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Toward 1-nm-EOT $Hf_{0.5}Zr_{0.5}O_2$ Ferroelectric Films

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Abstract

Ferroelectric characteristics of thin $Hf_{0.5}Zr_{0.5}O_2$ films are discussed toward 1-nm-EOT through differential C-V measurement. By thinning the film thickness, ferroelectric characteristics become clearer and are observable down to 1.5-nm-EOT.

1. Introduction

HfO_2 is the most popular high-k dielectric film in Si technology. There are several polymorphs in HfO_2. In the conventional Si process technology, the lowest-k monoclinic phase or amorphous films are used. To engineer the structural phase (to enhance the k-value), several methods have been challenged to form other polymorphs by doping other elements [1] or by employing non-equilibrium process such as rapid-thermal annealing [2]. Meanwhile, ferroelectric properties of doped HfO_2 have been reported [3-5]. This fact is quite impactful because not only k-value but also functionality will be introduced to CMOS technology.

There are, however, two concerns about ferroelectric HfO_2. One is the thermodynamic stability of its ferroelectricity, because we know the HfO_2 structural phase is sensitive to the thermal treatment dynamics [6]. The other is the thickness scalability of ferroelectric properties. Therefore, the objective of this paper is to discuss the thermodynamic stability of HfO_2-based ferroelectric films as well as to inspect ferroelectric properties in ~1-nm-EOT film.

2. Experimental

$Hf_{0.5}Zr_{0.5}O_2$ was investigated in this work for typical ferroelectric films. Various thickness films were prepared by rf-sputtering of $Hf_{0.5}Zr_{0.5}O_2$ target in Ar plasma on TiN film. Post-deposition annealing was typically performed in N_2 ambient at 500°C for 30s. The structural phase was identified by XRD, and Hf/Zr ratio was determined by XPS. Al electrodes were deposited on ferroelectric film. The *P-E* characteristics measurement is usually carried out to investigate ferroelectricity, but the differential *C-V* characterization, which is used in conventional semiconductor analysis, was used, because the leakage current observed in thin films should make the accurate *P-E* measurement increasingly difficult. Also from *C-V* characteristics we can determine the coercive electric field, E_c, quantitatively, as shown in **Fig. 1**.

3. Results and Discussion

$Hf_{0.5}Zr_{0.5}O_2$ films with thicknesses from 3 to 40 nm were

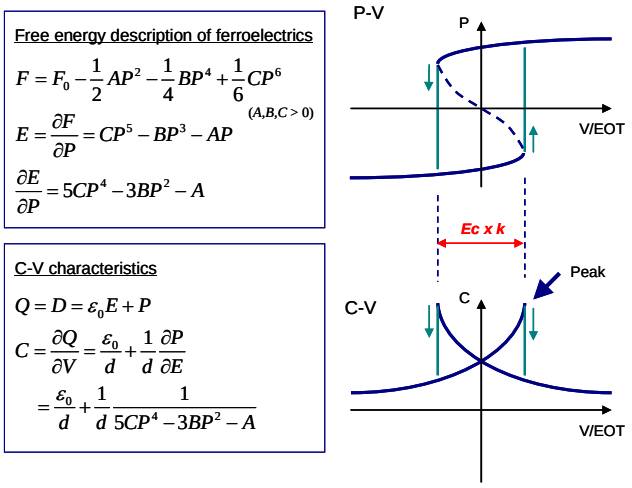

Fig. 1 Relationship of C-V measurement to ferroelectric characteristics. Due to the *P* dependent capacitance, characteristic C-V curvature with hysteresis is observed in ferroelectric MIM capacitor. The coercive electric field, *Ec*, can be estimated from the interval of peaks in the C-V curves. To sharpen the experimentally obtained C-V peaks, we took second order derivative of capacitance.

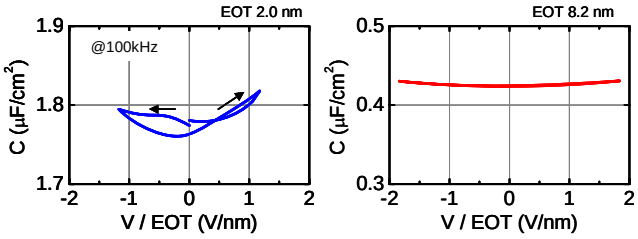

Fig. 2 Typical C-V characteristics of Al/$Hf_{0.5}Zr_{0.5}O_2$/TiN capacitors. Horizontal axis is normalized by EOT. Thin film shows clear hysteresis of capacitance, whereas the hysteresis was hard to be detected at thicker film.

investigated. **Figure 2** shows typical C-V characteristics of Al/thin $Hf_{0.5}Zr_{0.5}O_2$/TiN capacitors, in which *V/EOT* is used for comparing effective *Ec* in ferroelectric films with different thickness. (*E* x *k* = *V/EOT)*). Thin $Hf_{0.5}Zr_{0.5}O_2$ films (< EOT ~ 5 nm, physical thickness ~ 25 nm) show C-V characteristics of ferroelectricity, while thick ones does not. We can clearly see the ferroelectricity down to 1.4-nm-EOT, which is very promising for ferroelectric applications in scaled devices.

In addition, the *Ec* determined by the procedure described in Fig. 1 is shown as a function of EOT in **Fig. 3**. *Ec* x *k* value is constant or rather increasing with the decrease of EOT. This also supports potential advantage of thin EOT ferroelectricity in this system.

Next, the thermal stability of ferroelectric phase of $Hf_{0.5}Zr_{0.5}O_2$ is discussed. The phase transformation kinetics

in HfO_2 has been well described by *Johnson-Mehl-Avrami* law [6]. If the ferroelectric phase transformation is also described by the same kinetics, the nucleation of other phases in the ferroelectric phase limits the stability of the film. From the process point of view, the ramping up and down rate control in addition to the PDA temperature should be quite important. 20-nm-thick $Hf_{0.5}Zr_{0.5}O_2$ was annealed in N_2 at 600°C for 5 min and then the temperature was decreased with three kinds of the ramping-down rate of 150, 30 and 5°C/min. **Figure 4** shows XRD patterns of three samples. At higher ramping-down rate, symmetric phase becomes more evident and monoclinic one becomes weaker, and capacitance increases.

The fact that ferroelectric phase of $Hf_{0.5}Zr_{0.5}O_2$ is observed in thin film region suggests that the ferroelectric phase nucleation is strongly affected by the surface energy in addition to intrinsic property of $Hf_{0.5}Zr_{0.5}O_2$ system. Our experimental results indicate that pure ferroelectric phase of $Hf_{0.5}Zr_{0.5}O_2$ is with very narrow window to control and that it might be along the boundary between monoclinic and tetragonal phase. Therefore, it seems to be easy to achieve ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ phase, but not so easy to obtain its pure phase. In fact, it is reported that the ferroelectric phase is orthorhombic [2]. Since it is less symmetric structure compared to tetragonal or cubic, mixed phase may intrinsically be realized along the boundary.

To confirm this view, we have depicted the phase diagram of $Hf_{1-x}Zr_xO_2$ as functions of x and physical thickness, based on far-IR absorption results [7]. **Fig. 5** shows typical results in far-IR absorption for various thickness $Hf_{1-x}Zr_xO_2$. In thick case, clear monoclinic phase absorption is observed, while with the thickness decrease monoclinic phase disappears and high-symmetric phases appear. Although it is not clear, ferroelectric phase seems to appear along the boundary between monoclinic and high-symmetric phases.

On the other hand, pure ferroelectric phase is not necessarily for practical applications of ferroelectric films. Even though it is not the pure phase, remaining ferroelectric phase is quite robust and we should consider possible applications using the partial ferroelectric film.

4. Conclusions

$Hf_{0.5}Zr_{0.5}O_2$ includes ferroelectric phase down to 1.4-nm-EOT. Based on our experimental results, it is considered that the ferroelectric phase appears along the boundary between monoclinic and high-symmetric phases, and that it is in metastable state. Although its metastability depends on process and geometrical boundary conditions, this fact should be taken into account for the potential applications of ferroelectric HfO_2. We think the material properties are quite attractive.

Acknowledgements

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References

[1] K. Kita, *et al.*, Appl. Phys. Lett. **86**, 129906 (2005).

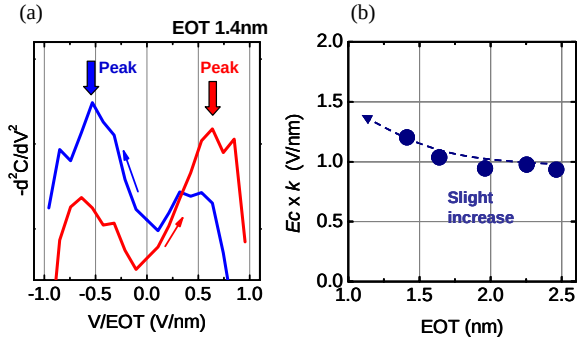

Figure 3 (a) Second order differential of C-V curve of 1.4-nm-EOT $Hf_{0.5}Zr_{0.5}O_2$. **(b)** *Ec* x *k* values of ferroelectric $Hf_{0.5}Zr_{0.5}O_2$ estimated from second order differential of C-V curvatures as a function of EOT.

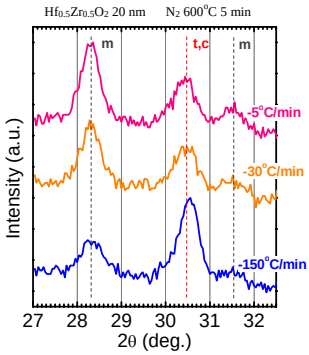

Figure 4 (a) XRD spectrum of $Hf_{0.5}Zr_{0.5}O_2$ films annealed at 600°C with various ramping-down rates. "m" and "t,c" denote the peaks identified to monoclinic phase and tetragonal or cubic phase, respectively. By lowering ramping-down rate, m-phase formation is surely facilitated.

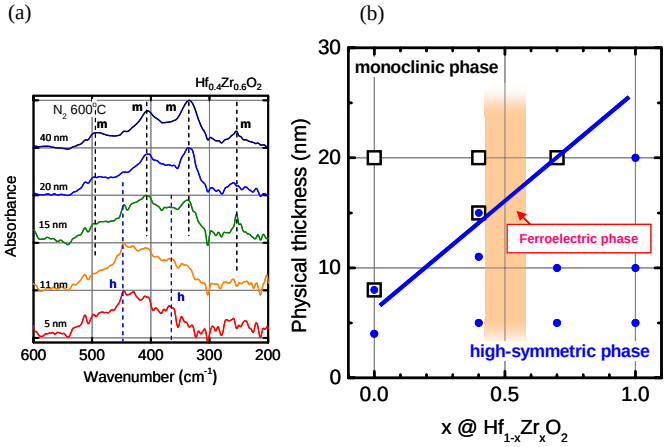

Figure 5(a) Far-IR absorption of $Hf_{0.4}Zr_{0.6}O_2$ films with various thickness stacked on SiO_2/Si substrate measured by FT-IR. "m" and "h" denote the peaks of monoclinic phase and high-symmetric phase, respectively. By thinning the film, two peaks (blue broken line) due to high symmetric phase appeared. **(b)** Local structural phase determined from far-IR absorption and ferroelectric characteristics of $Hf_{0.5}Zr_{0.5}O_2$ determined by C-V measurement. It is expected that the ferroelectric phase appeared along the boundary between monoclinic phase and high-symmetric phase (blue line).

[2] S. Migita, *et al.*, *Tech. Dig. Symp. on VLST technology* p.152 (2008).
[3] T. S. Boscke, *et al.*, Appl. Phys. Lett. **99**, 102903 (2011).
[4] J. Muller, *et al.*, Nano Lett. **12** (2012) 4318.
[5] M. H. Park, *et al.*, Appl. Phys. Lett. **102**, 242905 (2013).
[6] Y. Nakajima, *et al.*, *Tech. Dig. Symp. on VLST technology* (2011).
[7] K. Tomida *et al.*, *MRS Symp. Proc.* **811**, D10.9.1 (2004).