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Preparation and Characterization of Iridium Oxide Thin Films by DC Reactive Sputtering

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IrO_2 films are deposited by a dc magnetron sputtering method. It is found that IrO_2 films with columnar or equiaxed grain structure are obtained depending on the deposition temperature, oxygen partial pressure, and total pressure. The growth of IrO_2 film is well explained by the generic curve for system pressure as a function of O_2 content during the film deposition. The film shows a good reaction barrier property between Pt and poly-Si even after a furnace annealing at 750 °C.

1. INTRODUCTION

High dielectric thin films including $(Ba,Sr)TiO_3$, $Pb(Zr,Ti)O_3$ have received great interest for micro-electronic applications such as high density DRAMs and ferroelectric RAMs. As the electrodes of capacitors for these RAMs, Pt is widely used because of its excellent oxidation resistance and good electrical conductivity. However, some barrier materials are surely required to apply Pt electrode to conventional silicon process to prevent reaction between Pt and poly-Si. Rf-sputtered IrO_2 films have been suggested as a new electrode and a barrier material for Pt electrode of PZT capacitor.[1] However, few data have been available on the characteristics of the IrO_2 thin films. In this report the growth characteristics of IrO_2 films using reactive dc magnetron sputtering and the feasibility as a reaction barrier layer between Pt and poly-Si are discussed.

2. EXPERIMENTAL

A dc magnetron sputtering machine with 11 inch diameter metal Ir target was used to deposit IrO_2 thin films. 6 inch diameter Si wafers with (100) orientation coated with silicon oxide or doped poly-Si were used as the substrates. The films were reactively deposited in a mixture of Ar and O_2 at substrate temperatures of 25 °C and 200 °C. Total flow rate of Ar plus O_2 was varied from 15 to 25 sccm. The dc power, oxygen partial pressure, and postannealing conditions were varied to obtain the crystallized IrO_2 thin films. The evolutions of phase and morphologies were examined using X-ray diffraction (XRD), and scanning electron microscopy (SEM). The experimental variables are summarized in Table 1.

Table 1 Deposition Conditions

Target size	11 inch diameter
Substrate	SiO_2/Si and poly-Si/SiO_2/Si
Substrate temperature	25 - 200 °C
DC power	0.3 - 1.0 kW
Total gas flow rate	15 - 25 sccm
O_2 concentration	20 - 60 %
Anneal temperature	400 - 600 °C
Anneal ambient	oxygen

3. RESULTS AND DISCUSSION

, The variations of surface morphology and crystalline nature of the film with the sputtering power were first investigated. The sputtered films in a gas mixture of Ar/O_2=12/8 sccm were made under dc power ranging from 1.0 to 0.3 kW. All the deposited films were postannealed at 600 °C for 30 min in O_2 atmosphere. Figure 1 shows tilted-view SEM micrographs, in which the grain structure of the films are varied from nearly columnar to equiaxed one with increasing dc power. Figure 2 shows the XRD spectra. As the dc power increases, the Ir (111) peak becomes dominant and IrO_2 (110) peak vanishes. It is thus understood that the film containing both Ir and IrO_2 phase, whose grain structure is equiaxed, are formed under the high dc power. However, the grains are mostly columnar in the film with only IrO_2 phase. This phenomenon is explained by the generic curve for system pressure as a function of the oxygen gas flow rate.[2] When the oxygen flow rate is small, most of the supplied oxygen molecules are consumed by the oxidation of target or sputtered metal so that the total pressure is not so sensitive to the oxygen flow rate. However, there is an oxygen flow rate over which the total pressure increased almost linearly with increasing oxygen flow rate because all of the oxidizable species are already oxidized and the excess oxygen contributes to the total pressure. Figure 3 shows that the transition point discriminating the low and high oxygen partial pressure region moves to lower oxygen flow rate with decreasing dc power when the Ar flow rate is 12 sccm. In the cases of 0.3 kW and 0.5 kW, the transition points occur at oxygen flow rates of about 5 sccm and 9 sccm, respectively. Above these oxygen flow rates, a con-

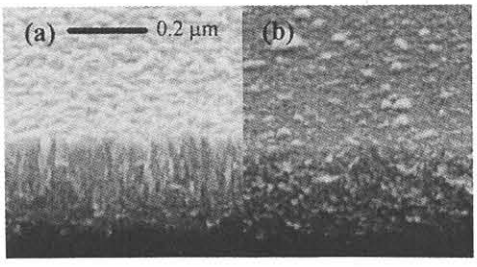

Fig. 1 SEM micrographs of IrO_2 films deposited at dc powers of (a) 0.3 and (b) 0.7 kW.

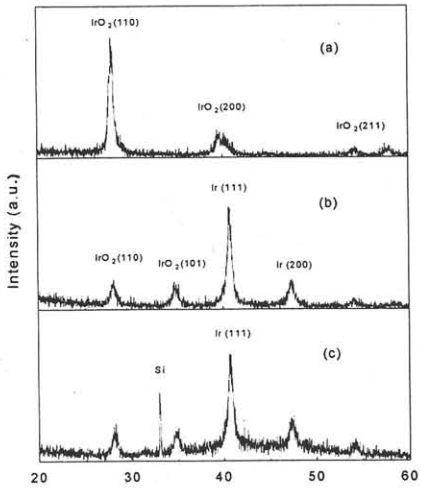

Fig. 2 XRD spectra of IrO_2 films deposited at dc powers of (a) 0.3, (b) 0.7, and (c) 1.0 kW.

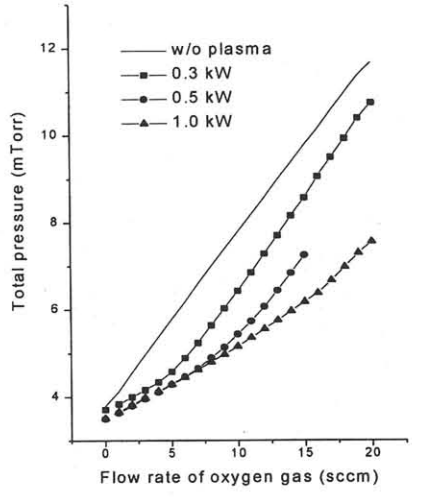

Fig. 3 Generic curves for system pressure as a function of oxygen gas flow rate at the various dc powers. The flow rate of Ar gas was fixed at 12 sccm.

stant volume of oxygen gas is consumed, independent of the flow rate of oxygen, and the formation of a stable oxide is favored. Therefore, only the film deposited at 0.3 kW with the Ar/O_2 ratio of 12/8 shows the stable IrO_2 phase as shown in Fig. 2. Figure 4 shows the XRD spectra of deposited films with different Ar/O_2 flow ratio at dc power of 0.3 kW. A mixed phase of Ir and IrO_2 is observed under 30 % oxygen concentration. Meanwhile, a complete and almost complete IrO_2 phases are obtained under the oxygen concentration of 60 % and 40 %, respectively. Figure 5 shows the SEM micrographs of the films deposited at different oxygen concentrations. The columnar and equiaxed grain structure is shown under the oxygen concentration of 50 % and 30 %, respectively.

Figure 6 shows the effect of deposition temperature and total pressure on the phase formation. The XRD spectra of the films deposited at 200 °C as shown in Figs.

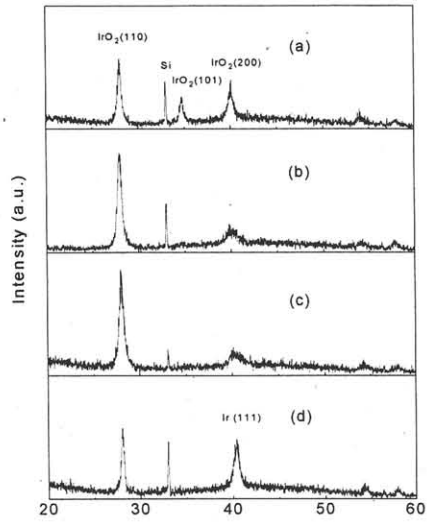

Fig. 4 XRD spectra of IrO_2 films deposited with Ar/O_2 flow ratio of (a) 8/12, (b) 10/10, (c) 12/8, and (d) 14/6.

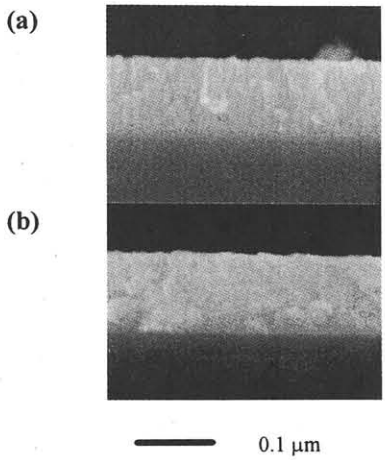

Fig. 5 SEM micrographs of IrO_2 films deposited with Ar/O_2 flow ratio of (a) 10/10 and (b) 14/6.

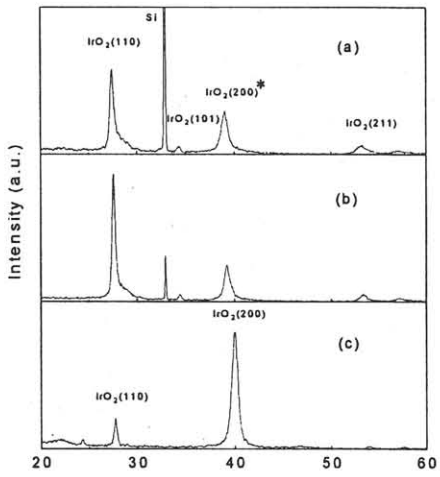

Fig. 6 XRD spectra of IrO_2 films deposited with (a) 0.5 kW, Ar/O_2=12/8 sccm, (b) 0.3 kW, Ar/O_2=14/6 sccm at 200 °C, and (c) 0.3 kW, Ar/O_2=9/6 sccm at 25 °C. The films were annealed at 400 °C, O_2 for 1 h.

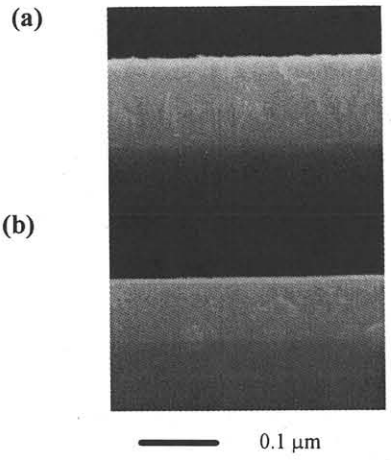

Fig. 7 SEM micrographs of IrO_2 films deposited with (a) 0.5 kW, Ar/O_2=12/8 sccm at 200 °C and (b) 0.3 kW, Ar/O_2=9/6 sccm at 25 °C.

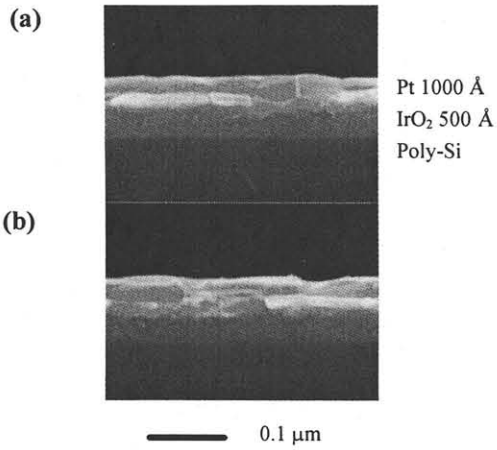

Fig. 8 SEM micrographs of Pt 1000 Å/IrO_2 500 Å/poly-Si/SiO_2/Si: (a) as-deposition and (b) after furnace annealing at 750 °C, N_2 for 30 min.

6(a) and 6(b), show strong IrO_2 (110) peak with a broad peak of IrO_2 (200)*, which is not attributed to the metallic Ir but supposed to be a shifted IrO_2 (200) due to the oxygen deficiency. From these results, it is considered that substrate temperature is a very important parameter when the deposition condition is close to the transition point in the generic curve. On the other hand, it is found that the film with different preferential orientation is deposited under different total pressure, as can be shown from the comparison between Fig. 6(c) and Fig. 4(c). The film with the deposition condition of 0.3 kW, Ar/O_2=9/6 sccm at 25 °C have the IrO_2 (200) preferential orientation. Figure 7 shows SEM pictures of the films in Fig. 6. Fully columnar and fully equiaxed structures are obtained under different deposition conditions. Figure 8 shows the excellent reaction barrier characteristics of the IrO_2 film. A 500 Å thick IrO_2 film sandwiched between 1000 Å thick Pt and 3000 Å thick poly-Si successfully prevents the inter-diffusion between them even after the annealing at 750 °C under N_2 atmosphere for 30 min. This characteristics is also confirmed by Auger electron spectroscopy analysis which is not shown in this report.

4. CONCLUSIONS

IrO_2 thin films are successfully deposited using dc reactive sputtering method. It is found that the crystalline nature, composition and morphology of the deposited films are strongly dependent on the oxygen partial pressure, total pressure, and substrate temperature. Single phase IrO_2 films are preferably obtained under high oxygen partial pressure at high substrate temperature. The film shows good barrier property between Pt and poly-Si up to 750 °C.

5. REFERENCES

1) T. Nakamura, Y. Nakao, A. Kamisawa, and H. Takasu, Appl. Phys. Lett. **65** (1995) 1522.
2) S. M. Rossnagel, J. J. Cuomo, and W. D. Westwood, *Handbook of Plasma Processing Technology*; Noyes, Park Ridge, (1989).