

# Characterization of Mesoporous Thin Films

The molecularly templated silica membranes and films were deposited by spin- and dip-coating on silicon wafer using sol-gel method. In this study, ordered three-dimensional structures of mesoporous silica films deposited on Si(001) substrate are determined by transmission electron microscopy (TEM) with electron diffraction (ED), conventional and grazing-incidence X-ray diffraction (XRD and GIXD), and X-ray reflectivity (XRR) measurements.

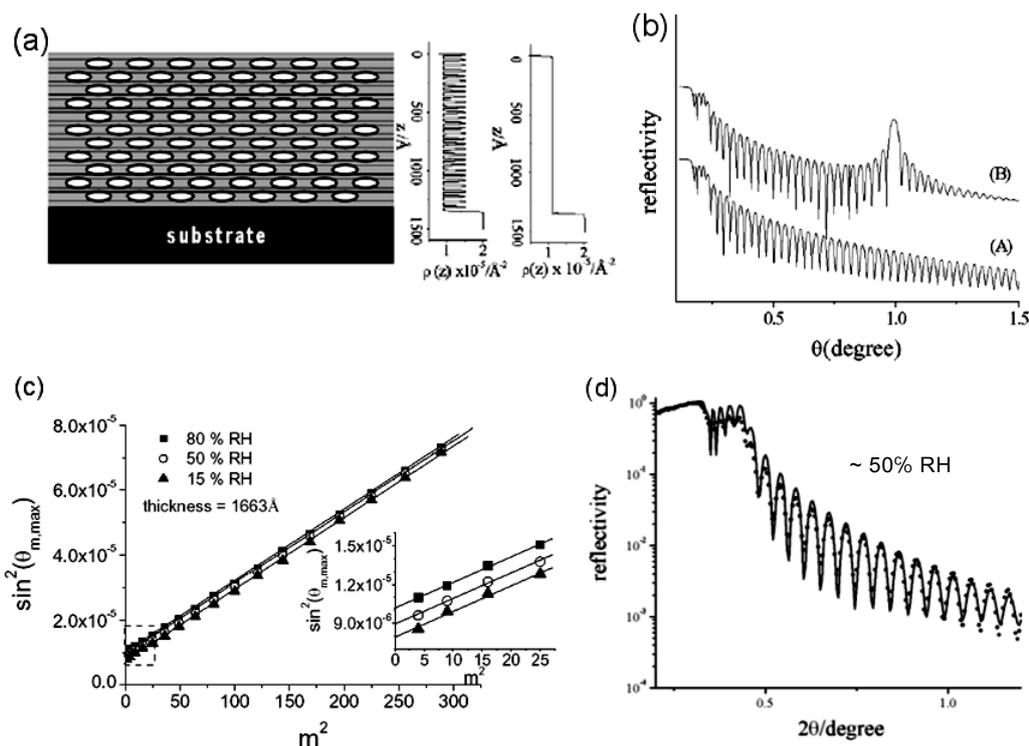
Mesostructured porous silica materials prepared through self-assembly of surfactants were first reported by Kresge et al. (1992) and Inagaki et al. (1993). These materials have highly ordered structures and can be synthesized with various morphologies, e.g., spheres, fibers, rods, monoliths and thin films. Other than powder, thin films have been considered as most promising materials due to their potential use in chemical sensors, membrane separation, optical and electronic devices.

Continuous thin films of surfactant-templated mesoporous silica were prepared either in self-support form or on top of porous or dense support. Synthesis of such thin films is preferable under acidic condition. The films have been grown from a homogeneous solution of reactants as well as by rapid solvent evaporation from a sol precursor coated on a solid support. Through an epitaxial-like growth, the mesochannels can be aligned under a

controlled reactant flow or on a modified anisotropic surface of a glass substrate or on a specific crystalline plane, i.e., (011) plane of a silicon wafer.

Since the pore structure and film texture of supported thin films were found to be affected by the substrate, and such films are usually used in applications together with its substrate, it is desirable to perform the structural characterization on the supported thin films instead of the films detached from their substrates.

In this study, the continuous nanoporous silica thin films were prepared on a Si wafer by dip- or spin-coating the silica sols with Brij-56 ( $C_{16}H_{33}(OCH_2CH_2)_{10}OH$ ) and Pluronic P123 ( $H(OCH_2CH_2)_{20}(OCH_2CH_2)_{70}(OCH_2CH_2)_{20}OH$  block copolymer) as templates. After the removal of the organic templates, the silica films exhibit high porosity and channel or pore structures of uniform pore sizes of 3 and 6 nm.



**Fig. 1** (a) A model of well-organized mesoporous film together with its electron density profiles assuming a series of two alternating layers (multi-layer model) and a model of homogeneous electron density distribution (single layer model) within the film. (b) Simulated XRR profiles using a single layer model (A) and a multi-layer model (B), (c) Plots of XRR data according to the modified Bragg equation for various RH, and (d) the XRR experimental data (o) and fit plot (-) of a spin-coated Brij-56 template-free mesoporous film.

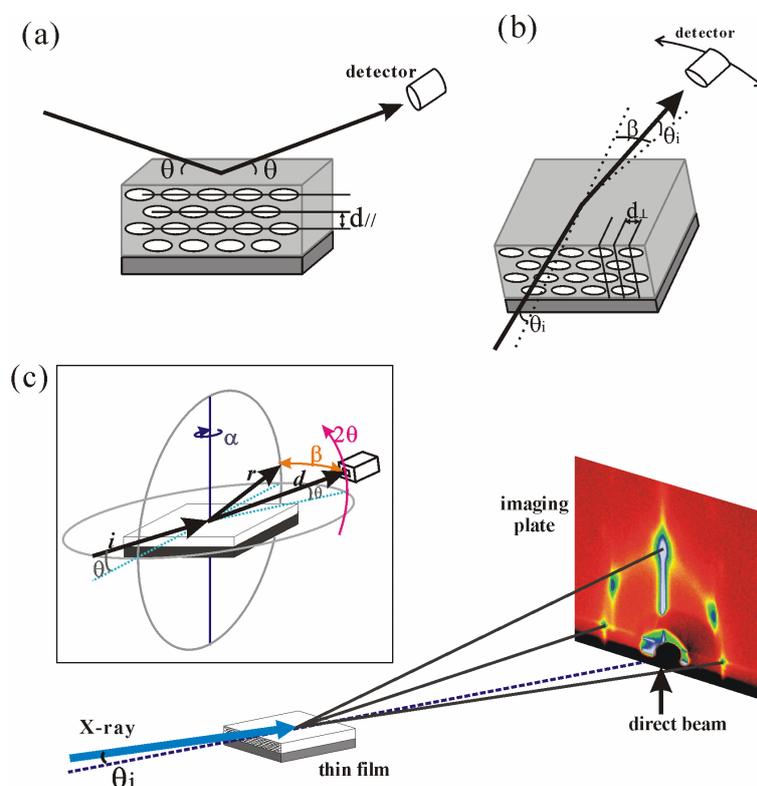
X-ray specular reflectivity (XRR) is a non-destructive technique to measure thin film properties such as film thickness, laterally averaged electron density distribution normal to the surface and interfacial roughness. Because the X-ray refractive index of air is 1 and that of matter is less than 1, when the X-ray beam impinges from air to a flat surface with incident angle ( $\theta_i$ ) below the critical angle  $\theta_c$ , the beam is totally reflected. At an incident angle higher than  $\theta_c$ , X-rays penetrate into the film with the intensity of the reflected beam dropping sharply. The larger the incident angle, the deeper the X-rays penetrate. The steeply decaying reflectivity curve is modulated by several oscillations known as the Kiessig fringes (Fig. 1d). Film thickness derived from the frequency of the Kiessig fringes is fitted into a modified Bragg equation (Fig. 1c & 1d):

$$\sin^2(\theta_{m,max}) = m^2(\lambda \cdot 2d)^2 + \sin^2(\theta_{c,film})$$

$\theta_{m,max}$  is the maximum of the  $m$ -th oscillation of the Kiessig fringes starting from the low end of  $\theta$ , and  $d$  is the film thickness. The densities of the P123-template-free mesoporous silica films deposited on Si (100) wafer were found to be lower than that of Brij-56 template-free films. It was also noted that the densities of these mesoporous films were sensitive to the relative humidity (RH) and the water uptake (Fig. 1c) due to the existence of hydrophilic Si-OH groups on the intrachannel surface. The thicknesses of P123 and Brij-56 template-free films

were analyzed by the Kiessig fringes with both single layer and multi-layer models for well-organized films with uniform pore packing arrangement throughout the films (Fig. 1a). The same frequency values of Kiessig fringes were obtained for multi- and single layer models as shown in Fig. 1b. However, for the multi-layer model consisting of a series of two alternating layers, there are out of plane diffraction peaks on top of the oscillations of the Kiessig fringes (profile B of Fig. 1b).

Reflection mode XRD is well established for the characterization and identification of structures of powdery mesoporous samples. However, the bundles of channels in mesoporous silica films are usually expected to pack and align themselves in a specific and preferred orientation at the air-solution interface or on a flat substrate. With such ordering of pores, only lattice planes parallel to the surface,  $d_{//s}$ , can be detected by XRD patterns in  $\theta - 2\theta$  scan mode as shown in Fig. 2a. In order to acquire information beyond the out-of-plane periodic lattice in the film, grazing incidence X-ray diffraction (GIXD) technique has been employed (Fig. 2b and c). The incident beam impinges on the surface with an angle  $\theta_i$ , which is often set at  $\theta_c$  in GIXD. A beam-stopper is used to shield the direct and total reflection beams in order to avoid signal saturation of the 2D image plate detector, while the point detector can scan either vertically ( $2\theta$ ) or horizontally ( $\beta$ ). The diffraction patterns of GIXD provide the bulk average information about lattice parameters of 2D structures in thin films.



**Fig. 2:** Schematic representations of (a) conventional out-of-plane  $\theta - 2\theta$  mode XRD; and (b) grazing incident in-plane mode XRD. (c) An illustration of the geometry used for 2D GIXD measurements,  $i$ ,  $r$ , and  $d$  represent the incident, reflected and in-plane diffracted beams.



jection of a  $[10\bar{1}]$  zone axis and the two-dimensional non-centered rectangular lattice is assumed as the projection of a  $[100]$  zone axis, an f.c.o. structure with  $a = 92$ ,  $b = 71$  and  $c = 128$  Å could be constructed. However, the top-view TEM images do not match the projection  $[010]$  zone axis of the f.c.o. model. The same inconsistencies also exist with a three-dimensional hexagonal structure and a b.c.c. structure. Consequently, structures I and II detected by the cross-sectional TEM can not belong to a single three-dimensional structure. Furthermore, TEM images with ED and lower magnification clearly show the irregularity of the channel direction.

In conclusion, the diffraction patterns of GIXD have been shown to provide information about lattice parameters of centered and noncentered rectangular two dimensional structures in a thin film. The uniformity over the film as well as the structure of the film relative to the substrate are assessed by cross-sectional TEM and ED techniques. The in-plane directional distribution of bundles of mesochannels in a film is estimated by transmission-mode XRD as well as by top-view TEM, and no preferred orientation has been revealed, although the mesochannels and mesopores are packed parallel to the substrate surface.

**BEAMLINE**

17B1 W20 X-ray Scattering beamline  
17A1 W20 X-ray Powder Diffraction beamline

**EXPERIMENTAL STATION**

X-ray scattering end station  
Powder X-ray diffraction end station

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**PUBLICATIONS**

- P.-H. Liu, K.-J. Chao, X.-J. Guo, K.-Y. Huang, Y.-R. Lee, C.-W. Cheng, M.-S. Chiu, and S.-L. Chang, *J. App. Cryst.* **38**, 211 (2005).
- K.-J. Chao, P.-H. Liu, and K.-Y. Huang, *C. R. Chimie*, **8**, 727 (2005).

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