Influence of Hf content on structure and electric properties of PHT thin films with self-buffered layer by PLD

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Abstract Three components of lead hafnate titanate ($\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$, PHT) thin films have been fabricated by pulsed laser deposition (PLD) on the Pt (111)/Ti/SiO₂/Si (100) substrates. In order to reduce the mismatch between the thin films and substrates, low temperature self-buffered layer is adopted. The effects of Hf content on structure and electric properties of PHT thin films have been investigated. The PHT near the MPB ($x=0.48$) shows the highest remnant polarization ($2P_r=93.23\mu\text{C}/\text{cm}^2$) and capacitance, even if its leakage current is a little worse than others. It should be noticed that the PHT ferroelectric films have a good performance after 2.15×10^{10} fatigue reversals, which indicates that PHT films as a promising material can be applied in ferromagnetic random access memory (FRAM).

Keywords Lead hafnate titanate; morphotropic phase boundary; ferroelectric thin film; pulsed-laser deposition (PLD); remnant polarization

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1. Introduction

Ferroelectric thin films with perovskite structure attract much attention for their fundamental properties and device applications, such as non-volatile ferroelectric random access memory (NVFRAM), infrared detectors, sensors and actuators, ferroelectric field-effect transistors. Lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, PZT) is one of the important ferroelectric materials owing to its good electrical properties. In the previous studies of PZT, many research groups made the effort to find the morphotropic phase boundary (MPB) as a result of its unique electrical properties and structure. The PZT phase diagram as accepted which is determined by Jaffe et al. [1] implies that MPB occurs around $x=0.52$. Mishra et al. [2] showed the electromechanical and dielectric response of PZT with $x=0.525$ is maximum, and, the maximum electromechanical response has been contributed [3] to the coexistence of tetragonal and rhombohedral phases around MPB. However, ferroelectric capacitors undergoing repeated switching (fatigue) tends to lose available remnant polarization. Improving the fatigue characteristics becomes a stringent problem. Watanabe et al. [4] found that the A-site or B-site substitution in BIT have received excellent fatigue properties. Schorn et al. [5] reported Hf^{4+} substituting for Zr^{4+} in PZT revealed a nice ferroelectric behavior and better fatigue performance. Lead hafnate titanate ($\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$, PHT), as a new kind of material, seems to be more suitable for FRAM

application. Compared with PZT, the component of MPB in PHT proved to be very similar. Jaffe et al. [1] have already reported both rhombohedral and tetragonal phase were observed in the range of $x=0.475-0.500$. Frantti et al. [6] found that PHT around $x=0.50$ contained both monoclinic and rhombohedral phase. Sawai et al. [7] found that there existed a structure distortion from tetragonal symmetry in PHT near $x=0.50$. Bedoya et al. [8] found that $\text{Pb}_{0.94}\text{Sr}_{0.06}\text{Hf}_{0.49}\text{Ti}_{0.51}\text{O}_3$ exhibits the best properties.

Several researches showed that the structural and thermal mismatch between the thin films and substrates has bad impact on the performance of ferroelectric capacitor [9]. Wu et al. [10] have put forward an idea that adopting low temperature self-buffered layer to reduce the mismatch and influence the preferred orientation of $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$. In the previous study, our research team members Lin et al. [11] have fabricated the $\text{PbHf}_{0.30}\text{Ti}_{0.70}\text{O}_3$ films with tetragonal structure successfully by using low temperature self-buffered layer. It is found that the low temperature self-buffer layer not only can improve the microstructure, but enhance the electric properties. In this paper, $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films were prepared for its component near the MPB. To make a comparison with $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$, $\text{PbHf}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and $\text{PbHf}_{0.70}\text{Ti}_{0.30}\text{O}_3$ films were also made. To characterize its ferroelectric behavior and electrical properties, PHT was made as a thin film capacitor. We adopted the low temperature self-

buffered layer to fabricate PHT films on the platinum coated silicon substrates and made an exploration on the electrical properties. The results reveal that the $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films show the highest remnant polarization and largest capacitance, but the highest leakage current. On the other hand, the fatigue measurements indicate that PHT films have better prospects development in FRAM.

2. Experimental

Pulsed laser deposition (PLD) has been widely used to produce the oriented ferroelectric thin films with its high reliability. Three components of PHT films were grown through the use of KrF excimer laser (Lambda Physik Complex 201, 248 nm). The PHT ceramics target was prepared by a conventional solid-state reaction technique from 99.99% pure powders (Pb_3O_4 , TiO_2 and HfO_2). To compensate the volatilization of Pb during the target of sintering and films deposition process, a wt.10% additional Pb_3O_4 is essential. Followed by the acetone, ethanol, and de-ionized water cleaning to substrates, substrates were prepared for the deposition of films. In the follow-up experiments, the self-buffered layer was grown at 300°C with the oxygen pressure of 20 Pa and the thickness was about 20nm. Then, the PHT film was deposited on the self-buffered layer at 600°C for 130nm. The annealing temperature was 600°C for 30 min.

The microstructures were measured by Bede D1 X-ray diffraction

(XRD). For the purpose of testing the performance of films, the metal/ferroelectric/metal (MFM) structure was applied. The nickel/gold top electrodes were chosen deposited by electron beam evaporation, whose areas are about $2.5 \times 10^{-4} \text{cm}^2$. The electric performance testing structure of PHT films was shown in **Fig.1**. The polarization–electric field (P-E) and fatigue curve were carried out by a Radiant Precision LC (RT2000) material analyzer. The capacitance-voltage (C-V) and leakage-voltage (I-V) tests were performed by Agilent 4294A and Agilent 4156C.

Fig.1 The test structure of $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ films with self-buffered layer.

3. Results and discussions

3.1 Structure Analysis

Fig.2 shows the XRD patterns of the $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ thin films. As we know, PHT has the similar structure with PZT [1]. The tetragonal (T) and rhombohedral (R) phases of PZT are distinguishable on XRD since the 200/020/002 set of reflections form a doublet and singlet for T and R phases respectively [2]. The XRD diagram of $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ proves the

coexistence of two phases. With increasing x from 0.48 to 0.52, the T phase of disappears, which means that the structure of PHT changes from two phases to R phase. Along with the x continuously increasing to 0.7, the structure is the similar as $x=0.52$.

Fig.2 XRD patterns of $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ thin films with self-buffered layer for $x=0.48, 0.52$ and 0.70 .

3.2 Electric Properties

Ferroelectric P-E hysteresis loops were tested as shown in **Fig.3**. The test frequency was about 100Hz. It can be seen that PHT films with different components reveal individual P-E hysteretic behaviors. The $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ thin film have the largest remnant polarization ($2\text{Pr}=93.23\mu\text{C}/\text{cm}^2$). Lin et al. [11] have showed the highest remnant polarization of $\text{PbHf}_{0.30}\text{Ti}_{0.70}\text{O}_3$ films is about $63\mu\text{C}/\text{cm}^2$. It is also

reported that the 2Pr of BTH and PZT films are about $45.7\mu\text{C}/\text{cm}^2$ and $69\mu\text{C}/\text{cm}^2$, respectively [12, 13]. Compared with these mainstream ferroelectric films, $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films reveal better ferroelectric performance. As shown in **Fig.4**, the $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films, whose component near MPB, reveal best ferroelectric performance. At MPB region, the polarization directions of electric domain is more than other regions and are easy to be polarized under the force of electric field. With increasing x from x=0.48 to 0.70, the remnant polarization decreases.

Fig.3 Ferroelectric P-E hysteresis of $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ films for x=0.48, 0.52 and 0.70.

Fig.4 Variation of 2Pr with component (x) of $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ thin films.

The capacitance and the leakage current of films were measured as shown in **Fig.5** and **Fig.6**. Capacitance is an important indicator for relating to the dielectric performance of film. The capacitance versus bias voltage was measured at room temperature and the test frequency was about 1MHz. As shown in **Fig.5**, the $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films appear the largest capacitance in all samples, which indicates the highest dielectric constant. This phenomenon is similar with the PZT near the MPB [2]. In previous research, the capacitance of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films measured at 1 KHz is about 760pF [14]. **Fig.6** shows the current density characteristics of PHT films. The PHT films with $x=0.48$ have worse insulation performance, compared with other PHT films. This behavior can be understood by considering the coexistence of two phases makes the

number of grain boundary and defects increase. As we know, the leakage current density is closely connected with the defects. The more the number of defects, the higher the current density. The loops of the films seen to be asymmetric as a result of the electrodes, test equipment and an internal electric field in the thin films.

Fig.5.The capacitance versus voltage curves of the $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ thin films for $x=0.48, 0.52$ and 0.70 .

Fig.6. Current density of $\text{PbHf}_x\text{Ti}_{1-x}\text{O}_3$ films for $x=0.48, 0.52$ and 0.70 .

The reliability of the ferroelectric films is another important factor of the application. Ferroelectric fatigue is much fatal for the electric apparatus based on the switchable polarization, such as NVFRAM. The fatigue properties of some PHT films were investigated in **Fig.7**. These measurements were processed in a switching electric field of ± 250 kV/cm. As the result shows, after 2.15×10^{10} switching cycles, the remnant polarization ($2P_r$) of the $\text{PbHf}_{0.52}\text{Ti}_{0.48}\text{O}_3$ and $\text{PbHf}_{0.70}\text{Ti}_{0.30}\text{O}_3$ films almost maintain the initial value. On the contrary, the $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films show a little bad fatigue performance for 15% degradation. In the previous studies, after 10^9 switching cycles, BTH and PZT thin films show a significant degradation of polarization (generally greater than or equal to 20%) [5, 15]. It was assumed that the fatigue is mainly due to the pinning

of domain walls by space charge or charged point defects near Pt electrodes [16]. Furthermore, the insulation performance of films, which often relates to the defects, has an impact on the fatigue. As discussed previously, the coexistence of two phases induce the number of defects increased. This is the reason why the fatigue performance of $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ is a bit poor compared to other PHT films.

Fig.7 The fatigue curves of PHT thin films for $x=0.48, 0.52$ and 0.70 .

From all the above results, it can be seen obviously that the $\text{PbHf}_{0.48}\text{Ti}_{0.52}\text{O}_3$ films near MPB show highest remnant polarization and capacitance, even if its leakage current and fatigue performances are little worse than other components. The cause of this phenomenon is the coexistence of two phases. As the structure of PHT changes to single phase, the ferroelectric and capacitance properties become worse. The

fatigue tests show that PHT has very good application prospects in FRAM.

4. Conclusion

In summary, three components of PHT thin films were fabricated on the Pt (111)/Ti/SiO₂/Si (100) substrates successfully by PLD and their properties have been tested. Compared with other components of PHT, the PbHf_{0.48}Ti_{0.52}O₃, whose component is close to the phase boundary, reveals better ferroelectric and capacitance properties, though its leakage current and fatigue performances are a bit poor. Furthermore, the PHT films show nice fatigue after 2.15×10^{10} switching cycles, which indicate PHT films have a vast practical future in FRAM.

Acknowledgements

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