

# Formation process and material properties of reactive sputtered IrO<sub>2</sub> thin films

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## Abstract

IrO<sub>2</sub> thin films were deposited by reactive sputtering in various O<sub>2</sub>/(O<sub>2</sub> + Ar) mixing ratios (OMR). The systematic study of the OMR effect on the properties of IrO<sub>2</sub> thin films has been reported. It was found that the formation of IrO<sub>2</sub> could be classified into two classes, depending on the O<sub>2</sub> flow ratio. At low OMR (10–30%), the Ir target and Si substrate were not oxidized and a high deposition rate and high crystallinity IrO<sub>2</sub> could be obtained. On the other hand, at high OMR (> 30%), the target and Si substrate were oxidized. It resulted in a lower deposition rate of IrO<sub>2</sub> and yielded poor structural properties. Moreover, the high OMR provided O atoms, incorporated into the IrO<sub>2</sub> thin film. This point could be confirmed by X-ray photoelectron spectroscopy. The excess O defects would also make the resistivity of IrO<sub>2</sub> increase as the samples were prepared at high OMR. The effect of substrate temperature on the resistivity was also discussed. It was found that the resistivity of the IrO<sub>2</sub> films decreased with an increase of the substrate temperature and a minimum resistivity of 70 μΩcm was obtained as films deposited at 600°C using 10% OMR. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** IrO<sub>2</sub>; Reactive sputtering; X-ray photoelectron spectroscopy; Resistivity

## 1. Introduction

There is tremendous interest in the development of (Ba, Sr)TiO<sub>3</sub> (BST) thin films as the dielectric material for Gbit dynamic random access memories (DRAMs) because of its high dielectric constant and good insulating properties [1,2]. In order to realize these high-dielectric films in DRAM applications, several integration strategies and processing issues must be investigated. One of the most important considerations is the choice of electrode material. Pt thin films are commonly used as a bottom electrode for high-dielectric capacitors, because they do not readily form an oxide in an oxidizing atmosphere and exhibit low resistivity

and good heat resistance. However, Pt layers have a problem in etching, and require additional diffusion barrier layers. These present obstacles to DRAM cell realization using Pt as the bottom electrode. Recently, other electrodes have been extensively investigated, such as the metallic oxides of transition metals. Dioxides of Ru, Ir, Os, and Rh, all crystallizing in the tetragonal rutile structure, have bulk metallic resistivities ranging from 30 to 100 μΩcm [3]. Among these conductive oxides, IrO<sub>2</sub> has the lowest bulk resistivity (~30 μΩcm). IrO<sub>2</sub> thin films have been successfully prepared by r.f. reactive sputtering. While excellent properties have been previously reported for IrO<sub>2</sub> films [4,5], there is lack of a systematic study of the effect of the O<sub>2</sub>/(Ar + O<sub>2</sub>) mixing ratio (OMR) during r.f. sputtering on the properties of IrO<sub>2</sub> thin films. This paper has focused on the influences of various OMR during the deposition on the deposition rate, crystal structure,

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chemical binding state. The effect of sputtering conditions such as substrate temperature and OMR on the resistivity has also been discussed.

## 2. Experimental

The sputtering target was a 1.5-inch disk of Ir (99.9%) metal. IrO<sub>2</sub> thin films were deposited on the *n*-type Si substrate with (100) orientation by r.f. magnetron sputtering. The Si substrate was cleaned by the standard RCA cleaning process and chemically etched in a dilute HF solution. The sputtering chamber was maintained at a base pressure of  $\sim 2 \times 10^{-7}$  torr by the use of a vacuum load-lock chamber and liquid nitrogen baffle. The substrate temperature during sputtering was varied from room temperature to 600°C. Reactive sputtering was carried out in an OMR which varied from 0 to 100%, keeping a sputtering pressure of  $5 \times 10^{-3}$  torr. In order to clean the target surface, 10 min pre-sputtering in an Ar atmosphere was carried out, followed by 10 min pre-sputtering in the gas mixture used for the deposition, then IrO<sub>2</sub> films were sputter deposited on the substrate. All films were prepared by a fixed power of 80 W and had the same thickness of approximately 200 nm.

The thickness of the film deposited on the Si substrate was determined by a Tencor Alpha step profiler. The crystal structures of Ir and IrO<sub>2</sub> films with the same thickness were determined by X-ray diffraction (XRD) with Cu K $\alpha$  radiation. Resistivity was measured by the four-point probe method. The chemical binding state of the films was investigated from Ir 4f and O 1s spectra obtained by X-ray photoelectron spectroscopy (XPS) using the monochromatic Mg K $\alpha$  radiation. In the XPS analysis, surface XPS spectra without ion etching were used for discussion, because the decomposition of IrO<sub>2</sub> was observed during the Ar ion etching, which was used in order to remove the contaminated layer on the film surface.

## 3. Results and discussion

Fig. 1 shows the deposition rate of the films deposited at room temperature as a function of OMR. Clearly, the deposition rate could be classified into the following three regions: (a) metal region; (b) high deposition-rate oxide region between 10 and 30% OMR; and (c) low deposition-rate oxide region above 30% OMR. At the metal region, only Ir films were formed, and the deposition rate was approximately 9 nm/min. It increased to 20 nm/min in the O<sub>2</sub> flow ratio region between 10 and 30%, at which IrO<sub>2</sub> films were formed. Then it decreased as the OMR was above 30%. The observed increase of the deposition rate from 9 nm/min to 20 nm/min may have been due to the increase of the molar volume, because the molar volume of IrO<sub>2</sub>

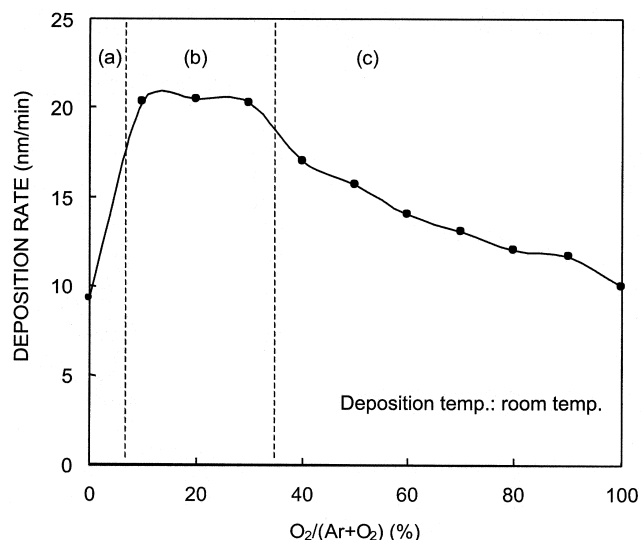


Fig. 1. Deposition rate of the films deposited at room temperature as a function of OMR.

was larger than that of Ir. In region (c), it was generally assumed that the decrease in the deposition rate was correlated to the decrease in the sputtering rate of the target because the compound was formed at the target surface, and O<sub>2</sub> makes the ion efficiency become smaller. This phenomenon is well-known in another reactive sputtering system, i.e. TiN formation in Ar and N<sub>2</sub> gases using a Ti target [6,7].

The corresponding XRD patterns of the samples prepared at room temperature under various OMRs are shown in Fig. 2. A single-phase Ir (cubic structure) was formed at the metal deposition condition and a single-phase IrO<sub>2</sub> (tetragonal structure) was formed above 10% OMR. For the films deposited at 10% OMR, a preferential orientation of the (110) plane was

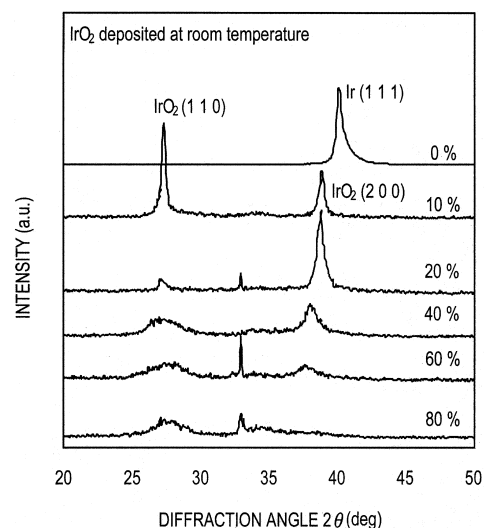


Fig. 2. XRD patterns of the samples prepared at room temperature under various OMR.

observed and the strong peak intensity indicated that  $\text{IrO}_2$  films were well crystallized. This orientation was the same as that obtained from the bulk  $\text{IrO}_2$  material. However, the preferential orientation plane changed from (110) to (200) as the  $\text{IrO}_2$  thin film was deposited at 20% OMR. Furthermore, it was found that the X-ray peaks became broad and weak as the films were deposited above 40% OMR. The (200) features were also shifted to lower angles, whereas the (110) features showed very little change in the peak positions. The increase of the linewidth broadening and the shifting to lower angles of diffraction peaks were attributed to microcrystallinity and local disorder. This means that the films came close to the amorphous or the fine grain structure as the films deposited above this OMR.

By comparing the deposition rate of  $\text{IrO}_2$  and the results of XRD, we were able to deduce the dominant factors that caused the preferential orientation changes and the linewidth broadening. This change in the deposition rate shown in Fig. 1 was attributed to being caused by the difference in the reaction process. In the metal region, Ir atoms were sputtered by a high energy Ar ion from the target and Ir films were deposited on the substrate. However, it is important to mention that the (111) orientation plane was obtained. This may be due to the fact that the Ir atoms that gained energy from the Ar ion had sufficient surface mobility to move to the lowest energy site (even the substrate was maintained at room temperature). It resulted in the lowest energy plane of the Ir (111) crystallinity forming. At OMR = 10%, Ir atoms were sputtered from the target and they reacted with oxygen at the substrate surface. This resulted in  $\text{IrO}_2$  films being deposited. Under these conditions, the Ir atoms still had high surface mobility, the same as that in pure Ar gas, and the lowest energy plane (110) could be obtained. However, at the 20%  $\text{O}_2$  flow, the surface mobility of Ir atoms was lower compared with that at 10% OMR or pure ambient Ar. Thus, the crystallinity formation followed the substrate orientation. It resulted in the (200) orientation being dominant. In the high OMR (above 40%), Ir-oxide layers were formed at the target surface (because the deposition rate decreased) and amorphous  $\text{SiO}_2$  was formed at the Si substrate. On the other hand, the surface mobility of the sputtered atoms obviously decreased. This resulted in the  $\text{IrO}_2$  films deposited by the sputtering of Ir-oxide and  $\text{IrO}_2$  (200) orientation becoming weak and broadening (like an amorphous structure) as the OMR increased. The other reason for the formation of amorphous like film in high  $\text{O}_2$  flow region was the excess oxygen atoms incorporated into the films.

The excess oxygen atoms incorporated into the  $\text{IrO}_2$  films could be confirmed by XPS measurement. Figs. 3 and 4 show the XPS spectra of Ir 4f and O 1s obtained from these  $\text{IrO}_2$  thin films. For the films deposited at

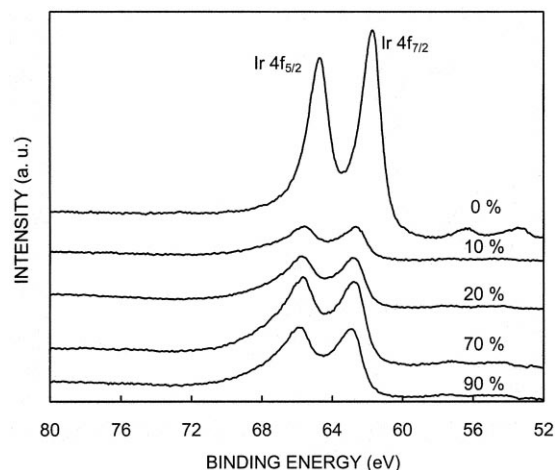


Fig. 3. Ir 4f XPS spectra for the films deposited at various OMR without substrate heating. No Ar ion etching was carried out.

0% OMR, the binding energies of Ir  $4f_{5/2}$  and  $4f_{7/2}$  were 64.7 and 61.7 eV, respectively. They agreed well with the values of pure Ir. For the films prepared above 10% OMR, the binding energy shifted to 65.6 and 62.7 eV for Ir  $4f_{5/2}$  and  $4f_{7/2}$ , respectively, which was consistent with the values of  $\text{IrO}_2$ . It implied that  $\text{IrO}_2$  was formed at 10% OMR. In the O-1s spectrum for the film prepared at 0% OMR, a peak corresponding to adsorbed oxygen was found at approximately 532.3 eV, because no Ar ion etching was carried out. For the films prepared at 10% OMR, the peak intensity increased gradually and the binding energy shifted to 533.4 and 531.2 eV. The 533.4 eV peak energy was attributed to the binding of Ir and O. The 531.2-eV peak was caused by the binding of O atoms to each other. For films prepared above 20% OMR, the binding energy of O 1s decreased to 531.3 or 531.2 eV and became dominating. This means that excess oxygen atoms were incorporated into the films. It would make

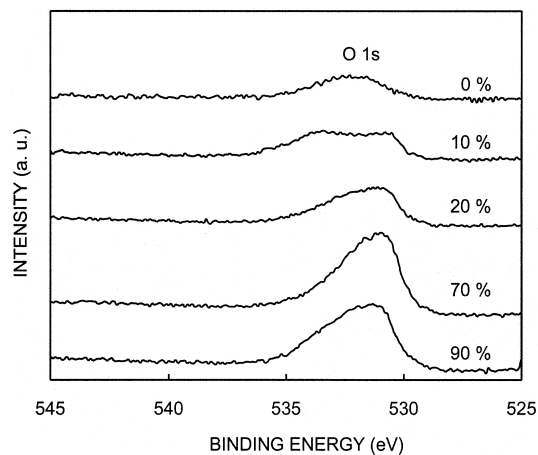


Fig. 4. O 1s XPS spectra for the films deposited at various OMR without substrate heating. No Ar ion etching was carried out.

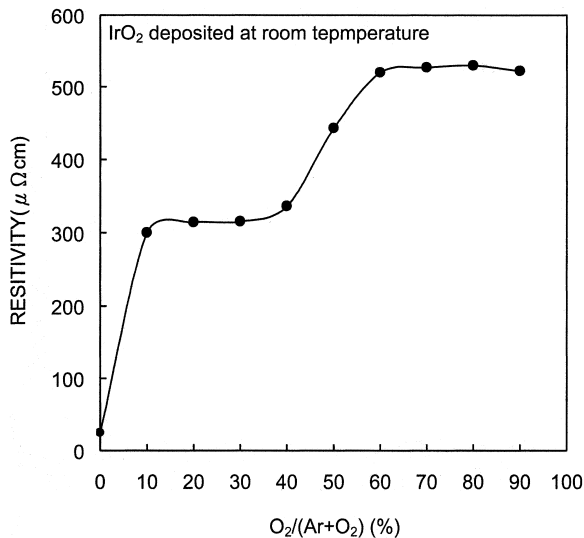


Fig. 5. Resistivity of the films prepared at room temperature as a function of the various OMR.

the IrO<sub>2</sub> present amorphous, which is consistent with the observation of the X-ray measurement.

A primary concern about the IrO<sub>2</sub> thin film is resistivity. Fig. 5 shows the resistivity as a function of the various OMR prepared at room temperature. At pure ambient Ar, the Ir films were formed, the resistivity was approximately 20 μΩcm. At 10–30% O<sub>2</sub> flow, at which the IrO<sub>2</sub> films were formed, the resistivity was approximately 300 μΩcm. Thereafter, the resistivity increases as the O<sub>2</sub> flow ratio increases. Increase of resistivity for the films deposited at above 40% OMR were considered to be caused by the disordered crystal and by the decrease of the grain size as seen from the X-ray data. An increase in impurity scattering due to excess O atoms is also probable.

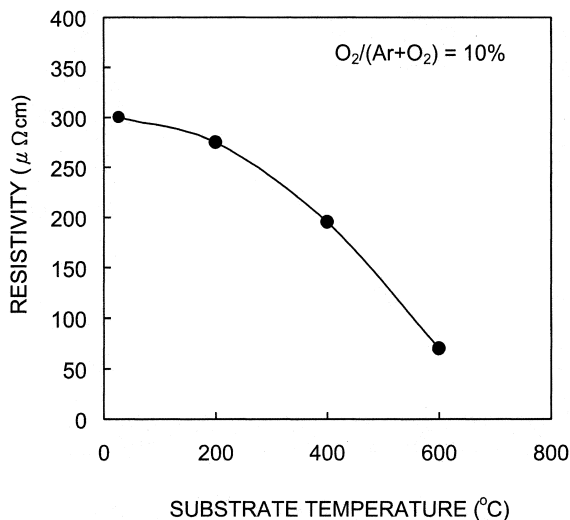


Fig. 6. Resistivity of the IrO<sub>2</sub> films deposited at 10% OMR as a function of substrate temperature.

In order to decrease the resistivity of IrO<sub>2</sub> films, the influence of the substrate temperature was studied under the OMR maintained at 10%. Fig. 6 shows the resistivity of the IrO<sub>2</sub> films deposited at 10% OMR as a function of substrate temperature. Resistivity decreased with an increase in the substrate temperature. The minimum resistivity value obtained was 70 μΩcm at 600°C. As the substrate temperature was increased, the enhancement of the surface mobility was expected to result in the formation of IrO<sub>2</sub> grains with increased size, leading to a reduction in grain boundaries in the IrO<sub>2</sub> films. This would be a plausible explanation of the observed decrease of the film resistivity. Nevertheless, IrO<sub>2</sub> still presented polycrystalline structure, and it resulted in IrO<sub>2</sub> having a higher resistivity than bulk ones.

#### 4. Conclusion

The formation of Ir and IrO<sub>2</sub> films was classified into three regions from the crystal structure and chemical binding state. The reactive process of IrO<sub>2</sub> was mainly classified into two processes. The oxidation of Ir atoms at the substrate surface was dominant in the high deposition-rate oxide region (10–30% OMR). In this region, the deposition rate was as high as 20 nm/min, and crystalline IrO<sub>2</sub> films were obtained. In the low deposition rate oxide region (above 30% OMR), oxidation at the target surface was dominant. In this region, fine grain or amorphous IrO<sub>2</sub> films were obtained. The resistivity of the IrO<sub>2</sub> films prepared at room temperature was minimal in the 10–30% OMR region. The resistivity of the IrO<sub>2</sub> films decreased with an increase in the substrate temperature and minimum resistivity of 70 μΩcm was obtained as the films were deposited at 600°C using 10% OMR.

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