Advanced Layer-by-Layer Annealing & Deposition Process for High-Quality High-k Dielectrics Formation

K. Iwamoto,[1] K. Tominaga,[1] T. Yasuda,[2] T. Nabatame[1] and A.Toriumi[2,3]
[1]MIRAI Project, Association of Super-Advanced Electronic Technologies (ASET), Japan
[2]MIRAI Project, Advanced Semiconductor Research Center (ASRC), National Institute of Advanced Industrial Science and Technology (AIST), Japan
[3]Departmeant of Materials Science School of Engineerring, University of Tokyo, Japan
Iwamoto.k@mirai.aist.go.jp

1. Introduction

ALD (Atomic Layer Deposition) is a promising technique for high-k gate dielectrics formation, primarily because it enables atomic-scale thickness control. ALD is carried out at low temperatures (typically 300°C) to attain self-limiting growth, while deposited films contain relatively large concentrations of the residual impurities such as C, H, and Cl originating from the ALD precursors. Impurity removal by post-deposition annealing is usually insufficient, most likely because desorption of the impurities from the deeper layer of films is slow. To overcome this problem, we propose an advanced ALD process which we name Layer-by-Layer Annealing and Deposition (LL-A&D). In LL-A&D, ALD growth by a small thickness (typically < 1nm) and subsequent annealing are repeated to complete the target thickness. Insertion of annealing treatments during the ALD cycles is expected to efficiently remove impurities before they are buried in the film. In order to test this concept, we have developed a multichamber system that integrates an ALD reactor with a rapid thermal annealing (RTA) furnace. In this paper, we investigate the effects of LL-A&D process both on the impurity reduction in the film and the interface structure modification.

2. Experimental Procedure

Process sequences for ALD and LL-A&D are shown in Fig. 1. Al_2O_3 films were grown on HF-last Si (100) at 250°C by ALD using $Al(CH_3)_3$ (TMA) and H_2O. $HfAlO_x$ (Hf/Al ratio 3/1) films were deposited on Al_2O_3 (0.5nm)/SiN(0.4nm)/Si(100) by ALD or LL-A&D using TMA, $Hf[N(CH_3)_2]_4$ and H_2O. RTA was performed under 1×10^{-4} Pa at 650°C for 30sec.

3. Result and Discussion

Figure 2 shows the intensity measured by thermal desorption spectroscopy (TDS) for Al_2O_3 grown by the ALD scheme. Main desorption species from Al_2O_3 has a mass number (m/e) of 28, which is presumably C_2H_4 formed by association of two residual CH_3 groups originating from TMA through a reaction such as $2CH_3 \rightarrow C_2H_4 + H_2$. Peak intensity of m/e=28 increases linearly with Al_2O_3 thickness up to 1.5 nm, and it saturates over 1.5 nm. This result indicates that, for effective removal of impurities, RTA needs to be performed before the thickness increases by 1.5 nm. Figure 3 shows the TDS spectra (m/e=28) for $HfAlO_x$ films prepared by three different process schemes. Desorption intensity for the $HfAlO_x$ film deposited by LL-A&D is about 50 % smaller than that for the $HfAlO_x$ film that was grown by conventional ALD with post-deposition RTA in O_2 ambient. Compared to the as-deposited $HfAlO_x$ film, the desorption intensity for LL-A&D is reduced to 1/3.

One of our big concern in LL-A&D process is that additional RTA treatments might cause interfacial SiO_2 growth. Figure 4 compares the Si_{2p} XPS spectra for an as-deposited ALD Al_2O_3 film and a LL-A&D Al_2O_3 layer. Thickness of the SiO_x layer estimated from these spectra was 0.19 and 0.42 nm for ALD and LL-A&D, respectively. Post-deposition RTA of the ALD-Al_2O_3 films forms approximately 0.5 nm-thick SiO_x layers at the interface. Thus, interfacial oxidation by LL-A&D is minimal as compared to conventional ALD with post-deposition RTA.

Impact of the impurity reduction on the electrical properties of the metal/Al_2O_3/Si capacitors is that the flatband voltage shift and hysteresis are well decreased by using LL-A&D process.

Acknowledgment

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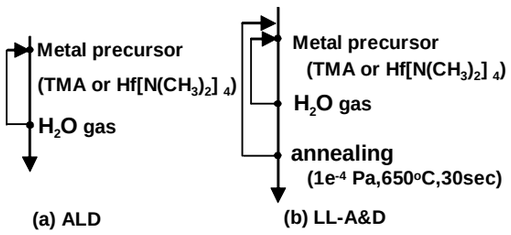

Fig.1 ALD and LL-A&D process flow

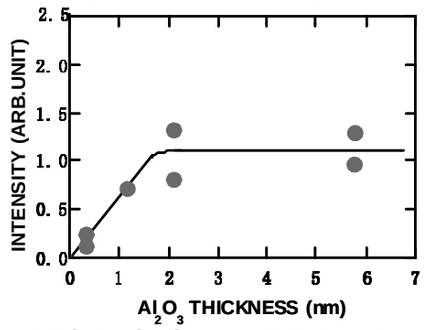

Fig. 2 Relationship between C_2H_4 intensity of TDS spectra and Al_2O_3 thickness.

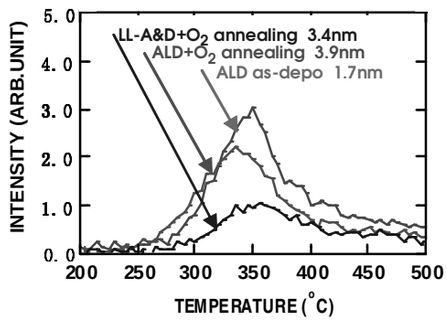

Fig. 3 TDS spectra for C_2H_4 of $HfAlO_x$.

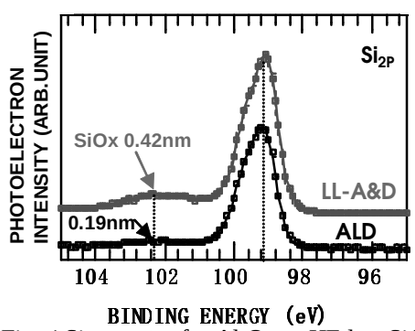

Fig. 4 Si_{2p} spectra for Al_2O_3 on HF-last Si(100) deposited by ALD and LL-A&D.