Paper

In-situ observation of a MEMS-based Pb(Zr,Ti)O$_3$ micro cantilever using micro-Raman spectroscopy

Masamichi NISHIDE,[†] Maresuke KUZUHARA,[*] Takeshi TAI,[*] Takashi KATODA,[*] Hitoshi MORIOKA,[**] Hiroshi FUNAKUBO,[***] Ken NISHIDA and Takashi YAMAMOTO

Department of Communications Engineering, National Defense Academy, 1–10–20 Hashirimizu, Yokosuka, Kanagawa 239–8686
[*]Department of Electronic and Photonic Systems Engineering, Kochi University of Technology, 185 Miyanokuchi, Tosayamada-cho, Kochi 782–8502
[**]Application Scientist XRD for Thin Film, Bruker AXS K.K., 3–9 Moriya-cho, Kanagawa-ku, Yokohama 221–0022
[***]Department of Innovative and Engineered Materials, Tokyo Institute of Technology, J2–43, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226–8502

The crystal structure and strain in a (100)/(001)-oriented PZT micro cantilever under applied voltage were characterized by in-situ Raman spectroscopy. A Pt/LaNiO$_3$/(100)/(001)PZT/LaNiO$_3$/Pt/Ti/SiO$_2$/silicon-on-insulator (SOI) multilayer structure was fabricated in a process based on a microelectromechanical system (MEMS). The volume fraction of the domain switching from a-domains to c-domains was monotonously increased with increases in the applied voltage. No compressive in-plane lattice strain was induced in the PZT film with the increases in the applied voltage. These results show that Raman spectroscopy is a useful method for in-situ observation of PZT micro cantilevers.
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1. Introduction

Lade zirconate titanate oxide (PZT) is a very important material for piezoelectric devices and nonvolatile memories because of their large volumes of piezoelectricity and ferroelectricity. Recently, microelectromechanical system (MEMS)-based micro cantilevers with PZT films (PZT micro cantilevers) have been fabricated for application in devices such as actuators and the sensors.[1)–4)] The tips of the PZT micro cantilevers move up and down with applied voltage, where a driving force of the PZT micro cantilevers is the piezoelectricity of the PZT films. It is known that there are two types of piezoelectricity mechanisms. One is the lattice strain caused by applied voltage and the other is the so-called extrinsic effect, such as domain switching from a-domains to c-domains or vice-versa (90° domain switching). Kim et al. reported the possibility that large volume piezoelectricity was induced by 90° domain switching in tetragonal PZT film.[5)] Investigation of the crystal structure and lattice strain in PZT micro cantilevers under applied voltage is therefore essential for improving the characteristics of PZT micro cantilevers. For PZT films deposited on planer substrates, a 90° domain switching phenomenon with an external electric field has been observed by Lee et al.[6)] and Nakajima et al.[7)] using synchrotron X-ray diffraction measurement and micro-Raman spectroscopy, respectively. There are only a limited number of experimental reports on actual devices, however, such as reports using focused X-ray diffraction.[8),9)] In this study, we employed micro-Raman spectroscopy to evaluate changes in the domain structure of PZT films in PZT micro cantilever under applied voltage. It can be measured in a short time and the micro-scale spatial resolution in ~1 μm.

2. Experimental procedure

PZT micro cantilevers have a Pt/LaNiO$_3$/PZT/LaNiO$_3$/Pt/Ti/SiO$_2$/silicon-on-insulator (SOI) multilayer structure. PZT films were deposited on LaNiO$_3$/Pt/Ti/SiO$_2$/Si substrates by the chemical solution method. The Pb/(Pb + Zr + Ti) and Zr/(Zr + Ti) ratios of the PZT film were 0.50 and 0.44, respectively, as evaluated by an X-ray fluorescence spectrometer. After spin coating, the as-deposited films were annealed at 250°C on a hot plate and rapid thermal annealing was performed at 650°C for crystallization. The PZT films were oriented mainly in the (100)/(001) direction, as determined using X-ray diffraction (XRD) measurement. The Pt and LaNiO$_3$ top electrodes were deposited on the PZT films by RF magnetron spattering. The obtained multilayer structure was fabricated to the piezoelectric micro cantilever by MEMS techniques reported elsewhere.[1)] A photograph and a schematic drawing of the micro cantilever are shown simultaneously in **Figs. 1**(a) and (b). The length, width and thickness of the micro cantilever were 1000, 240 and 5 μm, respectively. The thickness of the PZT films was 1.1 μm.

The Raman spectroscopy measurements were carried out using the Renishaw system 1000. A 514.5 nm-Ar$^+$ laser was used as an excitation source. The laser beam was focused at ~1 μm in diameter on a sample surface. A backscattering configuration was used for the measurement. The measurement point was the edge of the top electrode located at the middle of the micro cantilever, as shown in Fig. 1(b). The top electrode was connected to a ground and the applied voltage was changed from 0 to 13 V.

Changes in the volume fractions of the a- and c-domains and the lattice strain in the PZT films with the applied voltage were evaluated by Raman spectroscopy. It is known that the intensity of the A_1(TO)-modes are proportional to the volume fraction of the c-domain in tetragonal (100)/(001)PZT films.[10)] When the

† Corresponding author: M. Nishide; E-mail: ed10007@nda.ac.jp

(a)

(b)
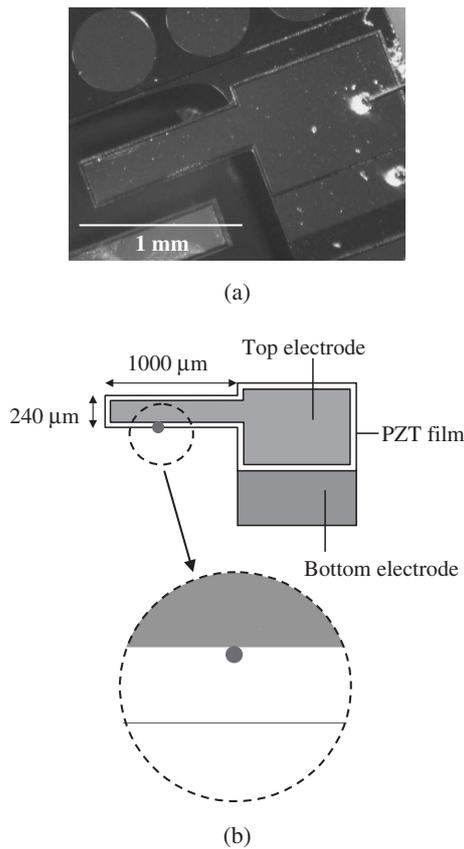
Fig. 1. (a) Photograph and (b) schematic drawing of the micro cantilever used in this study. The circle marker shows the measurement point located 500 μm from the top of the cantilever tip.
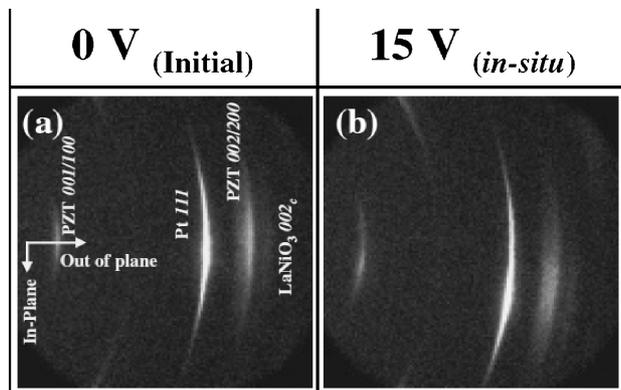
Fig. 2. XRD patterns of the micro cantilever under applied voltages of (a) 0 and (b) 15 V detected by 2D detector.[9]

Fig. 3. Raman spectra of the PZT film observed in (a) unpolarized, (b) parallel-polarized and (c) cross-polarized configurations.
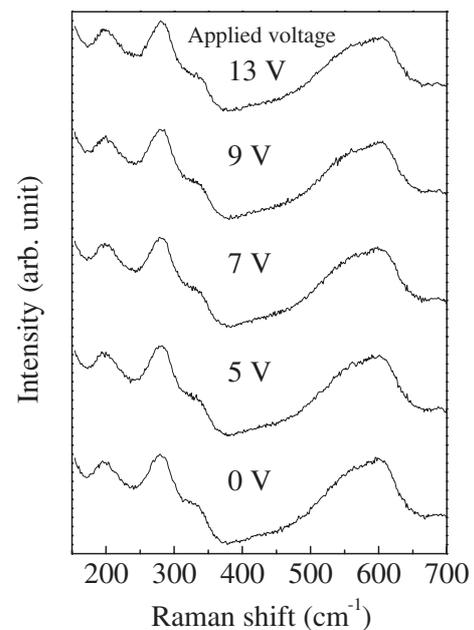
Fig. 4. Changes in Raman spectra with applied voltage for the PZT film obtained in an unpolarized configuration.

incident laser beam is perpendicular to the film surface, the intensities of the A_1(TO)-modes decrease with increases in the volume fraction of the c-domain. In addition, the lattice strain was also measured by Raman spectroscopy, which has been used extensively to detect strain in ferroelectric thin films.[11],[12]

3. Results and discussion

Figure 2 shows the XRD patterns of the PZT micro cantilever obtained using a 2D detector; this technique is described in Ref. 8). The PZT film was found to have a (100)/(001)-orientation, and no second phase was detected.

Figure 3 shows the Raman spectra of the PZT film obtained when the scattered light was unpolarized, and in a parallel-polarization configuration and a cross-polarization configuration. The Raman spectra show the intense phonon modes of E(2TO), $E + B_1$, A_1(2TO), E(3TO) and A_1(3TO) in the tetragonal phase, indicating that the PZT film was in tetragonal symmetry. In addition, there is no evidence of a second phase. For the cross-polarization configuration, the A_1(TO)-modes were not observed in accordance with the Raman selection rule. On the other hand, no such disappearance was observed in parallel-polarization configuration. This indicates some order of in-plane orientation.

Figure 4 shows the Raman spectra of the PZT film under applied voltages from 0 to 13 V obtained in an unpolarized configuration. Since the features of the Raman spectra were

Fig. 5.   Overlaid Raman spectra of the PZT film at 0, 9 and 13 V.

Fig. 7.   Applied voltage dependences of the peak shifts of the E(3TO) and A_1(3TO)-modes of the PZT film.

Fig. 6.   Applied voltage dependences of the intensities of the A_1(2TO)- (a) and A_1(3TO)-modes (b) of the PZT film.

dramatically with the applied voltage, and the shift amounts of the E(3TO)- and A_1(3TO)-modes were −0.2 and 2.7 cm⁻¹ at 13 V, respectively. For PbTiO₃, the peak positions of the E(3TO)- and A_1(3TO)-mode are shifted with hydrostatic pressure by 7.14 and −16.9 cm⁻¹/GPa, respectively.[13] The PZT film was in tensile strain at 13 V, therefore, indicating that no additional compressive in-plane lattice strain was induced in the PZT film. No obvious lattice strain was observed in the previous work using XRD measurement. The in-plane lattice parameters increased with the applied voltage, and the degree of the change at 15 V was less than 0.1%.[9] It is considered that the lattice strain was counteracted by the resilience of the bended Si substrates. The contribution of lattice strain due to the inverse piezo-electricity to the displacement of the micro cantilever is therefore considered to be small, and domain switching is considered to be the dominant driving force of the micro cantilever motion. These results are in close agreement with the micro cantilever study using XRD.[9] They indicate that micro cantilever movement can be evaluated using micro-Raman spectroscopy. Micro-Raman spectroscopy can, moreover, be applied to micro structured devices.

4.   Conclusion

In this study, in-situ Raman spectroscopy was carried out to characterize the domain switching of a PZT micro cantilever under applied voltage as well as the lattice strain. The volume fraction of the domain switching increased monotonously with increases in the applied voltage with no threshold voltage. No compressive in-plane lattice strain was induced in the PZT film by applied voltage. It is therefore considered that PZT micro cantilevers are driven mainly by domain switching, which results in bending of the micro cantilever. These results were in close agreement with a study of micro cantilevers using XRD. Raman spectroscopy is a useful method for evaluation of micro cantilever motion.

almost the same even after voltage was applied as shown in Fig. 4, the crystallographic symmetry of the PZT film was found to be unchanged. In order to analyze the Raman spectra precisely, the overlaid Raman spectra in the cases of applied voltages of 0, 9 and 13 V are shown in **Fig. 5**. As shown in Fig. 5, an intensity change with the electric field was observed for the A_1(TO)-modes, which decreased with increases in the applied voltage. On the other hand, the peak positions showed no significant change.

The intensities of the A_1(2TO) and A_1(3TO)-modes as functions of the applied voltage are shown in **Figs. 6**(a) and (b), respectively. As shown in Fig. 6, the intensities of the A_1(2TO) and A_1(3TO)-modes were monotonously decreased with increases in the applied voltage. This indicates that the a-domain volume fraction in the PZT film decreased and the c-domain volume fraction increased with increases in the applied voltage. In other words, domain switching from a-domains to c-domains occurs monotonously without a threshold voltage. It should be noted that the intensity of the A_1(TO)-modes decrease with the domain switching from the a- to c-domains in this measurement configuration (the incident direction of the excitation laser is parallel to the surface normal of the film), unlike in Ref. 10.

Figure 7 shows the peak positions of the Raman modes as functions of the applied voltage. The peak positions did not shift

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