Increase of Crystallization Temperatures of Ultrathin Al₂O₃ Films Caused by Si Diffusion during Annealing

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1. Introduction

In order to scale equivalent oxide thickness of gate dielectrics to 1 nm and below, alternative high-k dielectrics to SiO₂ will be necessary to satisfy current leakage requirements. However, to successfully introduce these materials into MOSFET devices, a number of material compatibility issues must first be solved such as the stability of gate stack structure against thermal treatments.

 Al_2O_3 is considered as a candidate of high-k material. Several groups have fabricated Al₂O₃-gate MOSFETs [1-3]. Thermal stability of Al₂O₃ film on Si is also studied [4-6]. However, it is noticed that results reported so far are confusing in that crystallization temperature studied ranges to higher than 1000 . Therefore, a widely from 700 systematic study is indispensable to understand the crystallization behavior in detail. In this paper, we use reflection high-energy electron diffraction (RHEED) and XRD to investigate the thermal stability of Al₂O₃ film, examining how annealing process and film thickness affect the crystallization temperature of amorphous as-deposited films. It is found that crystallization of Al₂O₃ film is influenced by Si diffusion into the film which arises during a relatively low temperature process.

2. Experimental

Si(001) substrates were prepared by conventional RCA cleaning and treated in 1% hydrofluoric acid solution for 30 s to obtain the hydrogen-terminated surface. Al₂O₃ films were deposited by atomic layer deposition at 300C using Al(CH₃)₃ and H₂O. Film thickness ranged from 3.2 to 32 nm as measured by ellipsometry.

Samples were cut from an as-deposited wafer into pieces and subjected to different annealing processes, as summarized in **Fig. 1**, either in a conventional RTA furnace at 1 atm or in an ultra-high vacuum (UHV) chamber equipped with *in-situ* heating stage and RHEED system. Crystallization was determined both by XRD and RHEED.

3. Results and Discussion

Advantage of the RHEED technique in ultrathin film region is demonstrated in Figs. 2 and 3. The annealing process shown in Fig. 1(a) was performed at 800 in 1 atm N₂. XRD data for the 32 nm film shows diffraction peaks, indicating the formation of -Al₂O₃ phase, while the 10 nm film does not show any diffraction peaks (Fig. 2). In contrast, Fig. 3 shows that RHEED can detect the crystallization of films as thin as 3.2 nm. Changes in RHEED image from halo-shaped patterns (Fig. 3(a)) to those exhibiting a series of streaks or rings (Fig. 3 (b) and indicate formation of crystalline structures. (c)) Crystallization of the 10 nm thick film after annealing was also confirmed by RHEED, which was not observable by XRD. Thus RHEED is a powerful technique to determine crystallization of ultrathin films.

The crystallization temperature of Al_2O_3 films was determined by RHEED as a function of film thickness in **Fig. 4**. The annealing process of Fig. 1(a) was performed in UHV. As is shown, when the film thickness is greater than or equal to 10 nm, the crystallization temperature is 800 and independent of film thickness. On the other hand, when the film thickness is thinner than 10 nm, the crystallization temperature increases with decreasing film thickness. This is a direct evidence of thickness dependent crystallization temperature of high-*k* films, which was first observed by RHEED.

Another important finding is that the heating rate has a strong influence on crystallization behavior. Figure 5 shows XRD results of 32 nm thick films heated at a slow rate of 1 /s (shown in Fig. 1(b)) and annealed at 800 and 900 in 1 atm N₂. In contrast to the result of Fig. 2 which was heated at a fast rate of 30 /s, no diffraction peak is detected. RHEED observation also confirmed that the crystallization does not proceed. Thus, even though slow heating rates generally yield fine crystal structures, in this case, it instead suppressed crystallization.

To investigate this unexpected effect from slow heating



Fig. 1 Illustrations of annealing processes examined in this study. T_{anneal} was ranged between 750 and 950 .





rates further, we tested three thermal treatments on 9.8 nm thick Al₂O₃ films; processes of Figs. 1 (c), (d), and (e) using the RTA furnace under 1 atm N₂. RHEED observations after thermal treatment confirmed that the sample heated at the fast heating rate (Fig. 1(c) process) indeed crystallized while the samples heated at the slow rate (processes of Fig. 1(d) and (e)) did not. We found it surprising that the heating rate used to bring the sample to the pre-annealing temperature of 550 (30 / s and 1 / s),as opposed to other variables such as the final annealing temperature, has a dominant role in determining whether the film crystallized or not.

It is noted that the slow heating rate also deteriorates the electrical property. Two samples with 6.3 nm thick Al_2O_3 were annealed by using processes shown in Fig. 1(a) and (d), both annealed at 750 for 30 s under $1\%-O_2/N_2$ in 1 atm. The capacitance equivalent thickness (CET) measured for a MIS structure was 2.5 nm for the Fig. 1(a) processed sample, whereas an increase of CET to 3.1 nm was observed in the Fig. 1(d) processed sample.

XPS spectra of the above 9.8 nm samples are shown in **Fig. 6.** Since the photoelectron escape depth through Al_2O_3 is 2.4 nm [7] and the film thickness of these samples is 9.8 nm, the XPS spectra in Fig. 6 should represent only the Al₂O₃ film itself without confounding effects from Al₂O₃/Si interface or Si substrate. We also note that the Al 2p and O 1s spectra (not shown) were essentially identical for all three samples.

The XPS spectra of the sample of Fig. 1(c) process show no evidence of Si in the Al₂O₃ film which, if present, would appear as a peak at a binding energy of approximately 103 eV. This binding energy corresponds to the chemical shift component (Si^{4+}) of Si 2p photoelectrons. The broad spectrum around 100 eV is the plasmon energy loss spectrum of Al 2p. In contrast, Fig. 1(d) processed sample shows a peak appearing at 103 eV. Appearance of the Si 2p signal suggests that Si atoms diffused from the Si



Fig. 3 RHHED images of (a) as-deposited Al₂O₃ films, (b) 3.2 nm film after annealing at 925 , and (c) 22.5 nm film after annealing at 850 for 30 s in UHV using the process in Fig. 1(a). Arrows indicate the appearance of ring or streak patterns.





and 850

Fig. 6 XPS spectra of Al₂O₃ (9.8 nm)/Si samples annealed in 1 atm N₂ using processes of Fig. 1(c), (d), and (e). Final temperatures were 950 for the processes of Fig. 1(c) and 1(d), respectively.

substrate into the Al₂O₃ layer. Coexistence of SiO_x (x<2) component and/or silicate phase is not clear because of the broad spectrum around 100 eV. Interestingly, the same Si 2p peak at 103 eV is observed in the sample of Fig. 1(e) process which was annealed only at 550 with a heating rate of 1 /s. These results suggest slow or prolonged heating even at temperatures below 550 are sufficient to drive Si diffusion from the substrate into the Al₂O₃ film. Increase of CET observed in case of adopting a slow heating rate is considered to be caused by the decrease of dielectric constant of Al₂O₃ film induced by the Si diffusion, although a possibility of concurrent formation of low dielectric constant layer at the interface can not be ignored.

Based on these findings, we suggest that the main source of variation of crystallization temperatures shown in Fig. 4 is Si diffusion into Al₂O₃ film. Although UHV annealing was performed at the high heating rate of 30 /s, only a small amount of Si diffusion at the Al₂O₃ interface is needed to increase the crystallization temperatures when films are as thin as 10 nm or less. We think this is also the case for the preceding reports that various thermal processes applied especially at low temperatures might have brought different content of Si in the film and thus resulted in the scattering of crystallization temperatures observed.

4. Conclusions

Crystallization behavior of ultrathin Al₂O₃ films is affected by the Si diffusion into film, which takes place during the annealing process below 550 . This effect might be emphasized in ultrathin film region which is the target thickness of high-k gate dielectrics. Thus in the annealing process of high-k gate stack, heating rate as well as the maximum temperature must be carefully controlled.

Acknowledgements

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References

- [1] A. Chin et al., Tech. Dig. VLSI Symp. (2000) 16.
- [2] D. A. Buchanan et al., IEDM Tech. Dig. (2000) 223.
- [3] J. H. Lee et al., IEDM Tech. Digest (2000) 645.
- [4] C. Krug et al., Phys. Rev. Lett. 85 (2000) 4120.
- [5] M. Copel et al., Appl. Phys. Lett. 78 (2001) 2670.
- [6] M. Kundu et al., J. Appl. Phys. 91 (2002) 492.
- [7] M. Kundu etal., Appl. Phys. Lett. 78 (2001) 1517.