Epitaxial Ferroelectric Thin Films on Silicon Substrates for Future Electronic Devices

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A lead lanthanum zirconate titanate \((\text{Pb}_{1-2/3-y}\text{La}_y)(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3, \text{PLZT})\) thin film with a thin-film bottom electrode of strontium ruthenium oxide \((\text{SrRuO}_3, \text{SRO})\) can be grown epitaxially on a (001) silicon substrate. Ceria \((\text{CeO}_2)\) and yttria-stabilized zirconia \((\text{YSZ})\) were used as a buffer layer. This paper discusses the orientation and domain structure of PLZT thin films on an SRO/CeO\(_2\)/YSZ buffer layer. All oxide thin films of the PLZT/SRO/CeO\(_2\)/YSZ heteroepitaxial structure were oriented toward (001). The CeO\(_2\) and YSZ grew epitaxially with a cube-on-cube alignment with the diamond structure of the silicon. The PLZT and SRO thin film rotates 45° in-plane with respect to the fluorite structure of CeO\(_2\). The remanent polarization of a \(\text{PbLa}_{0.03}\text{Zr}_{0.45}\text{Ti}_{0.55}\text{O}_3\) epitaxial thin film is 10 \(\mu\text{C/cm}^2\) and is smaller than that of a (001)-oriented epitaxial PLZT thin film with a platinum bottom electrode on a magnesia \((\text{MgO})\) substrate. The profiles of the reciprocal space mapping reveal that the PLZT epitaxial thin films were distorted into a pseudocubic structure by the tensile stress from the silicon substrate.

1. Introduction

Ferroelectric thin films have attracted much interest, both from the fundamental and applied aspects. These films are used in, for example, ferroelectric random access memories (FeRAMs), piezoelectric actuators, micro-electro-mechanical systems (MEMS), and pyroelectric detectors. \(\text{Pb(Zr}_{x}\text{Ti}_{1-x})\text{O}_3\) (PZT) and \((\text{Pb}_{1-2/3-y}\text{La}_y)(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3\) (PLZT) are promising materials for use as ferroelectric thin films. PZT thin films have already been prepared by several methods, for example, sputtering, metal organic chemical vapor deposition, chemical solution deposition, and pulsed laser deposition (PLD). PLD is a suitable method for preparing highly oriented multicomponent thin films. Using PLD, it is easy to transfer the stoichiometric composition of components, including volatile elements such as lead and bismuth, from the target to the thin film. Furthermore, it is also easy to realize multilayer structures if the targets are changed during the deposition process.

Epitaxial growth of thin films on a silicon substrate is considered to be a key technology for fabricating even thinner and smaller electronic devices in the future, because their leakage current and optical scattering are expected to be lower than those of polycrystalline films. These features are important for applications in devices such as metal-ferroelectric-semiconductor-field effect transistors (MFS-FETs), optical devices, and so on. However, the epitaxial growth of oxide thin films on a silicon substrate has some basic problems. First, the surface of the silicon is easily oxidized into amorphous silicon oxide by the oxygen in oxide films or the ambient atmosphere. No epitaxial oxide thin film can be prepared on the amorphous silicon oxide, because it cannot continue the crystallinity of the silicon. Secondly, most of the cations in the oxide film easily diffuse...
into the silicon substrate or react with the silicon. The secondary phase formed by diffusions or reactions disturbs the crystallinity of the silicon. Thus, an essential characteristic for epitaxial growth of an oxide thin film on a silicon substrate is low reactivity with silicon. Some typical oxides are alumina (Al₂O₃),⁵⁷ magnesia (MgO),⁶⁷ and yittria-stabilized zirconia (YSZ).⁸

YSZ thin film grows epitaxially on a silicon substrate. The epitaxial relationship between YSZ and silicon is \((001)\) of YSZ \(\parallel\) \((001)\) of silicon and \((100)\) of YSZ \(\parallel\) \((100)\) of silicon (cube-on-cube alignment).³¹ Perovskite compounds such as barium strontium titanate ((Ba,Sr)TiO₃) and strontium ruthenium oxide (SrRuO₃, SRO) are also grown epitaxially on YSZ thin film. However, the epitaxial relationships between YSZ and these perovskite compounds are \((011)\) of perovskite \(\parallel\) \((001)\) of YSZ.⁹ The polarization direction of a ferroelectric perovskite compound with a tetragonal phase is \((001)\). This indicates that the polarization of ferroelectric perovskite is rotated 45° with respect to the substrate surface. The polarization of a \((011)\)-oriented perovskite thin film is smaller than that of a \((001)\)-oriented one.

Ceria (CeO₂) also grows epitaxially with the cube-on-cube alignment on a YSZ thin film.⁹ Ceria (CeO₂) also grows epitaxially with the cube-on-cube alignment on a YSZ thin film.⁹ Recently, the CeO₂/YSZ double buffer layer has attracted much interest, because perovskite thin films orient toward the \((001)\) direction on a CeO₂ thin film. Electrode materials with a perovskite structure, such as \((\text{La}_{0.8}\text{Sr}_{0.2})\text{CoO}_3\) (LSCO) and \((\text{YBa}_2\text{Cu}_3\text{O}_{7-δ})\) (YBCO) have been prepared on a CeO₂/YSZ double buffer layer on a silicon substrate.¹⁰⁻¹⁵

Strontium ruthenium oxide (SrRuO₃, SRO) is promising as an electrode material because it has a simple perovskite structure. Another advantage for YBCO and LSCO is the controllability of the composition during the deposition process, because SRO consists of three elements. The epitaxial growth of SRO on a CeO₂/YSZ buffer layer has not been investigated fully. Furthermore, the domain structure, orientation, and polarization of an epitaxial PLZT thin film on SRO/CeO₂/YSZ heteroepitaxial structures on a silicon substrate are unclear.

In this paper, we describe how we formed a PLZT/SRO/CeO₂/YSZ/Si heteroepitaxial structure by the PLD method. We also discuss the relationship between the domain structure and the polarization property of the PLZT thin film.

2. Experimental procedure

First, we cleaned 2-inch \((001)\) silicon wafers with dilute HF acid to remove the amorphous SiO₂ layers on the surface. The YSZ, CeO₂, and SRO buffer layers were deposited by pulsed laser deposition. The wavelength of the KrF excimer laser was 248 nm. Ceramics of 8 mol% \(\text{Y}_2\text{O}_3\)-doped \(\text{ZrO}_2\), \(\text{CeO}_2\), and SRO with a 99.9% purity were used as targets. The depositions were carried out in \(7.3 \times 10^{-2}\) Pa under an oxygen flow at 740°C. The final thicknesses of the YSZ, CeO₂, and SRO were around 30, 30, and 100 nm, respectively.

The PLZT thin films were prepared on the SRO/CeO₂/YSZ thin films on a silicon substrate by a chemical solution method. The solution compositions were \(\text{Pb}_{1.13}\text{La}_{0.03}\text{Zr}_{0.45}\text{Ti}_{0.55}\text{O}_3\) and \(\text{Pb}_{1.13}\text{La}_{0.03}\text{Zr}_{0.2}\text{Ti}_{0.8}\text{O}_3\) (hereafter PLZT\(3_{20}/55\) and PLZT\(3_{20}/80\), respectively). The coated SRO/CeO₂/YSZ silicon wafers were heated by a hot plate at 350°C after spin coating. This process was repeated four times. Finally, the wafers were heated at 650°C in a furnace for 10 minutes under oxygen flow. The final thickness of the PLZT films was around 200 nm. The PLZT thin films were also prepared on platinum (Pt) coated MgO substrates with the \((001)\) orientation taken as the reference of polarization. The Pt thin film was prepared by radio frequency (RF) sputtering at 650°C and was grown epitaxially on the MgO substrate.

For the top electrode, a Pt thin film was prepared by RF sputtering the PLZT thin films at room temperature. The top electrode was 200 µm in diameter and 150 nm thick. After sputtering, the silicon wafers with the top electrodes were an-
nealed again at 600°C for 1 hour under an oxygen flow.

The phases and the orientations of the thin films were determined by X-ray diffraction (XRD, X-pert-Pro MPD, Philips). The microstructures of the thin films were observed with a transmission electron microscope (H-9000NAR, Hitachi). The D-E hysteresis loop of the PLZT thin film was measured with a ferroelectric tester in virtual ground mode (RT6000HS, Radiant).

3. Results and discussion

Figure 1 shows the 2theta-theta XRD profile of the PLZT3/45/55 thin film grown on the SRO/CeO2/YSZ multilayer structure on the (001) silicon substrate. No peaks were detected except for the (00l) peak. This indicates that the PLZT, SRO, CeO2, and YSZ thin films were oriented toward the (001) direction, which is perpendicular to the surface of the substrate.

Figure 2 shows the XRD pole profiles (in-plane measurement) of the PLZT3/45/55 thin films on the SRO/CeO2/YSZ structure on the (001) silicon substrate. The profiles show four poles corresponding to the (l0l) plane, indicating that the films grew epitaxially and have ø-scan patterns with a fourfold rotational symmetry. The rotation angle ø of the (202) peak of YSZ and CeO2 coincides with that of silicon. This indicates that each layer grew epitaxially with a cube-on-cube alignment on the silicon crystal. The (101) peaks of SRO and PLZT thin films with the perovskite structure are shifted 45° with respect to the YSZ, CeO2, and silicon. This indicates that these perovskite compounds rotate 45° with respect to the fluorite structure of the CeO2 crystal. The reason for this rotation is the difference between the lattice constants of the perovskite and fluorite structures. Figure 3 shows a schematic diagram of the epitaxial relationship between the perovskite, fluorite, and diamond structures. The lattice constants of the fluorite and diamond structures are 0.51 nm of YSZ and 0.54 nm of silicon, respectively. The mismatch between the lattice constants of YSZ and silicon (~5.6%) is relatively small. However, the lattice constants of the per-
ovskite and fluorite structures are 0.393 nm of pseudocubic SRO and 0.54 nm of CeO$_2$, respectively. The mismatch between the (100) direction of SRO and the (100) direction of CeO$_2$ is -27.2%, and the mismatch between the (110) direction of SRO and the (100) direction of CeO$_2$ is +2.9%.

Because of these two mismatches, the distance between the (110) planes of the SRO is larger than the distance between the (100) planes of the CeO$_2$, and as a result, the SRO crystal is subjected to a compressive stress. This compressive stress is believed to increase the (001) orientation of the PLZT thin film, because the a-axis is shorter than the c-axis.

Figure 4 shows the microstructure of the PLZT3/45/55 thin film on the SRO/CeO$_2$/YSZ/Si heteroepitaxial structure. An amorphous SiO$_2$ layer (around 7 nm) was observed on the interface between the YSZ and silicon. This SiO$_2$ layer was formed by the diffusion of oxygen in the later process, because the growth of the YSZ thin film was influenced by the crystallinity of the silicon. No reactive phase was observed at the interfaces between the CeO$_2$-YSZ, CeO$_2$-SRO, and SRO-PLZT.

Figure 5 shows the D-E hysteresis loops of the epitaxial PLZT3/45/55 and PLZT3/20/80 thin films on the SRO/CeO$_2$/YSZ/Si structure and the epitaxial PLZT3/45/55 on the Pt/MgO structure. The remanent polarization of the PLZT3/45/55 on the silicon substrate is 10 µC/cm$^2$. The remanent polarization of the PLZT3/45/55 on the Pt/MgO is 42 µC/cm$^2$. The remanent polarization of the
PLZT3/45/55 film on the silicon substrate is much smaller than that of the PLZT3/45/55 film on the Pt/MgO substrate.

The ratio of the c-axis to the a-axis of the lattice parameter increases with the amount of titanium in the PLZT. The remanent polarization of the PLZT3/20/80 thin film is expected to be larger than that of the PLZT3/45/55 thin film. However, the remanent polarization of the PLZT3/20/80 thin film is almost the same as that of the PLZT3/45/55 thin film. To understand this difference in the polarization properties of the PLZT thin films on the silicon and Pt/MgO substrates, the lattice parameters in and out of the plane of the PLZT film should be evaluated.

Figure 6 shows the reciprocal space mappings of the (204) planes of the PLZT3/45/55, PLZT3/20/80, and SRO thin films on the PLZT/SRO/CeO$_2$/YSZ/Si heterostructure. The (204) planes of the CeO$_2$ and YSZ thin films and the silicon substrate could not be detected, because they are rotated 45° in-plane with respect to the SRO and PLZT thin films, as shown in Figure 3. These profiles indicate the in-plane 90° domain structure of the PLZT thin film.

The in-plane and out-of-plane lattice parameters of each film and substrate are summarized in Table 1, and the lattice parameters of the PZT45/55, SRO, Pt, and MgO powders are summarized in Table 2. The lattice parameters of Pt and MgO coincide with the lattice constants of the powders. The crystal symmetry of the Pt thin film on the MgO substrate is cubic, because the...
The lattice parameter of the a-axis is the same as that of the c-axis. The Pt thin film is not distorted by the MgO substrate. The lattice parameters of the SRO thin films on the CeO$_2$/YSZ double buffer layer are slightly larger than those of the SRO powder and are spread out by the silicon substrate. The SRO thin film has a pseudocubic symmetry, because the in-plane lattice is almost the same as the out-of-plane lattice.

The lattice parameters of PLZT3/45/55 are different from those of the PZT45/55 powder.\textsuperscript{16} The in-plane lattice parameters of the PLZT3/45/55 film are slightly larger than those of the out-of-plane lattice. These lattice parameters indicate that the PLZT3/45/55 thin film has a (100) orientation (a-axis orientation) with a pseudocubic structure. The X-Y line in Figure 6 (a) indicates that the in-plane and out-of-plane lattice parameters are equal. Area A indicates that the polarization of the lattice is perpendicular to the surface, because the out-of-plane lattice parameter is larger than the in-plane parameter. Thus, the lattices of area A contribute to the remanent polarization. The remanent polarization of the epitaxial PLZT3/45/55 thin film on silicon is smaller than that of the epitaxial films on Pt/MgO (Figure 5) because part of the crystal contributes to the remanent polarization. This contribution is due to the in-plane distortion that occurs in the PLZT thin film due to the tensile stress applied from the silicon substrate. The PLZT lattice becomes aligned with the silicon substrate at the crystallization temperature of 650°C. Around 600°C, the thermal expansion coefficient of the PLZT ($6 \times 10^{-6}$ K$^{-1}$) is larger than that of silicon ($4 \times 10^{-6}$ K$^{-1}$).\textsuperscript{17} In the cooling process, the PLZT film contracts more than the silicon substrate. Thus, tensile stress is applied to the PLZT film from the silicon substrate. This tensile stress orients the PLZT film toward the (100) direction at the Curie temperature. Around 650°C, the thermal expansion coefficient of an MgO substrate ($14 \times 10^{-6}$ K$^{-1}$) is larger than that of the PLZT film.\textsuperscript{17} Thus, compressive stress is applied to the PLZT film from the MgO substrate. This compressive stress orients the PLZT film toward the (001) direction at the Curie temperature. The component of the (001) orientation (c-axis orientation) due to the compressive stress has been applied. However, the results shown in Figures 5 and 6 indicate that the effect of the silicon substrate on the polarization is larger than that of the mismatch.

The PLZT3/20/80 has two peaks, one at a-axis orientation and another at c-axis orientation, because the ratio of the a-axis to the c-axis is larger than in PLZT3/45/55. The lattice parameters of the component of the a-axis orientation are 0.398 nm for the a-axis and 0.397 nm for the c-axis. The lattice parameters of the component of the c-axis orientation are 0.396 nm for the a-axis.
and 0.411 nm for the c-axis. The component of the c-axis of PLZT increases with the amount of lead titanate. However, this indicates that most lattices of PLZT3/20/80 also have a pseudocubic structure. The stress affects the hysteresis of the PLZT thin film more than that of the composition. In the future, we plan to evaluate the imprint and the switching speed of this ferroelectric capacitor.

To improve the polarization property of epitaxial PLZT thin films on a silicon substrate, it is necessary to relax the tensile stress from the substrate and to increase the degree of (001) orientation, as described in this paper. We believe that the tensile stress can be relaxed by developing the buffer layer. In the future, we will also search for optimum materials for the epitaxial growth of perovskite films on silicon substrates.

4. Conclusions

This paper described the preparation of a PLZT/SRO/CeO$_2$/YSZ heteroepitaxial structure on a (001) silicon substrate and discussed the orientation of PLZT thin films on a SRO/CeO$_2$/YSZ buffer layer. All oxide thin films of the PLZT/SRO/CeO$_2$/YSZ heteroepitaxial structure were oriented toward (001). The CeO$_2$ and YSZ grew epitaxially with a cube-on-cube alignment with the diamond structure of the silicon. The PLZT and SRO thin films were rotated 45° in-plane with respect to the fluorite structure of the CeO$_2$. The remanent polarization of the PLZT3/45/55 epitaxial thin films was 10 µC/cm$^2$, which is smaller than that of a (001) oriented epitaxial film on an MgO substrate. The profiles of reciprocal space mapping reveal that the PLZT epitaxial thin films were distorted into a pseudocubic structure by tensile stress from the silicon substrate. The findings described in this paper indicate many interesting areas for future investigations into epitaxial PLZT films, and we plan to develop the properties of these films on silicon substrates in the near future.

References

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