20a-F10-8

Reinvestigation of the role of Ar in structural phase transformation of sputtered HfO_2

Univ. of Tokyo, °Takamasa Iwai, Takeaki Yajima, Tomonori Nishimura, Kosuke Nagashio, and Akira Toriumi

E-mail: iwai@adam.t.u-tokyo.ac.jp

[Introduction]

Thin amorphous (*a*-) phase HfO_2 initially transforms to metastable cubic (*c*-) phase due to the surface energy contribution, and then transforms to monoclinic (*m*-) phase[1,2] thermodynamically. We have noticed the effect of Ar introduced in HfO_2 deposited by the sputtering deposition (SPD) on the phase transformation, and found *c*→*m* transformation occured after Ar desorbtion from the film[3]. On the other hand, we also found that Ar desorbed only from the near-surface region of HfO_2, and that so much Ar remained in the film even after Ar desorption[4]. In this work, we discuss about the role of Ar in the *c*-*m* transformation in HfO_2 film in more detail, and show a clear picture of HfO_2 phase transformation by demonstrating a new result of phase-profiled HfO_2.

[Reinvestigation of the role of Ar in HfO_2]

The fact that the HfO_2 film becomes *m*-phase even though so much Ar remains in the film suggests that Ar is likely to suppress the *m*-phase nucleation but has nothing to do with grain growth of *m*-phase. In fact, we assumed the model that a limiting factor of the *c*-*m* transformation in HfO_2 is at the nucleation stage, and by employing the model, all of results so far obtained seems to be reasonably understandable. Namely, *c*-phase at the surface first becomes unstable due to Ar desorption, followed by the *m*-phase nucleation at the surface (**Fig.1**). Then, *m*-phase grows inside the film, regardless of Ar existence. To verify this model, further experiments are needed. So, we have prepared phase–profiled HfO_2.

[Sample preparation]

a-phase HfO_2 (30nm) was deposited on SiO_2(100nm)/Si substrate by Ar-SPD, followed by in-situ deposition of two kinds of 10nm-HfO_2 films. One is Y-doped HfO_2 (YDH) by co-SPD, and the other is HfO_2 by O_2-SPD (O-HfO_2). Then Ar desorption was measured from those samples by thermal desorption spectroscopy (TDS), which was actually the post deposition annealing (PDA) process in vacuum (UHV). Finally, the structural phase was analyzed by X-ray diffraction (XRD).

[Results and Discussion]

Several interesting results have been observed. (1) No Ar desorption was detected from YDH- and O-HfO_2-capped film. (2) In-plane-XRD results indicated that the structural phase of O-HfO_2 (10nm) was only *m*-phase without PDA. Furthermore, out-of-plane-XRD results of three kinds of films (YDH-cap, O-HfO_2-cap, and Ar-HfO_2) after PDA at 830ºC for 1 sec in UHV (**Fig.2**) shows that (3) *c*-phase remained in the bulk in YDH-capped case, while no difference was observed between in O-HfO_2-cap and Ar-HfO_2.

Those results directly indicate that *c*-*m* transformation through the film is limited only by the *m*-phase nucleation, and Ar is not directly involved in *m*-phase growth in the film. Thus it is possibly expected that an intentional *m*-phase nucleation inside the film may control the structural transformation in the whole film.

Finally one of the possible kinetic processes how Ar can suppress *m*-phase nucleation is discussed. By occupying the interstitial site in HfO_2 lattice, Ar might suppress the movement of O-atoms involved in *c*-*m* transformation as shown in **Fig.3,** in which red arrows indicate oxygen atom movements required for *m*-phase nucleation.

[Conclusion]

It is concluded that Ar does not directly suppress the *m*-phase growth but suppresses its nucleation. Ar desorption triggers the nucleation of *m*-phase at the surface. According to this model, *c*-*m* transformation could be controlled intentionally by forming the nucleation site at any position.

[References]

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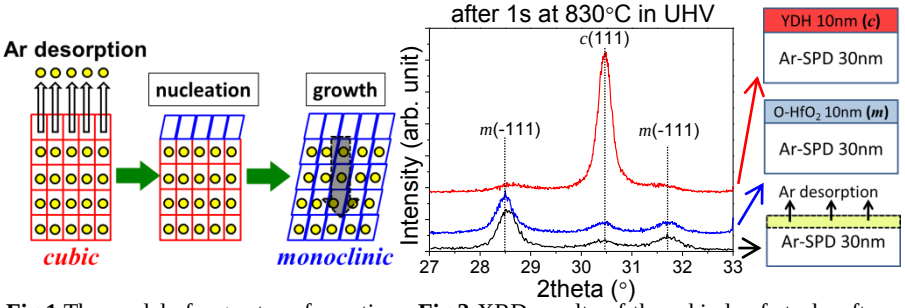

Fig.1 The model of *c*→*m* transformation of Ar-SPD-HfO_2 film. Ar suppresses only the *m*-phase nucleation at the surface.

Fig.2 XRD results of three kinds of stacks after PDA at 830ºC for 1sec in UHV.

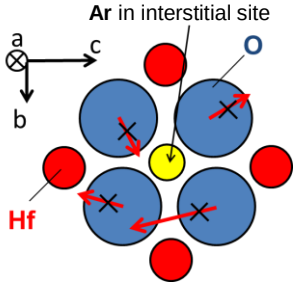

Fig.3 Schematic image of *c*-phase showing that Ar suppresses the movement of O-atom in HfO_2. The radii of O, Hf and Ar are 1.4, 0.83 and 0.7Å[5], respectively.