

## Role of Ar on Structural Phase Transformation of Sputtered HfO<sub>2</sub>

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### 1. Introduction

HfO<sub>2</sub> has three kinds of crystal phases under the atmospheric pressure such as cubic phase (*c*-phase, 2700°C~), tetragonal phase (*t*-phase, 1750°C~) and monoclinic phase (*m*-phase, ~1750°C).<sup>[1]</sup> And it is reported that when amorphous HfO<sub>2</sub> (*a*-phase) film is annealed at around 600°C, it initially crystallizes to *c*-phase (metastable at 600°C) and then transforms to *m*-phase (*c*→*m* transformation).<sup>[2,3]</sup> In addition, since it is expected that the dielectric constant of *c*-phase is much larger than that of *m*-phase<sup>[4]</sup>, it is practically important to understand the structural phase transformation of crystallized HfO<sub>2</sub>.

We have already studied the structural transformation kinetics from the cubic to monoclinic phase HfO<sub>2</sub>.<sup>[5]</sup> This paper discusses the crystallization and structural phase transformation of HfO<sub>2</sub>, focusing on Ar unintentionally introduced in the sputtering deposition (SPD) process. The results are compared with HfO<sub>2</sub> grown by the pulsed-laser deposition (PLD) in high vacuum condition.

### 2. Experimental

HfO<sub>2</sub> films were deposited by rf-sputtering in Ar and by KrF-PLD in high-vacuum on SiO<sub>2</sub>/(100)-Si wafers. The typical Ar flow in SPD was 22 sccm if not mentioned specifically. The thicknesses of HfO<sub>2</sub> and SiO<sub>2</sub> were about 30 and 2 nm, respectively. The post-deposition annealing (PDA) in the rapid thermal annealing (RTA) furnace was performed at various temperatures in N<sub>2</sub>, O<sub>2</sub> and in UHV ambient. The typical annealing profile in RTA-PDA is shown in Fig.1(a). The structural phase of HfO<sub>2</sub> was analyzed by XRD. In order to qualify the crystallinity of different phases of deposited HfO<sub>2</sub> film in PDA, the XRD peak area of *x*(*hkl*) (*x*=*m* or *c*) was represented by *I<sub>x(hkl)</sub>*. In this study, *t*-phase was not distinguished from *c*-phase. And the cubic phase ratio (*r<sub>c</sub>*) is defined by the following expression.

$$r_c = \frac{I_{c(111)}}{I_{c(111)} + I_{m(-111)} + I_{m(111)}}$$

Also, the thermal desorption spectroscopy (TDS) measurement was performed to identify what species were unintentionally involved in HfO<sub>2</sub> film.

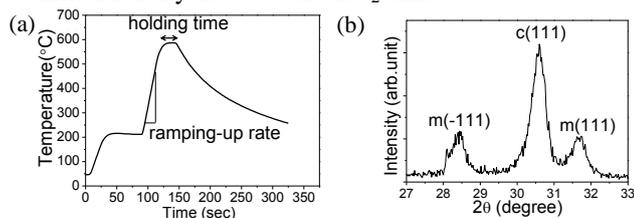


Fig. 1.

- (a) Typical annealing temperature profile with the time using RTA furnace.  
 (b) An example of XRD peaks of HfO<sub>2</sub> film after PDA.

### 3. Results and Discussion

First, the distinct difference between SPD- and PLD-grown HfO<sub>2</sub> films is discussed. Fig. 2 shows the TDS results of Ar desorption from SPD- and PLD-films. The desorption peak of Ar from SPD-film is approximately at the crystallization temperature. Of course, no desorption was observed in PLD-film.

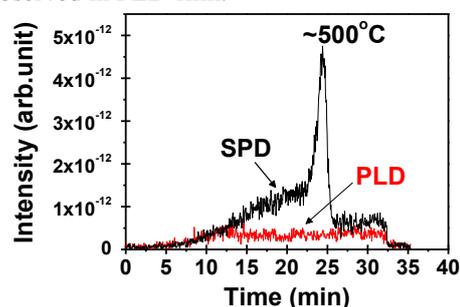


Fig. 2. Ar desorption intensity from SPD-film and PLD-film measured by TDS. The ramping-up rate was 20°C/min. The peak temperature of Ar was observed at about 500°C in SPD-film, and it approximately corresponds to the crystallization temperature.

Fig. 3 shows *r<sub>c</sub>* of SPD- and PLD-films in UHV-PDA at 600°C for several holding times. The *c*-phase in SPD-HfO<sub>2</sub> was maintained even in 1 hour PDA, while that in PLD-HfO<sub>2</sub> was considerably weakened in 30 min PDA, then almost disappeared in 1 hour. It means that *c*→*m* transformation of PLD-film is much faster than that of SPD-film. The apparent difference between SPD- and PLD-HfO<sub>2</sub> is whether Ar atoms are in the film or not, as shown in Fig. 1. Therefore, Ar is likely to suppress *c*→*m* transformation.

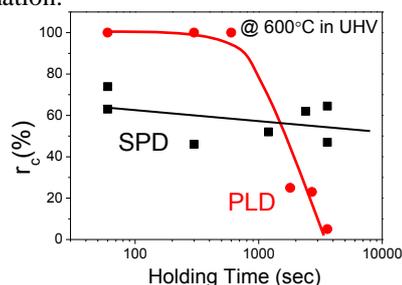
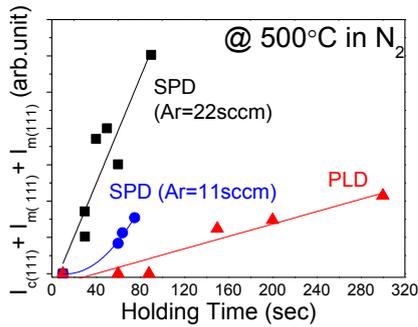


Fig. 3. *r<sub>c</sub>* of SPD-film and PLD-film. Samples were annealed at 600°C in UHV (ramping-up rate was 20°C/min).

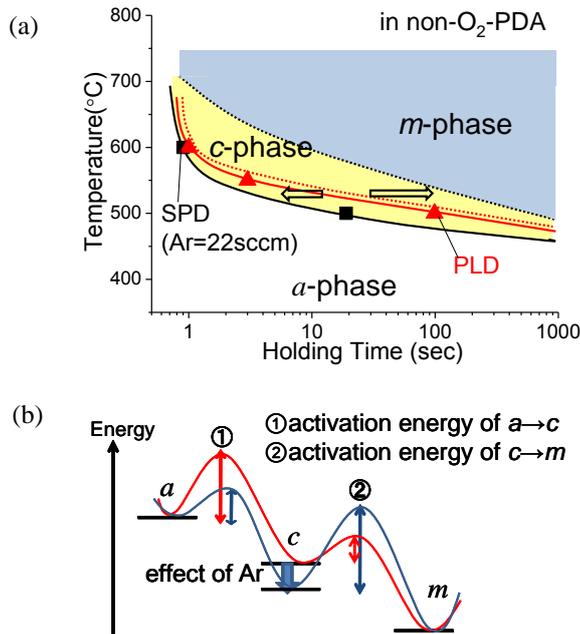
Next, the Ar flow in SPD process was reduced from 22 to 11 sccm. Fig. 4 shows the results of XRD peak area (*I<sub>c(111)</sub>*+*I<sub>m(-111)</sub>*+*I<sub>m(111)</sub>*) in N<sub>2</sub>-PDA at 500°C (ramping-up rate : 200°C/sec). This result clearly shows that the incubation time for the crystallization becomes shorter when more Ar is introduced into HfO<sub>2</sub>. Thus, it is experimentally concluded that Ar in the film accelerates the

crystallization, though it decelerates the  $c \rightarrow m$  transformation.



**Fig. 4.** Crystallinity (XRD peak intensity, I) of each film after annealed at 500°C in N<sub>2</sub> ambient as a function of the holding time in PDA. The incubation time can be estimated from this figure.

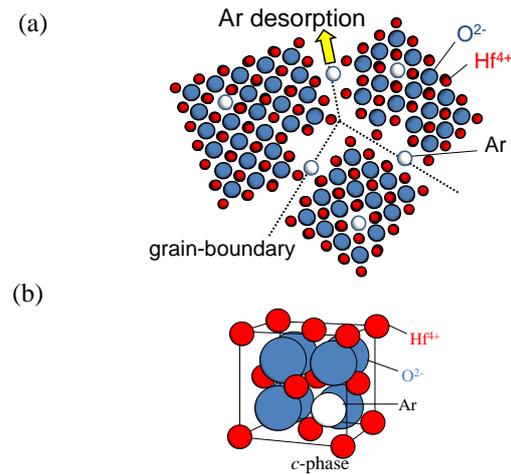
Now, the results discussed above are summarized in the time-temperature-transformation (TTT) diagram (Fig. 5). The solid squares and triangles represent the incubation time in PDA estimated from Fig. 4. Ar in the SPD-film causes easier crystallization and stabilizes the  $c$ -phase region, while the crystallization temperature of PLD-film is higher than that of SPD-film, and the  $c \rightarrow m$  transformation of PLD-film more easily occurs than that of SPD-film.



**Fig. 5.** (a) TTT diagram obtained from annealing in N<sub>2</sub> ambient. The plots show the incubation time of each film. Solid line is the border between  $a$ - and  $c$ -phase, and dotted line is the border between  $c$ - and  $m$ -phase. The ramping-up rate was 200°C/sec. Ar broadens  $c$ -phase region. (b) Energy diagram of  $a$ -,  $c$ - and  $m$ -phase. Ar reduces the activation energy of crystallization and stabilizes  $c$ -phase.

Finally, the physical model of Ar effect on the phase transformation of SPD-HfO<sub>2</sub> is discussed. When the crystallization ( $a \rightarrow c$  transformation) is initiated, Ar atoms

are likely to move toward the grain boundary and are ejected out of the film (Fig. 6(a))<sup>[6]</sup>. This corresponds to the large Ar desorption peak observed experimentally by TDS in Fig. 1. However, a few Ar atoms will remain inside the grain, and these atoms will be located at O-site of crystallized HfO<sub>2</sub> (Fig. 6(b)). As a matter of fact, O<sub>2</sub>-PDA strongly induces  $c \rightarrow m$  transformation<sup>[7]</sup>. Also, Ar atom is smaller than O<sup>2-</sup> ion, so according to Pauling's rule<sup>[8]</sup>,  $c$ -phase (coordination number : 8) will become more stable, although Ar atom is inert. Thus, we propose this may be the reason why Ar suppresses the  $c \rightarrow m$  transformation.



**Fig. 6.** (a) The model of Ar desorption. Ar atoms are ejected through the grain-boundary when crystallization occurs. But a few Ar atoms remain in the grain. (b)  $C$ -phase of sputtered film including Ar atom in the lattice. Ar atom replaces O-site and suppresses  $c \rightarrow m$  transformation.

#### 4. Conclusion

This paper discusses the effect of Ar on the crystallization and transformation of HfO<sub>2</sub> films. It seems that SPD-HfO<sub>2</sub> crystallizes when the desorption of Ar in the film is initiated. Therefore, the Ar desorption accelerates the HfO<sub>2</sub> crystallization. On the other hand, the remaining Ar in HfO<sub>2</sub> decelerates the  $c \rightarrow m$  transformation, and more stabilizes the region of higher- $k$  phase. The understanding of the phase transformation is quite helpful for controlling the dielectric properties of high- $k$  dielectrics.

#### Acknowledgements

This work was partly supported by a Grant-in-Aid for Scientific Research (S) by JSPS.

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