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

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1. Introduction

ALD (Atomic Layer Deposition) is a promising technique for high-k dielectric formation, enabling 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 < 1 nm) and subsequent annealing is 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. ALD films were grown on HF-last Si(100) at 250°C by ALD using Al(CH3)3 (TMA) and H2O. HfAlO3 (Hf/Al ratio 3/1) films were deposited on Al2O3 (0.5 nm)/SiO2(0.4 nm)/Si(100) by ALD or LL-A&D using TMA, Hf[N(CH3)2]4, and H2O. RTA was performed under 1×1017 Pa at 650°C for 30 sec.

3. Result and Discussion

Figure 2 shows the intensity measured by thermal desorption spectroscopy (TDS) for Al2O3 grown by the ALD scheme. Main desorption species from Al2O3 has a mass number (m/e) of 28, which is presumably C2H4 formed by association of two residual CH3 groups originating from TMA through a reaction such as 2CH3 → C2H4 + H2. Peak intensity of m/e=28 increases linearly with Al2O3 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 HfAlO3 films prepared by three different process schemes. Desorption intensity for the HfAlO3 film deposited by LL-A&D is about 50% smaller than that for the HfAlO3 film that was grown by conventional ALD with post-deposition RTA in O2 ambient. Compared to the as-deposited HfAlO3 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 SiO2 growth. Figure 4 compares the Si2p XPS spectra for an as-deposited ALD Al2O3 film and a LL-A&D Al2O3 layer. Thickness of the SiO2 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-Al2O3 films forms approximately 0.5 nm-thick SiO2 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/Al2O3/Si capacitors is that the flatband voltage shift and hysteresis are well decreased by using LL-A&D process.

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