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Atomic Layer Deposition of HfO_2 Films on Ge

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We investigated the growth characteristics and interfacial properties of HfO_2 films deposited on Ge substrate through atomic layer deposited (ALD) by using an in-situ medium energy ion scattering analysis. The growth kinetics of HfO_2 grown on a GeO_2/Ge substrate through ALD is similar to that grown on an SiO_2/Si substrate. However, the incubation period of HfO_2 deposition on Ge is shorter than that on Si. The HfO_2 grown on the GeO/Ge substrate shows a significant diffusion of Hf atoms into the substrate interface and GeO volatilization after annealing at 700°C. The presence of low-quality Ge oxide or suboxide may degrade the electrical performance of device.

Keywords : Atomic layer deposition, HfO_2, Ge, GeO, Growth, Annealing

I. Introduction

Ge has been considered as a replacement of Si as channel material for future high-speed CMOS technology because Ge exhibits high intrinsic carrier mobility. However, native germanium oxide is hygroscopic and water-soluble, hindering the processing and application of Ge CMOS devices. Thus, the lack of a sufficiently stable native oxide poses problems in obtaining high-quality surface passivation during device manufacturing.

There have been many attempts to use Ge as a channel material in high-speed FETs [1-4], because of its high low-field carrier mobility and small mobility band gap for low voltage scaling. However, the oxide layer poses a major problem. Chui et al and Bai et al reported the possibility of Ge-based MOS capacitors and transistors exhibiting superior electrical properties using high-k dielectrics [1,5].

Among the various techniques for depositing high-k gate dielectrics, atomic layer deposition (ALD) has drawn much attention as it can be used to fabricate ultrathin dielectric layers with excellent electrical characteristics and uniformity because its low-thermal-budget processing suppresses unstable intrinsic chemical nature of dielectric layer.

This study focused on the characteristics of HfO_2 films grown on GeO_2/Ge substrate through ALD and their interfacial reactions. The dependence of the interfacial layer on the electrical characteristics was also studied.

II. Experimental Procedures

In this study, we used p-type (100) Ge wafers of resistivity 1～2 Ω-cm. The Ge wafers were subjected to RCA cleaning and dipped in dilute HF to remove

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the Ge native oxides. After the wet-chemical cleaning, a Ge oxide layer was grown at the temperature of 300°C in a quartz furnace in an atmosphere of dry O_2.

The ALD of HfO_2 was performed in a hot-wall shower-head reactor. Using $HfCl_4$ and H_2O as a precursors, the HfO_2 films were grown at a substrate temperature of 300°C. The temperatures of $HfCl_4$ and H_2O were maintained at 170°C and at 14.5°C, respectively. N_2 gas was used as the flow gas as well as the purge gas. The process pressure for the feeding time was maintained at 250 mTorr.

In order to investigate the initial growth of the atomic-layer-deposited HfO_2 films, samples were transferred to an in-situ medium energy ion scattering (MEIS) chamber after each ALD deposition cycle. The MEIS analysis using the medium energy ion beam (~100 keV) is unique, and permits thin films to be quantitatively examined with a high depth resolution of ~3Å [6]. Moreover, the in-situ MEIS analysis can overcome some limitations associated with the ex-situ measurement analysis, such as surface contamination and modification. The MEIS measurement was performed using double-aligned 100 keV proton ion beam, which eliminates contributions from crystalline Si substrates. The incident beams were aligned in the [111] direction and the scattered beams were aligned in the [001] direction with a scattering angle of 125°. Therefore, the in-situ MEIS in the ALD environment provides insights into the growth kinetics during the initial stage of ALD.

Capacitance voltage (CV) characteristics were measured using an HP4284A LCR meter and the current voltage (IV) characteristics were determined using an HP4145B parameter analyzer. A Pt square electrode with an area of approximately 30×30 μm^2 was patterned through a photo-lithography process.

III. Results and Discussion

Fig. 1 shows the proton backscattering energy spectra of Hf atoms for the HfO_2 films grown on the Ge oxide layer. The change in the Hf peaks indicates an increase in the Hf coverage with slow growth rates. Because the leading edge of the Ge peak moves backward after the HfO_2 deposition (5 and 10 cycles), the MEIS results represent the smooth and uniform growth of ALD-HfO_2 on the Ge oxide underlayer. At a growth temperature of 300°C, the concentration of Ge decreases slightly after five ALD cycles.

Fig. 2 is a plot of the Hf coverage, measured through in-situ MEIS, as a function of the number of

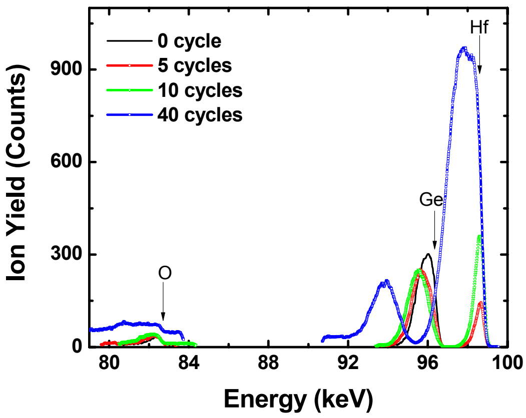

Figure 1. In-situ MEIS spectra of Hf, Ge, and O for HfO_2 films grown on the GeO underlayer with increasing growth cycles.

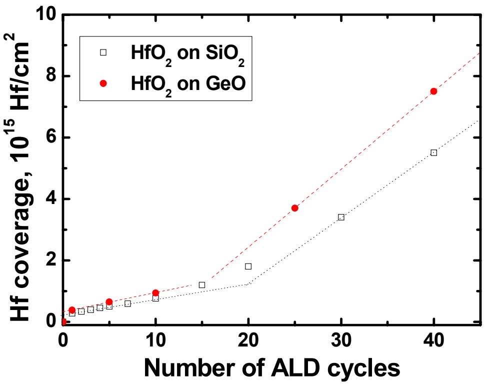

Figure 2. Hf coverage, measured through in-situ MEIS, as a function of the number of ALD cycles for depositing HfO_2 on SiO_2 and Ge oxide.

ALD cycles for depositing HfO_2 on SiO_2 and Ge oxide. In some aspects, the growth of HfO_2 on Ge oxide is similar to that on SiO_2 [7]. However, the induction period of HfO_2 deposition on Ge oxide is lower than that on SiO_2. The Hf coverage on Ge oxide after 25 ALD cycles is equivalent to that on SiO_2 after 30 ALD cycles. After more than 25 ALD cycles, the MEIS measurements indicated only a linear growth of the HfO_2 film on Ge oxide.

Fig. 3 shows the MEIS spectra for the as-grown and annealed samples (40 cycles). After the annealing treatment at 700°C, evidence of the diffusion of Hf atoms into the substrate interface can be clearly observed in the inset of Fig. 3. In addition, the volatilization of GeO occurs simultaneously with Hf diffusion. The desorption and volatilization of GeO after annealing generates a huge amount of defects and traps in the HfO_2 film [8–10]. Therefore, these phenomena tend to deteriorate the interface and the high-k film quality [11,12]. The results indicate that Ge (or GeO_x) is incorporated in the HfO_2 films, forms an HfGeOx layer.

Fig. 4 shows the CV characteristics measured at 10 kHz, 100 kHz, and 1 MHz for a Pt-gated MOS capacitor with an HfO_2 layer grown on GeO using 40 ALD cycles. The successful electrical properties of HfO_2 on GeO/Ge substrate can be attributed to the negligible Ge segregation and interface roughness due to the low thermal budget of the ALD process. The capacitance curve shows a heavy dependency on frequency. Interfacial Ge sub-oxide (GeOx; Ge^{1+}, Ge^{2+}, Ge^{3+}) could account for the high interfacial density of states [8,13]. The IV measurements showed high leakage and interfacial density of states that increase with the amount of Hf-O-Ge bonds after annealing at 700°C. Fig. 5 shows the corresponding leakage current behaviors for these samples. A CV curve could not be obtained after annealing owing to the Hf

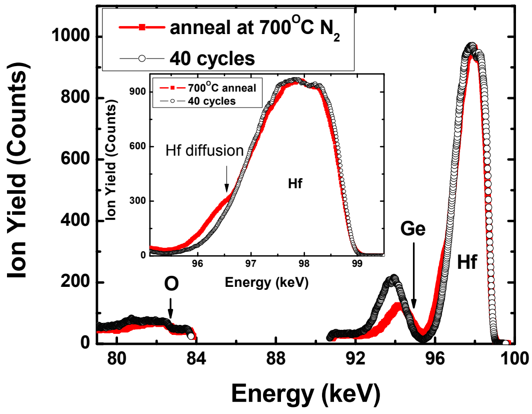

Figure 3. MEIS spectra for the as-grown and annealed HfO_2/GeO/Ge. Evidence of the diffusion of Hf atoms into the substrate is visible after the annealing treatment at 700°C.

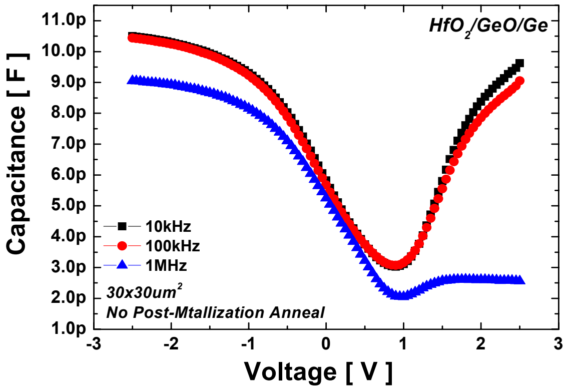

Figure 4. Capacitance voltage curves measured at 10 kHz, 100 kHz, and 1 MHz for a Pt-gated MOS capacitor with an HfO_2 film on GeO.

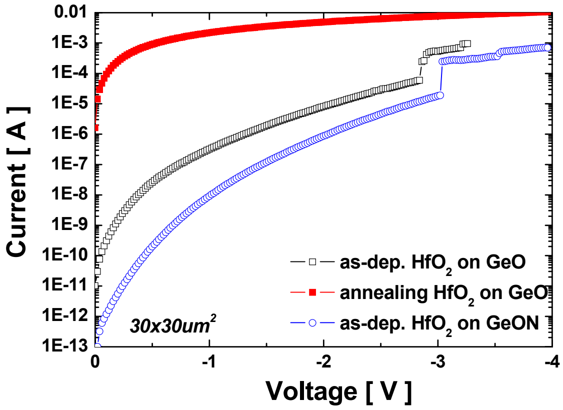

Figure 5. Leakage current behaviors for Pt/ALD-HfO_2/GeO capacitors.

diffusion and Ge desorption, which is further supported by the MEIS results shown in Fig. 3.

In another GeO_x formation mechanism, the Ge surface is nitridated by annealing in NH_3 at 600°C, which results in a Ge–O–N bond with a chemical state similar to the fully oxidized Ge^{4+} state [8]. HfO_2 on GeON/Ge substrate clearly results in a lower leakage current than that on GeO/Ge substrate. This indicates that the poor electrical properties of the Pt/ALD–HfO_2/Ge capacitors may be attributed to the different Ge oxidation states underneath the HfO_2 layer.

IV. Summary and Conclusions

HfO_2 films were deposited through ALD with the alternate exposure to $HfCl_4$ and water on the thermal oxide on both Si and Ge substrates. In both cases, the growth kinetics of the HfO_2 films on both substrates exhibit similar characteristics, except for the incubation regime. After the thermal treatment, the Hf mixes with Ge to form an HfGeOx layer, which cause the degradation of electrical properties of the device. Therefore, the interfacial reactions and the control of interfacial GeO_x played a crucial role in the electrical properties.

Acknowledgements

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