Stability origin of metastable higher-k phase HfO$_2$ at room temperature

Yasuhiro Nakajima, Koji Kita, Tomonori Nishimura, Kosuke Nagashio, and Akira Toriumi

Department of Materials Engineering, The University of Tokyo,
7-3-1 Hongo, Bunkyo, Tokyo 113-8656, Japan
Phone: +81-3-5841-7161, E-mail: nakajima@adam.t.u-tokyo.ac.jp

1. Introduction

Hf-based oxide is one of the most promising candidates for high-k dielectrics. Both theoretical and experimental researches revealed that higher-k HfO$_2$ could be achieved in the form of tetragonal- or cubic-HfO$_2$ [1, 2]. A typical example of experimental works is cubic Y-doped HfO$_2$. Another one is that cubic-HfO$_2$ is formed by annealing after Si-cap deposition on HfO$_2$ film (Si-cap PDA) [3,4]. However, we recently reported metastable higher-k phase of pure HfO$_2$ was obtained by the fast ramping-up rate annealing even without any gate electrode caps [5]. In this research, we investigate the stability origin of the metastable higher-k phase HfO$_2$ and discuss a plausible mechanism of Si-cap PDA.

2. Experimental

30-nm-thick HfO$_2$ or Y$_2$O$_3$ doped HfO$_2$ films were RF-sputtered on thermally grown ~100-nm-thick SiO$_2$. Some samples were covered with 30-nm-thick amorphous Si by EB evaporation. They were annealed in the RTA furnace at 600°C under various temperature programs in N$_2$. The structural phase of HfO$_2$ was characterized by XRD.

3. Results and Discussion

Fig. 1 shows XRD patterns of films annealed at various ramping-up rate of annealing temperature. The higher-k phase (cubic or tetragonal) peak intensity significantly increases by increasing ramping-up rate of annealing, whereas the monoclinic one decreases. To understand more quantitatively this correlation, the ratio of XRD peak intensity of the higher-k phase to the monoclinic one, hereafter *the higher-k phase ratio*, is shown in **Fig. 2**. It is clearly seen that the higher-k phase ratio increases monotonically with increasing the ramping-up rate. With Si-cap, it is totally shifted up but looks parallel with the case without Si-cap. **Fig. 3** shows the higher-k phase ratio as a function of holding time at 600°C. Without Si-cap, the higher-k phase is dominant at the initial stage of annealing, but it sharply decreases with the holding time. This means the higher-k phase obtained by the fast ramping-up rate annealing is metastable, and it recovers to the thermodynamically stable monoclinic phase. On the other hand, Si-cap PDA is quite effective to maintain the higher-k phase ratio. Thus, it can be concluded that Si-cap does not induce higher-k phase crystallization but suppresses the transformation of the higher-k phase to the monoclinic one. And the higher-k phase appearance is inherent to HfO$_2$.
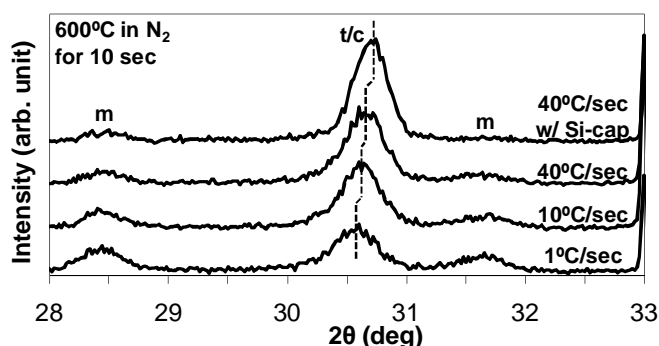

Fig. 1 XRD spectra of HfO$_2$/SiO$_2$/Si sorted by the ramping-up rate to 600°C. Only the top one shows with Si-cap case. "t/c" and "m" denote the tetragonal or cubic, and the monoclinic phases, respectively. Since it is difficult to distinguish the cubic phase from tetragonal one, in this paper "t/c" means the peak just as higher-k phase. Broken line indicates the shift of the peak top position. These films were almost (>90%) crystallized.
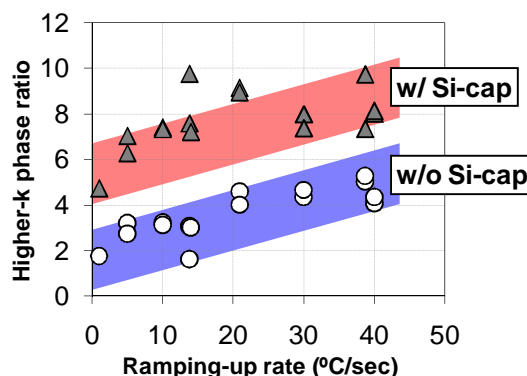

Fig.2 The XRD peak intensity ratio of the higher-k phase to the monoclinic phase as a function of the ramping-up rate.
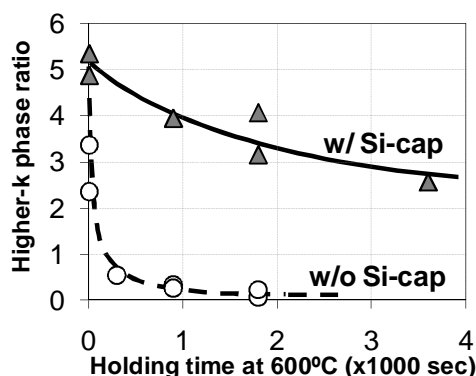

Fig. 3 Holding time dependence at 600°C of the higher-k phase ratio for w/ and w/o Si cap on HfO$_2$/SiO$_2$/Si.

In the case of slightly Y_2O_3 doped HfO (0.2%- and 1.2%-YDH) films with and without Si-cap, similar results shown in Fig. 3 were observed, although the higher-k phase ratio was enhanced (data not shown). This is also attributable to the fact that Y_2O_3 doping can enhance the nucleation of the higher-k phase, but the small amount of doping such as 0.2% or 1.2% is not sufficient to maintain the higher-k phase at 600 ℃.

We have proposed the origin of the higher-k phase HfO_2 appearance at 600˚C from the viewpoint of the size effect of crystallized grain at the initial nucleation stage. It was reported that higher-k phase becomes more stable with decreasing the grain size (increasing the surface/interface area) [6]. Since the grain size should be very small at the initial stage of crystallization, higher-k phase might be relatively stable. So, we can infer that amorphous HfO_2 first nucleates in the higher-k phase, followed by the grain size increase. When the grain size exceeds the critical one, the transformation of the higher-k phase to the monoclinic one will occur. This model reasonably explains the results as shown in Fig. 1 and 3.

Fig. 4 shows the (111) lattice spacing of the higher-k phase as a function of the higher-k phase ratio. This indicates that the metastable higher-k phase gradually changes with the higher-k phase ratio increase, and the lattice spacing approaches to the value of the cubic structure when the cubic structure at higher temperature is quenched to the room temperature. On the other hand, Y-doping can stabilize the cubic phase with larger lattice spacing toward the ideal higher-k phase structure. In fact, it is impossible to extend the bond length of pure HfO_2 at room temperature without transformation to the monoclinic phase. The Si-cap may pin the atom distortion at the top interface, and makes it easy to maintain the metastable higher-k phase HfO_2 after annealing.

Fig. 5 shows the schematic picture of the transformation between tetragonal and monoclinic in the atomic configuration. Because cubic phase must go through tetragonal to monoclinic, we focus the transformation in Fig. 5. The tetragonal lattice transforms to monoclinic one by Martensitic deformation, with elongation of b and c axis. In the monoclinic structure, coordination number of Hf is 7, and there are two zones paralleled with c axis. One is the plane that Hf bonds four Os, $O_{II}Hf_4$, and the other is that Hf bonds three Os, O_IHf_3. This is caused by the combination of lattice deformation with oxygen displacement. Therefore, one of the longest bonds is disconnected, and O_IHf_3 is formed. It should be noticed that (111) lattice spacing expands with the transformation to the monoclinic. That is to say, to maintain the metastable higher-k phase, the lattice spacing in Fig. 4 must be shrunk.

Interesting point is both of HfO_2 films with and without Si-cap is understandable based on the same picture in Fig. 5. This result supports the previous discussion that the appearance of the metastable higher-k phase is attributed to HfO_2 intrinsic property, and Si-cap PDA only makes it easy to obtain the higher-k phase after annealing.
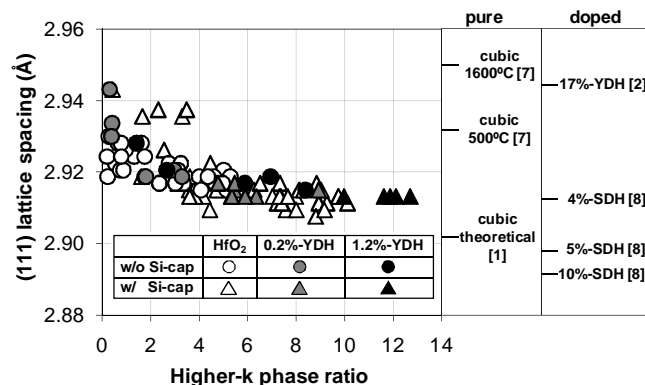
Fig. 4 The (111) lattice spacing derived from XRD peak position of the higher-k phase, as a function of the higher-k phase ratio. Data of cubic-, tetragonal-HfO_2, cubic-YDH, and tetragonal-SDH (Si-doped HfO_2) are shown in right frame [1, 2, 7, 8].
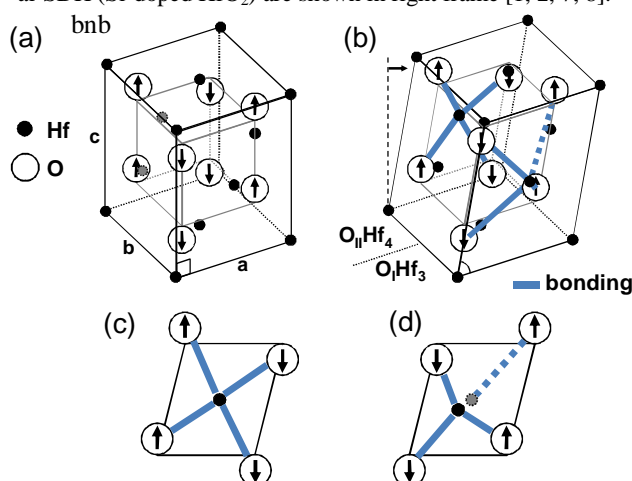
Fig. 5 Schematic picture of the transformation of (a)tetragonal phase to (b)monoclinic one. (c)View from [100] angle of $O_{II}Hf_4$, and (d)one of O_IHf_3. Broken line indicates disconnected bonding.

4. Conclusions

The metastable higher-k phase-HfO_2 obtained by the fast ramping-up rate annealing was investigated. The bonding distance of the higher-k phase approaches to the quenched cubic phase with increasing the higher-k phase ratio. This understanding should provide a new guideline for designing higher-k HfO_2-based gate dielectric films.

References

1. X. Zhao and D. Vanderbilt, *Phys. Rev. B* **65**, 233106 (2002).
2. K. Kita, *et al.*, *Appl. Phys. Lett.* **86**, 102906 (2005).
3. Y. Watanabe, *et al.*, *ECS Transactions* **11**, 35 (2007).
4. Y. Migita,*et al.*, *ECS Transactions* **19**, 563 (2009).
5. Y. Nakajima, *et al.*, *ECS Transactions* **28**, 203 (2010).
6. S. V. Ushakov, *et al.*, *Phys. Stat. Sol.* (b) **241**, 2268 (2004).
7. J. Wang, *et al.*, *J. Mater. Sci.* **27**, 5397 (1992).
8. K. Tomida, *et al.*, *Appl. Phys. Lett.* **89**, 142902 (2006).