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Formation Process and Material Properties of Reactive Sputtered IrO_2 Thin Films

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IrO_2 thin films were deposited by reactive sputtering in various $O_2/(O_2+Ar)$ mixing ratios (OMR). The formation of IrO_2 could be classified into two classes as depending on the O_2 flow ratio. At low OMR (10 ~30%), the Ir target and Si substrate are not oxidized and high deposition rate and high crystallinity IrO_2 can be obtained. At high OMR (> 30%), the target and Si substrate were oxidized. It results in a lower deposition rate of IrO_2 and yields poor structural properties. Moreover, the high OMR will provide excess O atoms incorporated into IrO_2, and it makes the resistivity of IrO_2 increase as the samples prepared at high OMR. On the other hand, the resistivity of the IrO_2 films decreased with an increase of the substrate temperature and a minimum resistivity of 70 μΩcm was obtained as films deposited at 600 ^oC using 10% OMR.

1. Introduction

There are tremendous interests in the development of (Ba, Sr)TiO_3 (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 DRAMs application, several integration strategies and processing issues must be investigated.

One of the most important considerations is the choice of electrode material. Pt thin film is commonly used as a bottom electrode for the high-dielectric capacitors, because it does not readily form an oxide in an oxidizing atmosphere and exhibits low resistivity and good heat resistance. However, Pt layer has a problem in etching and requires 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 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_2 has the lowest bulk resistivity (~30 μΩcm). IrO_2 thin films have been successfully prepared by rf reactive sputtering. While excellent properties have been previously reported for IrO_2 films [4,5], there is lack of a systematic study of the effect of the $O_2/(Ar + O_2)$ mixing ratio (OMR) during rf sputtering on the properties of IrO_2 thin films.

This paper focuses on the influences of various OMR during the deposition on the deposition rate, crystal structure, chemical binding state. The effect of sputtering conditions such as substrate temperature and OMR on the resistivity is also discussed.

2. Experimental

The sputtering target was a 1.5-inch disk of Ir (99.9%) metal. IrO_2 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 ~ 2×10^{-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 ^oC.

Reactive sputtering was carried out in an OMR varied from 0 to 100%, keep a sputtering pressure of 5×10^{-3} Torr. In order to clean the target surface, 10 min pre-sputtering in Ar atmosphere was carrier out followed by 10 min pre-sputtering in the gas mixture used for the deposition, then IrO_2 films were sputter deposited on the substrate. All films were prepared by a fixed power of 80 W and have the same thickness of about 200 nm.

The thicknesses of the films deposited on the Si wafers were determined by a Tencor Alpha-step profiler. Crystal structures of Ir and IrO_2 films with the same thickness were determined by X-ray diffraction (XRD) with Cu Kα 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 Kα radiation. In the XPS analysis, surface XPS spectra without ion etching were used for discussion, because the decomposition of IrO_2 was observed during the Ar ion etching, which was used in order to remove the contaminated layer on the film surface.

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3. Results and discussion

Figure 1 shows the deposition rate of the films deposited at room temperature as a function of OMR. Clearly, the deposition rate can be classified into the following three regions: (a) metal region, (b) high deposition-rate oxide region between 10~30% OMR, and (c) low deposition-rate oxide region above 30% OMR. At metal region, only Ir films were formed, the deposition rate is around 9 nm/min. It increases to 20 nm/min in the O_2 flow ratio region between 10 and 30%, at which IrO_2 films were formed. Then it decreases as the OMR is above 30%. The observed increase of the deposition rate from 9 nm/min to 20 nm/min may be due to the increase of the molar volume, because the molar volume of IrO_2 is larger than that of Ir. In region (c), it is generally assumed that the decrease in the deposition rate is correlated to the decrease in the sputtering rate of the target because the compound was formed at the target surface and O_2 makes the ion efficiency become smaller. This phenomenon has been well known in another reactive sputtering system, *e.g.* TiN formation in Ar and N_2 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) is formed at the metal deposition condition and a single-phase IrO_2 (tetragonal structure) is formed above 10% OMR. For the films deposited at 10% OMR, a preferential orientation of the (110) plane is observed and the strong peak intensity indicates that IrO_2 films are well crystallized. This orientation is the same as that obtained from bulk IrO_2 material. However, the preferential orientation plane

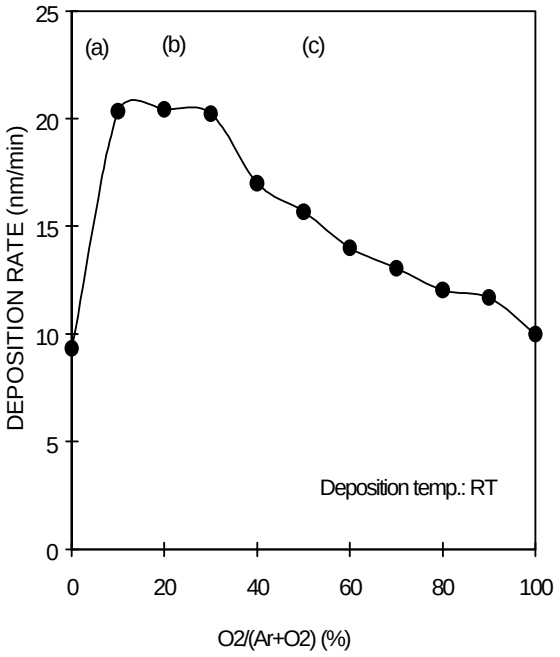

Fig. 1. Deposition rate of the films deposited at room temperature as a function of OMR.

changes from (110) to (200) as the IrO_2 thin film deposited at 20% OMR. Furthermore, it was found that the X-ray peaks become broad and weak as the films deposited above 40% OMR. Not only, the (200) features are also shifted to lower angles whereas the (110) features show very little change in the peak positions. The increase of the linewidth broadening and the shifting to lower angles of diffraction peaks are attributed to microcrystallinity and local disorder. This means that the films come close to the amorphous or the fine grain structure as the films deposited at above this OMR.

By comparing the deposition rate of IrO_2 and the results of XRD, it is able to deduce the dominant factors that cause the preferential orientations change and the linewidth broadening.

This change of the deposition rate shown in Fig. 1 is attributed to being caused by the difference of reaction process. In the metal region, Ir atoms are sputtered by high energy Ar ion from the target and Ir films are deposited on the substrate. However, it was worthy to mention that the (111) orientation plane was obtained. It may be due to the fact that the Ir atoms obtained energy from Ar ion and has sufficient surface mobility to move to the lowest energy site (even the substrate is maintained at room temperature). It results in the lowest energy plane of the Ir (111) crystallinity forming. As the small amount O_2 (10%) instead of Ar gas, Ir atoms are sputtered from the target and they react with oxygen at the substrate surface. This results in IrO_2 films being deposited. In this condition, the Ir atoms still have high surface mobility as the same as that in the pure Ar gas

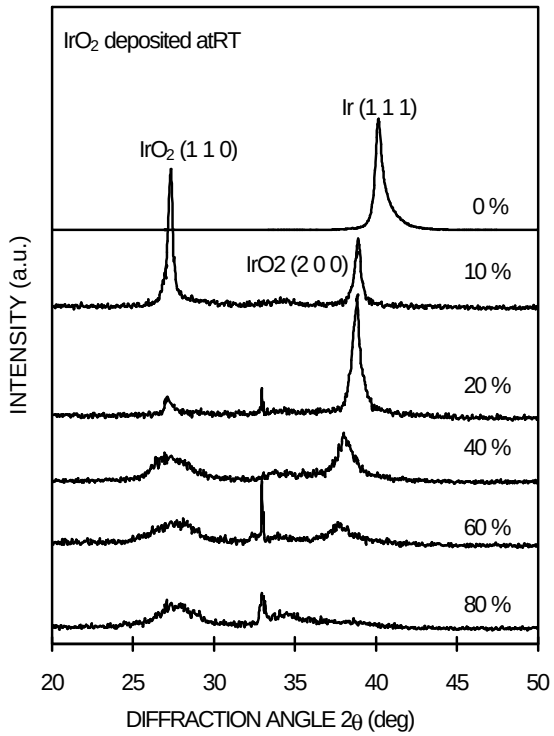

Fig. 2 XRD patterns of the samples prepared at room temperature under various OMR.

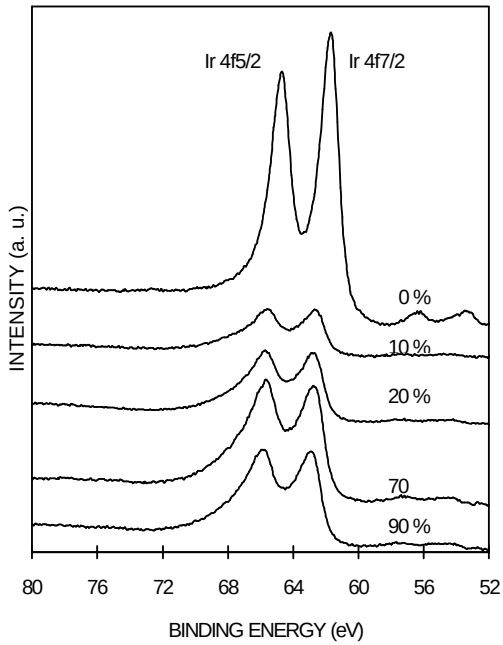

Fig. 3 Ir 4f XPS spectra for the films deposited at various OMR without substrate heating. No Ar ion etching was carried out.

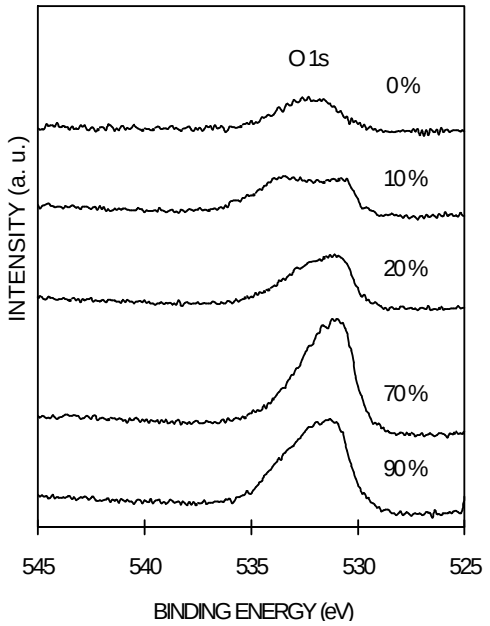

Fig. 4 O 1s XPS spectra for the films deposited at various OMR without substrate heating. No Ar ion etching was carried out.

and the lowest energy plane (110) can be obtained. However, at the 20% O_2 flow, the surface mobility of Ir atoms is lower as compared with that at the 10% OMR or pure Ar ambient.

Thus the crystallinity formation follows the substrate orientation. It results in the (200) orientation being dominant. In the high OMR (above 40 %), Ir-oxide layers are formed at the target surface (because the deposition rate decreases) and amorphous SiO_2 are formed at the Si substrate.

On the other hand, the surface mobility of sputtered atoms is obviously decreased. These result that the IrO_2 films are deposited by the sputtering of Ir-oxide and IrO_2 (200) orientation becomes weak and broaden (like amorphous structure) as the OMR increases. The another reason for the formation of amorphous like film in high O_2 flow region is caused by excess oxygen atoms incorporated into the films.

As concerning excess oxygen atoms incorporated into the IrO_2 films, it can be confirmed by XPS measurement. Figure 3 and 4 show the XPS spectra of Ir 4f and O 1s obtained from these IrO_2 thin films. For the films deposited at 0% OMR, the binding energies of Ir $4f_{5/2}$ and $4f_{7/2}$ are 64.7 eV and 61.7 eV, respectively. They agree well with the values of pure Ir. For the films prepared above 10% OMR, the binding energy shifted to 65.6 eV and 62.7 eV for Ir $4f_{5/2}$ and $4f_{7/2}$, respectively, which is consistent with the values of IrO_2.

It implied that IrO_2 has been formed at the 10% OMR. In the O 1s spectrum for the film prepared at 0 % OMR, a peak corresponding to adsorbed oxygen was found around 532.3 eV, because no Ar ion etching was carrier out. For the films prepared at 10% OMR, the peak intensity increased gradually and binding energy shifted to 533.4 and 531.2 eV.

The 533.4 eV peak energy is attributed to the binding of Ir and O. The 531.2 eV peak is caused by the binding of O atom and O atom. For films prepared above 20% OMR, the binding energy of O 1s decreased to 531.3 or 531.2 eV and becomes dominating. This means that excess oxygen atoms were incorporated into the films. It will make the IrO_2 present amorphous, which is consistent with the observation of X-ray measurement.

A primary concern about the IrO_2 thin film is the resistivity. Figure 5 shows the resistivity as a function of the various OMR prepared at room temperature. At pure Ar ambient, the Ir films were formed, the resistivity was around 20 μΩcm. At 10~30 % O_2 flow, at which the IrO_2 films were formed, the resistivity was about 300 μΩcm. Thereafter, the resistivity increases as the O_2 flow ratio increases. Increase of resistivity for the films deposited at above 40% OMR are considered to be caused by the disordered crystal and by the decrease of the grain size as seen from the X-ray data. Increase of impurity scattering due to excess O atoms is also probable.

In order to decrease the resistivity of IrO_2 films, the influence of substrate temperature was studied under the OMR maintained at 10%.

Figure 6 shows the resistivity of the IrO_2 films deposited at 10% OMR as a function of substrate temperature. Resistivity decreases with an increase of the substrate temperature.

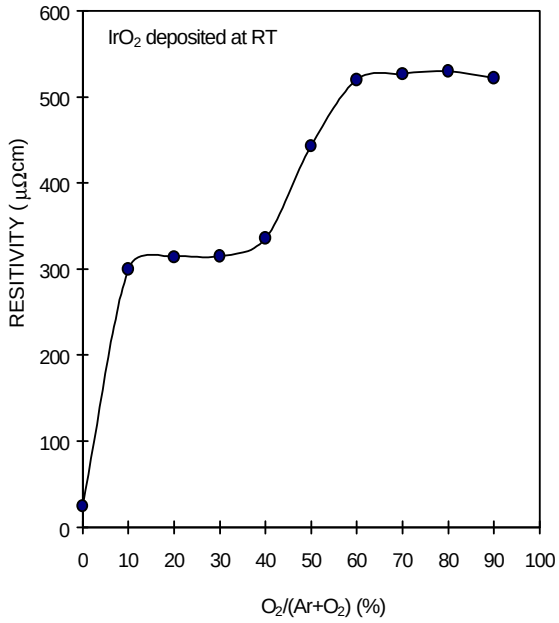

Fig. 5 Resistivity of the films prepared at room temperature as a function of the various OMR.

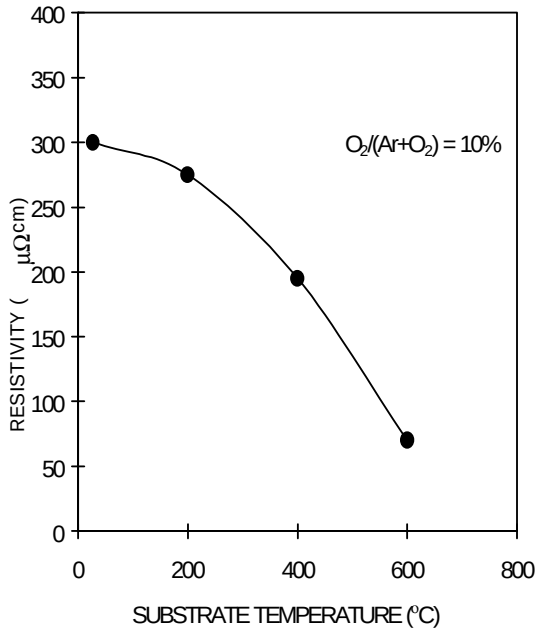

Fig. 6 Resistivity of the IrO_2 films deposited at 10 % OMR as a function of substrate temperature.

The minimum resistivity value obtained was 70 μΩcm at 600 °C. As the substrate temperature is increased, the enhancement of the surface mobility is expected to result in the formation of IrO_2 grains with increased size, leading to a reduction of grain boundaries in the IrO_2 films.

This would be a plausible explanation of the observed decrease of the film resistivity. Nevertheless, the IrO_2 still presents polycrystalline structure, and it results that the IrO_2 has higher resistivity than bulk ones.

4. Conclusions

The formation of Ir and IrO_2 films was classified into three regions from the crystal structure and chemical binding state. Reactive process of IrO_2 was mainly classified into two processes. 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 well crystalline IrO_2 films were obtained. In the low deposition rate oxide region (above 30% OMR), oxidation at the target surface was dominant. In this region, the fine grain or amorphous IrO_2 films were obtained.

The resistivity of the IrO_2 films prepared at room temperature was minimum in the 10~30% OMR. The resistivity of the IrO_2 fi
in the substrate temperature and minimum resistivity of 70 μΩ cm was obtained as the films deposited at 600°C using 10 % OMR.

Acknowledgement

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