been the most promising material so far. The advantages of Pt electrode are fast operating speed of devices due to low enough resistivity, good resistance to oxidation which causes the degradation of device property and low leakage current density because of the high work function difference with dielectric layer, etc. However the hillock formation, the need for buffer layer to prevent the formation of Pt-silicide and to improve the adhesion, and the etching difficulty prohibit further application. Recently RuO_2 which is a conductive oxide has been focused since it can overcome such problems.[1-9] In addition, RuO_2 is decidedly superior to Pt in the properties like fatigue, TDDB(Time Dependent Dielectric Breakdown).[5,10] But one of the disadvantages for using RuO_2 electrode in ferroelectric device is rough surface morphology. Depending on the roughness of bottom electrode, the property of the device built up on the electrode would be influenced. In particular, it is believed that the leakage current level of device strongly relies on the roughness of the electrode.

In this study, RuO_2 films were deposited by RF magnetron sputtering technique under different substrate temperature and O_2/Ar ratio. The phase formation, adhesion, composition, surface morphology and electrical properties were investigated. Especially, the microstructural control of film was attempted in the range without loosing adhesion, stoichiometric composition, and low resistivity. The change of resistivity according to reduction of the film thickness was also examined.

II. Experimental Procedure

Anhydrous RuO_2 powders (John Matthey; purity 99.98%, particle diameter 0.15~1 μm) recrystallized with annealing at 600°C for 2 hours were unidirectionally pressed to form 2" diameter RuO_2 sputtering target. Typical upper sputter type RF magnetron sputtering system was used. P-type (100) Si wafer was cut to 3 cm × 3 cm and each substrate was cleaned by aceton, alcohol and D.I. water in order for ten minutes each before the deposition.

In most deposition we fixed the process parameters such as target to substrate distance, base pressure, working pressure, and RF power. The O_2/Ar ratio was varied from 0/10 to 5/5 and the substrate temperature was either room temperature or 300°C during deposition (Table 1). Thickness of RuO_2 films was varied from 300Å to 4000Å to investigate the its effect on the film resistivity. Post annealing was carried out in the tube furnace between 400~700°C in O_2 or Ar ambient at atmospheric

Table 1. Deposition Conditions of RuO_2 Thin Films

target	2" RuO_2
substrate	P-type (100) Si
spacing (cm)	5
base pressure (torr)	$< 3.0\times10^{-6}$
O_2/Ar	0/10~5/5
sub-heating Temp. (°C)	Room Temp., 300
working pressure (torr)	1.0×10^{-2}
RF power (W)	45
power density (W/cm^2)	0.56

pressure for 15~270 minutes.

Thickness of the films was measured by α-step (Tencor stylus profilometer 200) and by scanning electron microscope (SEM, Hitachi S-3000). RuO_2 phases at different process conditions were determined by X-ray diffractometry (XRD, Rigaku, RAD-C, Cu Kα). We studied the adhesion between Si substrate and RuO_2 film by adhesive tape test. Composition ratio and surface density were ascertained with RBS (Rutherford Backscattering Spectrometry, NEC in USA, 5SBH-2). Surface morphology and the cross sectional microstructures were examined by an SEM (Hitachi, S-3000). Finally, the resistivity of the film was measured from the Van der Pauw method by Hall measurement (BIO-RAD, HL5200).

III. Results and Discussion

1. *Phase and composition analysis*

X-ray diffraction patterns of RuO_2 films deposited at room temperature are shown in Fig. 1(a). In all the range of O_2/Ar ratios, characteristic peaks are not shown. On the other hand, for the films deposited at 300°C(Fig. 1(b)), (002) Ru, (200) RuO_2, (101) RuO_2 phases are resulted in O_2/Ar ratios of 0/10, 1/9, 2/8~5/5 respectively. The formation of Ru phase in pure Ar ambient, in spite of using oxide target, is due to the fact that the supply of oxygen was not sufficient during the deposition. When oxygen was added to Ar, RuO_2 phase appeared and the preferred orientation changed from (200) to (101) as the amount of O_2 increased. In rutile structure, ion radius of oxygen and Ru, calculated from lattice parameter(a=4.4919Å, c=3.1066Å) and atomic site,[11] are 1.2324Å and 0.7115Å, respectively. Area ratio occupied by oxygen in (200) plane is 34.2% and in (101) plane is 46.5%. Since the content of oxygen is relatively low for the case of O_2/Ar ratio of 1/9, RuO_2 film is believed to be grown to (200) plane. Preferred orientation of the RuO_2 films in O_2/Ar ratio of 2/8~5/5 was (101) with the same reason.

In both room temperature and 300°C deposited films, there was not noticeable change in XRD peak intensity after the post-heat treatment, indicating the governing

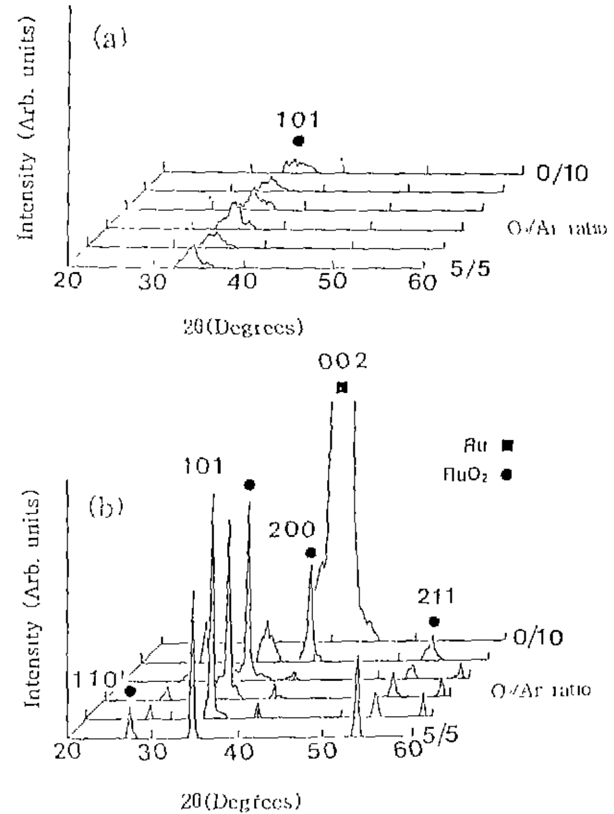

Fig. 1. XRD patterns from the films deposited in the O_2/Ar ratio of 0/10~5/5 (a) at room temperature and (b) at 300°C.

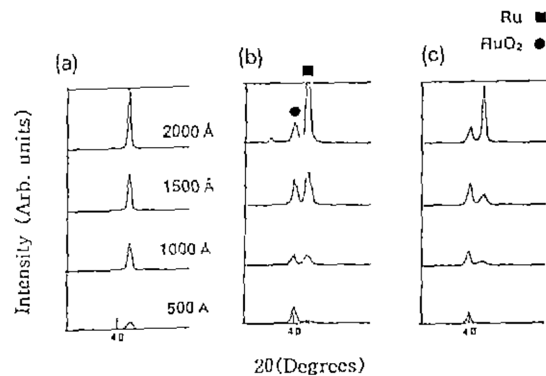

Fig. 2. XRD patterns from the films deposited in Ar only ambient at 300°C and post-annealed at 600°C in O_2 ambient for (a) 0, (b) 15 and (c) 30 minutes.

process parameter of the phase formation is the substrate temperature during the deposition rather than the annealing conditions. However, in the specimen of Ru film deposited only by Ar, metallic phase of Ru oxidized and the (200) RuO_2 peak intensity increased as the annealing time increased under the oxygen atmosphere (Fig. 2)

Bottom electrodes are supposed to experience higher temperature during the following process. For that reason, the thermal and mechanical stability of the electrode material with the substrate is very important

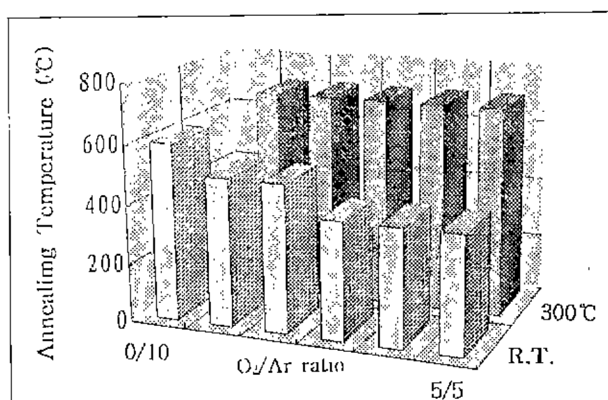

Fig. 3. Adhesion between substrate and RuO_2 thin film deposited at (a) room temperature and (b) 300°C as a function of various process conditions (Each bar represents the range of the good adhesion at a given deposition condition.).

while in service. Fig. 3 shows the adhesion of the films prepared at various conditions. Adhesion of the specimens deposited at room temperature is not good in general. It becomes worse as the oxygen partial pressure and the annealing temperature increase. Presumably the surface mobility to make ions or molecules placed in suitable lattice site was not sufficient to relax the strain of the films during the process. This piled-up strain is going to be relaxed during post annealing process and even the peeling of the film can be resulted. On the contrary, all the RuO_2 films deposited at 300°C show good adhesion except the specimen deposited only in Ar. This is because the metallic Ru phase oxidizes and changes to RuO_2 phase during the annealing process as we have observed in XRD patterns (Fig. 2). This phase transformation requires free volume of about 130% due to the molar volume expansion.

Effect of the O_2/Ar ratio on the composition was also investigated for the specimens having RuO_2 phases and good adhesion characteristics. O/Ru atomic ratios of films deposited in O_2/Ar ratio of 1/9, 3/7 and 5/5 were 2.0, 2.0 and 2.1, respectively, indicating stoichiometric composition of RuO_2

2. *Surface morphology*

RuO_2, like typical oxide material, has relatively high surface energy than metallic Ru. Therefore there is a tendency to grow with low surface energy facet planes when it is formed as crystal. It inherently ends up with rough surface morphology. Such surface roughness can be reduced by decreasing the size of the crystallites.

The surface and cross-sectional morphologies of the film grown at 300°C under the O_2/Ar ratio of 1/9 are shown in Fig. 4. Polycrystalline film consists of columnar structure of tiny crystallites of 300~500Å wide. Since the crystallites are small, surface flatness is relatively good and this result is comparable with the reported RuO_2 surface.[7] Whereas the crystallite size of the film deposited

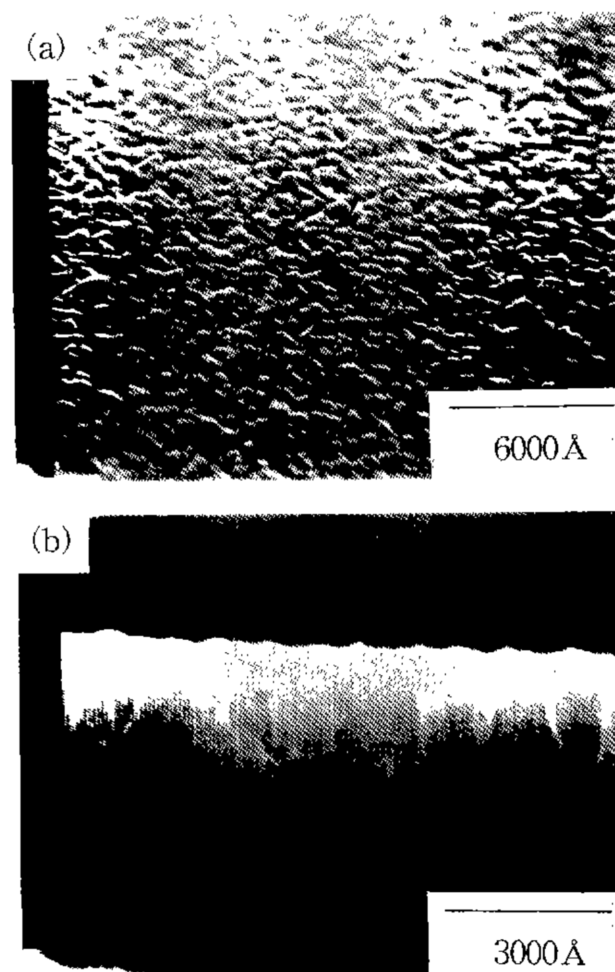

Fig. 4. SEM microphotographs of (a) surface and (b) cross section of the films deposited at 300°C in O_2/Ar ratio of 1/9.

under O_2/Ar ratio of 5/5 is about 1000~1500Å and the film surface becomes rougher as a result of well developed facet plane at the crystal tip (Fig 5).

Such change in surface morphology is related to the nucleation and growth rate of crystallites. When oxygen content in sputtering gas ($Ar+O_2$) is low, net flux of RuO_2 to substrate increases due to both increment of sputtering yield and reduction in re-sputtering effect by O^{2-} ion. It seems from the experimental results that the effect of surface mobility on the grain size due to the O_2/Ar ratio at the same substrate temperature is small enough to be overwhelmed by the effect of degree of supersaturation due to the charges in flux. Therefore the nucleation rate increases as the O_2/Ar ratio decreases due to the increase in flux and the film consists of small grains as a result.

Grain size also varies according to reduction of the film thickness. Fig. 6 clearly reveals that the grain size of 400Å thick films is smaller than that of 2000Å thick films shown in Figs. 4 and 5. This phenomenon is from the low crystallinity in the early stage of deposition,

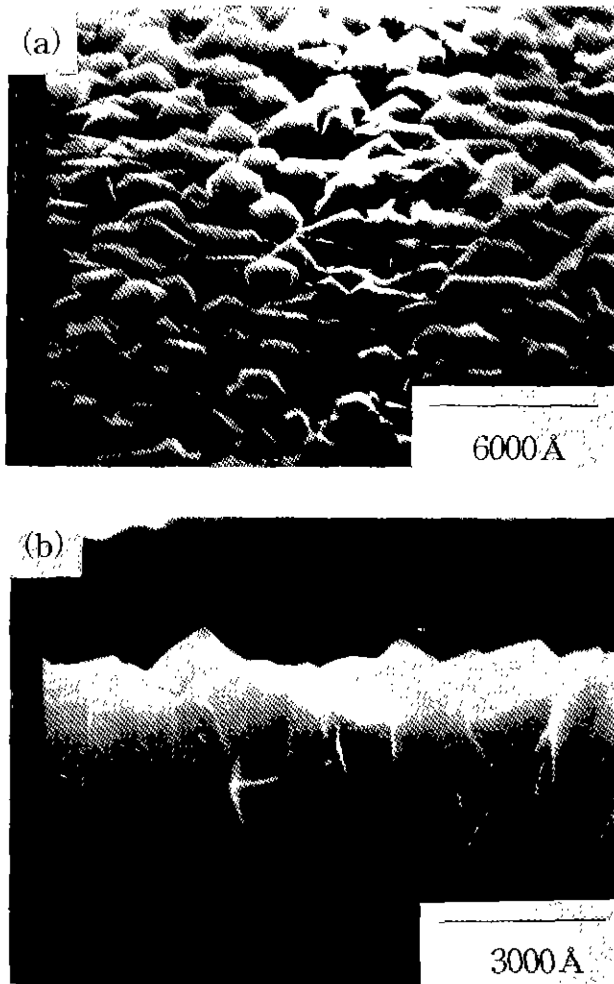

Fig. 5. SEM microphotographs of (a) suface and (b) cross section of the films deposited at 300°C in O_2/Ar ratio of 5/5.

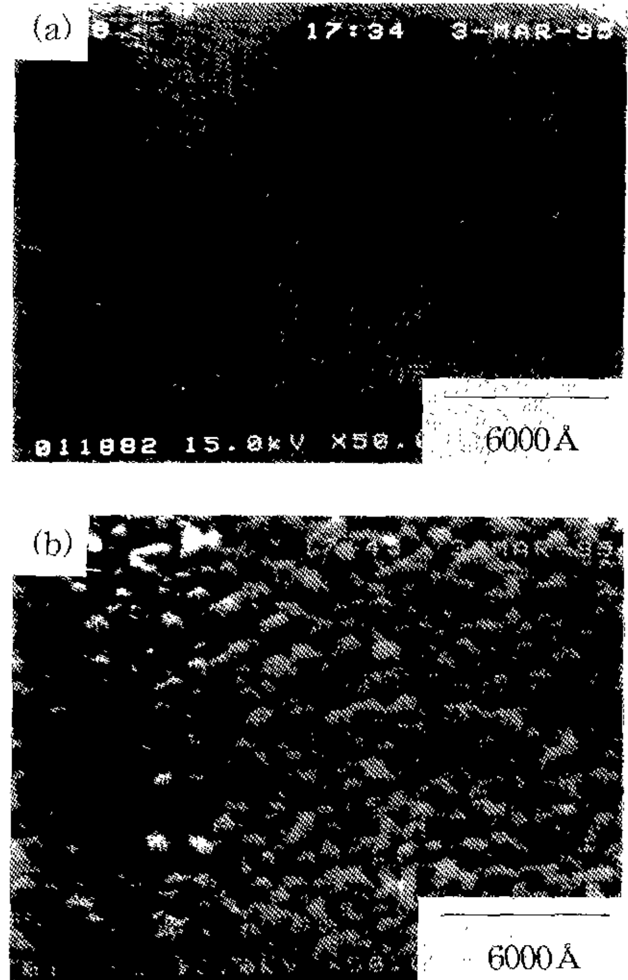

Fig. 6. Surface morphologies of 400Å-thick RuO_2 thin films deposited at 300°C in O_2/Ar ratio of (a) 1/9 and (b) 5/5.

which is observed often in growing of thin films.[7] Comparing the 400Å thick films deposited in O_2/Ar ratio of 1/9(Fig. 6(a)) with 5/5(Fig. 6(b)), 1/9 film is denser and smoother than 5/5 film, which is again related to the number and distribution of nuclei.

3. *Resistivity*

Resistivity of the films deposited at room temperature or 300°C before and after post-annealing is shown in Fig. 7. For the films deposited at room temperature, resistivity decreases slightly as the post-annealing temperature increases due to the densification, but it is still higher than that of the bulk. It is because the RuO_2 phase was not formed clearly even after the post-annealing process as explained previously. Resistivity of the films deposited at 300°C (2000~3000Å thick) ranges from 50 μΩ-cm to 70 μΩ-cm irrespective of annealing temperature and O_2/Ar ratio. The resistivity for the film deposited at 300°C is reproducible and shows a relatively little deviation compared to the films deposited at room temperature. The resistivity of film deposited only by Ar is 10 μΩ-cm and this low value is because of the formation of metallic Ru.

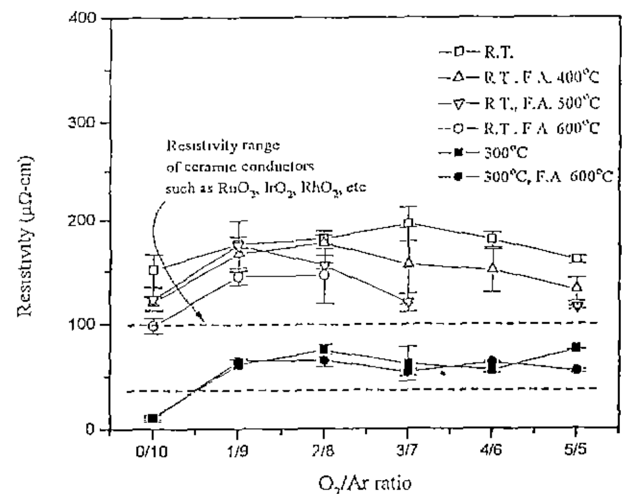

Fig. 7. Dependence of resistivity on the O_2/Ar ratio of RuO_2(or Ru) films deposited at room temperature and 300°C as a function of various process conditions.

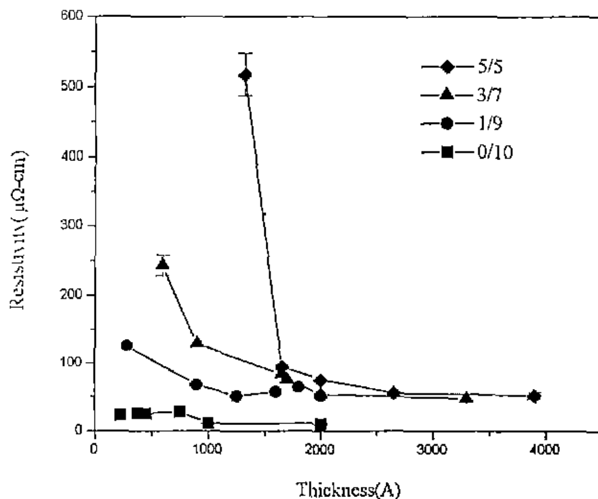

Fig. 8. Dependence of resistivity of RuO_2 films deposited at 300°C on the film thickness.

The variation of resistivity as a function of film thickness is shown in Fig. 8. The onset thickness where the drastic change in resistivity occurs decreases as the oxygen partial pressure decreases. Such shift in onset thickness implys again that the surface morphology governs the electrical property as stated above. Therefore the resistivity of the film deposited in O_2/Ar ratio of 1/9 can be maintained below 150 μΩ-cm even under 500Å. This is a good indication that the surface roughness can be decreased further by reducing the film thickness without loosing the resistivity.

IV. Conclusion

It has been found that the substrate temperature is more critical than the post-anneal condition. The microstructure of RuO_2 films deposited directly on Si substrates varies as a function of O_2/Ar ratio and film thickness. The grain size gets smaller and the film surface becomes smoother as the amount of oxygen and film thickness decrease. Resistivity of RuO_2 films deposited at 300°C ranged from 50 μΩ-cm to 70 μΩ-cm and it was insensitive to the O_2/Ar ratio. As the film thickness decreases the resistivity of the film increases. For the film deposited in O_2/Ar ratio of 1/9, the resistivity was reasonably low even at 500Å.

Consequently, it is recommended to control the oxygen partial pressure as low but not as low to form metallic Ru. By this way, RuO_2 film could be more advantageous being used as an electrode in ferroelectric devices.

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