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Effect of annealing conditions on formation of $SrRuO_3$ films by interfacial reaction of SrO/RuO_2 bi-layer films

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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 $SrTiO_3$ film 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 $SrRuO_3$, 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 $Ru(EtCp)_2$ [$Ru(C_2H_5C_2H_4)_2$] 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 $Sr(DPM)_2$ [$Sr(C_{11}H_{19}O_2)_2$] 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.

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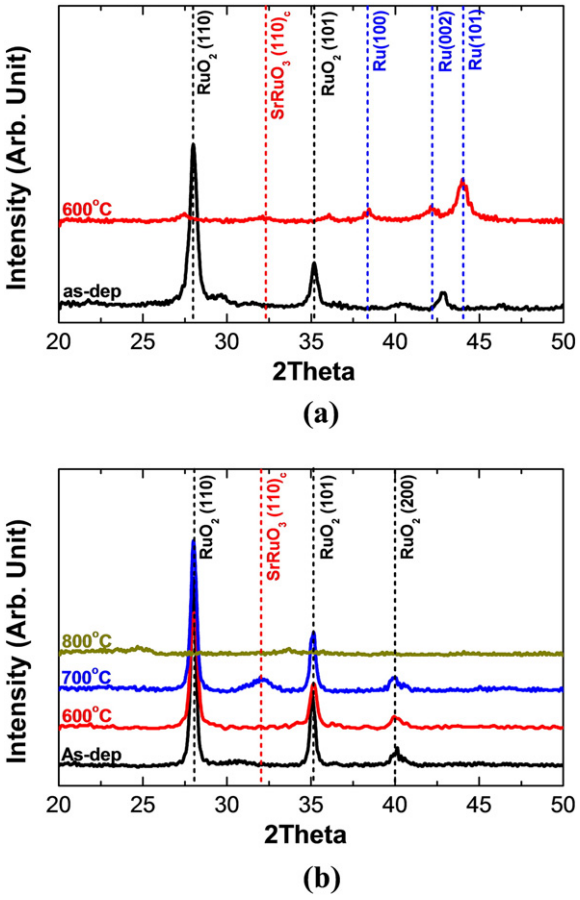

Fig. 1. XRD patterns of SrO(20 nm)/RuO_2(30 nm) bi-layer stack and samples annealed in a temperature range from 600 to 800 °C in a (a) 1 Torr N_2 atmosphere and (b) 1 Torr O_2 atmosphere for 10 min.

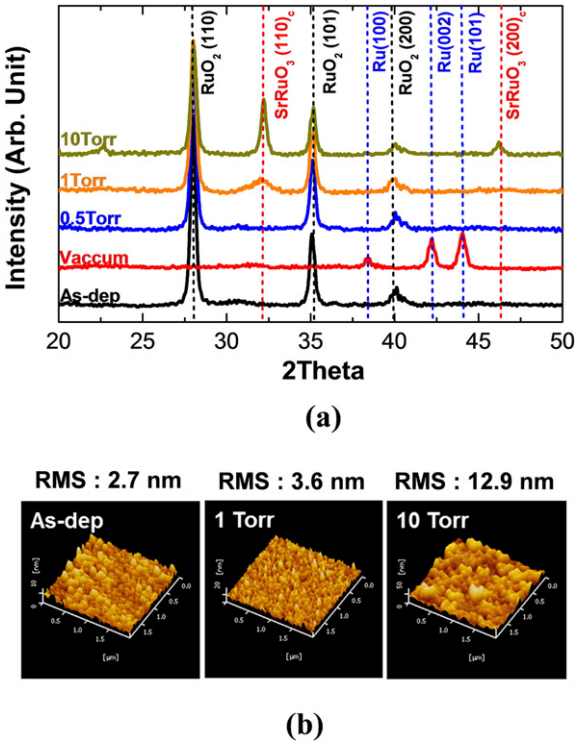

Fig. 3. (a) Annealing pressure dependence of XRD patterns and (b) the RMS roughness change of SrO(20 nm)/RuO_2(30 nm) bi-layer stack. All annealing processes were conducted in an O_2 atmosphere at 700 °C for 10 min.

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 a 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. 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

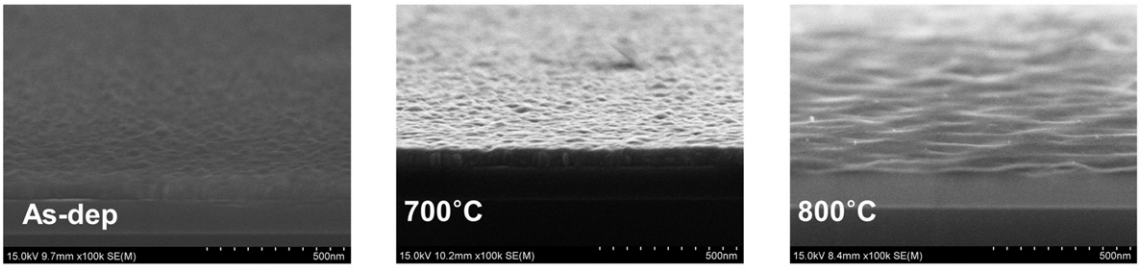

Fig. 2. Tilted SEM images of SrO(20 nm)/RuO_2(30 nm) at various annealing temperatures in a O_2 atmosphere.