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Electromechanical coupling factors of single-domain 0.67Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}−0.33 PbTiO\textsubscript{3} single-crystal thin films

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Thin films of single c-domain/single-crystal (1−x)Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}−xPbTiO\textsubscript{3} (PMN-PT) with x = 0.33 near a morphotropic boundary composition were heteroepitaxially grown on (110)SrRuO\textsubscript{3}/(001)Pt/(001)MgO substrates. The heteroepitaxial growth was achieved by rf-magnetron sputtering at the substrate temperature of 600 °C. After the sputtering deposition, the substrates were rapidly cooled from 600 °C to room temperature by atmospheric air gas at a cooling rate of 100 °C/min. The rapid cooling process enhanced the heteroepitaxial growth of the single c-domain/single-crystal PMN-PT thin films. Their electromechanical coupling factor \( k_t \) measured by a resonance spectrum method was 45% at resonant frequency of 1.3 GHz with phase velocity of 5500 to 6000 m/s for the film thickness of 2.3 \( \mu \)m. The observed \( d_{33} \) and \( d_{31} \) were 194 pC/N and \( −104 \) pC/N, respectively. The observed \( k_t \), \( d_{33} \), and \( d_{31} \) were almost the same to the bulk single-crystal values. The present PMN-PT thin films are applicable for a fabrication of GHz planar bulk acoustic wave transducers. © 2006 American Institute of Physics, [DOI: 10.1063/1.2188588]

Relaxor based ferroelectric single crystal (1−x)Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}−xPbTiO\textsubscript{3} (PMN-PT) exhibits an exceptionally high piezoelectric constants with a high electromechanical coupling factor at the morphotropic phase boundary (MPB) around \( x = 0.35 \). \textsuperscript{1,2} Thin films of PMN-PT will be useful for a fabrication of thin film acoustic transducers, if the thin films exhibit the high \( k_t \) and/or high piezoelectric constants similar to the bulk PMN-PT single crystals. Several deposition processes of PMN-PT thin films were reported.\textsuperscript{3} Their piezoelectric properties, such as \( d_{33} \) and \( d_{31} \) were evaluated. The piezoelectric coefficients were mostly smaller than bulk values \( d_{33}=2000 \) pC/N, although relatively high values \( d_{33}=1200 \) pC/N were recently reported at a trench structure.\textsuperscript{4} The \( k_t \) of PMN-PT thin films in a GHz range has been not evaluated, although the evaluation of \( k_t \) in a GHz range is essential for a fabrication of GHz acoustic devices. The differences in the electromechanical coupling and/or piezoelectric properties between the bulk and thin films are not well understood, since these PMN-PT thin films included a dislocated interfacial layer.\textsuperscript{5,6} For a better understanding of the ferroelectric behavior of the PMN-PT thin films, the deposition of a single-domain/single-crystal structure without the interfacial layer is essential. This letter describes the deposition of single c-domain/single-crystal PMN-PT thin films with \( x = 0.33 \) (0.67PMN−0.33PT) near the MPB composition and discusses their electromechanical coupling factor \( k_t \) measured in a GHz range in relation to their piezoelectric constants \( d_{33} \) and \( d_{31} \).

A planar rf-magnetron sputtering system was used for the deposition of 0.67PMN−0.33PT thin films. The sputtering system was described in a previous report.\textsuperscript{7} 4-in. powder target was used for the sputtering. The powder target was composed of a mixture of PbTiO\textsubscript{3}, PbO, MgO, Nb\textsubscript{2}O\textsubscript{5} and TiO\textsubscript{2} powder packed in a stainless shallow tray. The chemical composition of the mixed powder was 10% PbO-rich 0.67PMN−0.33PT. The substrates were (001)Pt/(001)MgO with buffer layer of (110)SrRuO\textsubscript{3} (SRO). A mixture of Ar and O\textsubscript{2} with ratio of 20 to 1 was introduced at 0.5 Pa, and rf power was set at 90 W. The substrate temperature was held at 600 °C during the deposition. After the deposition the substrates were rapidly cooled from growth temperature 600 °C to room temperature by a cooling gas of atmospheric air at 1 atm. The substrate holder with heating block was designed to have a small thermal capacity so that the substrates were easily cooled down by the air gas. The cooling rate was 100 °C/min. The growth rates of the sputtered films were 0.2 to 0.3 \( \mu \)m/h. Electron probe microanalyses suggested the chemical composition of the sputtered films was stoichiometric 0.67PMN−0.33PT. The thickness of the sputtered films was selected from 1 to 3 \( \mu \)m for the measurement of electromechanical coupling \( k_t \) and the piezoelectric constants.

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Typical X-ray diffraction (XRD) patterns of the sputtered 0.67PMN–0.33PT thin films near the MPB composition were shown in Fig. 1. The XRD θ–2θ pattern showed the sputtered film was highly (001) oriented PMN-PT structure [Fig. 1(a)]. The pole figure of (110) direction showed a strong four-fold intensity describing three-dimensional epitaxy, i.e., single-crystal structure [Fig. 1(b)]. The XRD analyses suggested the lattice parameters of the PMN-PT thin films at room temperature were \( a = 0.4014 \) nm, \( b = 0.4011 \) nm, \( c = 0.4046 \) nm, \( \alpha = 90.00^\circ \), \( \gamma = 90.02^\circ \), \( \beta = 89.91^\circ \). These lattice constants were obtained by measuring the four-circle diffraction angles of 17 peaks different from each other. The possible crystal structure of the present PMN-PT thin films is a tetragonal structure with \( a = b = 0.401 \) nm, \( c = 0.405 \) nm, and \( \alpha = \beta = \gamma = 90.00^\circ \). The room-temperature crystal phase of bulk PMN-PT near the MPB composition is rhombohedral and/or a mixture of rhombohedral and tetragonal phase.\(^7\) The crystal structure of the PMN-PT thin films were modified from the bulk structure, if the PMN-PT thin films truly comprised the tetragonal phase and/or rhombohedral phase, i.e., single-crystal structure \(^7\) without remarkable dislocated interfacial layer, although point defects were observed at the interface between the PMN-PT thin films and MgO substrates.\(^10\) The growth of the dislocated interfacial layer was possibly suppressed by the rapid cooling process.

The \( k_t \) and \( d_{31} \) and \( d_{33} \) were measured for the present 0.67PMN–0.33PT thin films. The experimental values were compared with the 0.67PMN–0.33PT single crystal values.\(^11,12\) In order to evaluate the \( k_t \), two ports planar bulk acoustic wave (BAW) resonator was fabricated using the PMN-PT thin films. The construction of the resonator is shown in Fig. 2. The \( k_t \) was evaluated by the resonance spectrum method recently developed for the evaluation of the BaTiO\(_3\) thin films.\(^13\) A pair of vacuum evaporated Au/Cr input and output electrodes of 80 \( \mu \)m in diameter were formed on the surface of the PMN-PT thin films. The SRO/Pt layer was common earth electrode. The spacing between the two electrodes was 60 \( \mu \)m. The resonator was composed of a pair of thin film resonator connected in series connection. The thickness of the PMN-PT thin films and MgO substrates were 2.3 \( \mu \)m and 300 \( \mu \)m, respectively. The resonance spectra were measured across the electrodes by a network analyzer (HP-8719D). Typical resonance properties were shown in Fig. 3. The fundamental resonance signal was observed at about 1.3 GHz [Fig. 3(a)]. The multi-reflection mode is superposed on the main resonant signals [Fig. 3(b)]. The multifrequency mode was caused by the acoustic multirefection of a longitudinal standing wave excited in the MgO substrate. The frequency of multirefection mode \( \Delta f \) is expressed by \( \Delta f = v_pMGO/2d \), where \( v_pMGO \) denotes the phase velocity in the MgO substrate.

![Fig. 1. Typical XRD patterns of the sputtered PMN-PT thin films with \( x = 0.33 \) near the MPB composition grown on (110)SRO/(001)Pt/(001)MgO substrates. (a) θ–2θ pattern, (b) pole figures of (110) direction. Contours are drawn from 27 to 213 on a logarithmic scale (PMN-PT film thickness: 2.3 \( \mu \)m).](image1.png)

![Fig. 2. Schematic construction of planar type two ports PMN-PT thin-film resonator.](image2.png)

![Fig. 3. Resonant properties of planar type two ports PMN-PT thin film resonator with \( x = 0.33 \) near the MPB composition for a different frequency range.](image3.png)
most the same to the bulk single domain/single crystal values, $d_{31} = -90$ pC/N, $d_{33} = 190p$C/N. The measurements included errors, since bulk elastic constants were used for the calculation of $d_{31}$ and $d_{33}$. In contrast, the measurement of the $k_s$ is less obscure. It is clear the $k_s$ measured in a GHz range is almost the same to the bulk single crystal, 95% of bulk single-domain/single crystals, although the PMN-PT thin films show the tetragonal structure contrary to bulk rhombohedral structure.

Synchrotron scattering XRD analyses of the PMN thin films suggest the sputtered PMN thin films under the present rapid cooling process comprise the B-site chemical ordered nanoregion that is suggested as an origin of relaxor behavior.15 The high electromechanical coupling observed in the present PMN-PT thin films may be also owed to the presence of the B-site chemical ordered nanoregion similar to the PMN thin films.

In conclusion single c-domain/single crystal 0.67PMN–0.33PT thin films near the MPB composition were fabricated by magnetron sputtering under rapid cooling process. Their piezoelectric constant and electromechanical coupling factor $k_s$ were almost the same to the bulk single-domain single crystals. The $k_s$ in a GHz range was found to be 45%. The present PMN-PT thin films have high potential in the fabrication of GHz BAW transducers and/or GHz planar resonator.

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