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Communications

Neutron Reflectivity on Nanoporous Poly(Methylsilsesquioxane) Thin Films

Ho-Cheol Kim,* Willi Volksen, and
Robert D. Miller

IBM Almaden Research Center, 650 Harry Road,
San Jose, California 95120-6099

Elbert Huang

IBM T.J. Watson Research Center,
Yorktown Heights, New York 10595

Gaiying Yang and Robert M. Briber*

Department of Materials and Nuclear Engineering,
University of Maryland,
College Park, Maryland 20742-7531

Kwanwoo Shin† and Sushil K. Satija

NCNR-NIST, Gaithersburg, Maryland 20899-8562

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Porous organic or inorganic thin films have gained much interest as low-dielectric-constant (low-*k*) materials for inter-metal dielectrics as the *k* value of porous materials decreases in proportion to the amounts of incorporated air ($k \sim 1$).[1] The pore size must be substantially smaller than device feature sizes to prevent problems such as localized structural collapse, metal short formation, etc. In addition, the low-*k* materials will ideally have a closed-cell pore structure and uniformly distributed pores.

Extensive studies have been performed for the structural characterization of nanoporous thin films using electron microscopy, X-ray, and neutron scattering, etc.[2,3] Most of these studies have focused on pore morphology, average pore size, and size distribution. A spatially uniform pore distribution is, however, one of the primary challenges with porous low-*k* materials because a localized higher porosity may lead to a structural failure during real chip fabrication processing when mechanical or thermal stresses are introduced (e.g., chemical mechanical polishing (CMP) or high-temperature process steps). In this communication, neutron reflectivity has been used to elucidate the porosity depth profile in thin films of nanoporous poly(methylsilsesquioxane) (PMSSQ) with toluene-d_8 and D_2O probes. As the observations discussed here indicate, neutron reflectivity revealed a highly selective sorption behavior of nanoporous PMSSQ and a localized higher porosity at the silicon substrate/porous PMSSQ interface. The results suggest that more careful control of

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* Authors to whom correspondence should be addressed. H.-C. Kim: e-mail hckim@us.ibm.com; tel 408-927-3725; fax 408-927-3310. R.M. Briber: e-mail rbriber@eng.umd.edu; tel 301-405-7313; fax 301-314-9601.

† Current address: Department of Material Science and Engineering, Kwang-Ju Institute of Science and Technology, Kwangju, Korea.

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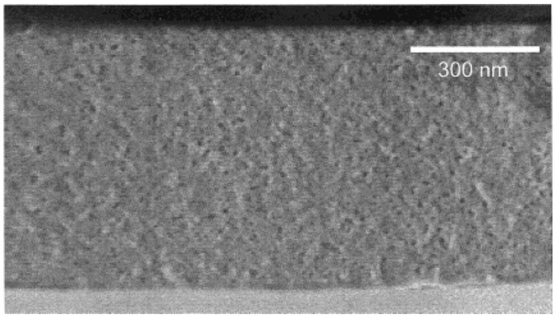

Figure 1. FESEM image of a nanoporous PMSSQ thin film generated with 20 wt % P(MMA-*co*-DMAEMA) loading.

pore distribution is required to prevent interfacial segregation as the thermo-mechanical stability of porous low-*k* materials has emerged as a major reliability concern of integration.

Nanoporous PMSSQ films were prepared by the so-called *sacrificial porogen (pore generator) approach*: the selective removal of the organic (porogen) phase from phase-separated mixtures of organic/inorganic polymers. Pore size, size distribution, and morphology are found to be strongly dependent on the amount and/or molecular architecture of porogen. Pores undergo morphological transition from closed-cell structure to interconnected bicontinuous structure based on the phase diagram of PMSSQ/porogen mixtures. PMSSQ was obtained from Dow Corning ($M_w = 15$ K) and used as received. Poly(methyl methacrylate-*co*-dimethyl amino ethyl methacrylate), P(MMA-*co*-DMAEMA), was used as a porogen in this study. P(MMA-*co*-DMAEMA) was synthesized by atom transfer radical polymerization (ATRP) ($M_w = 12$ K, $M_w/M_n = 1.1$).[4] Thin films were prepared by spin-casting homogeneous 1-methoxy-2-propanol solutions of PMSSQ and P(MMA-*co*-DMAEMA) on clean $^1/_2$-inch-thick silicon wafers. Heating the samples to 450 °C under an argon atmosphere generates optically homogeneous, nanoporous films. Films of dense PMSSQ and nanoporous PMSSQ with 20 wt % and 60 wt % loadings of P(MMA-*co*-DMAEMA), denoted PMSSQ-0, PMSSQ-20, and PMSSQ-60, respectively, were prepared for this study. The refractive indices of the films determined by a white light interferometer (Filmetrics, F20 thin film measurement system) were found to decrease with increasing amounts of P(MMA-*co*-DMAEMA) loading. Neutron reflectivity measurements were performed at the NG7 horizontal reflectometer of the National Institute of Standards and Technology (NIST) at Gaithersburg, MD. The nanoporous film on silicon wafer was placed in a cell that provides the ability to expose the film to either the vapor or liquid state of D_2O or toluene-d_8. The liquid cell consists of a spherical 4-in. quartz block with an O-ring for retaining toluene-d_8 or D_2O probes (~40 cm^3 volume space). The incident neutron beam entered and reflected through the thick silicon substrates for this study. The reflectivity was measured as a function of scattering vector $q_z = (4\pi/\lambda)\sin\theta$, where θ is the incident angle and λ is the wavelength. The wavelength was 4.76 Å, with a wavelength spread, $\Delta\lambda/\lambda$, of 1.0%.

Figure 1 shows a typical cross-sectional field emission scanning electron microscopy (FESEM, Hitachi S-4700 Scanning Electron Microscope) image of a nanoporous film, PMSSQ-20. The high-resolution image suggests that the pores have diameters of roughly ~10 nm, and within the limitation of the FESEM technique, the pores appear to be uniformly distributed throughout the thickness of the film. More accurate quantitative analysis of pore size and size distribution, such as small-angle X-ray scattering (SAXS) or neutron scattering (SANS), is needed, however, as the artifacts induced by the fracture of nanoporous films and resolution limit of FESEM make it difficult to extract quantitative values from the image. Independent SAXS studies determined the average pore diameter of 5.8 nm with a log-normal pore size distribution for PMSSQ-20.[5]

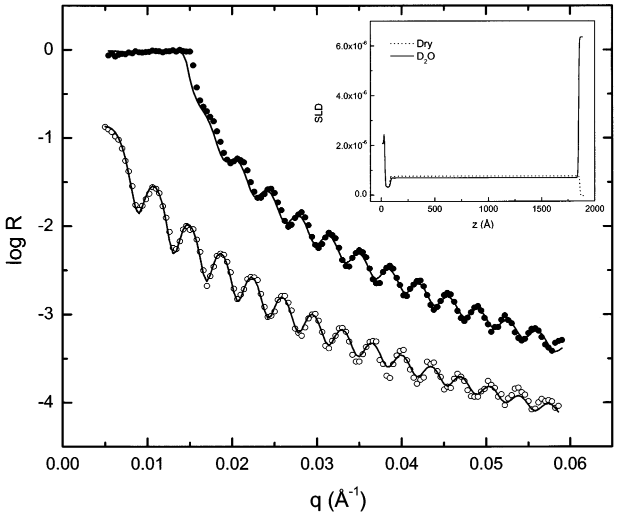

Figure 2. Neutron reflectivity for a nanoporous PMSSQ generated with 20 wt % P(MMA-*co*-DMAEMA) loading. Open and closed symbols are dry and water-contacted PMSSQ films, respectively. The inset shows the scattering length density profile normal to the surface that was used to calculate the reflectivity profile shown as the solid line.

The surface of dense PMSSQ is intrinsically hydrophobic and gives a static water contact angle of ~105°. The hydrophobicity meets the low moisture uptake requirement of low-*k* material for real on-chip applications. For Al-alloy (gap-fill) and Cu (damascene) integration, for example, moisture sorption must be less than 2 wt % at 100% relative humidity.[6] The neutron reflectivity data in this study confirm the low moisture uptake of nanoporous PMSSQ. Figure 2 shows the neutron reflectivity data (symbols) and model fits (lines) of a PMSSQ-20 with and without contact with the liquid phase of D_2O. The recursive Parratt formalism has been used to analyze the data.[7] The fit involves two layers (interface layer and bulk layer) and each layer has been modeled by three variables, i.e., SLD, layer thickness, and surface (interface) roughness. The SLDs of 0.88×10^{-6} (Å^{-2}) and 6.37×10^{-6} (Å^{-2}) were used for dense PMSSQ and D_2O, respectively, for calculating reflectivity curves, and the inset shows the scattering length density (SLD) profile obtained from the best fit. As shown in Figure 2, when the film is in contact with

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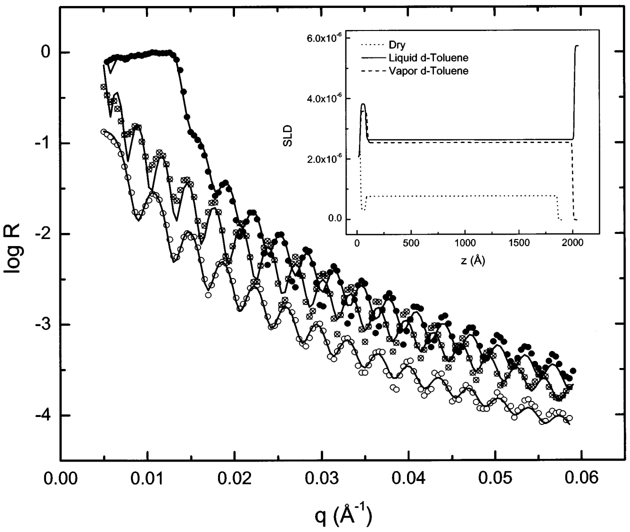

Figure 3. Neutron reflectivity for a nanoporous PMSSQ generated with 20 wt % P(MMA-*co*-DMAEMA) loading: (○) dry nanoporous PMSSQ; (●) nanoporous PMSSQ exposed to liquid phase of toluene-d_8; (⊗) nanoporous PMSSQ exposed to vapor phase of toluene-d_8. The inset shows the scattering length density profile normal to the surface that was used to calculate the reflectivity profile shown as the solid line.

liquid D_2O, the reflectivity profile at small values of q_z exhibits total external reflection below critical value of q_z due to the interface between porous film and D_2O. No significant change in the SLD and thickness of PMSSQ-20 film was observed by contacting it with D_2O, which indicates that water sorption of the nanoporous PMSSQ is negligible. This result is in good agreement with the previous quartz crystal microbalance (QCM) data that show less than 1% of moisture mass uptake of the nanoporous films.[8] It should be noted that a thin layer of lower SLD was found at the interface between nanoporous PMSSQ and silicon wafer. The porosity of this layer was determined as ~60% which is three times higher than the loaded porogen amount. The modulus of dense PMSSQ (5−7 GPa) is believed to be high enough to support the layer. Thickness of the higher porosity layer was measured at ~52 Å, which is approximately equal to $2R_g$ value of the P(MMA-*co*-DMAEMA) copolymer. The existence of this layer suggests a possibility of segregation of P(MMA-*co*-DMAEMA) copolymer at the interface.

The reflectivity profiles for PMSSQ-20 exposed to the vapor or liquid phase of toluene-d_8 are shown in Figure 3. For both liquid and vapor state of toluene-d_8, SLD of the bulk layer of the film increases uniformly throughout the entire film thickness when exposed to toluene-d_8, which indicates the uniform distribution of toluene-d_8 in the nanoporous PMSSQ. The interfacial layer of lower SLD of dry film shows higher SLD than the bulk layer when exposed to toluene-d_8 due to the higher concentration of toluene. This further substantiates the existence of a layer which has higher porosity than bulk, resulting from the interfacial segregation of P(MMA-*co*-DMAEMA) copolymer. As mentioned above, this result is in good agreement with a QCM study for quantitative analysis of the sorption behavior of nanoporous PMSSQ as a function of surface tensions of organic liquids.[8] According to the results, the nanoporous PMSSQ shows highly selective sorption behavior, and ~20% of sorption can take place by the PMSSQ-20 when it is exposed to the organic liquids (irrespective of the phase) whose surface tensions are below the critical value, 38−48 dyn/cm. The selective sorption behavior is explained by the capillary condensation described by the Kelvin equation. The most pronounced feature in Figure 3 is the changes in film thickness with sorption. The reflectivity data show about 8% increases in the film thickness for PMSSQ-20 with exposure to toluene-d_8 (from ~183 to ~198 nm). It is surprising that even though the film is fully cross-linked by heating to 450 °C, the nanoporous PMSSQ films actually can swell by an organic liquid such as toluene-d_8. Structural changes may take place by the swelling, but independent SAXS data argue against this possibility as no pore size difference was observed for the sample dried after soaking with toluene for 24 h. Similar swelling behavior was observed for PMSSQ-0 and PMSSQ-60 (data not shown). Approximately 3% and 9% increases in film thickness by exposure to toluene-d_8 were observed for PMSSQ-0 and PMSSQ-60, respectively.

In summary, the neutron reflectivity study revealed a selective sorption behavior and the depth profile of pore distribution of nanoporous PMSSQ. The nanoporous films swell by the sorption of toluene and show a localized higher porosity at the interface between porous films and silicon substrates. The spatial distribution of pores along the thickness direction of the thin films is controllable by modifying the interaction between the organic polymer and the substrate. It deserves a more thorough study and will be published separately.

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