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SPM Studies of Hydrogen-induced Degradation Mechanism in Ferroelectric Pt/PLZT/Pt Capacitors

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Abstract: It is well known that forming gas annealing in an ambient containing hydrogen causes severe degradation in the polarization hysteresis loop of a ferroelectric capacitor. To clarify the degradation mechanism, the effects of hydrogen on Pt/PLZT/Pt capacitors have been investigated using scanning probe microscopy (SPM) piezoelectric measurement. In the virgin state, the capacitor consists of ferroelectric domains at positive or negative remanent states. After hydrogen annealing, the local hysteresis loop for the domain in the positive (negative) remanent state shifted toward the negative (positive) voltage axis and positive (negative) polarization axis. It was found that the degradation of the polarization hysteresis characteristic originated from the shifts in the local hysteresis loops of each domain in the capacitor. The degradation of the polarization hysteresis loop can be explained combining the local shifted hysteresis loops for each domain. It was also found that each domain includes a non-switching portion, which causes the suppression of the saturation polarization

Key word: scanning probe microscopy, piezoelectric, ferroelectric capacitor, hydrogen annealing, PLZT

1. INTRODUCTION

It is well known that forming gas annealing in an ambient containing hydrogen causes severe degradation in the polarization-voltage (P-V) hysteresis curve of ferroelectric capacitors[1]. The freezing of the ferroelectric domain has been observed using a tunneling acoustic microscope[2]. The formation of polar hydroxil bonds is pointed out from Raman spectra[3], and the catalytic nature of Pt-electrode has been attributed[4]. However, there is still no fundamental understanding of the mechanism of the degradation process.

In this paper, to clarify the degradation mechanism, the local ferroelectric switching characteristic of Pt/(Pb,La)(Zr,Ti)O_3(PLZT)/Pt capacitors was investigated by means of the scanning probe microscopy (SPM) piezoelectric measurement technique[5,6]. Piezoelectric properties are always associated with the ferroelectric properties of the sample. Piezoelectric (d_{33}) and displacement-voltage (S-V) hysteresis loops exhibit a local switching characteristic where the tip is positioned over the sample, whereas the polarization-voltage (P-V) hysteresis loop exhibits a total polarization charge within a ferroelectric capacitor.

2. EXPERIMENTAL

The 260-nm-thick PLZT film was deposited on a Pt/SiO_2/SiO_2/Si substrate by using the sol-gel technique. The PLZT film was about 90% (111) oriented. Any non-180° domain could not be observed in the transmission electron microscopy (TEM) result. The Pt top electrode was deposited by dc sputtering and was then fabricated to the dimension

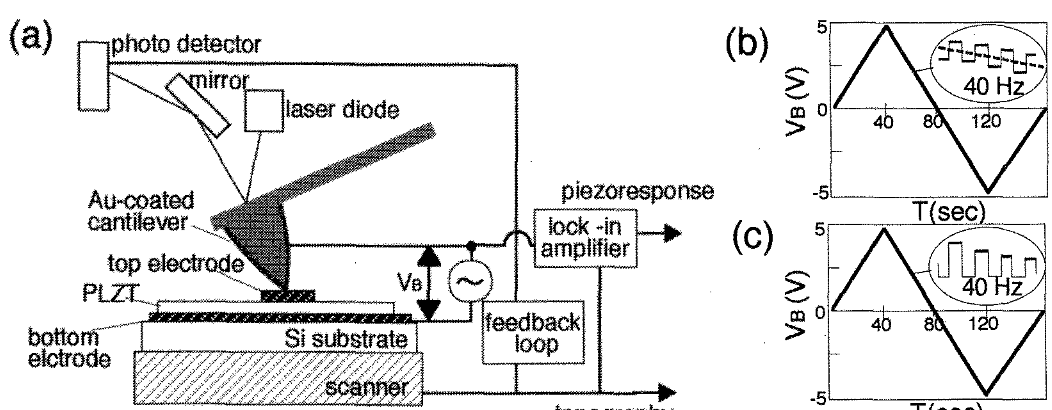

Fig. 1 (a) Schematic of the SPM piezoelectric measurement system, (b) profiles of a modulated ac voltage for d_{33}hysteresis loop, and (c) displacement hysteresis loop.

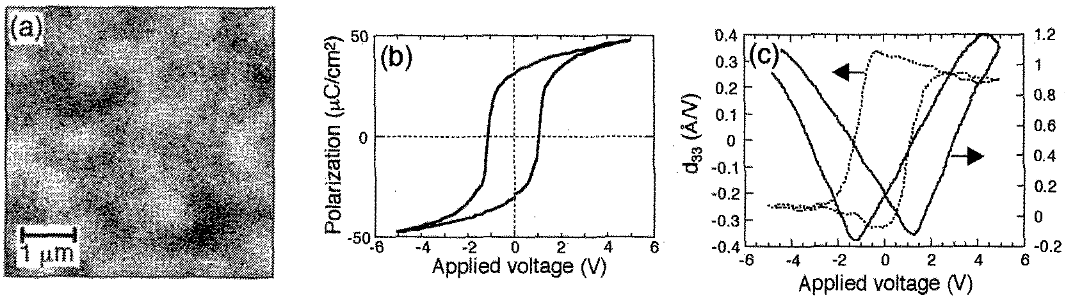

Fig. 2 (a) Piezoresponse (domain) image, (b) P-V hysteresis loop, and (c) d_{33} and S-V hysteresis loops for the virgin Pt/PLZT/Pt capacitor.

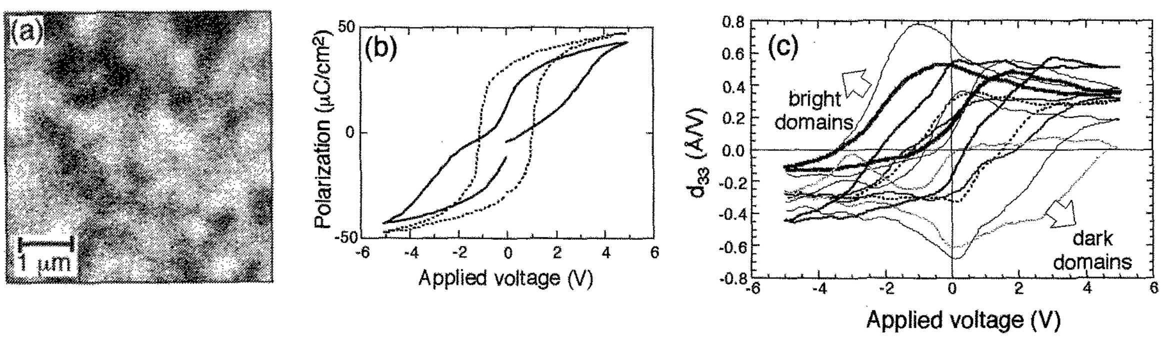

Fig. 3 (a) Piezoresponse image, (b) P-V hysteresis loops, (c) d_{33} loops for the Pt/PLZT/Pt capacitor after hydrogen annealing.

of 90×90 μm^2 by photolithography and ion milling. The capacitors were annealed in N_2+5% H_2 at 7.6 Torr, at 150 °C for an hour.

Figure 1 shows the schematic diagram of the experimental setup. A commercially available SPM (Seiko Instruments SPI3800) was employed in this study. The P-V hysteresis loops, the d_{33} hysteresis loops[5,6], and the S-V hysteresis loops[7] were obtained using an Au-coated tip probe at the top electrode of the capacitor in the contact force mode. The tip was positively biased with respect to the bottom electrode. To separate the piezoelectric signal from noise, a modulated ac voltage, as shown in Fig. 1(b) for the d_{33} hysteresis loop and Fig. 1(c) for the S-V hysteresis loop, was applied between the tip and the bottom electrode, and the SPM scanner displacement signal was detected by using a lock-in technique.

An image of the piezoelectric signal can be observed by scanning the tip over a certain area. An imaging voltage with an amplitude of 1 V and a frequency of 10 kHz was applied between the tip and the bottom electrode[6].

3. RESULTS AND DISCUSSION

Preliminary study of the domain structure of the virgin Pt/PLZT/Pt reveals a random distribution of domains measuring 0.5-1 μm in width (which is larger than lateral grain size in the PLZT film of about 200 nm), polarized $+P_r$ or $-P_r$ (Fig.2(a)). The dark and

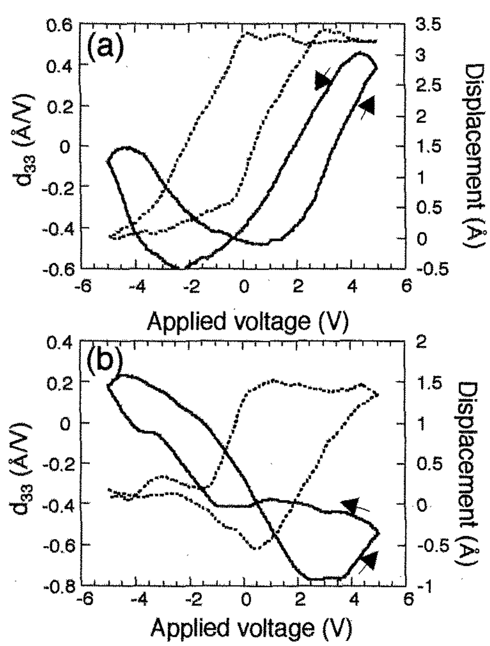

Fig. 4 d_{33} and S-V hysteresis loops for bright domain (a) and dark domain (b) of the hydrogen-annealed Pt/PLZT/Pt.

bright contrasts in the piezoresponse image are associated with remanent polarization states $+P_r$ and $-P_r$, respectively. The P-V hysteresis loop and a typical d_{33}, and S-V hysteresis loops for the virgin capacitor are shown in Fig. 2(b) and Fig. 2 (c), respectively. These curves show symmetrical voltage dependence.

After hydrogen annealing, The P-V hysteresis degraded into a propeller shape, and a suppression of about 15% of the saturation polarization and about 50% of the remanent polarization were observed (Fig.3(b)). The piezoresponse image of the Pt/PLZT/Pt capacitors after annealing in hydrogen is shown in Fig. 3(a). The bright and dark domains can also be seen with a higher domain contrast.

The local d_{33} hysteresis loops were measured by fixing the tip on each domain. For the bright domain, the loops are shifted upward and in the negative voltage direction along the voltage axis, whereas for the dark domain, the loops are shifted downward and in the positive voltage direction along the voltage axis(Fig. 3(c)). The absolute value of the voltage shift in the d_{33} hysteresis loop for the each domain, which depends the size of spontaneous polarization of each domain, differs from domain to domain.

The S-V hysteresis loops were measured for the one of the bright domains and one of the dark domains, as shown in Fig. 4. After hydrogen annealing the S-V loops became asymmetric in shape. The bright domain is difficult to expand at negative bias voltage and the dark domain is difficult to expand at positive bias voltage. The polarization state of the capacitor might be pinned during the hydrogen annealing and PLZT lattice could not reverse their position.

The voltage shift effects are similar to the thermal imprint phenomena[8,9], are explained to be caused by charge trapping at the electrode interface. The vertical shifts of the d_{33} hysteresis loops and asymmetric voltage dependence of the S-V hysteresis suggest that the domains include the non-switching area. The slight suppression of the saturation polarization might be correlated to the vertical shift of the hysteresis loops.

Thus the above microscopic study revealed the following. In the virgin state, positively or negatively polarized domains exist in the capacitor. After hydrogen annealing, local hysteresis of each domain shifts toward the upper left direction or lower right direction, depending on the initial polarization state. The pinched P-V hystersis loop after hydrogen annealing should be the summation of all local hystereses of domains. The small remanent polarization is due to the combined effects of the shifted loops, and the slight decrease in saturation polarization is caused by the non-switching portion within the capacitor.

4. CONCLUSION

The effects of hydrogen on Pt/PLZT/Pt capacitors have been investigated by SPM piezoelectric measurement. This approach enables the local characterization of switching properties. It was found that the degradation of the polarization hysteresis characteristic originated from the shifts in the local hysteresis loops of each domain in the capacitor. The degradation of remanent polarization can be explained by combining the local shifted hysteresis loops of each domain. It was also found that each domain includes a non-switching portion, which causes the suppression of the saturation polarization

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