Synchrotron Grazing Incidence X-ray Scattering and Reflectivity Analysis of Nano-structures and Patterns Supported with Substrates

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ABSTRACT

The grazing incidence X-ray scattering (GIXS) from structures within a thin film on a substrate is generally a superposition of the two scatterings generated by the two X-ray beams (reflected and transmitted beams) converging on the film with a difference of twice the incidence angle α_i of the X-ray beam in their angular directions; these two scatterings may overlap or may be distinct, depending on α_i. The two scatterings are further distorted by the effects of refraction. These reflection and refraction effects mean that GIXS is complicated to analyze. To quantitatively analyze GIXS patterns, a GIXS formula was derived under the distorted wave Born approximation. We applied this formula to the quantitative analysis of the GIXS patterns obtained for nano-structures and patterns fabricated with various polymer systems, which were supported with substrates. In addition, specular X-ray reflectivity studies were performed the nano-structures and patterns.

Keywords: grazing incidence X-ray scattering, specular X-ray reflectivity, nano-structure, nano-pattern

1 INTRODUCTION

Grazing incidence scattering can be used to overcome the limitations of conventional transmission scattering techniques with respect to extremely small scattering volumes, in particular for nano-structures and patterns [1-9]. Grazing incidence X-ray scattering (GIXS) has several important advantages over transmission X-ray and neutron scattering: (i) a highly intense scattering pattern with high statistical significance is always obtained, even for films of nanoscale thickness, because the X-ray beam path length through the film plane is sufficiently long; (ii) there is no unfavorable scattering from the substrate on which the film is deposited; (iii) sample preparation is easy and no additional sample treatment is required [1-9]. On the other hand, specular X-ray reflectivity (XR) technique has been used extensively for characterizing the layer structure, interface, surface roughness, and electron density and its profile along the thickness in single and multiple layer thin films [10,11]. Therefore, the GIXS technique becomes more powerful in the structural analysis of nano-structures and patterns when this technique is used together with the XR method.

In this study, we introduce the GIXS technique including its theory and advantages, and describe its extendability when used together with XR method. We have applied this GIXS technique with and without XR method for various nano-structures and patterns fabricated with a number of polymeric systems.

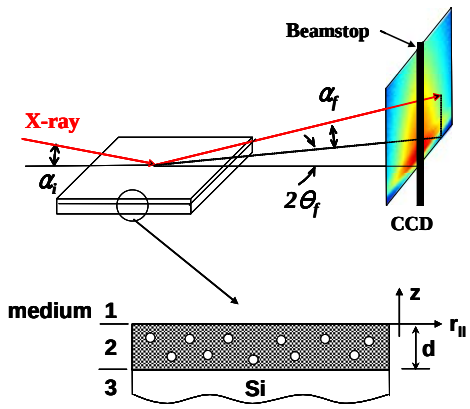

Figure 1 : Geometry of GIXS; an incident x-ray beam impinges on the surface of a thin film at an angle α_i, and then the scattered pattern is measured on a two-dimensional charge-coupled detector (2-D CCD), where α_f is the exit angle with respect to the film surface and $2\theta_f$ is the scattering angle with respect to the plane of incidence. A schematic structural diagram of a nanoporous dielectric film deposited onto a silicon substrate: medium 1, vacuum; medium 2, porous dielectric film; medium 3, silicon substrate. *d* is the thickness of medium 2 (i.e., the porous dielectric film).

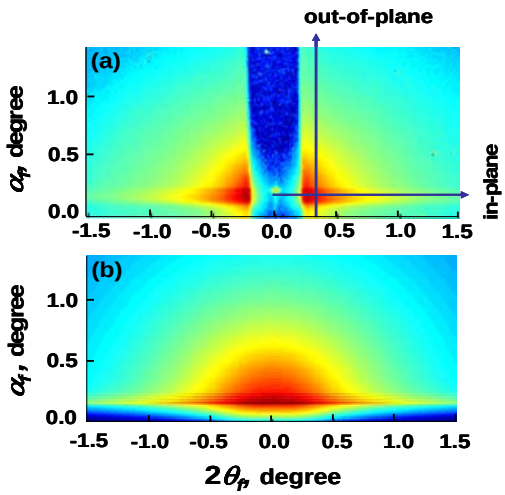

Figure 2 : (a) 2D GIXS pattern measured at α_i = 0.20° for a film derived from a PMSSQ precusor film loaded with 20 wt% porogen. (b) GIXS pattern calculated for the porous film in (a) using a GIXS formula [4,8]. In this calculation, pores were assumed to have a log-normal size distribution (r_0 = 3.73 and σ = 0.523: r_0 and σ are the pore radius corresponding to the peak maximum and the width in the radius distribution, respectively); the electron densities of the porous film and silicon substrate are 324 and 699.5 nm^{-3}, respectively, and the film thickness is 108 nm.

2 RESULTS AND DISCUSSION

Figure 1 shows a typical GIXS geometry and a schematic structural diagram of a nanoporous dielectric thin film deposited on a silicon substrate. The incident X-ray beam impinges onto the surface of the thin film at an angle α_i, and the scattered pattern is recorded on a two-dimensional charge-coupled detector (2D CCD); α_f is the exit angle with respect to the film surface, and $2\theta_f$ is the scattering angle with respect to the plane of incidence. Porous films are generally found to have a surface roughness of a few angstroms [10,12], which is much smaller than a typical nanoporous film thickness, i.e. less than 800 nm, so the volumes of the interfaces with air and the silicon substrate are much smaller than that of the porous film. Thus the perturbation of the scattering due to interfacial roughness is small for porous films coated on silicon substrates.

By adopting the distorted wave Born approximation [13-15], we have successfully derived a novel GIXS formula in order to quantitatively analyze GIXS data obtained from nano-structures and patterns [4,8]. The GIXS formula derivation [4,8] and its application in scattering data analyses [1-9] have been used to show that scattering from scatterers (i.e., pores or nano-structural elements) onto a substrate, buried in a film coated onto a substrate or both at the surface and buried in a film deposited onto a substrate results in four main types of processes: (i) the incident beam scatters without reflection; (ii) the scattered beam is reflected at the interface between the film and the substrate; (iii) the reflected beam scatters; (iv) the scattered, reflected beam is reflected once more.

A representative two-dimensional (2D) GIXS pattern is shown in Figure 2a, which was obtained at α_i = 0.20˚ for a 108 nm thick nanoporous polymethylsilsesquioxane (PMSSQ) film imprinted with a 20 wt% loading of a star-shape poly(ε-caprolactone) porogen [4]. Similar GISAXS patterns were obtained for nanoporous films prepared with other porogen loadings (data not shown). PMSSQ is an excellent dielectric material because its dielectric constant (k = 2.7–2.9) is lower than those of silicon dioxide materials (k = 3.9–4.3); it also has thermal stability up to 500˚C, a low moisture uptake, and good mechanical strength [10-12]. As can be seen in Figure 2a, bright striped patterns appear along the q_y direction at several exit angles α_f between the critical angles of the film and the silicon substrate ($\theta_{c,f}$ and $\theta_{c,s}$), which arise from intense scattering due to a type of standing-wave phenomenon and total reflection at the interface between the film and the substrate.

The GIXS patterns of the porous films imprinted with various porogen loadings can be fitted with the GIXS formula for hard spherical particles with a lognormal size distribution buried in the dielectric thin film, indicating that the pores are spherical in shape and have a sharp interface with the PMSSQ dielectric matrix. The GIXS data analysis provided all important structural parameters of the nanoporous dielectric thin films.

From the parameters determined with this procedure, 2D GIXS patterns can be generated using the GIXS formula. One of these patterns is shown in Figure 2b, which was calculated for the porous film imprinted with 20 wt% porogen loading. The calculated pattern is in good agreement with the measured pattern (Figure 2).

GIXS measurements can be conducted in-situ as a function of processing parameters (e.g., time, temperature, etc.) in nano-fabrication processes. This in-situ GIXS technique can make it possible to determine the mechanism of nano-structure (or nano-pattern) generation in the nano-fabrication.

One example is discussed here. For blend films of PMSSQ precursor and star-shape porogen, in-situ GIXS measurements were performed during both heating up to 400°C and subsequent cooling to room temperature [4]. Of the GIXS data obtained as a function of temperature and time, some representative one dimensional (1D) scattering profiles are presented in Figure 3. As can be seen in Figure 3, all the 1D scattering profiles were well fitted with the GIXS formula for hard spherical particles with a lognormal size distribution. The sizes of the porogen and the imprinted nanopores are summarized in Figure 4 as a function of the

temperature during the heating run as well as of the initial porogen loading.

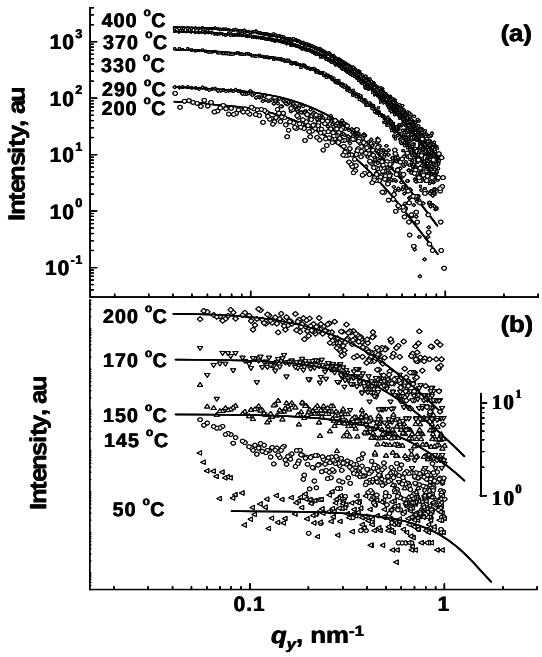

Figure 3 : In-plane GISAXS profiles at α_f = 0.17° of 2D GIXS patterns measured during heating (2.0 °C/min) of PMSSQ precusor film loaded with 10 wt% porogen under vacuum.

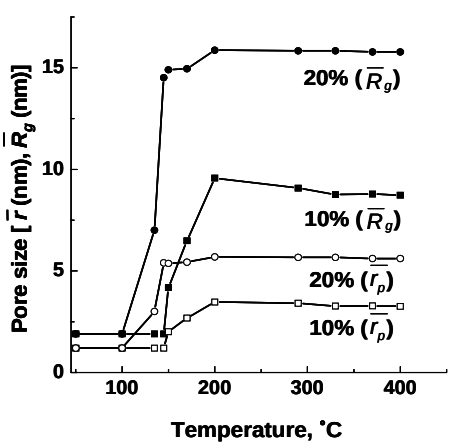

Figure 4 : Pore size variations determined from the GIXS analysis of the in-plane scattering profiles at α_f = 0.17° of 2D GIXS patterns measured during heating (2.0 °C/min) of PMSSQ precusor films loaded with 10 and 20 wt% porogen under vacuum. Here, $\overline{R_g}$ and $\overline{r_p}$ are the average radius of gyration and average pore radius of pores respectively.

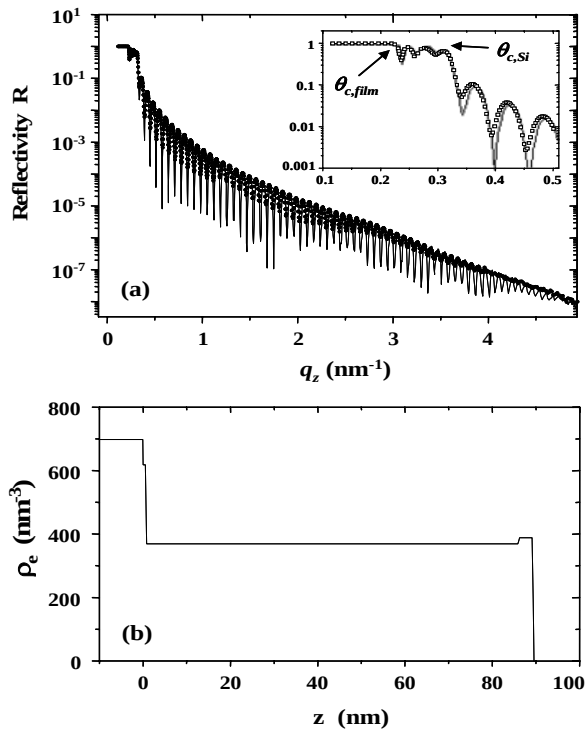

Figure 5 : (a) A representative X-ray reflectivity profile of a nanoporous PMSSQ film imprinted with 10 wt% porogen. The symbols are the measured data and the solid line represents the fit curve assuming a homogeneous electron density distribution within the film except for a thin surface layer, in which the electron density is slightly different. The inset shows a magnification of the region around the two critical angles: $\theta_{c,film}$ is the critical angle of the film and $\theta_{c,Si}$ is the critical angle of the Si substrate. (b) A model of the electron density distribution across the film thickness between the silicon substrate and air, which gives the best fit for the XR profile in (a).

Figure 5 shows a representative XR profile (Figure 5a), which was measured for a nanoporous PMSSQ film, and the data analysis results (Figure 5b). The XR data and analysis results indicate that a well-defined structure was developed in the porous film imprinted with 10 wt% porogen. This quantitative XR analysis provided important, detailed information on the surface, interface to the substrate, layer structure, electron density, and electron density gradient along the film thickness in the nanoporous dielectric thin films.

As described above, the 2D GIXS technique is a very powerful tool for characterizing the pore shape, size, size distribution, electron density, and porosity of nanoporous dielectric thin films of nanoscale thickness. Moreover, it was demonstrated that this GIXS technique becomes much

more powerful in analyzing the structure and properties of nanoporous dielectric thin films when used together with the specular XR method.

This quantitative GIXS and XR analysis has been extended for other nano-structures and patterns, which were prepared through many novel nano-fabrication processes [2,8,9,16,17].

In this study, all GIXS and XR measurements were conducted at the 4C1 and 4C2 SAXS beamlines of Pohang Accelerator Laboratory (Figure 6) [18-20].

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Figure 6 : Pohang Accelerator Laboratory at Pohang University of Science & Technology (POSTECH), Pohang, Republic of Korea.

REFERENCES

[1] B. Lee, Y.-H. Park, Y.-T. Hwang, W. Oh, J. Yoon, and M. Ree, Nature Mater., 4, 147, 2005.

[2] Y. Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J. Nelson, J.R. Durrant, D.D.C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, and M. Ree, Nature Materials 5 (2006) 197.

[3] B. Lee, W. Oh, Y. Hwang, Y.-H. Park, J. Yoon, K. S. Jin, K. Heo, J. Kim, K.-W. Kim and M. Ree, Adv. Mater., 17, 696, 2005.

[4] B. Lee, J. Yoon, W. Oh, Y.-T. Hwang, K. Heo, K. S. Jin, J. Kim, K.-W. Kim and M. Ree, Macromolecules, 38, 3395, 2005.

[5] B. Lee, W. Oh, J. Yoon, Y. Hwang, J. Kim, B. G. Landes, J. P. Quintana, and M. Ree, Macromolecules, 38, 8991, 2005.

[6] J. Yoon, K. Heo, W. Oh, K. S. Jin, S. Jin, J. Kim, K.-W. Kim, T. Chang and M. Ree, Nanotechnology, 17, 3490, 2006.

[7] K. Heo, K. S. Jin, W. Oh, J. Yoon, S. Jin and M. Ree, J. Phys. Chem. B, 110, 15887, 2006.

[8] B. Lee, I. Park, J. Yoon, S. Park, J. Kim, K.-W. Kim, T. Chang, and M. Ree, Macromolecules, 38, 4311, 2005.

[9] I. Park, B. Lee, J. Ryu, K. Im, J. Yoon, M. Ree, and T. Chang, Macromolecules, 38, 10532, 2005.

[10] J. Bolze, M. Ree, H. S. Yoon, S.-H. Chu, and K. Char, Langmuir, 17, 6683, 2001.

[11] W. Oh, Y.-t. Hwang, Y. H. Park, M. Ree, S.-H. Chu, K. Char, J. K. Lee, and S. Y. Kim, Polymer, 44, 2519, 2003.

[12] Oh, W.: Ph. D. Thesis, Pohang University of Science and Technology, Pohang, Korea, 2003.

[13] S. K. Sinha, E. B. Sirota, S. Garoff, and H. B. Stanley, Phys. Rev. B., 38, 2297, 1988.

[14] V. Holy, U. Pietsch, and T. Baumbach, High-Resolution X-ray Scattering from Thin Films and Multilayers, Springer-Verlag, Berlin, 1999.

[15] R. Lazzari, J. Appl. Crystallogr., 35, 406, 2002.

[16] J. Yoon, K. S. Jin, H. C. Kim, G. Kim, K. Heo, S. Jin, J. Kim, K.-W. Kim, and M. Ree, J. Appl. Cryst., 2007 (in press).

[17] J. Yoon, S. Y. Yang, K. Heo, B. Lee, W. Joo, J. K. Kim, and M. Ree, J. Appl. Cryst., 2007 (in press).

[18] J. Bolze, J. Kim, J.-Y. Huang, S. Rah, H. S. Youn, B. Lee, T. J. Shin, and M. Ree, Macromol. Res. 10, 2, 2002.

[19] C.-J. Yu, J. Kim, K.-W. Kim, G.-H. Kim, H.-S. Lee, M. Ree, and K.-J. Kim, J. Kor. Vac. Soc. 14, 138, 2005.

[20] M. Ree and I.S. Ko, Phys. High Tech. (Korea) 14 (2005) 2.