Nanopore Generation in Low Dielectric Organosilicate and SiCOH Thin Films

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Introduction

Advanced microelectronic devices have continued to shrink active device dimensions of integrated circuits (ICs) through the use of dense conductor-line wiring in multilevel structure and smaller features, in order to increase device density and performance and to reduce costs. However, shrink of device feature size causes severe resistance-capacitance coupling problems including signal delay, crosstalk noise between the metal interconnections. Since the delay, noise, and power consumption critically depend on the dielectric constant (k) of the separating insulator, has been focused on replacing the standard silicon dioxide (k=3.9~4.2) with new intermetal dielectric materials which have considerably lower dielectric constants [1, 2].

There has been much interest in incorporating nanoscale voids into dielectric materials in order to reduce their k value, and thus in producing low-k porous interdielectric materials. One approach to the development of low-k dielectric materials is the templated polycondensation of soluble organosilicate precursors in the presence of a thermally labile, organic polymeric porogen [3]. The other is SiOCH films have low dielectric constant as well as good mechanical strength and high thermal stability through PECVD[4].

In this study we explore the nanopore generation mechanism of organosilicate film using star-shape porogen and SiOCH film using *bis*-trimethylsilyl-methane (BTMSM) precursor.

Experimental

Film preparations. A polymethylsilsesquioxane (PMSSQ) precursor and triethoxysilyl-terminated six-arm poly(ε-caprolactone) (mPCL6) porogen were used in spin coating. The SiOCH films were deposited using a mixture of *bis*-trimethylsilylmethane (BTMSM) and oxygen gases in inductively coupled plasma chemical vapor deposition (ICPCVD) system. The flow rate ratio [BTMSM/(BTMSM+O_2)] was varied from 45 to 85 %, and the deposited films were annealed at 200, 300, and 400°C for 30 min in vacuum to investigate effect of post annealing.

Measurements. GISAXS and XR measurements were carried out to investigate pore size, size distribution, porosity and electron density. In particular, the organosilicate film samples were heated to 400°C at a rate of 2.0°C/min during GISAXS measurements to observe the process of pore generation within organosilicate precursor.

Results and discussion

It was found that the organosilicate film with 10% mPCL6 porogen component has $\bar{r}$ (average radius) = 2.45–2.47 nm with σ = 0.32–0.33 in the range 50–320°C. These radius values and radius distributions width are slightly larger than those ($\bar{r}$ = 1.86 nm and σ = 0.28) of the single porogen molecule. These results indicate that even in a PMSSQ precursor film loaded with 10 wt% mPCL6 porogen, limited aggregation of the porogen molecules takes place during the film formation process, and that the resulting porogen aggregates retain their size and size distribution until they undergo thermal degradation. Above 320°C, the size and size distribution of the pores imprinted in the film were found to be almost identical to those of the porogen aggregates that developed during the film formation process. These results indicate that above 320°C the porogen aggregates within the immobilized PMSSQ precursor matrix undergo sacrificial thermal firing without further aggregation. Thus the imprinted pores have sizes equivalent to those of the porogen aggregates.

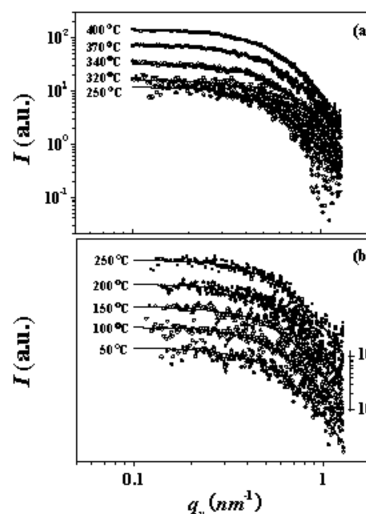

Figure 1. In-plane GISAXS profiles for dielectric thin films during heating run.

In SiOCH films, pores were generated in the range of 65-85% flow rate ratios. Also, all average pore radius from the films annealed at 400°C are slightly larger than those of lower annealing temperature. Also, the electron density of film is clearly lower for higher flow rate ratio. The electron densities were 414 and 549 nm^{-3} and the porosity were 38.9 and 19.0% for 85 and 45% flow rate ratio, respectively. Because more carbon atoms are incorporated into Si-O network can make more pores within the film, thus derives lower electron density and higher porosity. The electron density reduced with increasing annealing temperature. After post annealing, all the dielectric films underwent reduction of electron density, and this phenomenon was clarified for containing more carbon amount. The reduction of the electron density was due to that the removal of thermally unstable O-H related bonds by thermal annealing, while Si-CH_3 groups were stable during thermal process.

Conclusions

In organosilicate dielectrics, it was found that only limited phase separation took places during the blend film formation process. The formation of small porogen aggregates with a narrow size distribution might result from the favorable hybridization reaction of the porogen's reactive triethoxysilyl end groups with the reactive functional groups (i.e., ethoxysilyl and hydroxysilyl groups) of the PMSSQ precursor, which competes with the porogen aggregation that occurs via the condensation of the porogen molecules. Thus the reactive triethoxysilyl end groups of the porogen play a major role in minimizing the aggregation of the porogen molecules in the PMSSQ dielectric.

We have also shown that nanopores were generated within the SiOCH film, and their average pore radius increased with increasing carbon content. Also, electron density decreased followed by pore generation. In particular, we have demonstrated that the density of SiOCH films decreases with post annealing process. It is noted that the amount of carbon and post annealing in this work is the dominant factor that valuates the film characteristics.

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