Preparation of Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ thin films by MOCVD using ultrasonic nebulization

Choon-Ho Lee · Sun-Il Kim

Abstract Thin films of Pb(Mg$_{1/3}$,Nb$_{2/3}$)O$_3$ (PMN) and Pb(Mg$_{1/3}$,Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) were fabricated on Si and Pt/Ti/SiO$_2$/Si substrates by MOCVD using ultrasonic nebulization and their characteristics were investigated. PMN-PT films deposited at 350°C were annealed in a RTA (Rapid Thermal Annealing) system at 650°C for 30 sec to improve the micostructural properties. The crystallographic properties of PMN-PT films strongly depend on the content ratio of PbTiO$_3$. The content of pyrochlore phase in PMN-PT films decreased with the increase of Ti content and nearly single phase perovskite films were obtained at the composition of 80PMN-20PT. The PMN-PT films with perovskite phase showed a typical butterfly type C-V curve which verifies the ferroelectricity and had the relative dielectric constant of about 60.

Keywords PMN-PT film · Perovskite · MOCVD · Ferroelectrics

1 Introduction

Recently, thin films of lead magnesium niobate Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (hereafter PMN) and its solid solutions with PbTiO$_3$ (PT) have attracted considerable attention for their applications including ferroelectric nonvolatile memory, capacitors in high density microelectronics, micoelectromechanical system (MEMS) due to their good ferroelectricity, high dielectric constant and excellent piezoelectric properties [1–3]. These properties of PMN or PMN-PT films are known to depend on the crystal phase of

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films strongly, and particularly a little quantity of pyrochlore phase PMN degrades the dielectric and ferroelectric characteristics of the films [4]. So the main challenge in using these films is depositing pyrochlore-free perovskite phase films.

It is known that pure perovskite phase PMN ceramics can be made only by the columbite process, which involves the formation of *B*-site precursor oxides followed by reaction with PbO to develop a perovskite structure [5]. However this method is not applicable to thin film processing. Accordingly, it is very difficult to deposit single phase perovskite PMN films. There are various techniques to suppress the formation of pyrochlore phase films, such as sputtering, pulsed laser ablation, sol-gel and pyrolysis [6–9]. Among these, MOCVD is one of the most important techniques for practical application because of its high step-coverage, high deposition rate, good film uniformity and easy composition control [10, 11]. However there are few reports on MOCVD of these materials.

Recently, we have reported the deposition of PMN films by MOCVD using ultrasonic nebulization. In that study, we have found that the use of excess Pb condition and PbTiO$_3$ seed layer has an effect on the formation of perovskite phase PMN film [12]. In this study, PMN-PT films were made by this method and the effect of PbTiO$_3$ mole fraction on the crystallographic and structural properties of PMN-PT films were investigated.

2 Experimental

PMN-PT films were prepared on Si and Pt/Ti/SiO$_2$/Si substrate by MOCVD using ultrasonic spraying. The details of this method and the apparatus are described in a previous paper [13]. The source solutions were made by dissolving

Table 1 Deposition condition of PMN films

Concentration of precursors in the source solution	
$Pb(Mg_{1/3}Nb_{2/3})O_3$ source solution	
Pb[TMHD]$_2$	1.0 mol/l
Mg[TMHD]$_2$	0.59 mol/l
Nb(Eto)$_1$[TMHD]$_4$	0.67 mol/l
$PbTiO_3$ source solution	
Pb[TMHD]$_2$	1.0 mol/l
Ti(OiPr)$_2$[TMHD]$_2$	1.0 mol/l
Substrate temperate	350°C
N$_2$ gas flow rate	5000 sccm
O$_2$ gas flow rate	2000 sccm
Total gas flow rate	7000 sccm
Carrying rate of mist of source solution	0.5 cc/min

all the precursors for each metal component in a solvent. As the solvent, the mixture of 70 vol.% buthanol and 30 vol.% butyl acetate were used. The source reagent of Pb was lead tetramethyl-heptanedionate. The source reagents of Mg, Nb and Ti were magnesium tetramethyl- heptanedionate, niobium ethoxide tetramethyl-heptanedionate ([Nb(Eto)$_1$(TMHD)$_4$]) and Titanium-isopropoxide tetramethyl -heptanedionate ([Ti(i-Pr)$_2$(TMHD)$_2$]), respectively. Niobium ethoxide tetramethyl-heptanedionate was made by the 1:4 reactions of niobium ethoxide and tetramethyl-heptanedione. Titanium isopropoxide tetramethyl-heptanedionate was made by the 1:2 reactions of titanium isopropoxide and tetramethyl-heptanedione. All the depositions were carried out under atmospheric pressure.

The deposition conditions are summarized in Table 1. After the deposition of PMN-PT films, the films were annealed using the RTA process at a heating rate of 40°C/s under oxygen atmosphere. The PMN-PT films were annealed at 650°C for 30 sec.

The crystallographic properties of the prepared films were investigated by XRD (Philips, X'pert APD) and FE-SEM (Hitachi, S-4200) was used to study the surface morphology and cross-sectional image of the PMN-PT films. The chemical composition of films was analyzed by EPMA (Cameca, SX-50). To identify the formation of ferroelectric PMN-PT films with perovskite structure, capacitance-voltage characteristics were measured by Agilent 4294A Impedance analyzer.

3 Results and discussion

Firstly, the optimum deposition condition was confirmed to prepare perovskite-type PMN-PT film. The studies on the chemical composition of thin films were conducted with various Mg concentrations in the source solution to obtain stoichiometric PMN films. Fig. 1 shows the variations of chemical composition of PMN films as a function of the
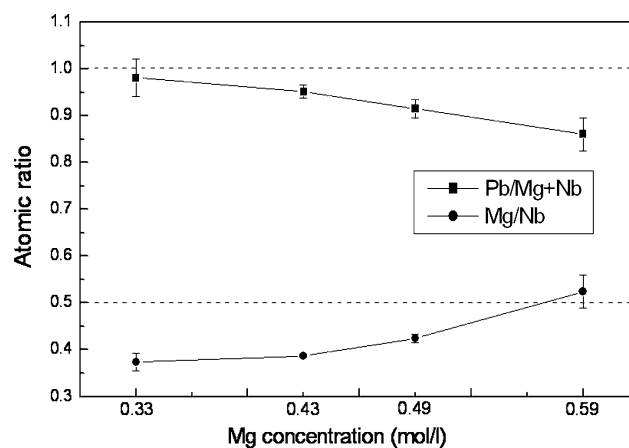

Fig. 1 Atomic ratios in the PMN films as a function of Mg mole concentration in source solutions

concentration of Mg source in the source solution at the oxygen partial pressure of 0.3 atm and the substrate temperature of 350°C.

As the Mg source concentration in the starting soluion increased, Mg/Nb ratio of the films gradually increased. The Mg source concentration for B-site stoichiometry of PMN films was 0.59 mol/l. The atomic ratios of Pb/[Mg + Nb] decreased as the Mg concentration increased. So, we have used the excess Pb concentration in the source solution to obtain the stoichiometric composition of PMN films.

Then we have deposited PMN-PT films with the mixed solution of sources for PMN and for PbTiO$_3$ (PT) varying the mixing ratio. The XRD patterns of RTA-treated PMN-PT films made with the various PT source concentration in the source solution were shown in Fig. 2. At low contents of PT, the films are composed of a large portion of pyrochlore phase and a small portion of perovskite phase. As the PbTiO$_3$ mole fraction increased, the pyrochlore phase of PMN-PT film decreased. This indicates that the incorporation of PbTiO$_3$ promotes a formation of peroveskite phase of PMN-PT films. There are some reports on the effect of Ti^{4+} substitution in B-site in PMN ceramics on the stabilization of perovskite phase [14]. PMN-PT film made with 80PMN-20PT source solution has nearly single perovskite phase as shown in Fig. 2(d).

Figure 3 shows the morphology of the surface and fractured cross-section of RTA-treated PMN-PT films having different phases. While the film with nearly single perovskite phase as shown in Fig. 3(a) have a dense and uniform microstructure, the film with a large portion of pyrochlore phase shows very porous and non uniform plate-like morphology as like Fig. 3(b). This result seems to have been caused not only by the difference of growth mechanism between the perovskite crystallite and the pyrochlore crystallite during deposition, but also by the difference in the volatility of Pb component during RTA process. From this figure, we can see
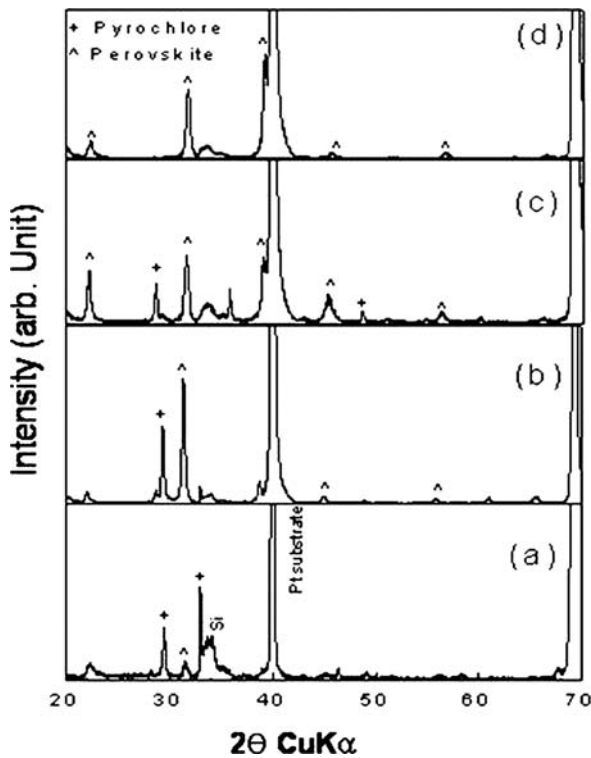
Fig. 2 X-ray diffraction patterns of RTA-treated PMN-PT film made with (a) 95PMN-5PT, (b) 90PMN-10PT, (c) 85PMN-15PT, and (d) 80PMN-20PT source solution

that PMN-PT films made with 80PMN-20PT in the source solution made a perfect solid solution of PMN and PT.

To investigate electrical properties of ferroelectric PMN-PT films with pervoskite structure, MFM (Metal-Ferroelectric-Metal) structure was fabricated by depositing the Pt top electrode by sputtering onto the PMN-PT films deposited on Pt/Ti/SiO$_2$/Si substrate. Figure 4 shows the capacitance-voltage curves of the RTA-treated PMN-PT films. In this measure a small ac signal of 1 mV amplitude and 100 KHz frequency was applied. The curie-temperature (Tc) of pure perovskite PMN is about $-15°$C and that of PMN-PT shifts to higher temperature with the content of PT. The PMN-PT films made with 95PMN-5PT source solution were paraelectric at room temperature as shown in Fig. 4(a). The nearly single perovskite PMN-PT films showed a typical butterfly type C-V curve due to ferroelectric switching as shown in Fig. 4(b). From these results, it is thought that we successfully obtained ferroelectric PMN-PT films with perovskite sturcture made by MOCVD using ultrasonic nebulization. But, the dielectric constant was about 60 at zero bias, which is very low value as a relaxor material. This seems to be caused by the presence of very small quantity pyrochlore phase in the films. The asymmetrical shape of this curve seems to be due to the difference of the deposition conditions between bottom electrode and top electrode [15].
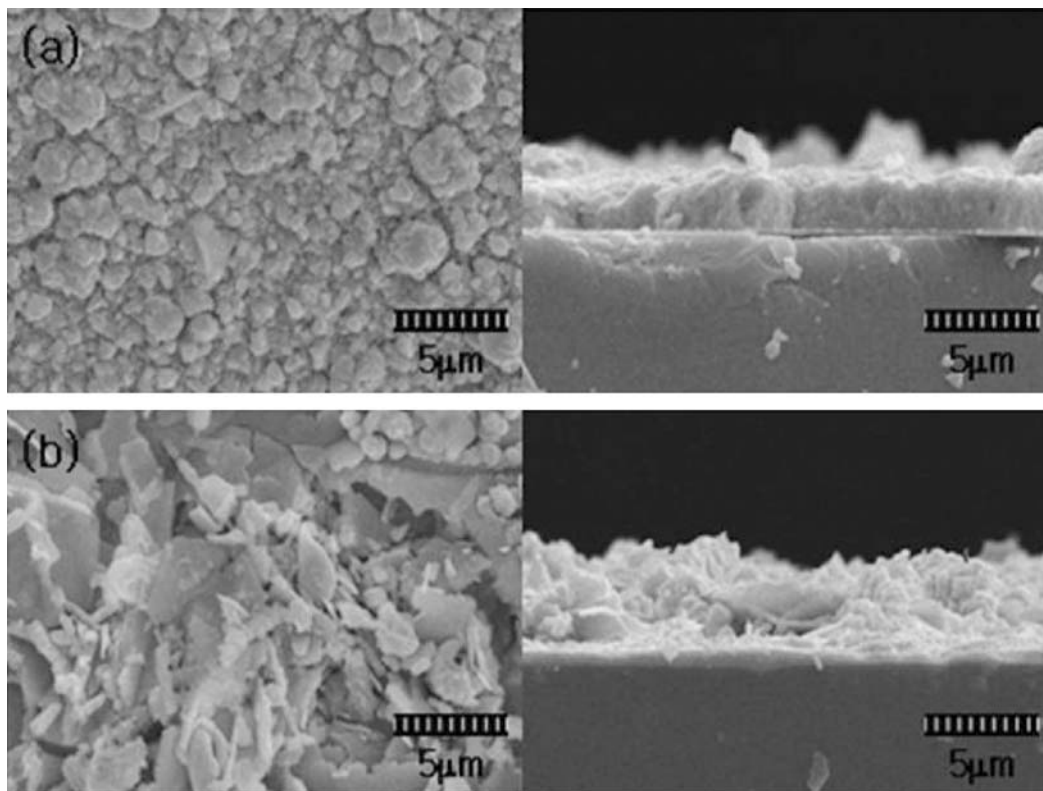

Fig. 3 SEM micrographs of the surface morphology and cross-sectional view of RTA treated PMN-PT films made with (a) 80PMN-20PT, (b) 95PMN-5PT source solution
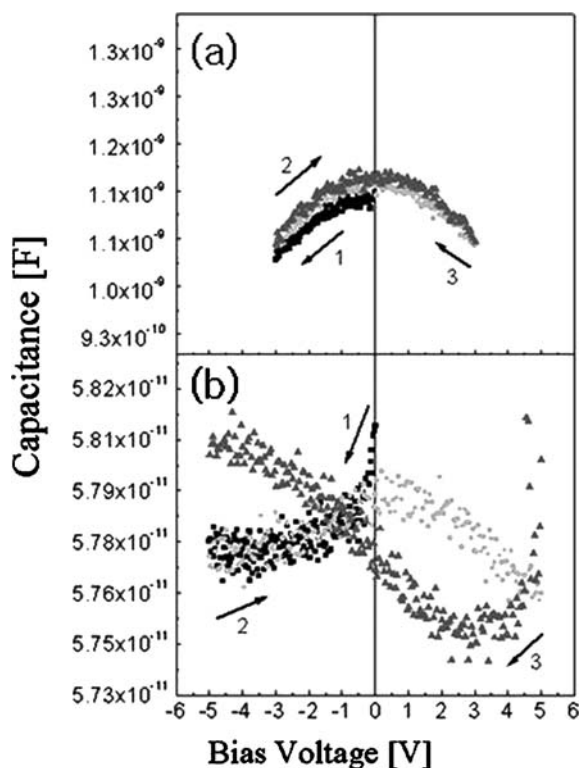
Fig. 4 Capacitance-Voltage characteristics of the RTA-treated PMN films made with (a) 95PMN-5PT, (b) 80PMN-20PT source solution

4 Conclusions

PMN-PT films were deposited on Si and Pt/Ti/SiO$_2$/Si substrate by MOCVD using the ultrasonic nebulization. The chemical composition for nearly stoichiometric PMN films was achieved at the deposition temperature of 350°C using

the source solution in which the concentrations of Pb, Mg and Nb components was about 1.0, 0.59 and 0.67 mol/l, respectively. Pyrochlore phase in PMN-PT films decreased with the increase of PT content and nearly single phase perovskite film could be obtained using 80PMN-20PT source solution. Perovskite PMN-PT films made with 80PMN-20PT source solution acted as a ferroelectric which show a typical butterfly type curve in C-V characteristics at room temperature and had the relative dielectric constant of about 60.

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