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Investigation of Domain Distribution in Patterned PZT Thin Films Using Raman Spectroscopy

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Domain distribution, crystallinity and ferroelectric properties of micro-patterned PZT thin films were characterized with polarized Raman spectroscopy. The patterned PZT film grown on the Pt bottom electrode had good crystallinity independent of the pattern size. On the other hand, the PZT film grown outside the Pt bottom electrode had poor crystallinity or almost amorphous. The *c*-domain volume was estimated to be 55% from the polarized Raman spectra on the Pt bottom electrode. These results demonstrate that Raman spectroscopy is a very useful means to characterize micro-patterned PZT films.

Key words: Raman scattering, $Pb(Zr_xTi_{1-x})O_3$ [PZT], thin film, domain distribution

1. INTRODUCTION

$Pb(Zr_xTi_{1-x})O_3$ [PZT] thin films are great interesting for applying to nonvolatile memory, micro actuator and pyroelectricity sensor because they have excellent ferroelectricity, piezoelectricity and pyroelectricity [1-3]. Recently, researches on the PZT films with micro-patterning were carried out for the miniaturization of the devices. It is known that the properties of PZT films (ferroelectricity, piezoelectricity and pyroelectricity) depend on film orientation, crystallinity and domain distribution. Also, considering the recent advancement in the integration technology, it is desirable to employ quick, nondestructive methods with high spatial resolution.

The most commonly used method to study PZT thin films is conventional X-ray diffraction (XRD) technique [4]. However spatial resolution is generally limited to several ten microns. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) have high resolution [5-6]. However, these techniques are destructive and need special sample treatment. In addition, the evaluation of domain volume with a high spatial resolution is an essential factor for PZT films. The main polar axis lies along *c*-axis, and the superior properties are appeared in this direction for tetragonal PZT films. Therefore, a volume of *c*-domain corresponding to the (001) orientation is the most effective parameter in the practical devices.

Raman spectroscopy has nondestructive, excellent spatial resolution and high sensitivity to the change in local coordination [7]. Especially, from the polarization analyses for epitaxial PZT thin films with different

c-domain volumes, the intensity of the A_1(TO) modes was found to be linearly scale with a *c*-domain volume and the Raman spectra can be used as probe for domain distribution in PZT thin films [8].

In this study, we applied Raman spectroscopy to characterization for domain distribution in micro-patterned PZT films.

2. EXPERIMENTALS

PZT films were deposited on patterned-(111)Pt/Ti/SiO_2/(100)Si substrates by metalorganic chemical vapor deposition (MOCVD). The growth temperature was fixed at 600 °C. $Pb(C_{11}H_{19}O_2)_2$, $Zr(O\text{-}t\text{-}C_4H_9)_4$, $Ti(O\text{-}i\text{-}C_3H_7)_4$ and high purity oxygen gas were used as the source materials. The Zr/(Zr+Ti) ratio and Pb/(Pb+Zr+Ti) ratio were controlled at 0.40 and 0.50, respectively [9]. Patterned-(111)Pt/Ti/SiO_2/(100)Si substrates were prepared with electron beam (EB) lithography technique. Pattern of the bottom Pt electrodes were striped with line widths of 500, 100, 50, 10 and 5 μm. Details of mask pattern used for characterization are described elsewhere [10]. Micro Raman spectroscopy was carried out using equipments SYSTEM 1000 (RENISHAW) and an Ar^+ laser of 514.5 nm was used as an excitation source. A diameter of the beam spot and the laser power were 1 μm and ~1 mW, respectively. Measuring time was fixed at 60 seconds. The backscattering configuration was used in the measurement. The sample stage was moved using a stepping motor. The transfer accuracy was 0.1μm. Line profile of the film thickness was measured using a surface-profile measuring system (DEKTAK 3).

3. RESULTS AND DISCUSSION

Figure 1 shows the optical micrographs of the patterned-(111)Pt/Ti/SiO_2/(100)Si substrates before PZT deposition. The pattern analyses of DEKTAK clearly indicate fine patterns with linewidths varied from 500 μm to 5 μm. Also, XRD measurements confirmed that the orientation of the Pt bottom electrodes is (111). However, due to the limitation of the spatial resolution [10], the narrow pattern less than 10 μm could not evaluated solely by XRD. Thus, the complementary data were obtained from Raman measurements.

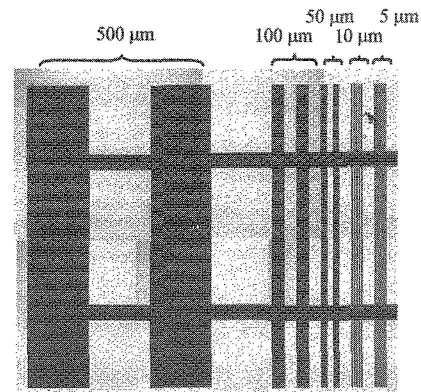

Fig. 1 Optical micrographs of patterned-Pt/Ti/SiO_2/(100)Si substrates. Line widths were 500, 100, 50, 10 and 5μm, respectively

Figure 2 shows the optical micrograph and Raman line profile of the 5-μm-width Pt bottom electrode. For the characterization of the Pt bottom electrodes, the well-known Si-LO band at 520 cm^{-1} is used as a probe. It is able to accurately distinguish the existence of the Pt bottom electrode by the intensity change of Si-LO phonon. Indeed, abrupt changes in the Raman intensity occur at Pt bottom electrodes. Note that the intensity of the Si-LO mode is greatly reduced on Pt electrodes, due to the screening effects of Pt. This highly metallic character of Pt, in turn, indicates the formation of high-quality electrodes with fine patterning of 5 μm.

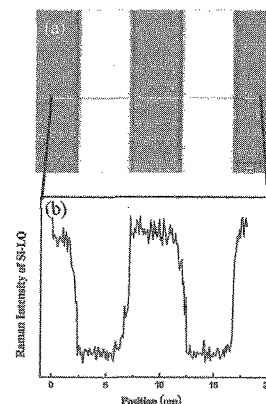

Fig. 2 The optical micrograph of Pt bottom electrodes designed with the line width of 5 μm [Fig. 2(a)] and the line profile of the Raman scattering intensities of Si-LO phonon (520 cm^{-1}) [Fig. 2(b)].

The PZT films were grown on these patterned-Pt electrodes. The thickness of the PZT films prepared on the outside of the Pt electrodes was as twice as that on the Pt electrodes. From XRD measurement, tetragonal (100)-/(001)-preferentially-oriented PZT films were grown on the Pt electrodes. On the other hand, random-oriented PZT films were grown on the outside the Pt electrodes with low crystallinity.

Figures 3(a) and (b) show the Raman spectra of PZT films grown on and outside of the 5 μm-width bottom Pt electrode, respectively. The tetragonal PZT belongs to space group symmetry C_{4v} (*P4mm*) and there are 12 Raman active modes (A_1, E and B_1). Raman peaks of E(1TO), A_1(1TO), A_1(1LO), E(2TO), E(silent) + B_1, A_1(2TO), E(3TO), A_1(3TO) and A_1(3LO) were observed as shown in Fig. 3(a). For PZT films grown outside Pt electrodes, the dominant Raman peak was LO phonon which originated from Si substrate, In contrast, PZT Raman bands are dominant for PZT films on Pt even with film thickness being of half of outside Pt electrodes. These results mean that the crystallinity of PZT film on the outside of the Pt bottom electrode was very poor or almost amorphous. Since lattice mismatch between PZT and Pt is smaller than that of between PZT and Si, the crystallinity of PZT film on the Pt bottom electrode is better than that of on the Si. These results were in good agreement with those obtained by XRD measurement [10].

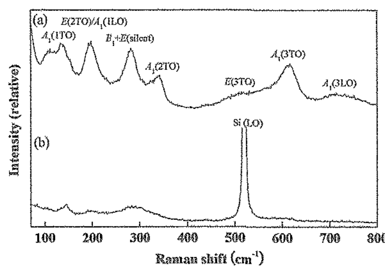

Fig. 3 The Raman spectra of PZT film grown on [Fig.3(a)] and outside [Fig.3(b)] of the 5 μm-width bottom Pt electrode.

Volume fraction of the c-domain and the polarization property were also characterized with Raman spectroscopy. Here, the intensity of the A_1(1TO) soft mode is used as a probe for domain distribution and polarization property [8, 11]. From the selection rule, the E-symmetry modes can be observed in the cross yz-polarization configuration, whereas the parallel zz-polarization configuration only yields the A_1-symmetry modes [12]. Domain distribution of PZT films grown on the Pt bottom electrode was characterized by zz-polarized Raman spectroscopy.

Figure 4 shows the zz-polarized Raman spectra of PZT films grown on Pt electrode with different widths. Note that Raman spectra are almost identical for different electrodes. This result indicates that PZT films have the same domain structure independence of the electrodes widths. The volume fraction of the c-domain of every PZT film was estimated to be almost the sum of 55%.

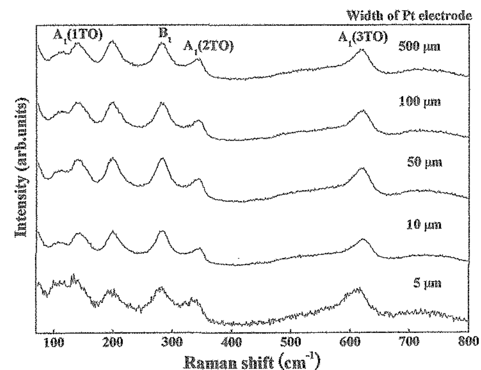

Fig. 4 The zz-polarized Raman spectra of PZT films grown on the bottom Pt electrodes with various widths.

In order to investigate the c-domain distribution of the PZT film on the Pt bottom electrode with a 5 μm width, line scan of the zz-polarized Raman spectrum was carried out. Figure 5(a) shows the surface image and scan position. Figure 5(b) shows a profile of c-domain distribution on lines calculated from the intensity of the A_1(1TO) soft mode [8]. The volume fraction of c-domain in PZT film was uniform on the Pt electrode and was estimated to be around 55 %. Estimated remnant

polarization from the volume fraction of the *c*-domain is also shown in Fig. 5(c) based on the fact that there is a linearly correlation between the A_1(TO)-mode intensity and remnant polarization [11]. The remnant polarization was estimated to be about 45 ~ 49 μC/cm^2 and had good uniformity on the Pt electrode.

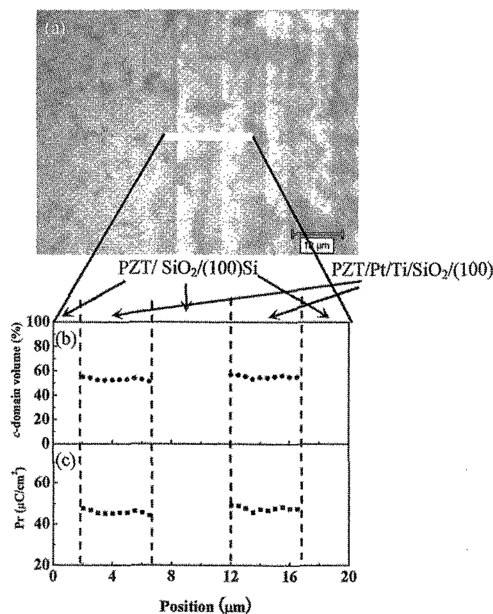

Fig. 5 The optical micrograph of PZT film grown on Pt bottom electrode with 5 μm widths [Fig. 5(a)] and the line profile of *c*-domain distribution [Fig. 5(b)]. Estimated remnant polarization from *zz*-polarized Raman spectra of this area is also shown in Fig. 5(c).

4. SUMMARY

Domain distribution, crystallinity and ferroelectric properties of micro-patterned PZT thin films were characterized with polarized Raman spectroscopy. Intensity of the Raman peaks of A_1(TO) modes were observed from PZT film grown on the patterned Pt bottom electrode. On the other hand, very weak Raman peaks originated from PZT phase were obtained from PZT film grown on the areas without the bottom Pt electrode. It was found that the PZT films grown on the patterned Pt bottom electrode had good crystallinity, and a *c*-domain volume of 55% independent of the pattern size. On the other hand, the PZT films grown without the Pt bottom electrode had poor crystallinity or almost amorphous. It was also found that Raman spectroscopy is a very useful means to characterize distribution of a volume fraction of the *c* domain and ferroelectricity of micro-patterned PZT films.

5. REFERENCES

[1] J. F. Scott and C. A. P. de Araujo, *Science* **246,** 1400-1405 (1989).

[2] O. Auciello, J. F. Scott, and R. Ramesh, *Phys. Today* **51,** 22-27 (1998).

[3] H. Han, X. Song, J. Zhong, S. Kotru, P. Padmini, and R. K. Pandey, *Appl. Phys. Lett.* **85,** 5310-5312 (2004).

[4] K. Saito, T. Kurosawa, T. Akai, T. Oikawa and H. Funakubo, *J. Appl. Phys.* **93,** 545-550 (2003).

[5] Y. Ding, J. S. Liu, I. Maclaren, Y. N. Wang and K. H. Kuo, *Ferroelectrics* **262,**1011-1020 (2001).

[6] M. Alexe and A. Gruverman, Nanoscale Characterization of Ferroelectric Materials, *Scanning Probe Microscopy Approach* (*Springer Verlag, Heidelberg,* 2004).

[7] M. Osada, M. Kakihana, S. Wada, T. Noma and W.-S. Cho, *Appl. Phys. Lett.* **75,** 3393-3395 (1999).

[8] K. Nishida, M. Osada, S. Wada, S. Okamoto, R. Ueno, H. Funakubo and T. Katoda, *Jpn. J. Appl. Phys.* **44,** L827–L829 (2005).

[9] S. Yokoyama, T. Ozeki, T. Oikawa and H. Funakubo, *Jpn. J. Appl. Phys.* **41,** 6705-6708 (2002).

[10] S. Yokoyama, K. Takahashi, S. Okamoto, A. Nagai, J. Minamidate, K. Saito, N. Ohhashi, H. Haneda, O. Sakata, S. Kimura, K. Nishida, T. Katoda and H. Funakubo, submitted to *Jpn. J. Appl. Phys.*

[11] M. Osada, K. Nishida, S. Wada, S. Okamoto, R. Ueno, H. Funakubo and T. Katoda, *Appl. Phys. Lett.* **87,** 232902-1-232902-3 (2005).

[12] S-H. Lee, H. M. Jang, H. H. Sung and H. Yi, *Appl. Phys. Lett.* **81,** 2439-2441 (2002).

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