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Influence of Temperature Annealing on the Crystallization, Hysteresis Loops and Leakage Current in Au/PZT/ Pt/TiO2/Si(100) Films Grown by Low Temperature MOCVD Method

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***Abstract*—PZT films were deposited on the Pt/TiO$_2$/Si(100) substrate at low temperature as low as 380 °C by metal-organic chemical vapor deposition (MOCVD) process. The effects of the temperature annealing by conventional furnace annealing (CFA) on the crystallization, hysteresis loops and leakage current of PZT films were investigated. After the annealing treatment, the films were transformed into polycrystalline PZT thin films with (001) and (100) orientation, respectively. Moreover, the crystal orientation (001/100) of the films were increased by the increases in the temperature of annealing. The improved ferroelectric behavior was influenced by grain orientation. The film with higher (001) orientation exhibited higher the remnant polarization (2*Pr*) and lower leakage current density. PZT at annealing temperature of 590 °C for 20 minutes exhibited the best ferroelectric properties. The 2*Pr* showed was about 24.80 μC/cm^2, when the applied voltage was ± 5V, and the leakage current density of the PZT films was about 1.697 × 10^{-5} A/cm^2 at ±5V.**

***Index Terms*—PZT films, MOCVD, annealing treatment, crystallinity, grain orientation.**

I. INTRODUCTION

Ferroelectrics are materials that undergo a spontaneous polarization, which can be controlled by an external strain, either mechanical or electrical. This polarization is due to atom displacements in the lattice along a preferred crystallographic direction, which depend on the type of the ferroelectric [1]. For applications in ferroelectric random access memory (FeRAM), recently, most studies were focused on obtaining high-quality lead zirconate titanate (PZT) films [1-3]. PZT film is a promising candidate for future FeRAM, which is a non-volatile memory utilizing ferroelectric material in order to maintain an electric charge.

The properties of the PZT films depend on many parameters, including composition, crystal structure, substrate films, film thickness and electrodes. In addition, the composition (Zr/Ti) ratio and crystal orientation, which significantly control the properties of PZT bulk, film thickness and film substrate interface, are also critical for improving the performance of PZT thin films [2]. The polycrystalline PZT films are common in practical devices and systems. The fundamental required properties and performances of the PZT films are strongly controlled by their microstructure including the size, shape and orientation of grains and their distributions. The optimal property of PZT crystals with Perovskite structure is generally at a given orientation [3]. Therefore, it is of interest to grow the textured films.

The growth of PZT films has been achieved by various methods, such as RF-sputtering [4], [5], pulsed laser deposition (PLD) [6], sol gel [7], and metal organic chemical vapor deposition (MOCVD). Among these thin-film processes, MOCVD is the most promising methods because the deposition of ferroelectric thin films can be achieved at low temperature [8] that is also very important in the integration process of FeRAMS in preventing the degradation of ferroelectric thin films and of the ferroelectric/semiconductor interface due to mutual diffusion and thermal damage [9]. In performing the low-temperature MOCVD of ferroelectric thin films such as PZT and Barium Stronsium Titanate (BST), several methods, such as seed layer method [10], photo-[11] or plasma-assisted [12] method, low-pressure method using surface reaction [13], and appropriate source materials combination method [14], have been previously reported. The seed layer method and appropriate source materials combination method are very useful for obtaining PZT thin films at low temperatures, in spite of their simplicity.

In this paper, we discuss the low-temperature MOCVD method to grow ferroelectric PZT films at a susceptor temperature as low as 380 ℃ by applying low-pressure surface reaction. The effects of the annealing temperature by conventional furnace annealing (CFA) on the crystallization, hysteresis loops and leakage current of PZT films are also discussed.

II. MATERIALS AND METHOD

The substrates used in this work were 8-inch silicon wafers with a platinum bottom electrode layer and a TiO$_2$ adhesion layer (Fig. 1). The generated substrate structure was Pt/TiO$_2$/Si(100). The PZT films were grown on the

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Pt/TiO_2/Si(100) substrate using a liquid delivery metal organic chemical vapor deposition (MOCVD) system named ″Doctor T″ developed by Yamagata University and WACOM R&D Co. Ltd., Japan. This MOCVD system features a novel instantaneous vaporizer and has excellent stability for depositing homogeneous films for large wafers. An 80-nm-thick film was deposited on the Pt bottom electrodes. In order to perform the low-temperature growth of ferroelectric PZT films, we demonstrated the low-temperature deposition using MOCVD at a susceptor temperature as low as 380 ℃ with the total pressure of 533 Pa. The source precursors used were $Pb(DMAMP)_2$ = 0.232 ccm, $Zr(MMP)_4$ =0.148 ccm, and $Ti(MMP)_4$ = 0.0 90 ccm and oxygen (O_2) and argon (Ar) were used as the oxidizing and carrier gases, respectively. The source materials used in this study and typical deposition conditions are summarized in Table I.

TABLE I: DEPOSITION CONDITIONS OF PZT SAMPLE

Pb sources	0.232 ccm
Ti sources	0.148 ccm
Zr sources	0.090 ccm
Substrate	Pt/TiO_2
Thickness of Pt	201 nm
Thickness of TiO2	17.74 nm
Thickness of PZT	80 nm
Carrier gas (Ar) flow rate	0.35 SLM
Oxygen gas flow rate	1.6 SLM
Susceptor temperature	380 ℃
Total pressure	533 Pa
Deposition time	40 min

For electrical characterization of the thin films, gold top electrodes were applied to the film surfaces using a shadow masking evaporation method. The top electrode structures were 300-μm-diameter circle patterned using shadow masks. The PZT films were annealed over a temperature range of 550 ℃ to 650 ℃ for 20 minutes by conventional furnace annealing in an O_2 atmosphere in order to crystallize the PZT films in the ferroelectric phase. X-ray diffraction (RAD-γ A type, Rigaku Denki Co. Ltd.) with CuKα radiation was used to examine the crystal orientation of the PZT films.

The polarization as a function of voltage (P-V) and current density as a function of voltage (J-V) were measured as deposited and after performing the thermal annealing process. A ferroelectric test system (Precision LC, Radiant Technology) was employed to measure the electrical properties by the drive terminal bottom electrode (Pt) that was connected to the drive of the precision LC as shown in Fig. 1. The systematic hysteresis loop behavior and relationship with J-V characteristics by applying two connections between drive terminal and top or bottom electrode have been reported in previous paper [18]. All measurements were carried out at room temperature.

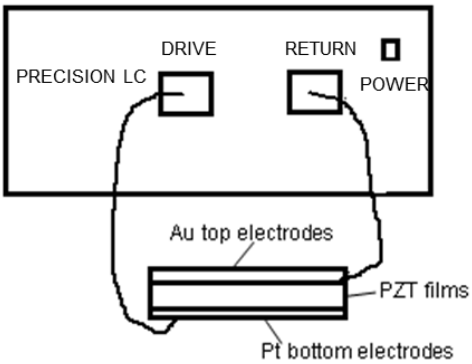

Fig. 1. Illustration model of drive precision LC connected to the Pt bottom electrode.

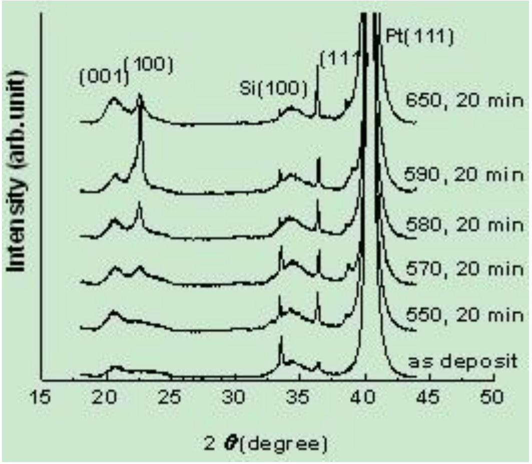

Fig. 2. XRD pattern of the PZT films crystallized at different temperature annealing.

III. RESULTS AND DISCUSSIONS

The effects of the different annealing processes on the structure of PZT thin film were characterized by x-ray diffraction (XRD). Fig. 2 shows the XRD pattern of the PZT films as deposited and after annealing over the temperature range from 550 ℃ to 650 ℃ for 20 minutes. The as-deposited PZT films shows a broad peak of (001) oriented crystal, whereas the (100) oriented crystal was obvious after annealing; both oriented crystal of (001) and (001) were improved by raising the temperature of annealing, and the films annealed at 590 ℃ for 20 minutes had an obvious larger peak for (100).

Fig. 3 shows the ferroelectric hysteresis loops dependence on the crystallization conditions. The P-V hysteresis loops were measured at a frequency of 100 Hz for the sample with an 80-nm PZT thickness and a capacitor area of 7.85×10^{-5} cm^2. The P-V hysteresis loops as deposited and annealed at 550 ℃ does not show a ferroelectric hysteresis loops, which is clearly related to the absence of a polycrystalline phase. On the other hand, the P-V hysteresis of the sample annealed at 570 ℃ to 650 ℃ shows ferroelectric hysteresis loops.

There were considerable changes in the shape of curves and the remnant polarization (2*Pr*) after annealed up to 550 ℃, where the 2*Pr* of the films increased with increasing annealing temperature, except for the loop at 650 ℃. The 650 ℃-annealed films became a linear P-V relation (Fig. 3d) due to the decreased the peaks of (001) and (100) oriented crystal in the PZT films. However, the hysteresis loops at

570 ℃ (Fig. 3a) and 580 ℃ (as shown in Fig. 3b) show paraelectric-like characteristics, but the 2*Pr* and ±Vc indicate improvements with increasing temperature up to 580 ℃. The 2*Pr* of each annealed film shows 1.128 μC/cm^2 for films annealed at 570 ℃ and 2.386 μC/cm^2 for films annealed at 580 ℃. The saturated P-V hysteresis is found at the temperature annealing of 590 ℃ (Fig. 2c), and it shows 2*Pr* of about 24.80 μC/cm^2 at an applied voltage of ± 5V. The grain size (dXRD) was calculated from the FWHM of the (100) and (001) diffraction peaks using the Scherrer's equation [15], dXRD = $K\lambda\beta$ cos θ, where λ is the x-ray wavelength, β is the FWHM of the diffraction line, θ is the angle of diffraction, and the constant K = 0.9. As shown in Table II, the remnant polarization was influenced by grain orientation. The improved 2*Pr* was probably related to the fact that the grain size of preferential orientation on planes (001) and (100). Moreover, the improvement of the 2*Pr* is determined by the grain orientation of (001).

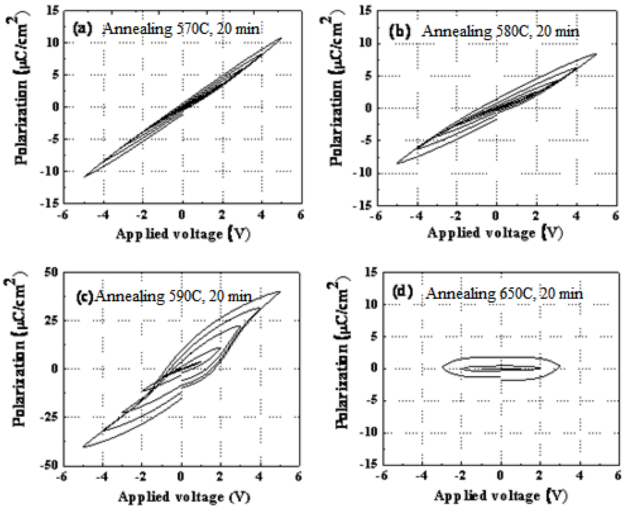

Fig. 3. Ferroelectric hysteresis loops dependence on the temperature annealing condition.

Furthermore, in preferentially (001) and (100) oriented polycrystalline PZT films, the number of grains could form a domain contributing to the average domain polarization [17]. It suggests that the grain size is the primary factor determining domain structure and consequently the electrical properties of ferroelectric films such as P-V hysteresis loops and leakage current density. In addition, the electrical properties of ferroelectric material are intrinsically determined by the domain structure and the mobility of domain walls.

The relationship between the grain size and domain structure has been previously reported by Rent *et al.* [16] that the grain size of ferroelectric films has strong influence on the domain structure and wall mobility based on TEM observations. They also reported and categorized the grain size into two domain structures. If the grain size is less than 150 nm, the domain structure is characterized by the predominance of single domains, and in large grain (>150 nm), domain structure is characterized by the predominance of multi domains. In the present study, the grain size of the (100) orientation crystal PZT annealed at 590 ℃ was more than 150 nm, and therefore the domain structure is characterized by the predominance of multi domains. On the other hand, the average grain orientation of (001) and (100) annealed at 570 ℃, 580 ℃ and 650 ℃ were 50-122 nm and the domain structure is characterized by the predominance of single domain.

In the domain structure predominance of multi domains, the domain structure can be easily changed by external field, therefore the film having large grains with a multi-domain-predominated structure can be easily switched leading to large remnant polarization [16-17]. As a result the PZT films annealed at 590 ℃ show better ferroelectric properties than other annealing temperatures. Conversely, in the single-domain-predominated structure, which usually has small grains had a small remnant polarization.

TABLE II: TEMPERATURE ANNEALING (TA) DEPENDENCE ON THE GRAIN SIZE (D) AND 2 *PR*

TA (℃)	*D* (nm)		2*Pr*
	I(100)	I(001)	
550	51,496	-	-
570	56,890	27,482	1,128
580	56,792	122,440	2,386
590	56,959	142,986	24,80
650	58,064	81,835	-

Fig. 4 shows the J-V characteristics of a sample at an applied voltage of ±5 V with a delay time of 100 ms. The PZT film annealed at 590 ℃ has an optimal leakage current density compared to the other temperature. The leakage current density was about 1.697×10^{-5} A/cm^2 at ±5 V for annealing temperature 590 ℃; and the film showed a large grain size of (100) oriented crystal (Table II). However, J-V characteristics of the PZT sample at 650 ℃ could not be measured due to large leakage current. The reason for this behavior is unclear, however we consider due to the relationship between the presence of poor crystalline PZT phase and a linear P-V hysteresis loop.

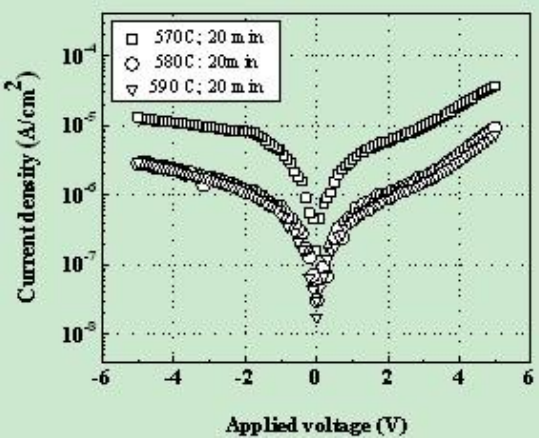

Fig. 4. J-V characteristic on the temperature annealing condition

IV. CONCLUSIONS

PZT films were deposited on a Pt/TiO$_2$/SiO$_2$/Si(100) substrate using low temperature MOCVD at temperature as low as 380 ℃. The ferroelectricity of the PZT films was influenced by grain orientation. The grain orientation of (100) and (001) increased with increasing annealing temperature, except for the PZT films annealed at 650 ℃. The 590 ℃ annealing temperature for 20 minutes exhibited good P-V hysteresis loops with 2*Pr* of about 24.80 μC/cm^2, and low leakage current density about 1.697×10^{-5} A/cm^2 at applied voltage of ±5 V. On the other hand, the 650 ℃ annealed films demonstrated a linear P-V relation due to the reduction of grain orientations of (100) and (001). The J-V characteristics could not be measured due to large leakage current. The future works related to the current research are recommended includes investigate the actual operation of PZT capacitors prepared by a low temperature processing.

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