Structural Characterization of Nanoporous Low-Dielectric Constant SiCOH Films Using Organosilane Precursors

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ABSTRACT

Synchrotron grazing incidence small-angle X-ray scattering and X-ray reflectivity analysis were performed to investigate the nanoporous structure of low dielectric constant carbon-doped silicon oxide films, which were deposited with plasma enhanced chemical vapor deposition from several silane precursors containing one to three vinyl groups with the aid of oxygen gas.

Keywords: grazing incidence small-angle X-ray scattering, specular X-ray reflectivity, low dielectric constant SiCOH film, plasma enhanced chemical vapor deposition, organosilane precursor

1 INTRODUCTION

Continuous improvements in device density and performance have been achieved through the feature size reduction and device dimensions are continually scaled down to the deep submicrometer level. Then the inter-metal capacitance effect coupled with line resistivity becomes a limiting factor for ultra-large-scale integration of integrated circuits. To reduce this problem, low dielectric constant (low-k) materials as interlayer dielectric and low resistivity conductors as metal lines such as copper, are required replacing the Al/SiO_2 interconnect technology [1]. Thus, much efforts have been devoted to developing new low-k dielectric materials to replace current workhorse dielectrics, namely silicon dioixde (k = 3.9 ~4.3) and silicon nitride (k = 6.07 ~ 7.0) [2-5].

Recently, carbon-doped silicon oxide (SiCOH) films have much attracted due to their low dielectric constant as well as good mechanical strength and high thermal stability [6]. In the present study, we prepared SiCOH dielectric films on silicon substrates with one of three silane precursors containing one to three vinyl groups (vinyltrimethylsilane (VTMS), divinyldimethylsilane (DVDMS), and tetravinylsilane (TVS)) as a precursor and oxygen as an oxidant gas by PECVD process, and subsequently annealed the as-deposited films at various thermal conditions in Ar ambient over the temperature range 400-450 °C. The resulting dielectric films were quantitatively investigated using grazing incidence small-angle X-ray scattering (GISAXS) and X-ray reflectivity (XR). This combined GISAXS and XR analysis provided details on the film structure, electron density, and electron density gradient along the thickness direction, as well as the pore shape, size distribution, and porosity in the film. And also we made a close investigation into the effect of post annealing on the structure of the films.

2 EXPERIMENTAL

A capacitively coupled plasma reactor was used where both O_2 and VTMS, DVDMS, and TVS precursors were introduced into the plasma through the shower head, which is also an upper electrode. Both gases were flown vertically toward the substrate on the bottom electrode. The film was deposited on silicon substrates as well as platinum-coated silicon substrates. Precursor flow rate was fixed at 10 sccm and O_2 flow rate was varied with total flow rate adjusted at 210 sccm with helium. The chamber pressure remained constant at 1 Torr. After the deposition, as-deposited films were annealed at 400, 450, and 450 °C for 0.5, 0.5, and 4 h in Ar ambient, respectively. GISAXS and XR measurements were carried out at the 4C2 and 3C2 beamline of the Pohang Accelerator Laboratory, respectively. Ellipsometric measurements were performed using a spectroscopic ellipsometer to obtain a refractive index of the films. The dielectric constant was obtained by capacitance-voltage measurement of the metal-insulator-metal structure (Al/0.3 μm thick film/Pt) at 1 MHz.

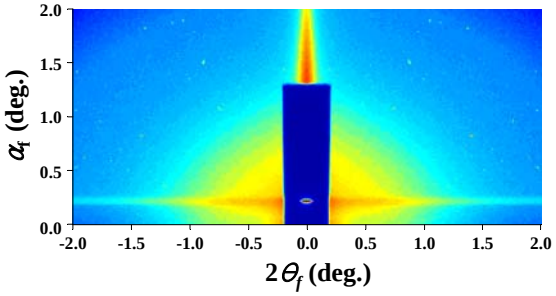

Figure 1 : 2D GISAXS pattern measured at α_i = 0.20° for a SiCOH film deposited with VTMS precursor and subsequently annealed at 450 °C for 4 h.

3 RESULTS AND DISCUSSION

The SiCOH dielectric thin films supported on silicon substrates were examined by GISAXS in order to extract information on the film structure. Figure 1 shows a representative 2D GISAXS pattern, which was measured for a SiCOH film deposited from VTMS precursor and subsequently annealed at 450 °C for 4 h. Similar scattering patterns were measured for the other SiCOH films. The measured scattering patterns were attempted to be quantitatively analyze the extracted scattering profiles using the recently derived GISAXS formula [3]. To analyze the scattering profiles using the GISAXS formula, we examined all possible scattering models (sphere, ellipsoid, cylinder and so on). We found that a sphere model [7] is the most suitable for the structures in the film prepared with VTMS precursor and subsequently annealed at 450 °C for 4 h. The scattering pattern was satisfactorily fitted, detailed structural parameters: average pore radius is 1.21 nm, the most populated pore radius 1.20 nm, and radius distribution 0.20. However, all other films showed featureless scattering patterns, suggesting that the films do not have pores, and otherwise have very small sizes of pores, which are much smaller than 1.21 nm observed for those in the film prepared with VTMS prepcursor.

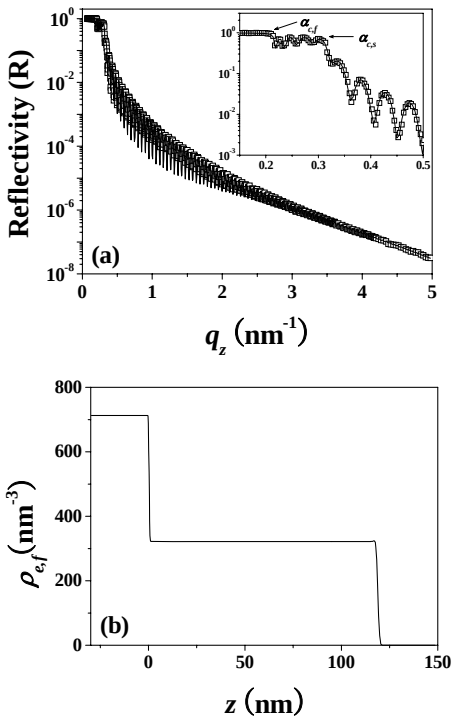

Figure 2 : (top) X-ray reflectivity profile of a SiCOH film deposited with a VTMS and annealed at 450 °C for 4 h. (bottom) Electron density distribution across the film thickness between the silicon substrate and air.

The films were further examined by XR measurements and data analysis. Figure 2 displays a representative XR profile and electron density distribution throughout the film, which was measured for a SiCOH film deposited with VTMS precursor and subsequently annealed at 450 °C for 4 h. The figure clearly reveals two critical angles of the film and substrate ($\alpha_{c,f}$ and $\alpha_{c,s}$) over the q_z range of 0.2-0.35 nm^{-1}. Oscillations between the two critical angles are also clearly discernible, which are the waveguide modes for X-rays confined in the film. The XR data were quantitatively analyzed using the Parratt formalism to obtain information on detailed structural parameters such as electron density, electron density gradient across the film thickness, surface roughness, and the film thickness [8]. The analysis provides the following structural details. The film thickness is precisely determined to be 118.4 nm, and the average film electron density $\rho_{e,f}$ is 321 nm^{-3}; here $\rho_{e,f}$ was obtained from the determined $\alpha_{c,f}$. The film surface roughness is only few angstroms, indicative of a very smooth surface. A very thin skin layer (0.7 nm thick) is detected with an electron density of 354 nm^{-3}. The other films were investigated in detail in the same manner using the XR technique.

For the measured data and the data analysis results, detailed discussions will be given.

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