Effect of annealing conditions on formation of SrRuO$_3$ films by interfacial reaction of SrO/RuO$_2$ bi-layer films

Ji-Hoon Ahn$^{a,*}$, Ja-Yong Kim$^{b,*}$

$^a$ Department of Electronic Material Engineering, Korea Maritime and Ocean University, 727 Taejong-ro, Yeongdo-gu, Busan 49112, Republic of Korea
$^b$ Research & Development Division, SK Hynix Semiconductor Inc., San 136-1, Ami-ri, Bubal-eub, Icheon-si, Kyoungki-do 467-701, Republic of Korea

Abstract

In this study, we investigated the effect of annealing conditions on the formation of SrRuO$_3$ films by the interfacial reaction of SrO/RuO$_2$ bi-layer films. We found that the annealing temperature and thickness of the SrO layer along with the annealing atmosphere were critical variables in the formation of the conformal SrRuO$_3$ film. By annealing SrO(20 nm)/RuO$_2$ bi-layer film at 700 °C in O$_2$ atmosphere at 1 Torr, the conformal SrRuO$_3$ film was formed. Finally, we evaluated the potential applicability of the SrRuO$_3$ film as a functional electrode for perovskite-structured dielectrics, and the dielectric constant of SrTiO$_3$ thin films deposited on the SrRuO$_3$ electrode increased by almost 2.5 times in comparison with that of a film on a Ru electrode.

1. Introduction

As the size of dynamic random access memory (DRAM) has been scaled down, perovskite-structured dielectric materials, such as SrTiO$_3$, have received considerable attention as DRAM capacitor dielectrics due to their high dielectric constant [1–4]. However, it is known that the dielectric constant of a SrTiO$_3$ film decreases abruptly due to inadequate crystallinity when the thickness decreases to a range applicable for a DRAM capacitor [5–6]. SrRuO$_3$ is a conductive oxide, which has a pseudo-cubic perovskite structure with a lattice constant of 3.93 Å, and the lattice mismatch between SrTiO$_3$ and SrRuO$_3$ is roughly 0.5% (whereas the lattice constant of perovskite-SrTiO$_3$ is 3.91 Å) [7]. Therefore, the SrRuO$_3$ film can be used as a functional bottom electrode to enhance the crystallinity and dielectric properties of perovskite-structured dielectrics in metal-insulator-metal (MIM) capacitors [8–10]. Furthermore, according to the International Technology Roadmap for Semiconductors, the combination of the perovskite-structured dielectric film and the SrRuO$_3$ thin film as a bottom electrode is the only potential solution for sub-15-nm-feature DRAM. Therefore, research on the deposition of conformal SrRuO$_3$ thin film is as important as developing new high-k materials with regards to continuous scaling of DRAM technology.

In this study, we investigated the effect of annealing conditions on the formation of SrRuO$_3$ films by the interfacial reaction of SrO/RuO$_2$ bi-layer films, because it is known that Ru or RuO$_2$, which is a component of SrO/Ru$_2$, is a redox active material and thermally unstable [11–12]. We also evaluated the potential applicability of the SrRuO$_3$ film as a functional electrode for perovskite-structured dielectrics.

2. Experimental details

SrRuO$_3$ thin films were prepared by the deposition of a SrO layer on a 30-nm-thick layer of RuO$_2$ (SrO/RuO$_2$ bi-layer stack) and post-annealing. RuO$_2$ film acted as the first layer and was formed by atomic layer deposition (ALD) on a SiO$_2$ substrate using Ru(EtCp)$_2$ [Ru(C$_2$H$_4$C$_6$H$_4$)$_2$] and oxygen at 230 °C. Ru(EtCp)$_2$ vapor was carried in argon gas though a bubbler at 50 °C. After RuO$_2$ deposition, a SrO layer was deposited by plasma-enhanced atomic layer deposition (PEALD) using Sr(DPM)$_2$ [Sr(C$_3$H$_7$O$_2$)$_2$] and oxygen plasma at 225 °C. Sr(DPM)$_2$ was dissolved in butyl acetate (0.2 M) and supplied to the reaction chamber by a liquid delivery system. After deposition of the SrO/RuO$_2$ bi-layer stacks, deposited samples were annealed to investigate the effect of the annealing conditions on SrRuO$_3$ formation.

X-ray diffraction (XRD, Rigaku) analysis using Cu K$_\alpha$ radiation ($\lambda = 1.5405$ Å) was used to determine the crystal structures of the annealed SrO/RuO$_2$ bi-layer samples. The morphology and surface roughness were observed using scanning electron microscopy (SEM, Hitachi S-4800) and atomic force microscopy (AFM, SPA400), respectively. To examine the dielectric properties of SrTiO$_3$ thin films (detailed deposition conditions were reported in a previous paper [3]), sputtered Pt dots were used as a top electrode, and the dielectric constant was measured using a C-V analyzer (Keithley 590) at a frequency of 1 MHz.
3. Results and discussion

First, we investigated the effect of annealing atmosphere and temperature on the formation of the SrRuO$_3$ film from 20-nm-thick SrO and 30-nm-thick RuO$_2$ bi-layer stacks. In a N$_2$ atmosphere, as shown in Fig. 1a, it was observed that the RuO$_2$ layer at the bottom of the bi-layer stack was reduced to metallic Ru. Therefore, it was impossible to obtain the SrRuO$_3$ film though annealing in the N$_2$ atmosphere.

However, in an O$_2$ atmosphere, the SrRuO$_3$(100) peak was observed at an annealing temperature of 700 °C, and there was no serious degradation of the morphology due to SrRuO$_3$ formation after annealing, as shown in Fig. 2. When the annealing temperature increased to 800 °C, all the peaks of RuO$_2$ and SrRuO$_3$ disappeared, and it was confirmed that the deposited SrO/RuO$_2$ bi-layer was removed, as shown in Fig. 1b. These results might be due to complete etching of the RuO$_2$ bottom layer after annealing under those conditions, because RuO$_2$ films can decompose to RuO$_4$, a volatile oxide, at such a high temperature [12].

Fig. 1. XRD patterns of SrO(20 nm)/RuO$_2$(30 nm) bi-layer stack and samples annealed in a temperature range from 600 to 800 °C in a (a) 1 Torr N$_2$ atmosphere and (b) 1 Torr O$_2$ atmosphere for 10 min.

Fig. 2. Tilted SEM images of SrO(20 nm)/RuO$_2$(30 nm) at various annealing temperatures in an O$_2$ atmosphere. (a) As-dep, (b) 700 °C, (c) 800 °C.

Fig. 3. (a) Annealing pressure dependence of XRD patterns and (b) the RMS roughness change of SrO(20 nm)/RuO$_2$(30 nm) bi-layer stack. All annealing processes were conducted in an O$_2$ atmosphere at 700 °C for 10 min.

Fig. 2c. These results might be due to complete etching of the RuO$_2$ bottom layer after annealing under those conditions, because RuO$_2$ films can decompose to RuO$_4$, a volatile oxide, at such a high temperature [12].

Fig. 3a shows the annealing pressure dependence of the XRD patterns when SrO(20 nm)/RuO$_2$(30 nm) bi-layer stacks were annealed in the O$_2$ atmosphere at 700 °C for 10 min. In vacuum annealing, the RuO$_2$ bottom layer changed to Ru, similar to the case of annealing in the N$_2$ atmosphere, and the intensity of the SrRuO$_3$ peak increased with annealing pressure. However, as shown in Fig. 3b, the root-mean-square (RMS) roughness measured by AFM also increased with annealing pressure. In other words, although the crystallinity of the SrRuO$_3$ film improved by increasing the annealing temperature to 10 Torr, the surface morphology was roughened, which can degrade the electrical properties of dielectric materials. Therefore, it is thought that the optimum annealing condition for the formation of the SrRuO$_3$ film is 700 °C in a 1 Torr O$_2$ atmosphere.

Next, we investigated the effect of the thickness of the SrO upper layer on the formation of SrRuO$_3$ film. Fig. 4a shows the XRD patterns of annealed SrO/RuO$_2$(30 nm) bi-layer stack films with variation of
the SrO layer thickness, and the SrRuO3 peak was observed, regardless of the thickness of the upper SrO layer. However, when the SrO thickness was less than 10 nm, as shown in Fig. 4b, the SrO/RuO2 bi-layer stack was partially etched, and a morphology-like morphology was observed. Based on these observations, Fig. 5 schematically shows the formation of SrRuO3 films through the interfacial reaction between SrO and the RuO2 layer. When the thickness of the SrO upper layer is sufficient to cover the entire surface without exposing the RuO2 bottom layer during the interfacial reaction, the conformal SrRuO3 film can be formed without serious morphological damage. However, when the SrO thickness decreases to less than 10 nm, as shown in Fig. 5b, the thickness of the SrO upper layer is insufficient to protect the RuO2 bottom layer, and the RuO2 layer is partially exposed during the annealing process. It is thought that the mushroom-like morphology is formed because etching of RuO2 occurs in the partially exposed regions. Therefore, to obtain conformal SrRuO3 films, the thickness of the SrO layer deposited on RuO2 should be thicker than a specified thickness to avoid etching damage, which, in our case, is about 20 nm.

Finally, to evaluate the applicability of the SrRuO3 film as a functional electrode for perovskite dielectrics, the dielectric properties of a 15-nm-thick SrTiO3 film deposited on SrRuO3 films, formed by annealing a SrO(20 nm)/RuO2(30 nm) bi-layer in a 1 Torr O2 atmosphere at 700 °C for 10 min.

(a)

(b)
underwent rapid thermal annealing at 600 °C for 10 min. Although it was difficult to observe the variation of the SrTiO₃ crystallinity because the XRD peak position of SrTiO₃ is very similar to that of SrRuO₃, the XRD peaks for annealed SrTiO₃ films on SrRuO₃ were shifted to a higher angle compared to the as-deposited sample, which indicated the crystallization of SrTiO₃. The dielectric constant of the SrTiO₃ film deposited on the SrRuO₃ electrode increased significantly compared to that of a film on a Ru electrode, as shown in Fig. 6, which means that our SrRuO₃ film formed from SrO/RuO₂ bi-layer film effectively acted as a functional electrode to enhance the dielectric properties of a perovskite-structured, high-k dielectric.

4. Conclusions

The effect of the annealing conditions on the formation of SrRuO₃ films by the interfacial reaction of SrO/RuO₂ bi-layer films was investigated. It was found that the annealing temperature, deposited SrO thickness, and annealing atmosphere were key parameters affecting the formation of conformal SrRuO₃ films. By optimization of the annealing conditions, the SrRuO₃ film effectively acted as a functional electrode for MIM capacitors, and the dielectric constant of the SrTiO₃ film deposited on the SrRuO₃ film increased remarkably by almost 2.5 times in comparison with that of a film on a Ru electrode.

References