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Preparation of Nb doped PZT film by RF sputtering

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ABSTRACT

Undoped lead zirconate titanate (PZT) and Nb doped lead zirconate titanate (PNZT) films formed on an Ir/Ti/SiO_2/Si substrate using an RF magnetron sputtering method were studied in detail. Films of about 3–4 μm thickness were deposited at a substrate temperature of 525 °C. X-ray diffraction measurement (XRD) shows that the obtained PZT and PNZT films are both strongly uniaxially oriented in the (100) direction of the perovskite structure, and TEM observation shows that the films have columnar structures. The addition of Nb results in changes of film electrical characteristics, particularly dielectric constant and hysteresis characteristics. Sputtered PNZT films (Nb 13 at.%) formed on silicon diaphragm structures generate 2 times more deflections than undoped PZT film formed on the same structure, thus demonstrating a superior piezoelectric performance. A sputtering method to directly form a PNZT film with high piezoelectric constant on a substrate at low temperature via electrodes finds a wide potential use in MEMS applications.

1. Introduction

Piezoelectric materials are being used in the driving parts of micropumps and other actuators. Improving the definition and performance of micropump requires miniaturization of the actuator structures in combination with advancement of MEMS technology and other semiconductor technologies [1]. To that end, researchers are putting a large effort in development of thin piezoelectric films to replace the conventional bulk piezoelectric materials to thin films.

Lead zirconate titanate (PZT) based materials are the most commonly used piezoelectric material because of its high piezoelectric coefficients. However, the piezoelectric performance of undoped PZT is not sufficient for many actuator applications. Therefore, relaxor type materials or modified PZT with an added third component are widely used. For example, it is well known that an addition of Nb to PZT improves the piezoelectric performance, and it has been widely practiced with bulk materials [2].

There are various methods for forming thin films of piezoelectric material, including sol–gel, sputtering, aerosol deposition and CVD [3–10]. Various approaches have been developed to obtain a film with a high piezoelectric coefficient including annealing films at 600 °C or higher, improving crystallinity through epitaxial growth using a monocrystalline substrate, or using modified PZT. Researchers are looking in particular at PNZT films in which Nb is added to PZT [11–17]. However, to date, no thin films with sufficiently high piezoelectric property together with a good compatibility with MEMS process have been achieved.

In this report, PZT film formed directly via electrode onto a Si substrate using the sputtering method is discussed. This film formation method is a versatile technique which enables us to easily form films with thickness of the order of a few μm. Films were also formed by adding Nb in order to improve the piezoelectric characteristics. We then characterized the film orientation and structure, and measured hysteresis characteristics. Both PZT and PNZT films were deposited on Si diaphragm structures in order to compare deflection performance.

2. Experimental procedure

Table 1 summaries the film formation conditions. PZT films were deposited using a magnetron sputter coater (Model STV4320, Shinko Seiki). Silicon wafers with 300 nm thick thermally-grown silicon dioxide film were used as our standard substrates. After a deposition of 20 nm Ti as an adhesion layer, 300 nm Ir is deposited as a bottom electrode, both by sputtering. A 4-inch diameter sintered body was used as a target, in which Pb composition was

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Table 1
Sputtering conditions.

Parameter	Conditions
Substrate	Ir(300 nm)/Ti(20 nm)/SiO_2/Si
Target	PZT: $Pb_{1.3}Zr_{0.52}Ti_{0.48}O_3$ PNZT: $Pb_{1.3}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_y$ $(0 \leq x \leq 0.2)$
Substrate temperature	525 °C
Gas composition	Ar + 2.5%O_2
Gas pressure	0.5 Pa
RF Power	200 W(2.55 W/cm^2)
Deposition rate	1 μm/h
Thickness	3–4 μm

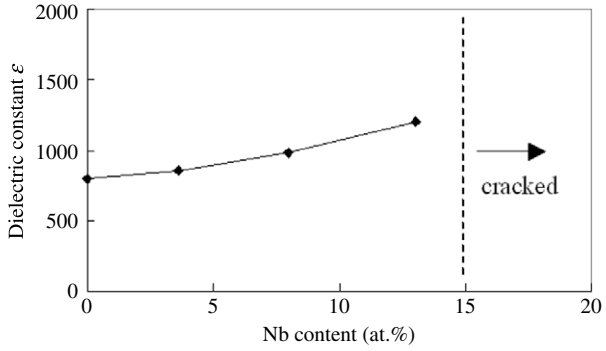

Fig. 1. Relationship between the Nb content in the target and dielectric constant ε of the PNZT film.

increased beyond its intended film stoichiometry in order to compensate for the loss of Pb during film formation. The target composition used is Pb:Zr:Ti = 1.3:0.52:0.48. At first, we used targets with various amounts of Nb content, $Pb_{1.3}(Zr_{0.52}Ti_{0.48})_{1-x}Nb_xO_y$ $(0 \leq x \leq 0.2)$, to examine the influence of Nb content. After we determined a suitable content as $x = 0.12$ which yields films with Nb content of 13%, we fixed our standard target composition as $Pb_{1.3}(Zr_{0.52}Ti_{0.48})_{0.88}Nb_{0.12}O_y$. We set substrate temperature to be 525 °C (substrate surface temperature), applied 200 W of RF power, set pressure in the chamber to 0.5 Pa, and used Ar + 2.5%O_2 as the sputtering gas. Film formation duration was typically 4 h, which yielded film thickness of 3–4 μm.

During the successive formations of the PZT or PNZT films, a thick insulating film begins to form on the inner walls of vacuum chamber and on a substrate holder. This results in the change in the inner wall potential which is initially at ground gradually changing into a floating potential. The change of the electric potential of the inner wall results in a poor film reproducibility. Because we intentionally make the substrate holder and the inner wall of vacuum chamber at a floating potential beforehand, we are able to form a thick PZT/PNZT film with a good repeatability. All our deposited films were evaluated without performing post-annealing nor polarization treatment after film formation.

3. Results and discussion

At first, we examined the Nb content dependence of PNZT films, using 0, 4, 13, 15, and 20 at.% Nb content in film. With 15 and 20 at.% of Nb content in film, cracks appeared in large regions of the film as a result of high residual film stress. Fig. 1 shows a dependence of the dielectric constant at 1 kHz on the Nb content in film (measured by Agilent impedance analyzer 4292A). The dielectric constant increases with an increase in Nb content, suggesting the higher performance of the PNZT films with the higher Nb content.

From these considerations, we have determined 13 at.% as a suitable Nb content and studied in detail, as it is having a high

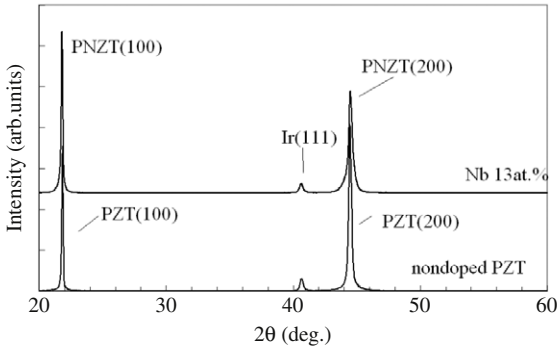

Fig. 2. XRD pattern of undoped PZT and PNZT films.

piezoelectric performance as predicted from high dielectric constant, while having no cracks.

Fig. 2 shows the X-ray diffraction (XRD; SA-HF3, Rigaku) patterns of PNZT film with 13 at.% Nb and undoped PZT. Strong diffraction peaks were observed near 21.9° and 44.6° with negligible peaks from impurity phase. So the obtained thin films are oriented in the (100) direction of perovskite in both undoped and doped cases.

Fig. 3 shows a cross-sectional transmission electron microscopy (TEM; H-9000NAR, Hitachi) image and electron beam diffractions of film with Nb added. Columnar structures grown in the film thickness direction can be observed in the image. The width of single column has a comparatively wide distribution from a few tens of nm to a few hundreds nm. Electron diffractions were taken at different locations of the film which revealed different diffraction patterns. This result indicates that the film's in-plane orientation axes are pointed randomly. No deposits or similar matters were found at grain boundaries.

The results of composition analysis by inductively-coupled plasma mass spectrometry (ICP; SPQ900SE, Seiko Instruments) of the obtained films, was Pb:Zr:Ti:Nb=1.1:0.42:0.45:0.13. Though the film was rich in Pb, no Pb or other deposits were found in either XRD or TEM analysis.

It is worth noting that Nb was incorporated in almost the same amount as the target composition. In the bulk ceramics PNZT, it is well known that no more than 3 at.% Nb can be incorporated in the perovskite structure without a pyrochlore phase formation [18,19]. But in the case of our films, a much higher content of Nb can be incorporated in the perovskite structure without losing the film quality, as evident from the increase of dielectric constant, film stress, and the fact that no deposits are found in XRD nor TEM analysis. As opposed to bulk ceramics, crystal growth in sputtered film occurs from atoms or ions decomposed by plasma at much lower temperature, so it is considered that impurity phase such as pyrochlore or surplus PbO are hardly formed. If the surplus Pb exists as 4+, and Nb^{5+} is incorporated into a perovskite B-site, Pb:Zr:Ti:Nb=1.1:0.42:0.45:0.13 is expressed as

$$Pb^{II}_{0.94}\square_{0.06}(Pb^{IV}_{0.076}Zr_{0.388}, Ti_{0.416}Nb_{0.120})O_3$$

(□ is A-site Pb vacancy) from charge compensation consideration [20].

Fig. 4 shows the P–E hysteresis (FCE-1, Toyo) characteristics of the obtained undoped PZT and PNZT films. The undoped PZT had a large coercive electric field exceeding 95 kV/cm whereas that of PNZT was only 49 kV/cm. PNZT exhibited better hysteresis characteristics which is expected to result in a better piezoelectric performance. As can be seen, the hysteresis of PNZT is in a state where the whole P–E loop is shifted to the right, suggesting that the polarization axes have been aligned in a certain direction beforehand. The reason is not clear, but we think that this is due to a stress exerted on the film. It has been reported that the tensile