Impacts of doped element on ferroelectric phase stabilization in HfO₂ through non-equilibrium PDA

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Abstract

Ferroelectric phase formation in HfO_2 is characterized from the viewpoint of thermal annealing transient as a function of Y-doping concentration including un-doped case. We have paid attention to ramp-up and ramp-down speed of post-deposition annealing in N_2 . This study demonstrates experimentally for the first time how the dopant stabilizes rather than forms ferroelectric phase of HfO_2 .

Introduction

It was recently reported that ferroelectric HfO₂ films were formed by doping various atoms [1, 2]. Although structural phase transformation in polymorphic HfO2 is often attributed to oxygen vacancy formation in doping, it has not been clearly understood how the dopant stabilizes the ferroelectric phase of HfO₂. Furthermore, un-doped HfO₂ actually shows the ferroelectric behavior as well [3]. Therefore, it is not appropriate for understanding and controlling the ferroelectric phase formation only whether HfO₂ shows ferroelectric characteristics or not. Meanwhile, we previously studied effects of thermal annealing transients on higher-k HfO₂ film formation. The results clarified a significant effect of the ramp-down process speed on specific structural phase stabilization [4]. Since ferroelectric HfO₂ is formed just between high-k and higher-k phase HfO2 in terms of doping concentration through empirical observations [5], ferroelectric phase HfO2 might be also quite sensitive to PDA transients.

In this work, we have studied the annealing transient as a function of dopant concentration. The ramp-up and ramp-down speed may be associated with the nucleation process of a certain crystalline phase of HfO_2 and the stabilization of the nucleated phase, respectively.

Experiments

HfO₂ was deposited by rf-sputtering on TiN substrate at room temperature. Y₂O₃ was doped into HfO₂ by co-sputtering. Typical HfO₂ thickness and Y concentration was estimated to be ~10 nm by GIXR and 1~3 % by XPS. In this study, we focused on the post-deposition annealing (PDA) transient of deposited HfO₂ in N₂ using the high-speed rapid-thermal-annealing (RTA) (As-Micro, Annealsys). The peak temperature was 600°C and 700°C, changing both ramp-up time (τ_1) to 600°C (700°C) and ramp-down time (τ_{\downarrow}) to 200°C, as shown in **Fig.** 1 (see the caption in Fig.1 for the definition of τ). The holding time was fixed to be 10 sec. Samples in PDA were inspected by XRD and P-V characteristics.



Fig. 1 Schematic image of PDA temperature control. τ_{\uparrow} and τ_{\downarrow} are defined by seconds per 100°C increase and decrease, respectively, between 200°C and highest temperature (600 or 700°C).

Results

The ramp-up process was first studied for un-doped HfO₂, because un-doped HfO₂ also exhibits ferroelectric properties. **Fig. 2** shows the remanent polarization 2Pr as a function of the monoclinic phase ratio r_m around 2θ ~30°, defined as follows.



Fig. 2 Relationship between the remanent polarization and r_m in un-doped HfO₂ films (10 nm) for two kinds of highest temperatures with several kinds of the ramp-up/ramp-down times.

PDA at 600°C causes higher Pr, while τ_{\uparrow} is not likely to affect Pr very much. It is noted that 2Pr is almost uniquely

determined by r_m , as previously discussed [6]. Therefore, we focus on the ramp-down process τ_{\downarrow} and 600°C for the highest PDA temperature.

Fig. 3 shows (a) XRD, (b) $2Pr-r_m$ relationship of 1.7 % (Y/Hf ratio) HfO₂ in PDA as a parameter of τ_{\downarrow} . It should be noted in (a) that the fast ramp-down process makes the monoclinic phase completely disappear in XRD, while P-E curve does not change so much (data not shown), because the monoclinic portion is still small. Here, the τ_{\uparrow} was fixed to be 2.5 sec. In (b), the unique $2Pr-r_m$ relationship holds good in non-equilibrium PDA cases as well.



Fig. 3 (a) XRD patterns and (b) A unique Pr- r_m relationship, for Y:1.7 % doped HfO₂ films for five kinds of ramp-down times. In the slow ramp-down process, monoclinic phase comes out, but the unique relationship in Pr- r_m is still true.

Fig. 4 shows 2*Pr* as a function of τ_{\downarrow} for three HfO₂ films (undoped, 1.0 %, and 1.7 % Y), in which $\tau_{\uparrow}=2.5$ sec. With the increase in Y concentration, less dependence of *Pr* on τ_{\downarrow} is observed, More interestingly, the extrapolated values of *Pr* to $\tau_{\downarrow}=0$ seem to converge at a given point. Namely, if we could carry out the perfect quenching in PDA, the same *Pr* ferroelectric properties might be observable even in un-doped HfO₂, and not different from doped cases in principle. With the increase in τ_{\downarrow} , *Pr* in Y:1.7 % sample does not change at all, while that in un-doped case is significantly degraded. The question is what is specific to doped HfO₂.



Fig. 4 2*Pr* as a function of ramp-down time for three kinds of samples. It indicates that no effect in Y: 1.7%, a small decrease in Y: 1.0 % and a significant decrease in un-doped case with the ramp-down time. The merged point at τ_1 =0 (infinite fast quenching process) seems to show the intrinsic polarization specifically involved in these HfO₂ stacks. The thickness was ~10 nm.

Discussion

The results particularly in non-optimized doped-HfO₂ show that ferroelectric properties are significantly sensitive to the ramp-down speed. In fact, it seems that $Pr=P_0$ exp($-\alpha \tau_{\downarrow}$). Although a huge number of ferroelectric HfO₂ results have been so far reported, no special cares for the PDA transient characteristics have been taken in most cases.

Another interesting point is that Pr value at $\tau_{\downarrow}=0$ looks the same for three samples as shown in Fig. 4. This fact suggests that the ferroelectric volume in HfO₂ at 600°C is the same for three samples. Dopant, Y in the present case, may stabilize the ferroelectric phase even in the quasi-equilibrium PDA, while un-doped HfO₂ cannot maintain the ferroelectric properties in such process. Fig. 5 schematically describes the energy landscape among monoclinic, tetragonal and ferroelectric (possibly orthorhombic) phases. The slow ramp-down process in PDA may change the energy landscape from the solid black to broken red lines, possibly due to a structural relaxation. Conversely speaking, a finite energy difference, Δ , can be maintained by the rapid ramp-down or by doping.



Fig. 5 The energy landscape in HfO₂ with many polymorphs. In doped HfO₂ or undoped one with rapid ramp-down process, a finite barrier, Δ (stabilizing the ferroelectric phase), may be maintained, while in a slow process for undoped case, ferroelectric phase may easily transform to monoclinic phase due to a structural relaxation which lowers the energy barrier.

Conclusion

We have demonstrated impacts of non-equilibrium PDA on ferroelectric phase formation among various polymorphs in HfO₂ for the first time. To stabilize the ferroelectric phase in HfO₂, kinetic control of the atom displacement in the phase transformation process should be considered. From the present experiments, it is concluded that the dopant works not as the ferroelectric former but the ferroelectric phase stabilizer. Another interesting finding is that the unique $2Pr-r_m$ relationship holds good in non-equilibrium PDA cases as well.

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