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Pore morphology of low-k SiC_xN_y films prepared with a cyclic silazane precursor using plasma-enhanced chemical vapor deposition

Hung-En Tu [a], Chun-Jen Su [b], U-Ser Jeng [b], Jihperng Leu [a,*]

[a] Department of Materials Science and Engineering, National Chiao Tung University, 1001 University Road, Hsinchu 30010, Taiwan
[b] National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan

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ABSTRACT

Low-k SiC_xN_y films were prepared using radio-frequency plasma-enhanced chemical vapor deposition (PECVD), with only 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane (VSZ) as the precursor; VSZ has cyclic Si–N–Si linkages and three pendent vinyl groups. At lower PECVD temperatures, SiC_xN_y films possess relatively low film densities, indicating the existence of a loose structure or voids within the cross-linked matrix structure. The pore morphology of SiC_xN_y films deposited at distinct temperatures were examined using grazing-incidence small-angle X-ray scattering, while the chemical bondings and structural information were analyzed using Fourier-transform infrared spectroscopy. At 100 °C, SiC_xN_y films without porogen displaying 4.9 nm pores and a mean pore spacing of 30.1 nm generated low-density films because Si-$(CH_2)_n$-Si and/or Si-$(CH_2)_n$-CH_3 could be incorporated free volume into the N–Si–C cross-linked structure under plasma deposition. At 300 °C, the N–Si–C cross-linked structure and the some organic phase were disrupted and transformed into a denser structure, reducing pore size (3.5 nm) and losing pore correlation. Thus, low deposition temperatures facilitate the formation of large pores and the ordering of the pores. Post annealing converted the 100 and 300 °C as-deposited SiC_xN_y films into loose and dense structures, respectively, and maintained slightly reduced pore size and pore correlation in the annealed films.

1. Introduction

As integrated-circuit dimensions are continually scaled down, the increase in propagation (RC) delay, crosstalk noise, and power dissipation in the interconnection become the limiting factors in the design of ultra-large-scale integrated devices [1]. To reduce the effective capacitance (k_{eff}) in the copper backend interconnection, low-k etch-stop/dielectric barrier materials such as silicon carbonitride (SiC_xN_y) ($k = 4.5–5.5$) [2] have been introduced in 45 nm nodes and beyond, following the implementation of low-k inter-layer dielectric (ILD) materials such as carbon-doped oxide and ultra-low-k dielectrics [3] and the scaling of their thickness [4,5]. Silicon carbonitride films have been typically prepared using plasma-enhanced chemical vapor deposition (PECVD) of multi-precursors such as $SiH_4 + NH_3$ (or N_2) + CH_4 [6,7] and $SiH(CH_3)_3 + NH_3$ [8]. Recently, single source precursors such as hexamethyldisilazane (HMDS) [9,10], and BASICN™ [11] have been examined for use in low-k SiC_xN_y applications, because compared with multi-precursors, single source precursors retain higher C content to achieve lower polarizability and improved etch selectivity. However, their dielectric constant values (4.5 to 3.8) are still too high for future integrations even their thickness is scaled down. To further reduce the dielectric constant of silicon carbonitride materials, the primary approach is to reduce the film density, in addition to the continued increase of C/Si ratio. A similar approach has been demonstrated for low-k SiC_xO_y inter-layer dielectric films by using single precursors with volumic cyclic structures, such as a 6, 8, or 10-membered Si–O ring [12,13] to introduce intrinsic and induced porosity for lowering the film's density.

This prompts us to explore a cyclic N–Si–N silazane precursor for a lower k SiC_xN_y films. In specific, 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane (VSZ) with 3 vinyl side-groups was used as a single precursor using radio-frequency (RF) PECVD technique at a low power density (0.15 W/cm^3). The deposition temperatures ranging from 25 to 400 °C yield low-k SiC_xN_y films with k from 3.6 to 4.6 [14]. Their film densities were 1.6–2.0 g/cm^3, which are considerably lower than the density of Si_3N_4 films ($k = 7.5$; $\rho = 3.1$ g/cm^3) [15] or SiC_xN_y (BASICN™ 400) films ($k = 4.3$; $\rho = 1.86$ g/cm^3) [11]. The low density of these SiC_xN_y films using VSZ precursor at low deposition temperatures indicates the existence of a loose structure or voids within the cross-linked matrix structure. Such SiC_xN_y films are of great interest as etch-stop/diffusion barrier in the copper interconnects because there is no need of adding a sacrificial porogen and post-treatment for removing the porogen. Yet, the origin of the low density of these SiC_xN_y films and the information about pore size and pore size distribution are still vague.

Although ellipsometric porosimetry [16] and positron annihilation spectroscop [17] have been successfully used in pore size characterization, a non-destructive, grazing-incidence small-angle X-ray scattering (GISAXS) technique can offer complete information of the pore shape,

* Corresponding author.
E-mail address: jimleu@mail.nctu.edu.tw (J. Leu).

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pore sizes, and pore size distribution, and any periodic pattern [18,19]. Thus, in this study, the pore morphology was examined using GISAXS and the chemical structures of the 100 and 300 °C as-deposited SiC_xN_y films were examined using Fourier-transform infrared (FTIR) spectroscopy. Moreover, the change in pore morphology induced by annealing performed at 400 °C for 3 h was investigated and discussed.

2. Experimental

PECVD was used to deposit SiC_xN_y films onto a silicon wafer by using a liquid monomer, VSZ (Gelest, Inc. 95%), as the matrix precursor. The deposition was performed in an RF (13.56 MHz) parallel-plate PECVD system. VSZ was vaporized at 60 °C to prevent condensation in the pipe and was then carried into the reactor by an Ar carrier gas. The deposition pressure and RF power were maintained at 12 Pa (90 mTorr) and 50 W (power density = 0.15 W/cm^3), respectively, without bias. The deposition temperatures were varied from 100 to 300 °C. Subsequently, the annealing step was performed at 400 °C for 3 h under an Ar atmosphere to generate the as-deposited SiC_xN_y films.

The chemical bondings of the SiC_xN_y films were examined using FTIR spectroscopy (MAGNA-IR Technology Protege 460) at a normal incident angle under the transmission mode. The FTIR spectra were collected using a total of 32 scans in the 500–4000 cm^{-1} range, at a resolution of 4 cm^{-1}.

Pore morphology was characterized using the GISAXS system at the BL23A beam-line of the National Synchrotron Radiation Research Center, Taiwan. All 2D GISAXS patterns were recorded using a Pilatus 1 M-F area detector, with an incident angle of 0.2° of the 10 keV X-ray beam (0.5 mm diameter); SAXS data were analyzed using the Guinier approximation to determine the size of the pores [20].

The densities of the porous SiC_xN_y films were calculated using an X-ray reflectivity (XRR) instrument (Bruker D8 Discover) equipped with a Cu K_α source ($\lambda = 0.154$ nm). The scanning region ranged from 0° to 2°. The XRR data were analyzed using LEPTOS simulation software to fit the density of the SiC_xN_y film.

3. Results and discussion

In order to understand the growth mechanism of the SiC_xN_y films prepared by PECVD using VSZ precursor, the deposition rate of SiC_xN_y films as a function of deposition temperatures was first examined and illustrated in Fig. 1. The deposition rate of SiC_xN_y films increased with increasing deposition temperature up to 200 °C, after which the deposition rate slightly decreased. It exhibited two types of growth mechanism; namely, surface-reaction-controlled growth between 25 and 200 °C, while mass-transfer-controlled growth between 200 and 400 °C.

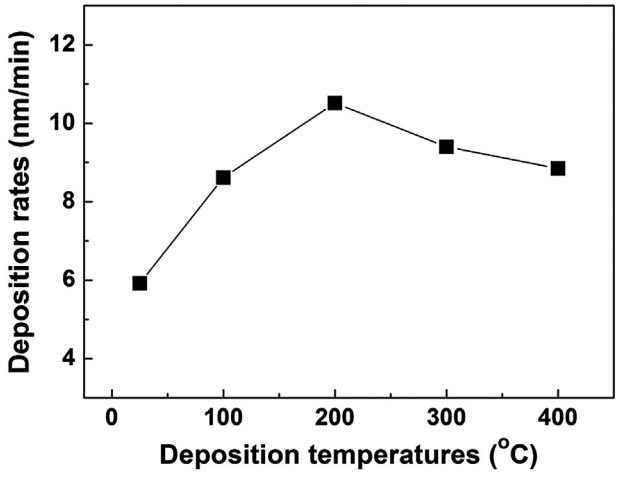

Fig. 1. Deposition rate of the SiC_xN_y films as a function of deposition temperatures.

GISAXS was used to examine the pore morphology of low-k SiC_xN_y films as-deposited at 100 and 300 °C and to study any additional change in morphology after annealing the films at 400 °C for 3 h. Fig. 2 presents the 2D GISAXS patterns of the low-k SiC_xN_y films as-deposited at 100 and 300 °C and after annealing at 400 °C for 3 h. The scattering images of the SiC_xN_y films as-deposited at 100 °C and after annealing at 400 °C (Fig. 2a and b) display two notable vertical streaks in the lateral direction, revealing a highly ordered structure possessing a mean spacing, as detailed in the following paragraph. By contrast, no ordered peaks were observed when examining films deposited at 300 °C and then annealed at 400 °C (Fig. 2c and d). The vertical streak in the GISAXS pattern indicates a spatially ordered arrangement in which the distance between pores is correlated in the horizontal direction [21,22], but not in the vertical direction, in films deposited at a low temperature (100 °C); this spatial ordering was absent in films deposited at higher temperatures such as 300 °C. Moreover, no noticeable change was detected in the scattering patterns of as-deposited films (Fig. 2a and c) and post-annealed films (Fig. 2b and d).

Next, the in-plane and out-of-plane intensities of the scattering patterns (Fig. 2) were extracted, and their corresponding GISAXS scattering profiles relative to scattering wavevector (q) are presented in Figs. 3 and 4. At the low-q regions of the in-plane scattering profiles of SiC_xN_y films deposited at 100 °C (Fig. 3a), the intensity peak revealed a spatial arrangement of pores displaying a specific correlation distance. The maximal intensities of SiC_xN_y films as-deposited at 100 °C and post-annealed appeared at q_p values of 0.2085 and 0.2128 nm^{-1}, respectively. Using the formula $L = 2\pi/q_p$ [22], the dominant mean distances between pores were estimated to be 30.1 and 29.5 nm for as-deposited and post-annealed films, respectively, which resulted from the occurrence of a marginally short-range ordering, parallel to the sample surface. The result also shows that an ordered and rigid pore structure of the film can be maintained at the high post-annealing temperature of 400 °C for 3 h.

In the case of the SiC_xN_y films deposited at 300 °C and post-annealed at 400 °C, no maximal intensity peak was detected in the profiles (Fig. 4a), suggesting that the pores in these films were randomly distributed.

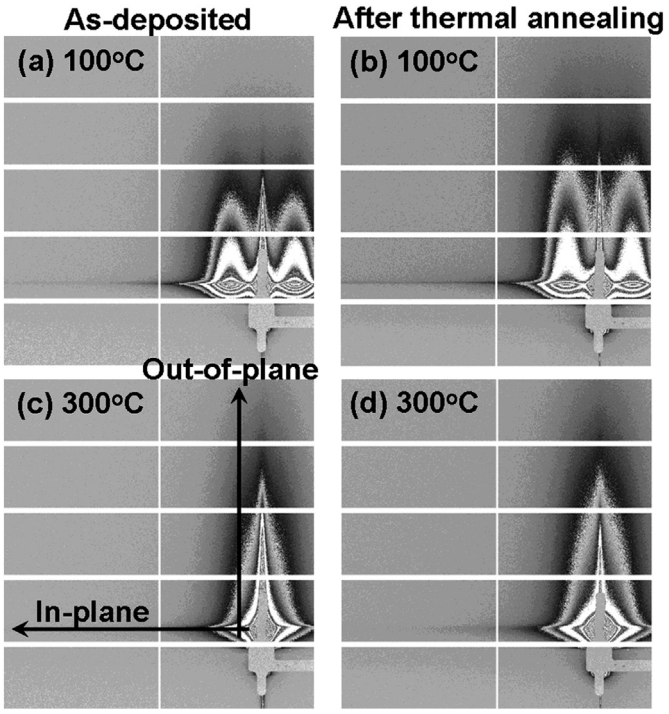

Fig. 2. 2D GISAXS scattering patterns of the SiC_xN_y films at different deposition temperatures: 100 °C and 300 °C, using only VSZ precursor, as-deposited and after thermal annealing at 400 °C.