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Thermal stability of pulsed laser deposited iridium oxide thin films at low oxygen atmosphere

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ABSTRACT

Iridium oxide (IrO_2) thin films have been regarded as a leading candidate for bottom electrode and diffusion barrier of ferroelectric capacitors, some process related issues need to be considered before integrating ferroelectric capacitors into memory cells. This paper presents the thermal stability of pulsed laser deposited IrO_2 thin films at low oxygen atmosphere. Emphasis was given on the effect of post-deposition annealing temperature at different oxygen pressure (P_{O2}) on the crystal structure, surface morphology, electrical resistivity, carrier concentration and mobility of IrO_2 thin films. The results showed that the thermal stability of IrO_2 thin films was strongly dependent on the oxygen pressure and annealing temperature. IrO_2 thin films can stably exist below 923 K at P_{O2} = 1 Pa, which had a higher stability than the previous reported results. The surface morphology of IrO_2 thin films depended on P_{O2} and annealing temperature, showing a flat and uniform surface for the annealed films. Electrical properties were found to be sensitive to both the annealing temperature and oxygen pressure. The room-temperature resistivity of IrO_2 thin films with a value of 49–58 μΩ cm increased with annealing temperature at P_{O2} = 1 Pa. The thermal stability of IrO_2 thin films as a function of oxygen pressure and annealing temperature was almost consistent with thermodynamic calculation.

1. Introduction

The development of diffusion barrier materials preventing the silicidation as well as the diffusion of oxygen is an important integration issue in dynamic random access memories (DRAMs) and ferroelectric random access memories (FeRAMs) [1]. Iridium oxide (IrO_2) belongs to the family of electrically conductive transition metal dioxides crystallized in a tetragonal rutile structure. Owing to its conductive nature, high chemical stability, and effective diffusion barrier for oxygen, IrO_2 thin film has been regarded as a leading candidate for the bottom electrode of ferroelectric capacitors even though its material cost is relatively high [2–4]. However, some process related issues, such as the thermal stability of IrO_2 thin films in various ambient, need to be considered before integrating ferroelectric capacitors into memory cells.

In accordance with these diverse applications, there is a growing need to develop easy and reliable methods for growing IrO_2 thin films. Various methods, such as reactive magnetron sputtering [5,6], pulsed laser deposition [7], sol–gel [8], chemical vapor deposition [9], and thermal preparation [10], have been employed for this purpose. However, most of those studies were mainly focused on the fabrication process or properties of IrO_2 thin films. It was reported that IrO_2 thin film is thermally stable maintaining its phase up to a high temperature of 1073 K under oxygen ambient of atmospheric pressure [11]. It was also reported that IrO_2 thin film was dissociated under a certain annealing condition, especially at low pressure, and lost its diffusion barrier property [12]. In the practical application of IrO_2 thin films as the bottom electrode of $Pb(Zr,Ti)O_3$ (PZT) and $(Ba,Sr)TiO_3$ (BST) ferroelectric capacitors, the decomposition of IrO_2 is a notable phenomenon because it is usually heated (about 873 K) at a low oxygen pressure (about 1 Pa) prior to depositing PZT or BST films [13,14]. Therefore, the thermal stability of the bottom electrode in such high-temperature deposition at low oxygen pressure must be investigated.

At present, the thermal stability under low oxygen pressure (P_{O2}) of IrO_2 films prepared by sputtering and thermal oxidation has received much attention. Cha [15] studied the deoxidization phenomenon of sputtered IrO_2 films and pointed that IrO_2 films deoxidized at 873 K under P_{O2} = 2.66 Pa. Sanjines [16] had shown that sputtered IrO_2 films decomposed at about 673 K in air and 473 K in vacuum. Peuckert [17] determined that thermally prepared oxide layers on iridium decomposed between 850 and 900 K in ultrahigh vacuum. The influence of oxygen partial pressure during deposition and annealing process on the physical properties of conducting films is important since the oxygen vacancies played as electrical donors in conducting oxide films [18]. Although there is

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much experimental proof that annealing conditions under low oxygen pressure can significantly affect the thermal stability of IrO_2 films, systematic studies of the effect of annealing conditions in those vacuum ambient on the microstructure as well as electrical resistivity of IrO_2 films are still quite limited.

Compared with other preparation methods, pulsed laser deposition (PLD) technique is regarded as one of the most effective ways due to its uniformity, reproducibility and simplicity, showing the highest conductivity in the literature focused on IrO_2 films [19]. However, as far as we know, the thermal stability of pulsed laser deposited IrO_2 films at low oxygen atmosphere has never been reported in the literature.

In the previous study, we have reported the preparation of IrO_2 thin films by PLD technique [20], and the post-deposition annealing in air ambient of IrO_2 thin films were also reported [21]. In the present study, the thermal stability of pulsed laser deposited IrO_2 thin films with annealing temperature and oxygen pressure were systematically investigated to understand the effect of the structure changes caused by various oxygen partial pressures during annealing process on the electrical property modifications. Moreover, thermodynamic analysis was used to explain the experimental results.

2. Experimental

IrO_2 thin films with a thickness of about 500 nm were deposited on Si (1 0 0) substrates by a PLVD-362 equipment using a target of iridium metal. IrO_2 films were reactively deposited under a substrate temperature of 773 K and P_{O2} = 20 Pa at an energy density of 2.0×10^4 mJ/cm^2. The detailed experimental conditions were described elsewhere [13]. To investigate its thermal stability in vacuum ambient, the deposited IrO_2 films were subjected to an in situ annealing process (773–973 K for 30 min) in vacuum as a function of P_{O2} (1–20 Pa).

The crystal structure of the as-deposited and annealed films was examined by X-ray diffractometer (XRD) using the 2θ–θ scan with Cu Kα radiation. The surface morphology was investigated by field emission scanning electron microscopy (FESEM). Atom force microscopy (AFM) was used to measure the surface morphology and roughness of the films, operated in tapping mode. The electrical resistivity, carrier concentration and carrier mobility of IrO_2 thin films were measured at room temperature by Hall measurement with the van der Pauw method.

3. Results and discussion

According to our previous study, IrO_2 films can stably existed up to a high temperature of 1073 K in an air atmosphere [21]. However, such an excellent thermal stability of IrO_2 can be affected by P_{O2} and annealing temperature (T_{ann}) during annealing process. Fig. 1 shows the XRD patterns of IrO_2 films with the annealing temperature during various ambient. As shown in these XRD patterns, it is found that IrO_2 films are maintained up to only 973 K at P_{O2} = 20 Pa. When the annealing temperature decreases to 873 K, the IrO_2 phase remains stable at P_{O2} = 1 Pa or higher. At vacuum ambient (<10^{-5} Pa), IrO_2 is completely reduced to Ir, whereas IrO_2 phase still remains stable at an annealing temperature of 773 K. These results suggest that IrO_2 phase may be thermally unstable at low P_{O2} and the decomposition temperature decreased with decreasing P_{O2}.

The decomposition phenomenon of IrO_2 under low P_{O2} may bring about the losing of its ability as a diffusion barrier in the application of IrO_2 films as a diffusion barrier of BST capacitors on poly-Si [15], which is usually deposited at a temperature of 773–873 K under low P_{O2} (about 1 Pa), thus it is necessary to

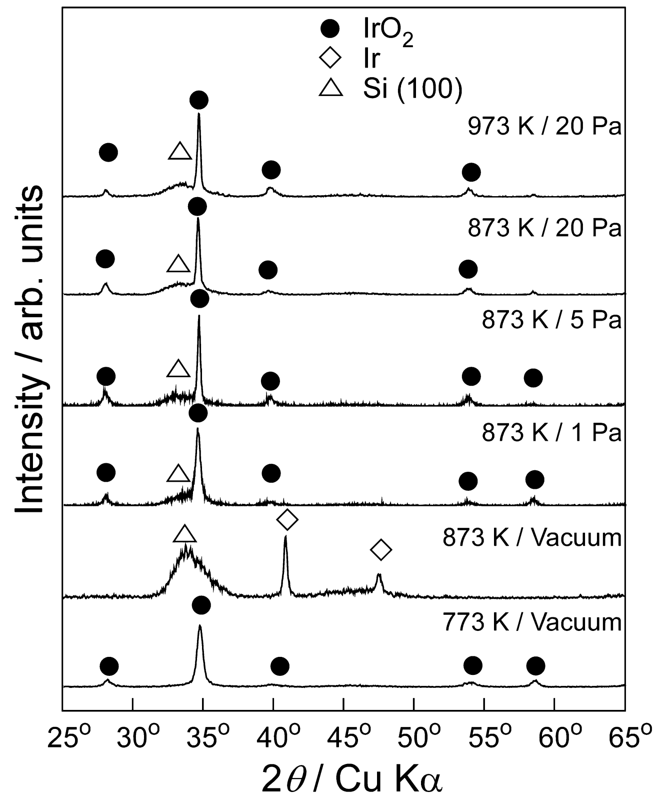

Fig. 1. X-ray diffraction patterns of IrO_2 films deposited on 773 K after being annealed at different conditions.

identify the stably existed temperature at low P_{O2} for PLD IrO_2 films. Fig. 2 shows the XRD patterns of IrO_2 films deposited at 773 K after being annealed at P_{O2} = 1 Pa under different temperatures. As it can be seen, IrO_2 films remains stable at an annealing temperature of 823–923 K under P_{O2} = 1 Pa, which can satisfy the requirement of the application of IrO_2 films in BST capacitors. However, when the annealing temperature was increased to 973 K, IrO_2 peaks entirely disappear, and only Ir peaks exist, indicating that the pulsed laser deposited IrO_2 films remain stable below 923 K at P_{O2} = 1 Pa. The IrO_2 films in the present study have a higher thermal stability than the previous reports [15–17].

For the optimized IrO_2 films in low oxygen pressure, the changes of film microstructure and properties after being annealed were investigated. The surface morphology of the deposited IrO_2 thin films at 773 K and annealed films at 873–973 K under P_{O2} = 20 Pa are presented in Fig. 3. As can be seen that the surface of the deposited IrO_2 films existed with much porosity, while the surface became more solidified and homogeneous after being annealed at 873–973 K. The average grain size was about 55 nm for deposited IrO_2 films, while the grain size of the annealed films at 873 K, 923 K, 973 K were about 80 nm, 85 nm, and 100 nm, respectively (Fig. 3(b–d)), showing a little increase in the grain size with increasing annealing temperature. The increase in IrO_2 average grain size with the increasing annealing temperature can be related to the interface merging processes induced by the thermal annealing [22], enhancing the interaction among the seed particles and causing the formation of bigger IrO_2 seeds. This phenomenon was consistent with the results of annealed IrO_2 films in air ambient [21].

Fig. 4 presents the effect of annealing temperature (T_{ann}) at P_{O2} = 1 Pa on surface morphology of IrO_2 films deposited at 773 K. Compared with the deposited films (Fig. 3(a)), the image showed a flat and uniform surface. However, at P_{O2} = 1 Pa, the average grain size of IrO_2 was about 45 nm for T_{ann} = 773 K, and 50–60 nm