Low-k SiC_xN_y Etch-Stop/Diffusion Barrier Films for Back-End Interconnect Applications

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Abstract

Lower k and low-leakage silicon carbonitride (SiC_xN_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_xN_y films as etch-stop/diffusion barrier (ES/DB) layer for copper interconnects in this study. SiC_xN_y films with k values between 3.0 and 3.5 were fabricated at T≦ 200 ºC, and k~4.0-4.5 at 300-400 ºC. Precursors with vinyl groups yielded SiC_xN_y films with low leakage, excellent optical transmittance and high mechanical strength due to the formation of cross-linked Si-$(CH_2)_n$-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_3N_4 (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 carbonitride (SiC_xN_y) films become the primary approach to replace silicon nitride because oxygen-doped SiN films show poor diffusion barrier effectiveness. Silicon carbonitride 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 evolutional approach, incorporation of more carbon and/or even small portion of porosity are undertaken to further reduce the k-value of SiC_xN_y films. Recently, single source precursors such as hexamethyldisilazane [5] and BASICN™ [6] have been used for preparing dense low-k SiC_xN_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_y/porous SiC_xN_y, exhibiting 12% porosity, by performing plasma deposition of dimethylsilacyclopentane and NH_3 and then using UV to cure the samples. Opportunely, recent introduction of selective metal-capping 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_xN_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_xN_y films were characterized and discussed. Preliminary work on UV-assisted thermal annealing of as-deposited SiC_xN_y films will be also addressed.

2. Experimental

RF (13.56 MHz) PECVD was used to deposit SiC_xN_y or hybrid SiC_xN_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^3) without bias, unless stated otherwise. The deposition temperatures were varied from 100 ºC 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 SiCN films was examined. The burn-out step was performed at 400 °C for 3 h in an Ar atmosphere.

Chemical bonding in the SiC_xN_y or hybrid SiC_xN_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_xN_y films was deduced from the film density that was determined using an XRR instrument (Bruker D8 Discover) equipped with a Cu K_α source (λ = 0.154 nm). The XRR data were analyzed using LEPTOS simulation software. The dielectric constant (k) of the SiC_xN_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 nanoindentor (MTS Nano Indenter XP System) equipped with a Berkovich tip, in continuous mode, to obtain the reduced modulus (E_r). The transmittances and absorption in UV and visible range of SiC_xN_y thin films were measured by Hitachi U-3900H spectrophotometer.

3. Results and Discussion

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

Low-k SiC_xN_y films with k values of 3.6–4.6 were developed and prepared by RF PECVD at 25 to 400 ºC, using 1,3,5-trimethyl-1,3,5- trivinyl-cyclotrisilazane (VSZ) as a single precursor (with 3 vinyl groups) and Ar as the carrier gas. At lower deposition temperatures (≤ 200 ºC), the vinyl groups of the VSZ are broken and form cross-linked Si-$(CH_2)_n$-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 SiC_xN_y films, which results in a lower density (1.60-1.76 g/cm^3) 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 ≥300 ºC, the cyclic N-Si-N linkages are broken up and reform into a dense Si-N structure with the disappearance of CH_x bonds, reducing both pore size (to 3.5 nm) and pore correlation. This results in a higher density (1.8-2.0 g/cm^3) 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 SiC_xN_y 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 ºC at 20% ECH loading, porogen incorporation dropped, leading to increased film density. Optimized processing parameters facilitated the fabrication of low-k porous SiC_xN_y 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 SiC_xN_y 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 SiC_xN_y films are summarized in Table II. In general, precursors with vinyl groups such as VSZ and DVTMDS yielded SiC_xN_y 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.* n^2 (n = refractive index), shows SiC_xN_y films prepared by MTSCP possess much lower dielectric constant at deposition temperature < 200 ºC, but about the same order at 400 ºC compared to those by VSZ and DVTMDS precursors.

The dielectric constant of SiC_xN_y films prepared by using DVTMDS precursor show dielectric constant, k~3.2-4.5 (see Fig. 1) with density (1.26-2.04 g/cm^3) and elastic modulus of 4.1-76.9 GPa (Fig. 2) for deposition temperature from 25 to 400 ºC. In comparison, for MTSCP precursor, its SiC_xN_y films has dielectric constant, k~3.0-4.5 with density (1.19-1.96 g/cm^3) and elastic modulus of 4.0-138.0 GPa (Fig. 2). A lower k SiC_xN_y 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 SiC_xN_y films using VSZ precursor was reduced from 1.5×10^{-6} to 4.0×10^{-8} A/cm^2 at 1 MV/cm, upon increasing the deposition temperature from 25 ºC to 400 ºC as shown in Fig. 3. The conduction mechanism in the low-k SiC_xN_y 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 SiC_xN_y film deposited at 400 ºC [11]. Fig. 4 shows the low leakage current of SiC_xN_y films deposited at 350 ºC using DVCTMDS 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 SiC_xN_y films is of interest to patterning when they are used as an etch hard mask or ES/DB layer. SiC_xN_y films using VSZ, DVTMDS precursors and deposited at 300 ºC possess higher transmittance than that using MTSP, presumably due to the existence of the cross-linked Si-$(CH_2)_n$-Si linkages.

4. Summary

SiC_xN_y films with k values between 3.0 and 3.5 were fabricated at T≦ 200 ºC, and k~4.0-4.5 at 300-400 ºC. 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 SiC_xN_y films with low leakage current, excellent optical transmittance, and high mechanical strength due to the formation of cross-linked Si-$(CH_2)_n$-Si linkages. UV treatment at elevated temperature of as-deposited SiC_xN_y films is being studied if dielectric constant and mechanical properties can be further improved.

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Table I. Compositions of various precursors

Precursors	Composition ratio relative to Si		
	Si	C	N
VSZ	1	3	1
MTSCP	1	7	1
DVTMDS	1	4	0.5

Table II. Film densities and refractive indices of SiC_xN_y films deposited at various substrate temperatures

Substrate temperature (℃)	Density (g/cm^3)			Refractive index		
	MTSCP	DVTMDS	VSZ	MTSCP	DVTMDS	VSZ
25	1.19	1.26	1.6	1.44	1.51	1.52
100	1.33	1.28	1.67	1.48	1.51	1.53
200	1.48	1.43	1.76	1.55	1.54	1.55
300	1.70	1.67	1.83	1.79	1.61	1.64
400	1.96	2.04	2.0	1.88	1.90	1.81

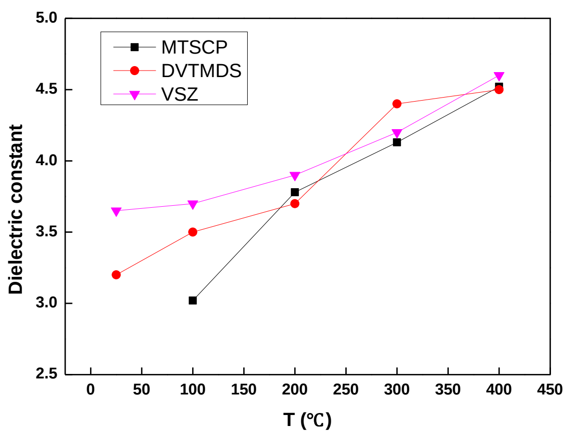

Fig. 1 Dielectric constants of SiC_xN_y films deposited at various temperatures

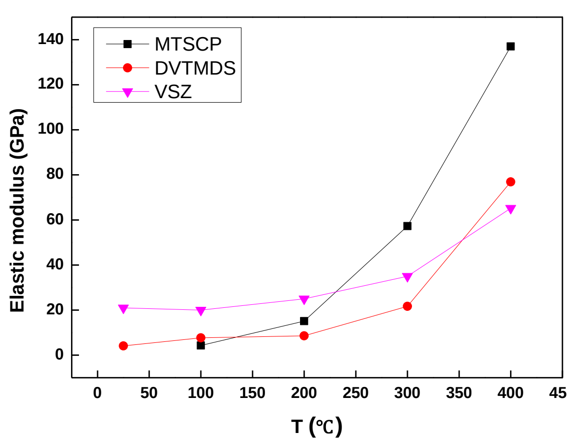

Fig. 2 Elastic modulus of SiC_xN_y films deposited at various temperatures

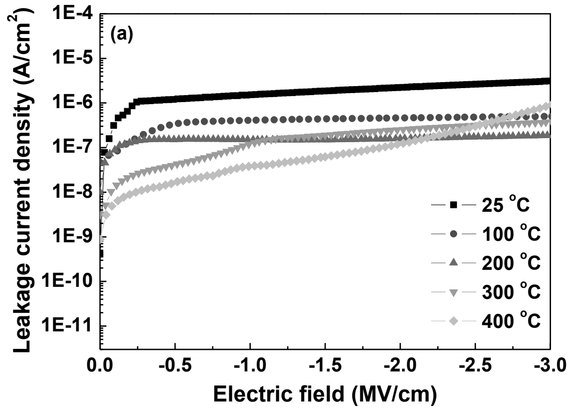

Fig. 3 Leakage current of SiC_xN_y films deposited at various temperatures using VSZ precursor

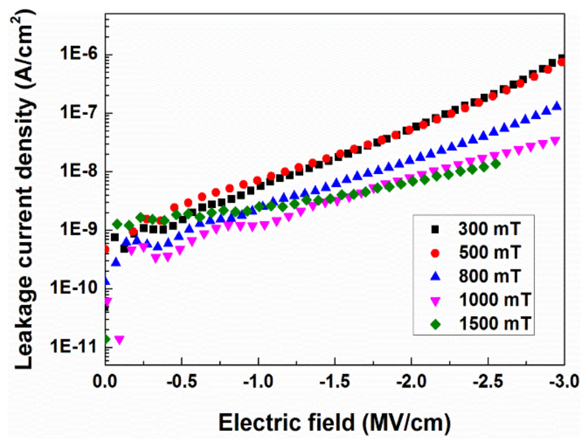

Fig. 4 Leakage current of SiC_xN_y films deposited at various pressure at 350 °C using DVCTMDS precursor

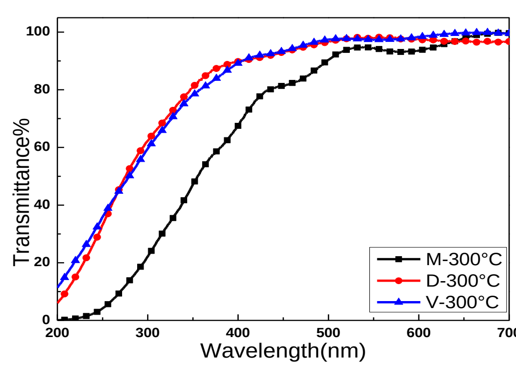

Fig. 5 Optical transmission spectra of SiC_xN_y films deposited at 300 °C