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MOCVD growth of epitaxial $SrIrO_3$ films on (111)$SrTiO_3$ substrates

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Abstract

$SrIrO_3$ films were grown on (111)$SrTiO_3$ substrates at 650 to 700 °C by metal organic chemical vapor deposition (MOCVD). Stoichiometric films were obtained above 650 °C for a wide range of input gas flow rate of Ir source under a fixed rate for a Sr source. $(001)_m$-oriented monoclinic $SrIrO_3$ films with in-plane 3-varian were epitaxially grown and their rocking curve full width at half maximum (FWHM) of $(001)_m$ peaks were forward to be narrow, i.e. 0.075°. Average surface roughness (*Ra*) of such film was 0.30 nm, which suggests that the surface is smooth. Resistivity at room temperature was about 1300 μΩ cm and (111)-oriented epitaxial $Pb(Zr_{0.4}Ti_{0.6})O_3$ films with smooth surfaces were successfully grown on these $SrIrO_3$ films. Good ferroelectricity characteristics comparable to those on $(111)_c SrRuO_3 // (111)SrTiO_3$ was obtained except for the large coercive field (E_c) values.

Keywords: MOCVD; FeRAM; $SrIrO_3$; Perovskite-type structure

1. Introduction

Thin films of $Pb(Zr,Ti)O_3$ (PZT) have been widely investigated for ferroelectric random access memories (FeRAM), actuators and optical switching applications due to the superior ferroelectric, piezoelectric and electro-optical characteristics of PZT. These characteristics are also well known to strongly depend on the choice of the electrode material [1–6]. Oxide electrodes with the cubic-perovskite structure, such as $SrRuO_3$ [1,5], $(La,Sr)CoO_3$ and $LaNiO_3$ [6], are known to improve the electrical properties of PZT because of their crystal-structure similarity and good lattice matching with PZT.

Electrical properties of PZT films are also known to strongly depend on the orientation of the film due to the polar characteristics of PZT [7,8]. Especially, (111)-oriented PZT films have been widely investigated as FeRAM and actuators owing to the high stability of the switching charge [9] and the large piezoelectric response [10]. Techniques to obtain (111)-oriented PZT films have been established not only for the epitaxial growth using substrates with epitaxial buffer layers, but also for the fiber-textured films on (111)-self-oriented Pt layers i.e. local epitaxial technique [11].

However, (111)-oriented oxide electrodes, that are essential for obtaining (111)-oriented PZT films with good properties, commonly show rougher surfaces in comparison with other orientations [12]. The rough surface of an oxide electrode results in PZT films with rough surfaces. This is a big problem especially for optical application, in which flat surfaces and thinner films are required to decrease the operating voltage of the FeRAM.

To use oxide electrodes with crystal structure different from that of the cubic perovskite, e.g. hexagonal-based ones, is one solution to overcome this problem. In the present study, $SrIrO_3$ films were prepared. $SrIrO_3$ has a hexagonal-based crystal structure (crystal symmetry is monoclinic) and relatively low conductivity of 4000 μΩ cm at room temperature [13–15]. So far the reports on the preparation of $SrIrO_3$ film have been rare. The goal of the present study was to grow epitaxial $SrIrO_3$ films on (111)$SrTiO_3$ substrates by metal organic chemical vapor

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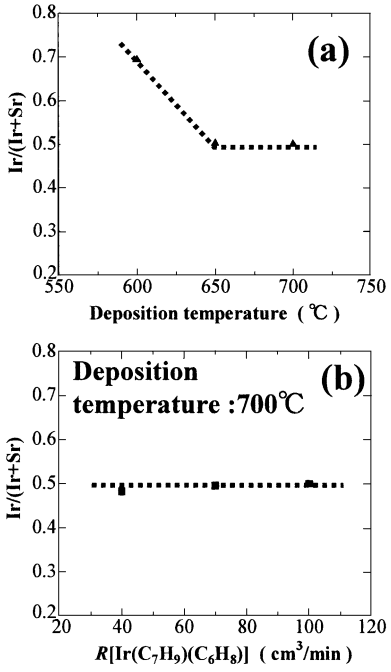

Fig. 1. Ir/(Ir+Sr) ratio of $SrIrO_3$ films as a function of (a) deposition temperature and (b) the input gas flow rate of Ir, $R[Ir(C_7H_9)(C_6H_8)]$, deposited at 700 °C.

deposition (MOCVD) for the first time. Crystal structure and electrical properties of the $SrIrO_3$ films were investigated and compared with those of the $SrRuO_3$ films, that are the most widely used oxide electrodes. In addition, electrical properties of PZT films grown on $SrIrO_3$ films were also compared with those of $SrRuO_3$ films.

2. Experimental details

$SrIrO_3$ films of 60–70 nm in thickness were prepared by MOCVD using $Sr(C_{11}H_{19}O_2)_2(C_8H_{23}N_5)_x$, $Ir(C_7H_9)(C_6H_8)$, and O_2 gas as source materials. Films were grown on (111)$SrTiO_3$ substrates at 600 to 700 °C under a reactor pressure of 1.3×10^3 Pa. The composition of the films was controlled by the input gas flow rate of the Ir source keeping the flow rate fixed for the Sr source. The theoretical input gas flow rate of the Ir source, $R[Ir(C_7H_9)(C_6H_8)]$, was defined elsewhere [16]. 60–70-nm-thick $SrRuO_3$ films were also grown on (111)$SrTiO_3$ substrates by MOCVD. Details of the MOCVD growth of $SrRuO_3$ were reported elsewhere [17]. 90-nm-thick (111)$Pb(Zr_{0.4}Ti_{0.6})O_3$ thin films were grown on $SrIrO_3$- and $SrRuO_3$-covered (111)$SrTiO_3$ substrates at 540 °C by MOCVD using $Pb(C_{11}H_{19}O_2)_2$, $Zr(t\text{-}C_4H_9O)_4$, $Ti(i\text{-}C_3H_7O)_4$, and O_2 gas as source materials [18].

The crystal structure of the films was investigated by X-ray diffraction (XRD) using four-circle goniometer. The chemical composition of the films was determined by wavelength-dispersion-type X-ray fluorescence spectrometer (PANalytical PW2404). Resistivity was measured by the four-probe method. Surface roughness was measured by scanning probe microscopy (SPM) and was estimated as an average surface roughness (*Ra*). Ferroelectric properties of the $Pt/Pb(Zr_{0.4}Ti_{0.6})O_3/SrIrO_3$ and $Pt/Pb(Zr_{0.4}Ti_{0.6})O_3/SrRuO_3$ capacitors were measured by ferroelectric tester Toyo technica, FCE-1 after the preparation of a 100 μmϕ Pt on $Pb(Zr_{0.4}Ti_{0.6})O_3$ film by electron beam evaporation as top electrodes.

3. Results and discussion

3.1. Preparation of $SrIrO_3$ and $SrRuO_3$ films on (111)$SrTiO_3$ substrates

Fig. 1(a) shows the composition change of the deposited films with the deposition temperature in the range from 600 to 700 °C. The films grown at 600 °C were Ir-rich, but the stoichiometric composition, Ir/(Ir+Sr)=0.5, was reached for films grown above 650 °C. On the other hand, Fig. 1(b) shows the composition change with $R[Ir(C_7H_9)(C_6H_8)]$ at 700 °C. Stoichiometric films were obtained irrespective of $R[Ir(C_7H_9)(C_6H_8)]$ from 40 to 100 cm^3/min. Hence, it seems that stoichiometric $SrIrO_3$ films are obtained above 650 °C for a wider $R[Ir(C_7H_9)(C_6H_8)]$ condition, suggesting the existence of a wide "process window". Parallel observations were made for MOCVD growth of $SrRuO_3$

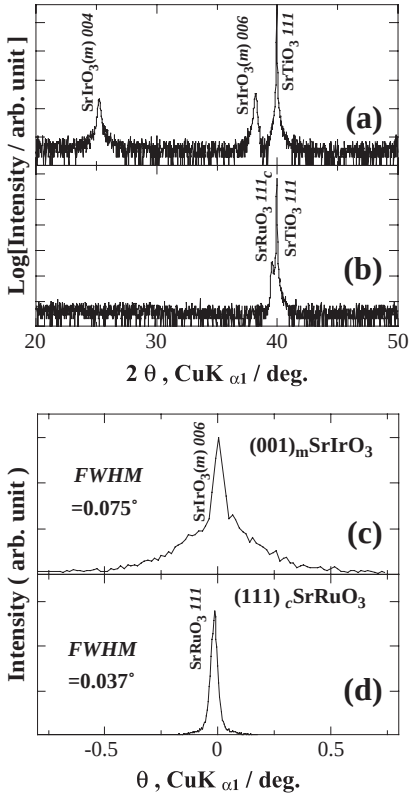

Fig. 2. XRD patterns of (a) $SrIrO_3$ and (b) $SrRuO_3$ thin films and rocking curves of (c) monoclinic $SrIrO_3(006)_m$ diffraction peak and (d) $SrRuO_3(111)_c$ diffraction peak for the films deposited at 700 °C on (111)$SrTiO_3$ substrates.