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Orientation and film thickness dependencies of (100)- and (111)-oriented epitaxial $Pb(Mg_{1/3}Nb_{2/3})O_3$ films grown by metal organic chemical vapor deposition

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Abstract

(100)- and (111)-oriented epitaxial $Pb(Mg_{1/3}Nb_{2/3})O_3$ films with 500 and 1300 nm in thickness were grown by metal organic chemical vapor deposition. Remained strain was almost relaxed because the crystal structure of the films was almost the same as that of bulk $Pb(Mg_{1/3}Nb_{2/3})O_3$. Relative dielectric constant showed the maximum value against the temperature that depended on the measurement frequency. Maximum relative dielectric constant, ε_r(max.), and the temperature showing ε_r(max.), T(max.), decreased and increased with the frequency, respectively, are in good agreement with reported data for the bulk. ε_r(max.) and T(max.), respectively increased and decreased with the film thickness and (111)-oriented films showed larger value than that of the (100)-oriented one. Ferroelectricity was observed for all films up to 297 K and monotonously decreased with increasing temperature. Saturation polarization value increased with the film thickness and (111)-oriented films showed larger value than (100)-oriented ones. On the other hand, the coercive field decreased with increasing film thickness, but was almost independent with the film orientation.

Keywords: $Pb(Mg_{1/3}Nb_{2/3})O_3$ epitaxial film; Thickness dependency; Orientation dependency; Dielectric property; Ferroelectric property

1. Introduction

$Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is one of well-known relaxor ferroelectric materials with diffused phase transition [1]. This is also known as an end member of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solution system that has been widely investigated for capacitor and piezoelectric transducer applications due to its large dielectric constant and piezoelectric properties near the morphotropic phase boundaries, respectively [2]. Film form of $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solution has been also investigated for the applications in high density capacitors and microelectromechanical system (MEMS) using piezoelectric materials, so called piezo-MEMS [3]. However, the number of researches for $Pb(Mg_{1/3}Nb_{2/3})O_3$ films itself is relatively small compared with $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ solid solution films.

Seo et al. [4] reported that the crystal structure changes with film thicknesses from 35 to 370 nm for (100)-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$ epitaxial films. On the other hand, *Nagarajan* et al. reported the strong film thickness dependency of the lattice parameter for 10% $PbTiO_3$ substituted (100)-oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$ epitaxial films from 100 to 400 nm in thickness [5]. They explain this dependence by the strain effect from the substrate. However, the investigation on the film thickness

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dependency beyond 1000 nm in thickness has been hardly reported. Our group reported the strong film thickness dependency of the dielectric constant, ε_r, for wide range of film thickness from 100 nm to 2000 nm [6]. This is different from previous reports because the obvious strain change with film thickness was not detected by the relaxation of the remained strain mainly due to the relatively thick film. In addition, this strong film thickness dependency of ε_r cannot be explained by the widely discussed so-called "dead-layer model'' [7]. In this model, the inverse of the capacitance has a linear relationship with film thickness having a positive intercept value at 0 nm in thickness. However, a linear relationship was not obtained in our previous study. One possibility to explain the strong film thickness dependency of ε_r observed in the previous study is the change of the temperature dependency of ε_r with film thickness because ε_r was previously measured at the fixed temperature, room temperature.

On the other hand, orientation dependencies of the dielectric and ferroelectric properties have been reported for various ferroelectric films [8,9]. This is because ferroelectric materials have polar characteristics. However, the film orientation dependency has been hardly reported for $Pb(Mg_{1/3}Nb_{2/3})O_3$ films.

In the present study, (100)- and (111)-oriented epitaxial $Pb(Mg_{1/3}Nb_{2/3})O_3$ films with different film thickness were grown by metal organic chemical vapor deposition (MOCVD) and temperature dependencies of the dielectric and ferroelectric properties were systematically investigated for the first time.

2. Experimental procedure

$Pb(Mg_{1/3}Nb_{2/3})O_3$ films with 500 and 1300 nm in thickness were grown on $(100)_cSrRuO_3$//(100)$SrTiO_3$ and $(111)_cSrRuO_3$//(111)$SrTiO_3$ substrates at 650 °C by pulsed MOCVD. The details on the pulsed MOCVD have already been reported elsewhere [10]. $Pb(C_{11}H_{19}O_2)_2$, $Mg(C_{14}H_{25}O_2)_2$ (Asahi Denka Corp.) and $Nb(OC_2H_5)_5$ were respective used as

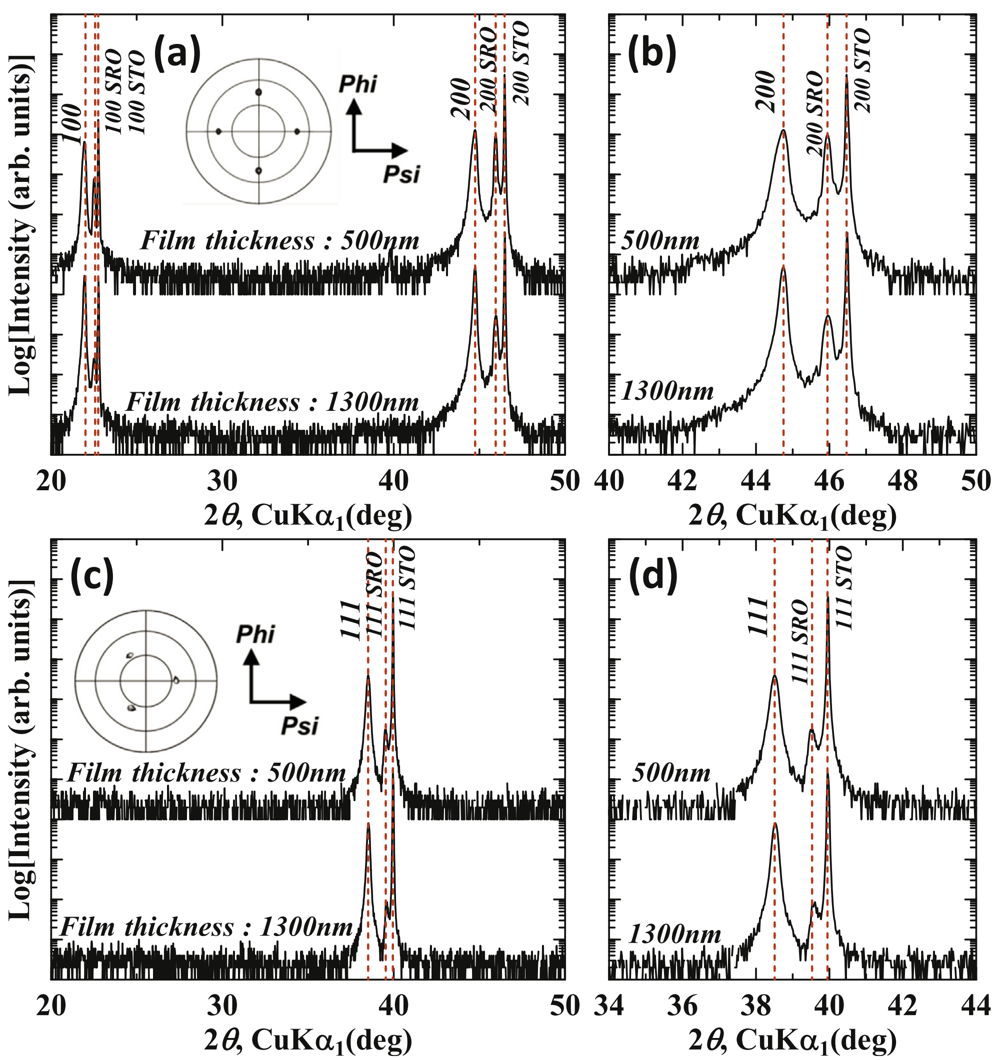

Fig. 1. XRD θ -2θ scan data for 500 nm and 1300 nm thick films grown on (a, b) $(100)_cSrRuO_3$//(100)$SrTiO_3$ substrates and (c, d) $(111)_cSrRuO_3$//(111)$SrTiO_3$ substrates. (b) and (d) respective show the enlarged ones of (a) and (c) near $SrTiO_3$ *200* and *111*. X-ray pole figures measured at fixed 2θ angle corresponding to $Pb(Mg_{1/3}Nb_{2/3})O_3$ *101* for 1300 nm thick films are shown as inserted figures.