Electrical properties of ferroelectric Y-doped Hf–Zr–O thin films prepared by chemical solution deposition

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Y-doped Hf–Zr–O (Y-HZO) films have been prepared by chemical solution deposition. It is shown that good ferroelectric property can be obtained for the Y-HZO film with a Y concentration of 3.2% after 800 °C crystallization annealing at a reduced pressure of 50 Pa. It is also demonstrated that the reduced pressure pre-annealing at temperatures as low as 400 °C is effective to obtain good ferroelectric properties, regardless of the crystallization annealing ambient. This is presumably because the pre-annealing under reduced pressure promotes the formation of nuclei in the orthorhombic phase. © 2022 The Author(s). Published on behalf of The Japan Society of Applied Physics by IOP Publishing Ltd

1. Introduction

Hafnium-dioxide (HfO2)-based ferroelectric materials have attracted much attention for integrated circuit applications such as nonvolatile memories and advanced MOSFETs.1–6 One of the reasons for the matching of HfO2-based ferroelectric materials with silicon electronics is that the HfO2-based materials exhibit good ferroelectric properties even in thin films less than 10 nm. In addition, they have a larger bandgap than conventional ferroelectric materials such as Pb(Zr,Ti)O3 (PZT) and (Bi,La)4Ti3O12 (BLT). Thus, the HfO2-based ferroelectric materials are suitable to scale nonvolatile memory and gate insulator applications. In particular, a ferroelectric-gate field effect transistor (FET)7–13 is one of the promising applications. HfO2 has been used as a high permittivity gate dielectric in Si-MOSFETs since the chemical reaction of HfO2 with Si substrate, forming the SiO2 interfacial layer, is not so serious.14 Hence, using the HfO2-based ferroelectric material as a gate dielectric, we can expect a ferroelectric-gate FET with good electrical properties, which is scalable, and high-density implementation would be possible for nonvolatile memory applications as in the flash memory. It is interesting to note that the first report on the device appeared about 60 years ago15, and that the revival of ferroelectric-gate FET is not only due to the nonvolatile memory applications, but also the potential of steep slope transistors using the negative-capacitance effect which has been discussed recently.16–19

There are several crystalline phases in HfO2-based materials and the stabilization of the orthorhombic phase (o-phase), which is the meta-stable phase, is important to obtain ferroelectric properties.20–23 The stabilization of the o-phase can be commonly obtained by doping the other elements, such as Si, Y, La in HfO2.24–28 It is also well known that the o-phase can be obtained in the Hf–Zr–O (HZO) system, resulting in good ferroelectricity.6,24 In addition, the doping effects of Si, Y, La in the HZO films have been investigated.25–28

To fabricate HfO2-based ferroelectric materials, atomic layer deposition (ALD),24 has been widely used, and pulsed laser deposition (PLD) and sputtering have been also used.26,29 On the other hand, chemical solution deposition (CSD) is one of the promising techniques for thin film deposition at low cost, and with low-cost facilities and interest in the CSD technique of HfO2-based materials seems growing. Various kinds of dopants were examined in HfO2 by the CSD technique for the comparative study of doping elements30–39 and the CSD technique has also been applied to deposit HZO films.40,41

In the CSD process of HfO2-based materials, deposition conditions, particularly the annealing environment, which significantly affects the ferroelectric properties, have to be investigated. We have reported the ferroelectricity of Y-doped HZO thin films prepared by the CSD and have demonstrated that the reduced pressure crystallization annealing is effective to obtain the ferroelectric orthorhombic phase.42,43 However, details of Y concentration and annealing pressure dependences on ferroelectric properties have not been reported yet. In this paper, we report the dependence of Y concentration and crystallization pressure on the CSD ferroelectric Y-HZO films along with the film thickness dependence. In addition, the impact of consolidation annealing (pre-annealing) is demonstrated. Preliminary experimental results of reduced pressure pre-annealing were presented in the meeting on ferroelectric materials and their applications (FMA-39) extended abstract.44 In this paper, details of the pre-annealing effect on the electrical properties of the Y-HZO films are presented and its mechanism is discussed.

2. Experimental procedure

The sample preparation procedure is similar to that reported in our previous works.42,43 Pt/Ti/SiO2/Si is used as a substrate. First, the source solution was prepared using hafnium (IV) acetylacetonate [Hf(acac)4], zirconium (IV) acetylacetonate [Zr(acac)4] and yttrium (III) acetylacetonate [Y(acac)3] as precursors which were dissolved in propionic acid (PrA). The source solution was prepared in an air environment without using a glove box. Y concentration in the source solution was varied from 0.6% to 9.3%. In this paper, we use mol% of Y to the total amount of Y, Hf, and Zr in the source solution as Y concentration. Then, the source solutions of Y-HZO were spin-coated on 1.5 × 1.5 cm2 Pt/Ti/SiO2/Si substrate and dried on a hot plate in the air ambient. The crystallization was carried out by rapid thermal annealing (RTA) at 800 °C for 3 min under various pressures.
from 1 to 1000 Pa. To examine the Y concentration dependence, the samples were crystallized at a fixed pressure of 50 Pa, and to examine the crystallization pressure dependence, Y concentration was fixed at 3.2%. Some samples were crystallized at 800 °C for 3 min in N2 (1 atm) or O2 (1 atm) for comparison. The thickness of Y-HZO films was typically 33 nm which was obtained by a one-time coating of the source solution. Y-HZO films with thicknesses of 22 and 80 nm were also fabricated to examine the thickness dependence by adjusting the spin-coating speed and the number of coating procedure. After the Y-HZO film formation, Pt top electrodes with a thickness of 100 nm were deposited through a shadow mask on Y-HZO samples using sputtering with Ar to fabricate metal-ferroelectric-metal capacitor structure for electrical measurements.

In this paper, two kinds of annealing sequences were employed. To examine the Y concentration and crystallization pressure dependence, one-step crystallization was employed at 800 °C. The other annealing sequence is a two-step annealing process with a pre-annealing (or consolidation annealing) step, followed by crystallization annealing. In this annealing sequence, the samples were pre-annealed at 400 °C at 50 Pa, in N2 (1 atm), and in O2 (1 atm) for 10 min for consolidation. After the samples were removed from the RTA reactor and exposed to air, they were reloaded in the RTA reactor and then proceeded to the crystallization annealing at 800 °C for 3 min. We examined the effect of pre-annealing ambient at first. After the samples were pre-annealed at 50 Pa, in N2 (1 atm), or in O2 (1 atm), the crystallization was carried out at 50 Pa and electrical properties were characterized. Next, we examined the effect of reduced pressure (50 Pa) pre-annealing for the Y-HZO films crystallized at 1 atm of nitrogen and oxygen ambient. Consequently, 5 samples were fabricated to discuss the effect of pre-annealing.

The thickness of the films was measured by a step profilometer (Alphastep-D500 by KLA tencor). The crystallinity of films was characterized by XRD (X’Pert PRO MRD Epi from PANalytical). Polarization-electric field (P-E) characteristics of all samples were measured by TOYO Corporation Model FCE-1 at 1 kHz.

3. Results and discussion

3.1. Y concentration dependence

Figure 1 shows XRD patterns of Y-HZO films prepared by CSD with Y concentrations of 0.6%, 3.2%, 6.3%, and 9.3%. All films were crystallized at 800 °C at 50 Pa. It is found that when the Y concentration is as small as 0.6%, diffraction peaks from the monoclinic (m) phase around 28.5° and 31.5° are observed along with a small peak from the orthorhombic, tetragonal, or cubic (o/t/c) phase around 30.5°. Hence the film has a mixed phase of monoclinic and o/t/c phases. When the Y concentration is larger than 3.2%, the main diffraction peak is from the o/t/c phase and peaks from the monoclinic phase are hardly seen. It can be seen that the peak position for the Y-HZO film with a Y concentration of 6.3% is slightly shifted to the high angle side, which suggests the formation of the tetragonal phase as we will see the different electrical properties. When the Y concentration is 9.3%, the diffraction peak is shifted to the low angle side, which is presumably due to the expansion of the lattice as the doping concentration increases. Similar behavior of the peak shift was reported for CSD La-doped HZO and Ce-doped ZrO2 films.45,46

The P-E loops of the Y-HZO films with Y concentrations of 0.6%, 3.2%, 6.3%, and 9.3% along with the current responses are shown in Fig. 2. When the Y concentration is 0.6%, the P-E loop exhibits the straight line, which shows the film has paraelectric nature. This is consistent with the XRD results showing the monoclinic phase in Fig. 1. When Y concentrations were 3.2%, P-E hysteresis loops can be obtained with clear current response peaks, which indicates the film has ferroelectricity. A remanent polarization as large as 10 μC cm−2 was obtained. When Y concentration is 6.3%, a pinched and slim hysteresis loop was observed with small current response peaks, which is presumably because the film contains the tetragonal phase, as suggested by the XRD patterns of Fig. 1. When Y concentration is 9.3%, the hysteresis shrinks and shows paraelectric-like behavior and the current response peak is hardly seen. From these results, it was found that a Y concentration of around 3.2% is suitable to obtain good ferroelectric properties.

An example of endurance characteristics of the CSD Y-HZO film with a Y concentration of 3.2%, crystallized at 800 °C is shown in Fig. 3. The data were taken by applying 2 MV cm−1 triangular pulses. Although a slight wake-up effect was observed, the difference of remanent polarization between the initial measurement and after 10⁷ cycles is not so large. Further study is now underway on the endurance characteristics of CSD Y-HZO films and the details will be reported elsewhere.

3.2. Effect of crystallization annealing pressure

Next, we examined the ferroelectric properties of the Y-HZO films with a Y concentration of 3.2% by varying the pressures during the crystallization annealing at 800 °C. Figures 4 and 5 show XRD patterns and P-E loops of the Y-HZO films crystallized at 800 °C for 3 min at pressures varying from 1 to 1000 Pa, respectively. When Y concentration is fixed at 3.2%, no significant difference is observed for the XRD patterns of the Y-HZO films crystallized at various pressures. A diffraction peak from the o/t/c phase around 30.5° is dominant for all samples examined in this work. Correspondingly, ferroelectric P-E hysteresis loops were obtained for all samples as shown in Fig. 5. Relatively good ferroelectric properties were obtained when the Y-HZO films were crystallized at 50 and 100 Pa. Slight degradation of the P-E loops was observed for
the Y-HZO films crystallized at lower and higher pressures, which is presumably related to oxygen vacancies in the films. As shown later, if the film was crystallized in O₂ at the same annealing condition, we could not obtain good ferroelectric properties. Hence, it is demonstrated that reduced pressure crystallization annealing is effective to obtain good ferroelectric properties, which is consistent with our previous work,⁴²) and that the annealing pressure of 50–100 Pa is suitable to obtain good ferroelectric properties.

### 3.3. Thickness dependence

Previous reports suggest that ferroelectric phase formation in HfO₂-based materials significantly depends on film thickness and it is generally thought that ferroelectricity is degraded in thick films. Although there is a report of ferroelectricity in the approximately 1 μm thick Y-doped HfO₂ film fabricated by PLD,⁴⁷) it was reported that the ferroelectric properties were degraded in HZO films prepared by ALD and sputtering when the thickness is more than 30 nm.⁴⁸,⁴⁹) Hence, we examined electrical properties of an 80 nm thick Y-HZO film by CSD along with thinner (22 nm) film in this work. Figure 6 shows P-E loops of Y-HZO films prepared by CSD with thicknesses of (a) 22 nm and (b) 80 nm. Y concentration is 3.2% and the film was crystallized at 800 °C for 3 min at 50 Pa as in the previous section. P-E loops of Y-HZO films with a thickness of 33 nm were already shown in Fig. 5(c). We can observe the ferroelectric P-E loops in both samples and it is found the P-E loops of the 22 nm thick Y-HZO film are tilted, which suggests the existence of a dielectric dead layer. On the other hand, when the film thickness is increased to 80 nm, ferroelectric P-E loops with good squareness were observed. We also observed ferroelectric properties for the Y-HZO film with a thickness of 160 nm (data not shown). It is interesting to note that the clear ferroelectric hysteresis loops were observed for the Y-HZO films prepared by CSD even when the film thickness is more than 80 nm. The stabilizing mechanism in such thick films prepared by CSD is not clear at present, but Y doping is one of the candidates to enhance the stability of the ferroelectric phase. In addition, another possibility is carbon incorporation in the film which also enhances the stability as discussed in our previous report.⁵⁰)

### 3.4. Impact of pre-annealing

Since we observed that reduced pressure crystalline annealing is effective to obtain ferroelectric properties, it is interesting to examine how and at what temperature range the reduced pressure annealing affects the crystallization. We next examined the effect of the pre-annealing (consolidation annealing) process performed at 400 °C. At first, the impact of the pre-annealing environment is focused on. Figure 7 shows P-E loops of the Y-HZO films fabricated with pre-annealing (a) at 50 Pa, (b) in N₂ (1 atm), and (c) in
After the pre-annealing, three samples were crystallized together by RTA at 800 °C at a reduced pressure of 50 Pa. In Fig. 7, (a) “50 Pa–50 Pa,” (b) “N2–50 Pa,” and (c) “O2–50 Pa” indicate that 400 °C pre-annealing was performed at 50 Pa, in N2, and in O2, respectively. When the sample was pre-annealed at 50 Pa, clear ferroelectric properties were obtained as shown in Fig. 7(a). On the other hand, when the pre-annealing was performed in N2 and O2 atmosphere, ferroelectric P–E loops were also observed, which is due to the reduced pressure crystallization annealing. However, the Y-HZO films fabricated with N2 and O2 pre-annealing showed degraded P–E loops with increased leakage, compared to the Y-HZO films fabricated with 50 Pa pre-annealing.

A more pronounced effect of reduced pressure pre-annealing was observed when the Y-HZO films were crystallized in N2 (1 atm), or O2 (1 atm). Figures 8(a) and 8(b) show P–E hysteresis loops of the Y-HZO films fabricated with 400 °C pre-annealing at a pressure of 50 Pa, and then crystallized at 800 °C for 3 min (a) in N2 (1 atm) and (b) in O2 (1 atm), respectively. For comparison, P–E loops for the Y-HZO films crystallized at the same condition without a pre-annealing process (one-step crystallization) are shown in Fig. 5.

O2 (1 atm), respectively. After the pre-annealing, three samples were crystallized together by RTA at 800 °C at a reduced pressure of 50 Pa. In Fig. 7, (a) “50 Pa–50 Pa,” (b) “N2–50 Pa,” and (c) “O2–50 Pa” indicate that 400 °C pre-annealing was performed at 50 Pa, in N2, and in O2, respectively. When the sample was pre-annealed at 50 Pa, clear ferroelectric properties were obtained as shown in Fig. 7(a). On the other hand, when the pre-annealing was performed in N2 and O2 atmosphere, ferroelectric P–E loops were also observed, which is due to the reduced pressure crystallization annealing. However, the Y-HZO films fabricated with N2 and O2 pre-annealing showed degraded P–E loops with increased leakage, compared to the Y-HZO films fabricated with 50 Pa pre-annealing.

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Fig. 7. $P$–$E$ loops of Y-HZO films prepared by CSD, pre-annealed at 400 °C, (a) at 50 Pa (50 Pa-50 Pa), (b) in N$_2$ (N$_2$-50 Pa), and (c) in O$_2$ (N$_2$-50 Pa), respectively. All samples were crystallized at 800 °C at 50 Pa after pre-annealing.

Figs. 8(c) and 8(d), respectively. It is found that good ferroelectric $P$–$E$ loops were observed when the reduced pressure pre-annealing was performed regardless of the crystallization annealing environment. Figure 9 shows XRD patterns for the Y-HZO films fabricated with 400 °C pre-annealing at 50 Pa, followed by the crystallization of 800 °C at 50 Pa. For all samples, a diffraction peak from o/t/c phase was observed at around 30.5° and diffraction peaks from the m-phase are negligible. The full width at half maximum of the o/t/c peak is larger when the sample was crystallized at 50 Pa, suggesting the small grain size. In fact, a low leakage current of about $1 \times 10^{-6}$ A cm$^{-2}$ at 1 MV cm$^{-1}$ was observed for the Y-HZO films fabricated with 50 Pa pre-annealing and 50 Pa crystallization. On the other hand, almost no ferroelectric property was observed if the film was crystallized in N$_2$ and O$_2$ ambient without reduced pressure pre-annealing as shown in Figs. 8(c) and 8(d).

From these results, it can be concluded that the reduced pressure pre-annealing, which was carried out at a temperature of 400 °C, is effective to obtain ferroelectric properties. Simultaneous thermogravimetry/differential thermal analysis (TG/DTA) for HfO$_2$ precursors shows an exothermic reaction takes place around 350 °C, which corresponds to the oxide formation. Hence, the reduced pressure annealing in the initial stage of crystallization is supposed to be effective to obtain...
ferroelectric orthorhombic phase. Furthermore, once the nuclei or small crystallites of the orthorhombic phase are formed at low temperature, good ferroelectric properties can be obtained even when the high-temperature crystallization annealing was performed in O₂ ambient. The results obtained in this work suggest that the formation of nuclei of the orthorhombic phase around 400 °C is important to obtain good ferroelectric properties and the reduced pressure pre-annealing is believed to be effective to create nuclei of the orthorhombic phase even at low temperatures, presumably because of the introduction of oxygen vacancies.

4. Conclusions

Y-doped HZO films have been prepared by CSD with varying Y concentration and crystallization pressure. When Y concentration in the source solution was 3.2%, good ferroelectric properties were observed, whereas the paraelectric-like behavior was observed for the films with lower (0.6%) and higher (9.3%) Y concentrations. The effect of crystallization pressure was also investigated and relatively good ferroelectric P-E loops were obtained when the Y-HZO film was crystallized at 50–100 Pa. Ferroelectric P-E loops were confirmed for the Y-HZO films with thicknesses of 22–80 nm. Furthermore, the impact of pre-annealing at temperatures as low as 400 °C was investigated. It was demonstrated once the film was pre-annealed at 400 °C under a reduced pressure of 50 Pa, good ferroelectric properties were observed regardless of the ambient during the crystallization annealing. The presented results suggest that the reduced pressure annealing at as low as 400 °C during the CSD process is effective to form the nuclei or crystallites of the ferroelectric orthorhombic phase and to obtain good ferroelectric properties after the crystallization annealing. The concept presented in this work would be also applicable to HZO-based thin films prepared by other methods such as ALD.

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