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Plasma-enhanced atomic layer deposition of low temperature silicon dioxide films using di-isopropylaminosilane as a precursor

Donghyuk Shin, Heungseop Song, Minhyeong Lee, Heungsoo Park, Dae-Hong Ko*

Department of Materials Science and Engineering, Yonsei University, Seoul 03722, Republic of Korea

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ABSTRACT

Silicon dioxide (SiO_2) films were deposited on Si (100) substrates with plasma-enhanced atomic layer deposition (PE-ALD) technique at 50, 100, and 200 °C, using di-isopropylaminosilane as a silicon source and oxygen (O_2) plasma as an oxident. Self-limiting growth was confirmed with saturated growth-per-cycle (GPC) of ~1.7 Å at a constant O_2 plasma time of 1.0 s while the GPC of the PE-ALD SiO_2 film decreased with the O_2 plasma time at a low temperature of 50 °C. In our experiment, the highest GPC of ~2.0 Å was achieved when the O_2 plasma time was 0.3 s. Along the change of deposition temperature, an activation energy for thermal dehydroxylation was estimated from the gradient of the Arrhenius plot. Also, film properties were investigated with varying O_2 plasma time. PE-ALD SiO_2 film exhibited a disparity in wet etch rate and stoichiometric composition dependent on the in-cycle O_2 plasma time. According to our experimental results, PE-ALD SiO_2 film at a low temperature of 50 °C, presented high GPC and refractive index value of typical SiO_2 film compared to thermal ALD SiO_2.

1. Introduction

Silicon dioxide (SiO_2) films have been most widely used in the semiconductor industry for applications in silicon-based electronics, such as interconnect dielectrics, gate spacer, gate dielectric, and diffusion barriers [1–4]. SiO_2 films can be obtained through the thermal oxidation process at high temperature on Si substrates [5]. However, as devices are scaling down to a smaller size, alternative deposition systems are required for low-temperature film deposition, improved step coverage, and high film thickness uniformity. From this perspective, the atomic layer deposition (ALD) process has been evaluated as a suitable deposition method due to its excellent step coverage as well as the advantages of a low temperature process.

Furthermore, plasma-enhanced atomic layer deposition (PE-ALD) has been highlighted for its high conformality and uniformity at very low temperatures, providing a solution for the problems of conventional plasma-enhanced chemical vapor deposition technology with respect to spacer deposition techniques [6]. In particular, PE-ALD technique is suitable for Spacer Defined Double Patterning because of the low temperature deposition capability of SiO_2 films on Spin-on carbon hardmask (SOC or SOH) [6]. Widely used in sub-45 nm nodes, SOC is a high carbon containing polymer solution (C > 80%) and it is very important to minimize any carbon loss, due to carbon oxidation, during subsequent silicon oxide deposition by keeping the deposition temperature as low as possible [7,8].

Among the silicon precursors for PE-ALD SiO_2 films, aminosilane groups have attracted great attention for their desirable reactivity of functional groups and high stability against safety problems [9–11]. Recently, there has been a lot of research on aminosilane precursors, such as tris-dimethylaminosilane, bis-diethylaminosilane, and bis-tertiarybutylamino-silane [12–17]. Di-isopropylaminosilane (DIPAS, $SiH_3N(C_3H_7)_2$) has been proposed as a promising silicon precursor, for its low-temperature processability and high growth-per-cycle (GPC) compared to other precursors [18,19]. Latest researches on PE-ALD SiO_2 films using DIPAS as a Si source, have been conducted actively with, such as density-functional theory simulations [20] and experimental investigations on SiO_2 films for thermal and PE-ALD process [21,22]. However, we do not have a detailed research outcome on the saturation behavior of GPC along with oxygen (O_2) plasma treatment and corresponding changes in SiO_2 film properties during the PE-ALD deposition at low temperature such as 50 °C.

In this work, we demonstrate the results of the PE-ALD process, using DIPAS as the precursor and O_2 plasma as the oxidant for SiO_2 film deposition at 50, 100, and 200 °C. The overall process time was optimized based on the saturation behavior of GPC along with the changes of the four process parameters. Mainly, we focused on the reduced film GPC for increasing O_2 plasma time, and evaluated properties of PE-ALD SiO_2 film related to plasma parameters. In addition, reaction kinetics as to film GPC was investigated with the variation of O_2 plasma time and the deposition temperatures. Also, film property in connection with O_2

* Corresponding author.
E-mail address: dhko@yonsei.ac.kr (D.-H. Ko).

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plasma time was extensively inspected using spectroscopic analysis.

2. Experimental details

SiO_2 films were deposited in the commercial PE-ALD reactor manufactured by ASM Genitech Korea Ltd., equipped with a direct capacitive-coupled plasma with a radio frequency of 27.12 MHz. DIPAS, which has high vapor pressure, i.e. ~13,000 Pa at 50 °C, was introduced to the reactor, via a bypass-type vessel. The entire PE-ALD process was performed in the order of DIPAS dose, DIPAS purge, O_2 plasma exposure, and O_2 plasma purge. For the plasma exposure step, O_2 plasma was executed with a RF power of 400 W. Argon and O_2 flow were continued during the process time as a carrier gas and oxidant. The reactor pressure was maintained at 267 Pa and the tested deposition temperatures were 50, 100, and 200 °C. All SiO_2 films were deposited on c-si substrates, without other cleaning treatment.

The refractive index and thickness of SiO_2 films were measured with Spectroscopic ellipsometry (alpha-SE model from J. A. Woollam Co. Ltd.). The wavelength of ellipsometry was 180 nm and the spectral range was from 380 to 900 nm. Ellipsometry data were fitted with the Cauchy optical model to extract the refractive index of SiO_2 films. The thickness of the SiO_2 film deposited under the process of record (POR) recipe was examined by High-resolution transmission electron microscopy (HR-TEM) along with the ellipsometry. Secondary ion mass spectroscopy (CAMECA IMS 7f magnetic sector SIMS) was also performed to quantitatively analyze the impurity concentration in the SiO_2 films. For SIMS measurement, Cs^+ primary beam at 6 kV with a current of 10 nA was used to evaluate the carbon and nitrogen concentration in the SiO_2 film. Chemical bonding and composition of the SiO_2 films were examined using Auger electron spectroscopy (AES, Model: PHI 700 Xi). For AES depth sputtering, 0.5 keV Ar + ions were irradiated at an incident angle of 75 degrees from the direction perpendicular to the film. For the binding energy measurement, depth profiling of High-resolution X-ray photoelectron spectroscopy (HR-XPS, K-alpha model from Thermo VG, U. K.) was performed with a monochromated Al Kα X-ray source (hν = 1486.6 eV) along with a pass energy of 100 eV and step size of 0.1 eV. Generated photoelectrons were passed through a 180 degrees double focusing hemispherical analyzer with 128-channel detector. Also, XPS depth sputtering was executed using 500 eV Ar ions for raster size of 2 mm × 2 mm. For the calibration of binding energy, Si—Si binding energy, 99.3 eV, within the Si 2p spectrum was selected as a reference. Wet etch test was also carried out at 22 °C using 1% dilute hydrofluoric (DHF) in which 50% HF aqueous solution and deionized water were mixed in a volume ratio of 1:49.

3. Results and discussion

3.1. Film growth rate and reaction kinetics

PE-ALD SiO_2 films were deposited at 50, 100, and 200 °C and the thickness of the film was first evaluated at the center of the wafer using ellipsometry. The GPC of the SiO_2 film was obtained by using the film thickness at 30, 60, and 90 cycles. Fig. 1 shows the saturation behaviors of the PE-ALD SiO_2 films as a function of DIPAS dose time, DIPAS purge time, O_2 plasma time, and O_2 purge time. To confirm the self-limiting growth, 1 process parameter time among the above 4 parameter times was changed during the deposition while the other 3 parameter times were kept constant for a sufficiently long time. In Fig. 1(a), (b), and (d), saturated growth rate was observed with a GPC of ~1.7 Å, which was a relatively high value compared to other Si precursors [13,23], at a fixed O_2 plasma time of 1.0 s. However, as shown in Fig. 1(c), GPC of the PE-ALD SiO_2 films as a function of O_2 plasma time decreases, not showing a typical saturation growth rate curve [13]. A similar result has been reported by M. Putkonen et al. where the growth rate first decreased with increasing ozone or oxygen plasma time and then became saturated [24]. Our experimental results show that O_2 plasma time plays a critical role in determining the GPC of PE-ALD SiO_2 film using DIPAS. How this decrease in GPC affects the property of PE-ALD SiO_2 film will be discussed in detail later.

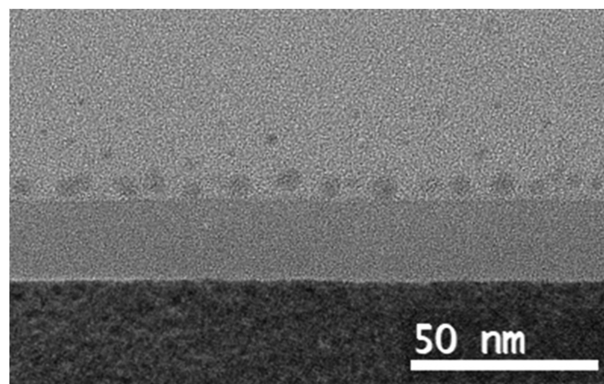

Fig. 2. High-resolution TEM image of 100 cycle PE-ALD SiO_2 film with optimized process conditions, 0.3/1.0/0.3/1.0 (DIPAS dose/DIPAS purge/O_2 plasma/O_2 purge). SiO_2 film thickness measured by TEM was 21 nm.

Fig. 2 illustrates the High-resolution TEM image of 100 cycle PE-ALD SiO_2 film under optimized process conditions, 0.3, 1.0, 0.3, and 1.0 s for DIPAS dose, DIPAS purge, O_2 plasma, and O_2 purge. Film thickness measured by TEM was about 21 nm, which corresponds well to the thickness of 20.9 nm in Ellipsometry. According to TEM and Ellipsometry results, GPC of PE-ALD SiO_2 film under POR recipe is about 2.0 Å/cycle. Latest reports done by Y.S. Lee et al. [21] showed that a GPC of 1.2 and 2.3 Å was obtained at 150 and 250 °C, respectively, for thermal ALD SiO_2 deposition using DIPAS, clearly indicating that the GPC decreased as the deposition temperature decreased: our results of 2.0 Å GPC at 50 °C are significantly meaningful since it shows that PE-ALD SiO_2 deposition using DIPAS and O_2 has the advantage of being a low temperature process with a comparable growth rate.

Fig. 3(a) shows the GPC of PE-ALD SiO_2 film according to O_2 plasma time at different temperature conditions. GPC of the PE-ALD SiO_2 films using various Si precursors decreased with deposition temperature and the ratio of GPC at the temperature of 200 and 50 °C was about 0.7–0.8 [13,23–25]. In the case of PE-ALD Al_2O_3 film, it was experimentally proven that the GPC of the film is governed by the number density of

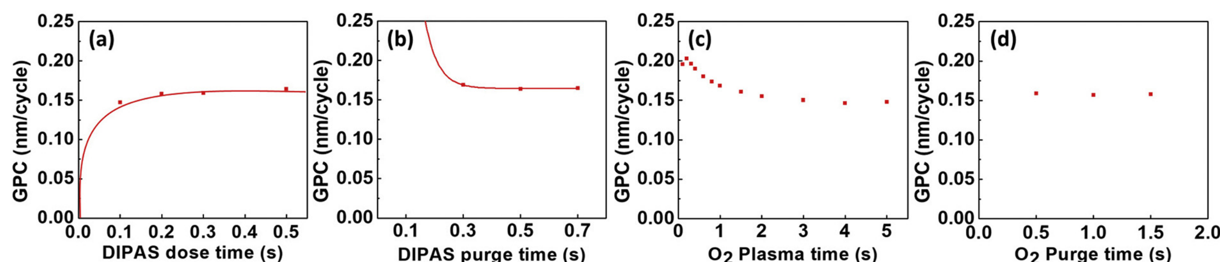

Fig. 1. The growth-per-cycle, GPC, of the PE-ALD SiO_2 film as a function of (a) DIPAS dose time, (b) DIPAS purge time, (c) O_2 plasma time, and (d) O_2 purge time.

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