



## Research paper

# Effect of annealing temperature on electrical and reliability characteristics of HfO<sub>2</sub>/porous low-*k* dielectric stacks



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## ABSTRACT

Atomic layer deposited thin HfO<sub>2</sub> film has been demonstrated to act as a pore-sealing layer and a Cu diffusion barrier layer used in porous low-*k* dielectrics. This study investigates the effect of annealing temperature on the electrical characteristics and reliability of the dielectric stacks with HfO<sub>2</sub> and porous low-*k* films. The experimental results reveal that annealing improved electrical performance and reliability, but increased the dielectric constant. However, the resulting dielectric constant of the annealed HfO<sub>2</sub>/porous low-*k* dielectric stacks following oxygen plasma treatment was still lower than that of the dielectric stacks without annealing, indicating that annealing improved the properties of HfO<sub>2</sub>/porous low-*k* dielectric stacks. Annealing at 400 °C improved electrical characteristics, reliability, and Cu barrier performance more than did annealing at 600 °C because at 600 °C annealing, the grain boundaries of the crystallized HfO<sub>2</sub> film provide a conduction path and cause the breakage of the porous low-*k* film. However, the HfO<sub>2</sub>/porous low-*k* dielectric stacks that were annealed at 600 °C exhibited greater resistance against damage by oxygen plasma.

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## 1. Introduction

Porous materials with a low dielectric constant (low-*k*) are used as inter-level dielectrics (ILDs) between Cu conductors to reduce the resistance-capacitance (RC) delay and power consumption, and to increase the signal-to-noise ratio in advanced integrated circuits [1–3]. However, the integration of such porous low-*k* dielectrics into back-end-of-line (BEOL) Cu interconnects must overcome increasing challenges, such as film delamination, moisture absorption, Cu diffusion, and plasma damage [4–6]. Issues of integration can seriously degrade electrical properties and reliability. To mitigate these issues when porous low-*k* dielectrics are used as ILDs, the top surface of the film must be sealed. Pore sealing methods involve either plasma treatment with inert gas or the deposition of a thin film as a pore-sealing layer [7–9]. Self-assembled molecules (SAM) or specific atomic layer depositions (ALD) are extensively used as pore sealing layers [9–11]. The ALD method is favored because it can provide conformal deposition. Therefore, the pores in the low-*k* dielectric at both the surfaces and the sidewalls in the trench or via can be effectively sealed.

To prevent possible Cu migration into a porous low-*k* dielectric, which shortens the dielectric breakdown time, a barrier metal (TiN or TaN) must be deposited onto the surface of the film during the integration of the

BEOL structure [12]. However, this barrier metal causes low-*k* dielectric degradation in a manner similar to Cu, and the relatively large resistance of barrier metals increases the resistance of the Cu conductor. These adverse effects become stronger as the dimension of Cu interconnects is scaled down. Accordingly, if an ALD-deposited pore-sealing layer can prevent the penetration of Cu into porous low-*k* dielectric, then the traditional barrier metal will no longer be required for Cu interconnects, further reducing RC delay.

Our previous work proposed a new scheme for improving the characteristics of a porous low-*k* dielectric by capping an HfO<sub>2</sub> film using the ALD method [13]. This HfO<sub>2</sub> film was demonstrated to function as not only a pore-sealing layer but also a Cu barrier layer and a protective layer against oxygen plasma for a porous low-*k* dielectric. ALD-deposited HfO<sub>2</sub> films reportedly contain carbon impurity or dangling bonds, the number of which can be reduced by thermal annealing [14, 15]. However, when the annealing temperature exceeds 550 °C, the HfO<sub>2</sub> film crystallizes, degrading its characteristics because the formed grain boundaries act as leakage and diffusion paths [16,17]. Therefore, this study investigates the effects of annealing temperature on the electrical characteristics and reliability of HfO<sub>2</sub>/porous low-*k* dielectric stacks.

## 2. Experiments

The porous low-*k* material is a SiCOH film, deposited on p-type (100) silicon substrates by plasma-enhanced chemical vapor

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deposition (PECVD). The porous low-*k* films were deposited from diethoxymethylsilane (DEMS) and alpha-terpinene (ATRP) as a matrix and a porogen precursor, respectively. A small amount of oxygen was also introduced as an oxidant. The deposition temperature, pressure, and power were 300 °C,  $1.0 \times 10^4$  Pa, and 600 W, respectively. After deposition, UV curing with 200–450 nm wavelength was performed for 300 s to remove the organic porogen to form porous low-*k* dielectric film with pore size and porosity of 1.4 nm and 12%, respectively, which were determined from the isotherm of ethanol adsorption and desorption using ellipsometric porosimetry (Semilab, Mode PS-1100). The thickness and the dielectric constant of the resulting porous low-*k* dielectric were about 100 nm and 2.56, respectively.

After the formation of the porous low-*k* film, the HfO<sub>2</sub> film using TEMAH (Hf[NCH<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>4</sub>) and ozone (O<sub>3</sub>) as a precursor and an oxidant, respectively, was deposited on the top surface using an ALD. The deposition cycle was 10 cycles with the resulting thickness of approximately 1.0 nm. One ALD cycle consisted of an oxidant pulse, a N<sub>2</sub> purge, a TEMAH pulse, and a N<sub>2</sub> purge. The oxidant and TEMAH pulse lengths of were 0.015 and 0.25 s, respectively. The N<sub>2</sub> purge time was 5 s. N<sub>2</sub> was used as carrier and purge gas. The O<sub>3</sub> delivery system generated 132 g/m<sup>3</sup> O<sub>3</sub> in N<sub>2</sub>-diluted environments. The HfO<sub>2</sub> film was deposited at a temperature of 200 °C. After capping an HfO<sub>2</sub> film, the fabricated dielectric stacks were annealed in a N<sub>2</sub> environment at 400 °C and 600 °C for 30 s using rapid temperature annealing tool. Then, a metal electrode of aluminum (Al) or Cu with area of 900 μm<sup>2</sup> and thickness of ~10 nm was deposited on the top surface of the dielectric stack through shadow mask using thermal evaporation method. The fabricated metal-insulator-silicon (MIS) capacitors were used to measure the capacitance–voltage (C-V), current–voltage (I-V), and time-dependent-dielectric-breakdown (TDDB) characteristics. The measurements were performed at room temperature (25 °C). A semiconductor parameter analyzer (HP4280A) was used for the C-V measurement operated at the frequency of 1 MHz. The I-V and TDDB measurements were performed using by electrometer (Keithley, 6517A).

### 3. Results and discussion

Annealing of the HfO<sub>2</sub>/porous low-*k* dielectric stack changes both the HfO<sub>2</sub> and the porous low-*k* films. Table 1 presents changes in the properties of HfO<sub>2</sub>, porous low-*k* films, and the dielectric stack after annealing at 400 °C and 600 °C. Annealing reduced the thicknesses of all films, including the stack. The reduction of the thickness of the porous low-*k* films and the HfO<sub>2</sub>/porous low-*k* dielectric stacks increases with annealing temperature. For the HfO<sub>2</sub> films, the thickness reduction decreases upon annealing at 600 °C. Upon annealing an HfO<sub>2</sub> film that was deposited on Si substrate, the thickness of the bulk HfO<sub>2</sub> film was reduced and interfacial layer growth at the HfO<sub>2</sub>/Si interface was observed. The thinning of the bulk HfO<sub>2</sub> film is weakly related to the annealing temperature, but the interfacial layer growth becomes stronger as the annealing temperature is increased. These two competing effects cause thinning to be less as the annealing temperature increases. However, in the HfO<sub>2</sub>/porous low-*k* dielectric stack, an interfacial layer cannot form because the HfO<sub>2</sub> film is deposited on the porous low-*k* film. Therefore, no interfacial layer grows upon annealing, and only thinning of the HfO<sub>2</sub> and the porous low-*k* films is observed. The structures of

all films were analyzed herein by XRD, which revealed that all of the as-deposited films were amorphous. All films still remained amorphous structure upon annealing at 400 °C. However, as the annealing temperature was increased to 600 °C, the HfO<sub>2</sub> film became crystallized, whereas the porous low-*k* film still remained amorphous. The detected peak positions in XRD spectra of the HfO<sub>2</sub> film and the HfO<sub>2</sub>/porous low-*k* dielectric stack annealed at 600 °C were identical, indicating that the crystallization phase of the HfO<sub>2</sub> films on the Si substrate was similar to that on the porous low-*k* film. The chemical composition of the films was determined by AES analysis, which revealed that the amount of carbon was reduced by annealing and the reduction increased with the annealing temperature. The amount of carbon in the HfO<sub>2</sub> films declined to 4.49% and 2.68% from 7.24% upon annealing at 400 °C and 600 °C, respectively. For the porous low-*k* films, the corresponding reductions were 1.36% and 2.86%, indicating that the porous low-*k* films undergo a smaller loss of carbon than the HfO<sub>2</sub> films upon annealing, because the carbon atoms in the HfO<sub>2</sub> films are not strongly bonded in the film, and so can be easily removed by annealing at high temperatures. The porous low-*k* films are SiCOH, in which most carbon atoms are associated with Si-CH<sub>3</sub> or Si-CH<sub>2</sub>-Si bonds, which are not easily broken by annealing. The loss of carbon in the porous low-*k* films was suspected to involve the removal of carbon dangling bonds from porogen residues [18].

Fig. 1 presents the Hf concentration within the porous low-*k* films determined from AES depth profile analysis. The Hf concentration within the dense low-*k* film is provided as a reference. Our earlier study reported that the Hf precursor during HfO<sub>2</sub> film deposition in an ALD chamber can seal the pores in the surface of a porous low-*k* film [13]. As HfO<sub>2</sub> film is deposited onto the dense low-*k* film, fewer Hf atoms diffuse into the low-*k* film. Annealing did not change the Hf concentration within the dense low-*k* film (not shown), but slightly changed the Hf concentration in the porous low-*k* film. As displayed in Fig. 1, annealing at 400 °C or 600 °C slightly increased the Hf concentration at the surface of the porous low-*k* film. Upon annealing at 400 °C, the diffusion of Hf atoms into the porous low-*k* film was not detected as the Hf concentration profile in the porous low-*k* film was similar to that in the unannealed sample. However, upon annealing at a high temperature of 600 °C, Hf atoms diffused more deeply into the porous low-*k* film, indicating that annealing at high temperatures above 600 °C drives more Hf atoms to diffuse into the porous low-*k* film.

The C-V characteristics of the MIS capacitors with HfO<sub>2</sub>/porous low-*k* dielectric stacks that underwent annealing at various temperatures were measured. Fig. 2 plots the obtained dielectric constant of the HfO<sub>2</sub>/porous low-*k* dielectric stacks that were annealed at 400 °C or 600 °C. The measured dielectric constant of the as-deposited HfO<sub>2</sub>/porous low-*k* dielectric stack is 2.85. Annealing increased the dielectric constants of the stacked samples. As described above, annealing of the HfO<sub>2</sub>/porous low-*k* dielectric stack caused the upper HfO<sub>2</sub> film to become more stoichiometric and to have fewer defects, and the Hf atoms to diffuse into the porous low-*k* film. An amorphous and stoichiometric HfO<sub>2</sub> film with few defects reportedly has a higher dielectric constant than that of a non-stoichiometric film with more defects [19]. Furthermore, the diffusion of Hf atoms into the porous low-*k* film and their presence in the pores increased the dielectric constant of the porous low-*k* film. These two mechanisms are responsible for the increase in the dielectric constant of the HfO<sub>2</sub>/porous low-*k* dielectric

**Table 1**  
Changes in physical properties of HfO<sub>2</sub>, porous low-*k*, and HfO<sub>2</sub>/porous low-*k* dielectric stack films after annealing at 400 °C and 600 °C.

Sample	Thickness reduction (%)		Film structure		Carbon atomic reduction (%)	
	400 °C	600 °C	400 °C	600 °C	400 °C	600 °C
Porous low- <i>k</i>	0.71%	5.77%	Amorphous	Amorphous	1.36%	2.86%
HfO <sub>2</sub>	6.92%	4.85%	Amorphous	Crystallized	2.75%	4.56%
HfO <sub>2</sub> /porous low- <i>k</i> stacks	5.50%	8.47%	Amorphous	Crystallized	2.68% <sup>a</sup>	4.68% <sup>a</sup>

<sup>a</sup> Detected HfO<sub>2</sub> film.

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