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FERROELECTRICITY OF LEAD-ZIRCONATE-TITANATE THIN FILMS PREPARED BY LASER ABLATION

TOSHIO OGAWA*, HIDEO KIDOH*, HIDEYUKI YASHIMA**, AKIHARU MORIMOTO** AND TATSUO SHIMIZU**
*Murata Manufacturing Co,Ltd., Nagaokakyo, Kyoto 617, Japan
**Department of Electronics, Faculty of Technology, Kanazawa University, Kanazawa 920, Japan

ABSTRACT

Lead-zirconate-titanate films were prepared by excimer laser ablation. The coercive field of films deposited on MgO substrates with an electrode was lower than that of films deposited on sapphire substrates. Laser fluence influenced the grain and crystalline size, resulting in a change in the Ec. Film thicknesses were varied over a range from 0.3 to 2.4μm, with the thinnest film showing a large remanent polarization even at an applied effective voltage of 5V.

INTRODUCTION

Recently, lead-zirconate-titanate (PZT) thin films have attracted great attention for use in nonvolatile random access memory devices[1]. We have prepared PZT films by excimer-laser ablation and reported that little fluctuation in composition was observed between the film and the target[2,3]. We, moreover, reported the ferroelectricity of the PZT films prepared by laser ablation[3,4]. The electrical properties of these films are similar to those of films prepared by other methods such as rf-magnetron sputtering[5] and metalorganic chemical vapor deposition (MOCVD)[6].

However, as described below, some problems remain in applying these films to memory devices. One of them is the switching voltage level[7]. Because the standard thickness of the PZT film we have prepared is in a range of between 1 and 2μm, more than 20V of applied voltage is necessary for obtaining a large remanent polarization (of more than 20μC/cm^2). The basic requirements of PZT films in ferroelectric memory devices are that they can be switched at low voltages (5V or less), and have both a sufficiently large remanent polarization (P_r), and a large number of read/write cycles. The voltages required for switching depend on the coercive field (E_c), film thicknesses, and the shape of the hysteresis loop (squareness). We have therefore attempted to prepare a film with a low E_c and smaller thickness in order to obtain one which can be switched at low voltages that are compatible with the operating voltages used in Si integrated circuits (ICs).

EXPERIMENTAL

Details of the apparatus used in preparing the PZT films are similar to those described previously[4]. Film deposition was carried out by the ablation of a PZT ceramic target in a vacuum chamber at an O_2 gas pressure of 133Pa (1Torr) using an ArF excimer laser. The ceramic target was a single-phase pellet of $Pb(Zr_{0.52}Ti_{0.48})O_3$ with 1 wt.% of Nb_2O_5, which had a high relative dielectric constant (ε_r) and low mechanical quality factor (Q_m). The substrates were r-plane sapphire and single-crystal MgO (100) with and without an Ni-alloy electrode[8]. The nominal substrate temperature (T_n) was measured by inserting a thermocouple into the substrate holder during film deposition. The real substrate surface temperature (T_s) was corrected from T_n by using the correction curve

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determined previously using both a thermocouple on the substrate surface and a radiation thermometer. The laser energy used for the ablation was between 65 and 250 mJ/shot, which corresponds roughly to a laser fluence of 2.6-10 J/cm²•shot. T_s was fixed at 530°C in these experiments. After the ablation, the films were cooled to room temperature over 3 hours in vacuum. The film preparation conditions are summarized in Table I.

X-ray diffraction (XRD) measurements were carried out using Cu-Kα at room temperature to investigate the film structure. The morphology of the films was inspected using scanning electron microscopy (SEM). In order to investigate the electrical properties of the film, after deposition of PZT film on MgO substrate with 1mm width Ni-alloy electrode, Ni-alloy or Au film electrode was deposited as upper electrode. The overlapping area of the upper and the lower electrodes was 1mm². We measured the relative dielectric constant (ε_r) and the dielectric loss factor ($\tan\delta$) at 1kHz using an LCR meter, and observed the film's D-E hysteresis loop using a Sawyer-Tower circuit at 60Hz.

Table I. Preparation conditions of the PZT films.

Laser	ArF excimer laser
wavelength	193 nm
pulse width	10 nsec
repetition rate	5 shots/sec
laser energy	65 - 250 mJ/shot
laser fluence	3.5 - 10J/cm²•shot
gas pressure	O_2 133Pa (1Torr)
substrate temperature	530°C
target	$Pb(Zr_{0.52}Ti_{0.48})O_3$
substrate	MgO(100), r-plane sapphire

RESULTS AND DISCUSSION

Substrate dependence

The D-E hysteresis loops of the films deposited on MgO and r-plane sapphire substrates with the Ni-alloy electrode are shown in Fig.1. These films were prepared at a laser fluence of 3.5J/cm²•shot. Although the P_r of the film on MgO substrate is larger than that on a sapphire substrate, the E_c on MgO is smaller than that on sapphire. Even in the case of film prepared on MgO, however, applied effective voltages of greater than 20V, which are too high to be compatible with IC operating levels, are necessary to obtain a large remanent polarization (> 20μC/cm²). Therefore, films with a lower E_c and/or smaller thicknesses are desirable.

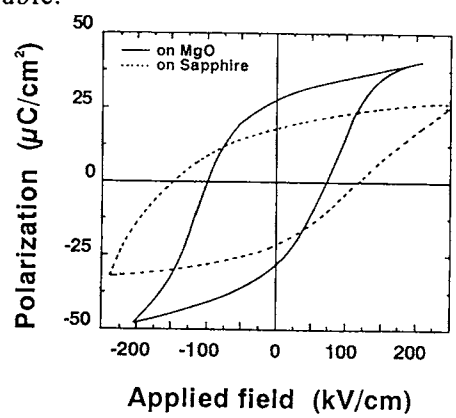


Fig.1 D-E hysteresis loops of the PZT films.

Laser fluence dependence

At first, we tried to decrease the Ec by increasing the crystalline and/or grain size. Generally, the Ec of ferroelectric ceramics such as $BaTiO_3$ and PZT decreases with increasing grain and/or crystalline size. The most popular method to enlarge the crystalline size is by raising the substrate temperature. Some problems, however, exist with this method such as reevaporation of the element due to its high vapor pressure and reactions between the film and either the substrate or electrode. Accordingly, we tried to enlarge the crystalline size without increasing the substrate temperature. In order to do so, it is necessary to provide excess energy to the growing surface. One of the characteristic phenomena of the laser ablation method is the existence of a plume, an emission of light caused by excited materials being ejected from the target. This phenomenon suggests that atoms ejected from the target have a relatively high energy compared with those released by thermal evaporation. Furthermore, the size of a plume increases with increasing laser fluence, which suggests that the amount of excited atoms arriving at the substrate increases when the ablation is held at a higher laser fluence. In light of this, we expected that increasing the laser fluence would enhance migration at the growing surface and enlarge the crystalline size, resulting in a decrease in the Ec. Therefore, we investigated the influence of laser fluence on film properties such as film composition, crystallinity, and the ferroelectric properties of the film deposited on a MgO substrate.

The film composition is almost the same as that of the target[3]. From XRD measurements, we confirmed that all the films prepared at a laser fluence range of between 2.6 and 10 J/cm^2•shot are almost perovskite single phase and oriented in the (100)/(001) direction. Figure 2 shows the laser fluence dependence of the crystalline size calculated from the full width at half maximum (FWHM) of the perovskite (100)/(001) XRD peak of the film deposited on MgO substrate without the electrode, and indicates that crystalline size increases with laser fluence. Considering this result, we expected that the crystalline and/or grain size deposited on the electrode would also increase with increasing laser fluence. The (111) oriented PZT films were obtained on a Ni-alloy electrode. SEM photographs of the films deposited on the electrode at different laser fluences are shown in Fig.3. From these photographs, we confirmed that grain size also increases with laser fluence. In light of the results shown in Fig.2 and Fig.3, we expected that the Ec of the film would be reduced by increasing the laser fluence.

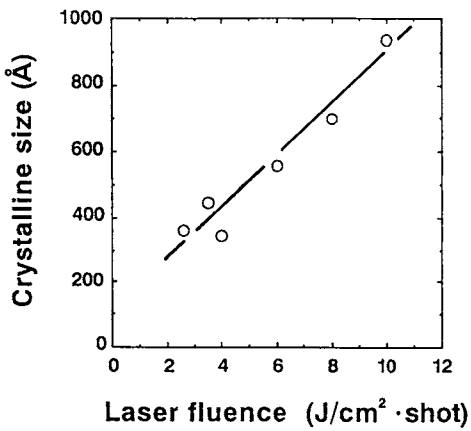
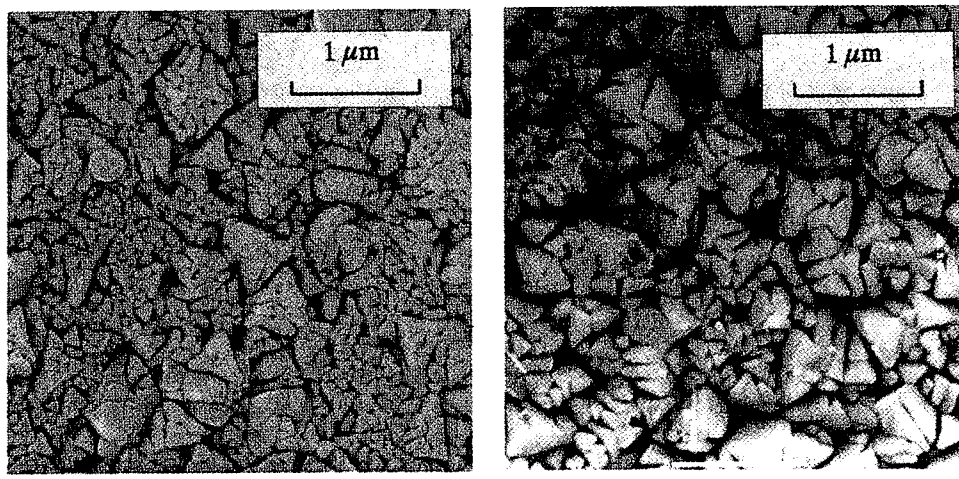


Fig.2 The effect of laser fluence on the crystalline size of the film.



(a) 3.5J/cm²•shot (b) 9.2J/cm²•shot

Fig.3 SEM photographs of the film deposited on MgO with an electrode.

Figure 4 shows the laser fluence dependence of Ec. In this figure, the values shown for the various Ec's were measured when the Pr was set at 20 μC/cm². The value of Ec decreased with increasing laser fluence as expected. The decrease in Ec, however, was only about 10%, so a significant decrease in the switched voltage was not realized by changing the laser fluence. The dielectric properties of the film are summarized in Table II.

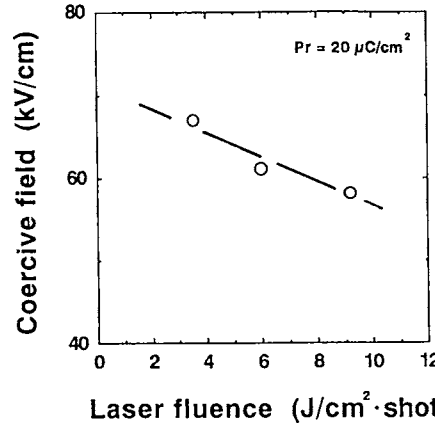


Fig.4 The dependence of Ec on laser fluence .

Table II. Dielectric properties of the PZT films.

laser fluence (J/cm²•shot)	film thickness (μm)	ε_r	tanδ (%)
3.5	1.2	512	10.7
6.0	1.8	886	9.5
9.2	1.5	635	8.8

Film thickness dependence

Next, we focused on varying the film thickness in order to reduce the applied voltage. In doing so, we varied it between 0.3 and 3.6μm by changing the deposition time while the laser fluence was fixed at 7J/cm²•shot. From an XRD measurement, we confirmed that all the films deposited on MgO substrate without the electrode were almost entirely perovskite phase and were oriented in a (100) or (001) direction. The film thickness dependence of the FWHM with a (100)/(001) XRD peak is shown in Fig.5. The value of the FWHM was nearly constant, suggesting that the crystalline size was also nearly constant over a film thickness range of 0.3 to 3.6μm. On the other hand, the lattice constants of the PZT films became larger with decreasing film thickness, probably as a result of a lattice mismatch between PZT films and MgO substrates. At any rate, no significant degradation of film crystallinity due to a decrease in film thickness was recognized in this film thickness range.

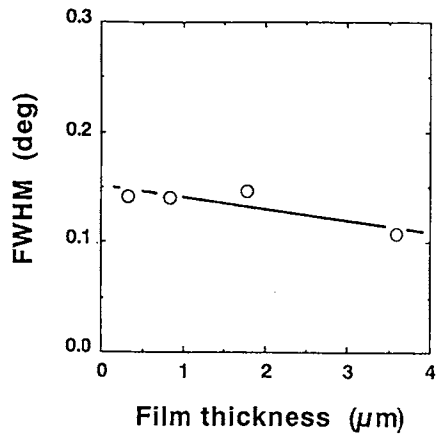


Fig.5 The dependence of the FWHM of the perovskite (100)/(001) peak on film thickness.

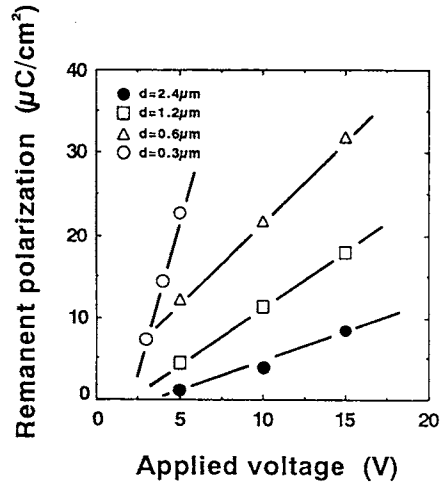


Fig.6 The relationship between applied voltage and P_r in PZT films of various thicknesses.

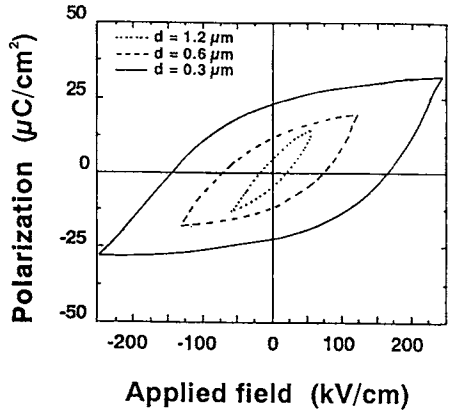


Fig.7 D-E hysteresis loops of PZT films of various thicknesses. (Applied voltage of 5V).

Figure 6 shows the applied voltage dependence of the P_r of the films with different thicknesses. By decreasing the film thickness, we observed that the voltage necessary for obtaining the same level of P_r became smaller. Figure 7 shows the D-E hysteresis loops of films of various thicknesses. The film with a thickness of 0.3μm showed a large P_r (20μC/cm²) even at an applied voltage of 5V. From the results shown in Fig.6 and Fig.7, we confirmed that films of submicron thicknesses have low access voltages which are compatible with standard Si IC operating levels.

SUMMARY

PZT films were deposited on MgO (100) substrates with an Ni-alloy electrode by excimer laser ablation, and the following results obtained:
(1) Laser fluence influenced the crystalline and grain size and the coercive field. Films with low E_c were obtained by increasing the laser fluence.
(2) As film thicknesses were varied between 0.3 and 2.4μm, the thinnest film showed the largest P_r even at an applied voltage of 5V.

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