Low Temperature Formation of Silicon Oxide Thin Films by Atomic Layer Deposition Using NH3/O2 Plasma

Jong-Sik Choi,a,1 Bong Seob Yang,a Seok-Jun Won,c Jun Rae Kim,a Sungin Suh,a Hui Kyung Park,d Jaeyeong Heo,d,z and Hyeong Joon Kim,a,z

aDepartment of Materials Science and Engineering, Seoul National University, Gwanak-Gu, Seoul 151-744, Korea
bThin Film/CMP Technology Team, Memory Division, Samsung Electronics Co. Ltd., Hwasung-City, Gyeonggi-Do 445-701, Korea
cTechnology Development Team, LSI Division, Samsung Electronics Co. Ltd., Gijeong-Gu, Yongin-City, Gyeonggi-Do 446-711, Korea
dDepartment of Materials Science and Engineering, Chonnam National University, Gwangju 500-757, Korea

High-quality silicon oxide (SiO2) thin films are deposited by plasma-enhanced atomic layer deposition (PEALD) using bis(diethylamino)silane as a Si precursor and ammonia/oxygen plasmas at a substrate temperature of 150°C. The SiO2 films are formed at a growth rate of ~0.137 nm/cycle in high purity. The overall quality of the PEALD-SiO2 films is assessed by infrared spectroscopy, Auger electron spectroscopy, and current-voltage analysis. The quality of the films formed at low temperature using the combination of ammonia/oxygen plasmas compares well with deposition at higher temperatures (350°C) using oxygen plasma only.

Silicon oxide (SiO2) thin films are widely used in semiconductor and display devices as capping layers, gate spacers, etch stoppers, antireflection layers, and gate dielectrics. The move away from the use of silicon in channel layers toward deposited layers such as amorphous oxide semiconductors will require gate dielectric layers to be grown at low-temperatures.1,2 Passivation layers for flexible displays must also be deposited below 200°C because of the low thermal stability of flexible organic substrates. The International Technology Roadmap for Semiconductors (ITRS) predicts that 3-dimensional structures will become important for development of future memory device technologies. In these regards, atomic layer deposition (ALD) has been highlighted as a process for deposition of high-quality SiO2 films at low temperatures.3-6 In addition this technique gives good step coverage and control of thickness on the nanometer size.7,8 Thermal-ALD enables fast deposition of SiO2 thin films using catalysts, such as pyridine, ammonia, and trimethylaluminum.9-12 The use of plasma in addition to thermal-ALD can allow lower growth temperatures to be used through the generation and deposition of reactive radicals from the plasma.9,13

Silicon precursors used for ALD-SiO2 film growth include chlorine-based precursors such as dichlorosilane (SiH2Cl2) and tetra- chlorosilane (SiCl4). However, these generally show low adsorption probabilities at reactive surface sites, resulting in slow growth rates. Application of these precursors therefore requires an exposure of ~106 L (~107 Torr s), which corresponds to an actual reactant exposure time of ~50 s or longer.9-12 They require a relatively high growth temperature (>300°C) to facilitate ligand exchange reactions during oxidation.14-17 To overcome these problems, alternative organosilane precursors that feature high reactivity at low growth temperatures have been actively researched. One class of Si precursors are amino-group-based derivatives such as tetrakis(dimethylamino)silane, bis(dimethylamino)silane, and bis(diethylamino)silane.18

In this study, high-quality SiO2 films were formed by PEALD using bis(diethylamino)silane (BDEAS, H2Si[(N(C2H5)2]2) precursors with the aid of ammonia (NH3) and oxygen (O2) plasma. The films were formed with low impurity levels and growth per cycle (GPC) was ~0.137 nm/cycle at 150°C. It was revealed that NH3 plasma exposure prior to the O2 plasma step catalyzed the removal of adsorbed hydrogen-based ligands on the growth surface and helped to formation of a strong Si–O–Si backbone structure, yielding denser SiO2 films. The quality of the SiO2 films grown at 150°C using both the NH3 and O2 plasma was comparable with that of films grown at 350°C, only using O2 plasma. The combination of NH3 and O2 plasma allowed low growth temperatures to be used for the ALD reaction while maintaining the overall quality of the film. The synergetic reaction developed may be further exploited for formation of other high-quality oxide films at low growth temperatures.

A PEALD system (ASM Genitech Co.) with direct capacitive-coupled plasma (CCP) was used to deposit SiO2 thin films. A radio frequency of 13.56 MHz was applied to a showerhead located at the top of the reactor and a heater forming an electric ground was located below the plasma region. BDEAS (DNF Co. Ltd., Korea) was used as a silicon precursor. Argon was used as a carrier gas as well as plasma activation gas to ignite the plasma. The deposition sequence was as follows: BDEAS pulse (1 s)/Ar purge (5 s)/NH3 pulse (0.3 s)/NH3 plasma (0.5 s, 50 sccm, 200 W)/O2 pulse (0.3 s)/O2 plasma (2 s, 100 sccm, 200 W)/Ar purge (5 s). The source injection time of 1 s was sufficient to provide saturated growth. For comparison, in some film depositions the NH3 pulse and plasma steps were omitted and only the O2 plasma steps were performed. The process pressure was 3 Torr. The growth temperature was varied from 150 to 350°C for the films formed only using the O2 plasma. The SiO2 film growth using the NH3/O2 plasma was performed at 150°C to evaluate its feasibility for low temperature growth.

The film thickness was measured using a single wavelength ellipsometer (Gaertner, L116D, USA). The film thickness was also double-checked by X-ray reflectivity (XRR, PANalytical, X’Pert PRO MRD) analysis (the difference was less than 5%). The chemical composition of the deposited films was analyzed by Auger electron spectroscopy (AES). The hydrogen content of the PEALD-SiO2 films was investigated using Fourier transform infrared spectroscopy (FTIR). The wet etch rate (WER) of the SiO2 films was used to evaluate the relative density of the films. The PEALD films and thermally-grown films were compared by dipping into an aqueous solution of 0.5% HF prepared using deionized water. A metal-oxide-semiconductor (MOS) capacitor was fabricated for electrical analysis with a stack of highly-doped p-Si/SiO2/Pt. Current density–voltage (J–V) characteristics were measured using an HP 4145A semiconductor parameter analyzer.

A set of film growth experiments was conducted to confirm growth behavior as a function of deposition temperature using BDEAS and O2 plasma (without NH3 plasma). The GPC results, shown in Fig. 1a, indicate that over the temperature range 150–350°C the GPC was 0.115–0.122 nm/cycle, with a declining trend at higher growth temperatures. At higher growth temperatures it is believed that a denser film develops because the high temperature allows a more thermodynamically stable structure to form. Also, different surface chemistry, i.e., less number of surface hydroxyl groups at higher growth temperatures.
that fluent nucleation of SiO₂ proceeds on the Si substrate. In the case of a SiO₂ film deposited using the NH₃/O₂ plasma at 150°C, the film grown using only O₂ plasma (≈0.122 nm/cycle) at the same growth temperature (150°C). At a growth temperature of 150°C, a characteristic linear increase in film thickness with increasing number of growth cycles was also observed for both films, as shown in Fig. 1b. No obvious incubation cycle was seen and Figure 1b indicates that fluent nucleation of SiO₂ proceeds on the Si substrate.

Figure 2a shows the FTIR spectra of the SiO₂ films deposited at different growth temperatures using only O₂ plasma. It is noteworthy that the peak assigned as the Si–N bond at 890 cm⁻¹ was not detected in any spectra, suggesting complete oxidation occurred during the film growth. The main vibrations observed are Si–O stretching modes in any spectra, suggesting complete oxidation occurred during the film growth. The main vibrations observed are Si–O stretching modes at ≈1130, and ≈2300 cm⁻¹, respectively. The proportion of Si–O vibrations relating to the network structure increases with growing temperature while the Si–O vibrations for the cage structure gradually disappear. The cage structure is in general observed for porous SiO₂ as shown in Fig. 2a. These FTIR observations are consistent with the growth rate behavior shown in Fig. 1a. For the case of a SiO₂ film deposited using the NH₃/O₂ plasma at 150°C, the intensity of the Si–H bond is dramatically reduced compared to that of the film deposited using only O₂ plasma at the same temperature, as shown in Fig. 2b. In addition, the Si–O vibration for the cage structure almost disappears from the films grown using a combination of NH₃/O₂ plasma, while the peak is prominent when only O₂ plasma is used. These differences clearly suggest that the NH₃ plasma applied before the O₂ plasma plays a crucial role in forming high density Si–O–Si backbones with low H content.

We speculate that the NH₃ plasma step before the O₂ plasma effectively removes hydrogen-related species generated during the ligand exchange reaction, contributing to formation of high density films. The film density was measured by XRR analysis; however, only marginal differences were observed (≈2.0–2.1 g/cm³). The film density was therefore indirectly estimated by measuring the WERs (wet etch rates) of the grown films in dilute HF solution. The WERs of both PEALD-SiO₂ films deposited using NH₃/O₂ plasmas at 150°C and O₂ plasma at 350°C were ~4.0 ± 0.2 nm/min. These WERs were slightly higher than that of a thermally-grown SiO₂ film (≈2.5 ± 0.2 nm/min). A higher WER (≈8.0 ± 0.4 nm/min) for the SiO₂ film grown at 150°C with O₂ plasma was obtained, indicating its lower film density. These results indicate that dense, high-quality SiO₂ film can be formed at relatively a low growth temperature of 150°C by using a combination of NH₃ and O₂ plasmas.

AES spectra of the SiO₂ films grown using the NH₃/O₂ plasma at 150°C and a thermally-grown film are presented in Fig. 3. This figure shows that residual nitrogen and carbon impurities from unreacted Si precursor ligands inside the bulk sample are below the detection limit of the AES instrument for the PEALD-SiO₂ film formed using NH₃/O₂ plasmas. Interestingly, a small nitrogen signal is detected at the interface of the SiO₂ film and the Si substrate. It is believed that nitrogen atoms, which may from the unreacted Si precursor or from...
NH$_3$ plasma,$^{23,24}$ may be incorporated during the initial stage of the film formation on a Si substrate.

Electrical properties of capacitors based upon the various SiO$_2$ films were compared by measuring the $J$–$V$ characteristics. The 350°C-grown SiO$_2$ film formed using only O$_2$ plasma, a 150°C-grown SiO$_2$ film using NH$_3$/O$_2$ plasma and a thermally-grown SiO$_2$ film were analyzed. Figure 4 shows that all the films were good electrical insulators with breakdown fields higher than 10 MV/cm.

BDEAS appears to be a good Si precursor for SiO$_2$ film growth using PEALD techniques. However, PEALD-SiO$_2$ films formed using only O$_2$ plasma at low temperatures had lower density attributed to incomplete removal of hydrogen-related species and limited formation of a strong Si–O–Si network structure. This is supported by the higher WER ($\sim$8.0 ± 0.4 nm/min) of the PEALD-SiO$_2$ film deposited at 150°C than that ($\sim$4.0 ± 0.2 nm/min) of the film deposited at 350°C using O$_2$ plasma. Based on the structural analysis of the deposited SiO$_2$ films, it is concluded that the addition of the NH$_3$ plasma step prior to O$_2$ plasma exposure promotes efficient removal of hydrogen-related ligands generated during the ligand exchange reaction and helps to form a more complete Si–O–Si network bond. Although a detailed mechanism of the precursor ligand chemistry and removal are not yet fully understood, our strategy of using different plasma exposure steps may be applied to the formation of other metal oxide films of high-quality at low growth temperature.

Acknowledgments

This work was supported by Samsung Electronics. Financial support by Chonnam National University, 2012 is also acknowledged. Jong-Sik Choi and Bong Seob Yang contributed equally to this work.

References