Low-k SiC$_x$N$_y$ Etch-Stop/Diffusion Barrier Films for Back-End Interconnect Applications


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Abstract

Lower k and low-leakage silicon carbide nitride (SiC$_x$N$_y$) films were fabricated using single precursor by using radio-frequency (RF) plasma-enhanced chemical vapor deposition (PECVD). We explored precursors with (1) cyclic-carbon-containing structures, (2) higher C/Si ratio, (3) multiple vinyl groups, as well as (4) the incorporation of porogen for developing low-k SiC$_x$N$_y$ films as etch-stop/diffusion barrier (ES/DB) layer for copper interconnects in this study. SiC$_x$N$_y$ films with k values between 3.0 and 3.5 were fabricated at $T \leq 200$ °C, and k ~ 4.0-4.5 at 300-400 °C. Precursors with vinyl groups yielded SiC$_x$N$_y$ films with low leakage, excellent optical transmittance and high mechanical strength due to the formation of cross-linked Si-(CH$_2$)$_x$-Si linkages.

1. Introduction

In order to alleviate RC delay issue in the backend interconnection, there is a continued drive in reducing the effective dielectric constant ($k_{eff}$). This has necessitated aggressive $k$- and thickness scaling of interlayer dielectrics (ILD) and dielectric diffusion barrier/etch-stop layer (DB/ES). On the ILD, air-gap was announced for Intel’s 14 nm node, following several generations of carbon-doped oxides or SiCOH scaled down from 3.4 to ~2.5 [1]. PECVD Si$_x$N$_y$ (k ~ 6.5) was first used as DB/ES layer due to its excellent diffusion barrier property and etch selectivity in the via-first dual damascene scheme. Later, silicon carbide nitride (SiC$_x$N$_y$) films become the primary approach to replace silicon nitride because oxygen-doped SiN films show poor diffusion barrier effectiveness. Silicon carbide nitride films are typically prepared by performing PECVD of multi-precursors such as silane/ammonia (or nitrogen)/methane [2, 3] and trimethylsilane/ammonia [4]. In the evolution approach, incorporation of more carbon and/or even small portion of porosity are undertaken to further reduce the k-value of SiC$_x$N$_y$ films. Recently, single source precursors such as hexamethyldisilazane [5] and BASICN$_{TM}$ [6] have been used for preparing dense low-k SiC$_x$N$_y$ films (k ~ 5.0-5.5) by using PECVD because these films display low defects (i.e., low leakage current) and higher etch selectivity due to high C/Si ratio [7]. Yet, its etch selectivity and diffusion barrier effectiveness may become an issue if k is drastically reduced down to ~4.0, in addition to possible degradation of the mechanical strength. To overcome the barrier effectiveness, a sandwiched structure may be the best option. A conservative approach was proposed by Nguyen et al. [8], who prepared a dielectric barrier bilayer of dense SiN$_x$/porous SiC$_x$N$_y$, exhibiting 12% porosity, by performing plasma deposition of dimethylsilacyclopetane and NH$_3$ and then using UV to cure the samples. Opportunely, recent introduction of selective metal-cappping materials such as CoW(P) [9] to passivate copper lines may relax the requirements on ES/DB layer and allow the k-value of the etch-stop layer, with or without using sandwich structure, to be scaled aggressively to advance the $k_{eff}$ scaling, for example, by incorporating porosity [10].

This paper reports our recent development of PECVD lower k SiC$_x$N$_y$ films using single precursors with (1) cyclic-carbon-containing structures, (2) higher C/Si ratio, or (3) multiple vinyl groups, as well as (4) the incorporation of porogen. The dielectric constant, film density, elastic modulus, optical properties such as refractive index and optical transmission, and leakage behavior of low-k SiC$_x$N$_y$ films were characterized and discussed. Preliminary work on UV-assisted thermal annealing of as-deposited SiC$_x$N$_y$ films will be also addressed.

2. Experimental

RF (13.56 MHz) PECVD was used to deposit SiC$_x$N$_y$ or hybrid SiC$_x$N$_y$/porogen films onto silicon wafers using a single precursor (VSZ, DVTMDS, MTSCP with various C/Si and N/Si ratios, and vinyl groups summarized in Table I) as the matrix precursor in the presence or absence of epoxycyclohexane (ECH) as a porogen, and Ar as carrier gas. The deposition pressure and RF power were maintained at 90 mTorr and 50 W (power density = 0.15 W/cm$^2$) without bias, unless stated otherwise. The deposition temperatures were varied from 100 °C to 400 °C. Moreover, the effect of porogen loading in the gas feed (total flow rate, 20 sccm) on the porosity and pore morphology of SiC$_x$N$_y$ films was examined. The burn-out step was performed at 400 °C for 3 h in an Ar atmosphere.

Chemical bonding in the SiC$_x$N$_y$ or hybrid SiC$_x$N$_y$/porogen films was examined using FTIR spectroscopy in transmission mode. Pore morphology was characterized using a BL23A GISAXS instrument at the National Synchrotron Radiation Research Center, Taiwan. All 2D GISAXS patterns were recorded using an area detector at a fixed incident angle of 0.2° of the 10-keV X-ray beam (diameter, 0.5 mm). Pore size was extracted from the GISAXS data by using the Guinier approximation. The porosity of the porous SiC$_x$N$_y$ films was deduced from the film density that was determined using an XRR instrument (Bruker D8 Discover) equipped with a Cu K$_\alpha$ source ($\lambda = 0.154$ nm). The XRR data were analyzed using LEPTOS simulation software. The dielectric constant (k) of the SiC$_x$N$_y$ films was calculated from the capacitance-voltage (C-V) measurement obtained using the metal-insulator-semiconductor (MIS) using multiple dot sizes. Refractive index and film thickness was measured using an n&k Analyzer 1280 (n&k Technology, Inc.). Nanoindentation tests were performed using a nanoindenter (MTS Nano Indenter XP System).
3. Results and Discussion

3.1 SiC₅N₅ films prepared by VSZ precursor with and without ECH porogen [7, 11]

Low-k SiC₅N₅ films with k values of 3.6–4.6 were developed and prepared by RF PECVD at 25 to 400 °C, using 1,3,5-trimethyl-1,3,5-trivinyl-cycloctasilazane (VSZ) as a single precursor (with 3 vinyl groups) and Ar as the carrier gas. At lower deposition temperatures (≤ 200 °C), the vinyl groups of the VSZ are broken and form cross-linked Si-(CH₂)₂-Si linkages, in the plasma polymerization process. However, most of the cyclic VSZ structures are preserved to create free volume (4.9 nm pore size) in the SiC₅N₅ films, which results in a lower density (1.60–1.76 g/cm³) and a lower dielectric constant (k~3.6–3.9), with a fairly good elastic modulus of 22-25 GPa. When the deposition temperature is raised to 2300 °C, the cyclic N-Si-N linkages are broken up and reform into a dense Si-N structure with the disappearance of CH₃ bonds, reducing both pore size (to 3.5 nm) and pore correlation. This results in a higher density (1.8–2.0 g/cm³) and a higher dielectric constant (4.2–4.6), with an excellent elastic modulus of 35-65.2 GPa.

When ECH porogen was added, the porosity of SiC₅N₅ films deposited at 100 °C increased from 2.4% to 21.8% when ECH loading was increased from 0 to 30%, above which the porosity remained nearly constant because of high film shrinkage (> 15.9%). The pore size decreased slightly from 4.1 to 3.7 nm when ECH loading increased to 30%, above which the pores became larger. If deposition temperature was raised to 200 °C at 20% ECH loading, porogen incorporation dropped, leading to increased film density. Optimized processing parameters facilitated the fabrication of low-k porous SiC₅N₅ films exhibiting 21.8% porosity, 3.7-nm pores, a k value of 3.18, and an elastic modulus of 7.7 GPa. [11]

3.2 SiC₅N₅ films prepared by using DVTMDS and MTSCP precursors

Next, we explore precursors with high carbon content, i.e., 1, 3-divinyl-1,1,3,3-tetramethyldisilazane (DVTMDS; C/Si=4; linear chain with 2 vinyl groups) and MTSCP (C/Si=7; cyclic structure). The film densities and refractive indices of PECVD SiC₅N₅ films are summarized in Table II. In general, precursors with vinyl groups such as VSZ and DVTMDS yielded SiC₅N₅ films with higher film density presumably due to its enhanced degree of crosslinking, compared to those films deposited by MTSCP precursor without vinyl side group. The dielectric constant at optical frequency, i.e., n² (n = refractive index), shows SiC₅N₅ films prepared by MTSCP possess much lower dielectric constant at deposition temperature < 200 °C, but about the same order at 400 °C compared to those by VSZ and DVTMDS precursors.

The dielectric constant of SiC₅N₅ films prepared by using DVTMDS precursor show dielectric constant, k~3.2–4.5 (see Fig. 1) with density (1.26–2.04 g/cm³) and elastic modulus of 4.1-76.9 GPa (Fig. 2) for deposition temperature from 25 to 400 °C. In comparison, for MTSCP precursor, its SiC₅N₅ films have dielectric constant, k~3.0–4.5 with density (1.19-1.96 g/cm³) and elastic modulus of 4.0-138.0 GPa (Fig. 2). A lower k SiC₅N₅ films with k ~3.0 is possible using MTSCP precursor of high C/Si ratio.

3.3 Leakage current and mechanisms

The leakage current density of SiC₅N₅ films using VSZ precursor was reduced from 1.5x10⁻⁶ to 4.0x10⁻⁸ A/cm² at 1 MV/cm, upon increasing the deposition temperature from 25 °C to 400 °C as shown in Fig. 3. The conduction mechanism in the low-k SiC₅N₅ films was dominated by Schottky emission in the low field (< 1.5 MV/cm), but changed to Frenkel-Poole emission in the high field (> 1.5 MV/cm), only for SiC₅N₅ film deposited at 400 °C [11], Fig. 4 shows the low leakage current of SiC₅N₅ films deposited at 350 °C using DVTMDS precursor under various pressures. Schottky emission was the main conduction mechanism for electric field < 3 MV/cm.

3.4 Optical transmittance

The optical property of SiC₅N₅ films is of interest to patterning when they are used as an etch hard mask or ES/DB layer. SiC₅N₅ films using VSZ, DVTMDS precursors and deposited at 300 °C possess higher transmittance than that using MTSP, presumably due to the existence of the cross-linked Si-(CH₂)₂-Si linkages.

4. Summary

SiC₅N₅ films with k values between 3.0 and 3.5 were fabricated at T ≥ 200 °C, and k=4.0–4.5 at 300–400 °C. The cyclic structure in VSZ precursor with or without porogen, and the high C/Si ratio in MTSCP precursor enable the reduction of dielectric constant, k ≤ 3.5. Precursors (VSZ and DVTMDS) with vinyl groups yielded SiC₅N₅ films with low leakage current, excellent optical transmittance, and high mechanical strength due to the formation of cross-linked Si-(CH₂)₂-Si linkages. UV treatment at elevated temperature of as-deposited SiC₅N₅ films is being studied if dielectric constant and mechanical properties can be further improved.

Acknowledgement

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References
Table I. Compositions of various precursors

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<tr>
<td>MTSCP</td>
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<tr>
<td>DVTMDS</td>
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Table II. Film densities and refractive indices of SiC_{x}N_{y} films deposited at various substrate temperatures

<table>
<thead>
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<th>Substrate temperature (°C)</th>
<th>Density (g/cm³)</th>
<th>Refractive index</th>
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<tr>
<td>400</td>
<td>1.96 2.04 2.0</td>
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Fig. 1 Dielectric constants of SiC_{x}N_{y} films deposited at various temperatures

Fig. 2 Elastic modulus of SiC_{x}N_{y} films deposited at various temperatures

Fig. 3 Leakage current density (A/cm²) vs. Electric field (MV/cm) for SiC_{x}N_{y} films deposited at various temperatures using VSZ precursor

Fig. 4 Leakage current density (A/cm²) vs. Electric field (MV/cm) for SiC_{x}N_{y} films deposited at various pressure at 350 °C using DVTMDS precursor

Fig. 5 Optical transmission spectra of SiC_{x}N_{y} films deposited at 300 °C