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Complementary neutron and X-ray reflectivity for structural characterization of porous thin films

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Abstract

Neutron reflectivity (NR) and X-ray reflectivity (XR) have been measured for a silicon-gel-derived porous thin film, deposited on an oxide silicon wafer. The complementary NR and XR data provide a better determination of the film structure. With the two critical wavevectors for total reflection of neutrons and X-rays measured for the film, we have extracted the hydrogen content of the film. We have also discussed the strategy of using XR NR as a contrast to study the three-phase porous thin films.
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Keywords: X-ray reflectivity; Neutron reflectivity; Porous thin film; Contrast variation

1. Introduction

Low dielectric constant is one of the principal considerations in the selection of materials for advanced integrated circuit applications [1]. In recent developments, silicon-based porous materials, of a density much less than unity, have demonstrated many characteristics desired for inter-layer dielectric materials [1]. It is realized that the structure of a porous thin film influences strongly the related electric properties and mechanical strength. In addition, the pore size in the film needs to be small (compared to the feature size of microelectronic devices) and uniformly distributed for practical applications [1]. These requirements place strong demands on controlling and characterizing the microstructures of the thin films (for instance, silicon-gel-derived films) of a porous structure for low dielectric constant.

X-ray reflectivity (XR) and neutron reflectivity (NR) have long been used in revealing the depth density profiles and surface/interfacial structures of thin films of layering characteristics [2,3]. In this study, complementary XR and NR are adapted for studying a porous thin film. Since porous thin films usually have a large porosity ($\gtrsim 50\%$) and a low density or low scattering length density (SLD), the critical wavevector transfer of the films for total neutron or X-ray reflection Q_c is usually small, especially for neutrons ($\sim 0.005\,\text{Å}^{-1}$). High-resolution reflectivity is therefore advantageous in the studies on porous films. In this report, we discuss the strategy of using NR and XR as a contrast in revealing the porosity, the skeleton density and the hydrogen content of porous thin films.

2. Contrast variation for Q_c

The real part of the SLD ρ_r of a thin-film material determines the critical wavevector transfer $Q_c = 2(4\pi\rho_r)^{1/2}$ of the film for total neutron or X-ray reflection. For a smooth layer containing two phases, the mean critical wavevector averaged from the two phases is

$$Q_c^2 = 16\pi[(1-p)\rho_{1r} + p\rho_{2r}], \quad (1)$$

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where p is the volume ratio of phase 2 with an SLD of ρ_{2r}. For a porous film, namely $\rho_{2r} = 0$ for the pore phase, Eq. (1) reduces to $Q_c^2 = 16\pi(1-p)\rho_{1r}$. The chemical composition of the skeleton material of the porous film, determining the skeleton SLD ρ_{1r}, can be examined by the contrast S of the two Q_c values of the film measured for NR and XR, namely,

$$S = Q_{c,x}/Q_{c,n} = \left(\rho_{1r,x}/\rho_{1r,n}\right)^{1/2} = \left(\sum_i (b_{i,x})/\sum_i (b_{i,n})\right)^{1/2}. \quad (2)$$

In Eq. (2), x and n denote symbols for X-ray and neutrons, respectively, with b_i for the scattering lengths of the atoms in the film. Note that the density of the skeleton is not necessarily identical to the dense, non-porous prototype [4]. When the pores of the film are filled with organic solvent with a known and non-trivial ρ_s value, the porosity of the film can be determined from the shift ΔQ_c of Q_c of the film measured, with $p = [2(\Delta Q_c)Q_c + (\Delta Q_c)2]/16\pi\rho_s$ derived from Eq. (1). Once the porosity is determined, the skeleton density can be deduced.

However, the situation becomes complicated with existing sealed pores where no solvent can be filled. Thus, after saturated with solvent, the film becomes a three-phase system, namely the skeleton, the sealed pores, and the open pores (filled with solvent or solvent vapor) [5]. In this case, NR can provide an additional contrast to solve the skeleton density, open pole volume fraction p_1, and sealed pore volume fraction p_2. Three contrast conditions will be needed to solve the three parameters: e.g., XR for an as-prepared porous film and the film with solvent in the open pores, together with NR for the later case. The three conditions can be expressed as

$$Q_{c,x}^2 = 16\pi(1-p_1-p_2)\rho_{1,x} \quad \text{(XR)}, \quad (3.1)$$

$$Q_{c,x}^{s2} = 16\pi[(1-p_1-p_2)\rho_{1,x} + p_1\rho_{s,x}] \quad \text{(XR with solvent)}, \quad (3.2)$$

$$Q_{c,n}^{s2} = 16\pi[(1-p_1-p_2)\rho_{1,n} + p_1\rho_{s,n}] \quad \text{(NR with solvent)}. \quad (3.3)$$

Note that while Eqs. (3.2) and (3.3) are necessary, Eq. (3.1) can be either from XR or NR, since these two are linearly proportional and represent the same relation. Of course, there is no loss in having XR, NR, and more conditions obtained from deuterated solvent for contrast variation, as they can serve as a consistency check and give a better accuracy in the three parameters p_1, p_2, and ρ_1 determined from the over-sampling. Three-phase porous films have also been discussed previously [6].

3. Experimental section

A xerogel film was spun from an organic solvent slurry on a Si(0 0 1) wafer with a 1000 Å thick SiO_2 overlayer. The xerogel film, of ~5000 Å thickness, was then cured through a sol–gel process and dried under atmospheric pressure. Composition $SiO_{2.2}C_{0.6}$ for the film was determined using Rutherford back-scattering spectrometry (RBS). However, information of hydrogen was missing in the measurement, since hydrogen, being lighter than the α-particles used in RBS, did not possess a back-scattering signal [6]. Nevertheless, existence of hydrogen in this type of porous films has been observed by Wu et al. using modified RBS with forward scattering of α-particles [6].

XR for the xerogel sample (92 × 64 mm) was measured on the eight-circle diffractometer at the wiggler beamline BL17B in the National Synchrotron Radiation Research Center. Three pairs of slits were used to shape a monochrome beam of 8 keV (1.55 Å) photons into a highly collimated beam of dimensions of 0.6 mm × 0.2 mm ($H \times V$) at the sample position. The setup, described in our previous report, provided a Q-resolution of 0.0003 $Å^{-1}$ in the reflectivity measurement [7]. On the other hand, with the long-wavelength 8.8 Å neutron beam of the MINE-2(C3-1-2-2) neutron reflectometer at the JRR-3 M reactor, Japan, reflectivity scan down to $Q = 0.0025\,Å^{-1}$ with a resolution of 0.0002 $Å^{-1}$ for the film was achieved.

4. Result and discussion

Inset of Fig. 1 shows the high-resolution XR of the xerogel film, with two clear maxima at $Q_{c,x} = 0.0145 \pm$

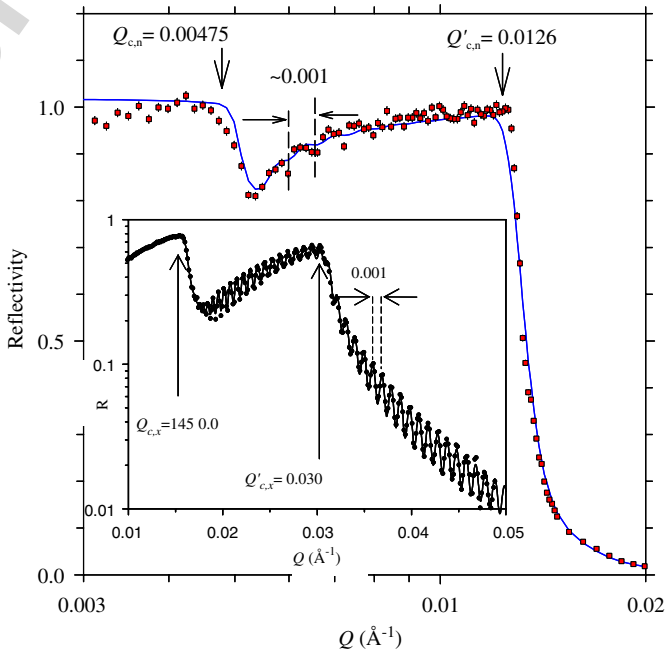

Fig. 1. NR and XR (inset) data for a xerogel film. In the inset, XR data exhibit clearer oscillation characteristics than NR data between the two intensity maxima, due to a better contrast of the film with air and the SiO_2 layer for X-rays. The solid curve in the inset is a simulation dominated mainly by a 5800 Å thick xerogel layer of density 0.50 ± 0.03 g/cm^3, sitting on a SiO_2 layer ($d = 2.18$ g/cm^3). Note that SLD of SiO_2 is close to the Si substrate. With similar density (0.5 g/cm^3) and thickness (5740 Å), we can reproduce a reasonable reflectivity profile for neutron data (solid curve). In the neutron case, the SLD of SiO_2 differs significantly from that for the Si substrate, and has to be taken into account in the fitting process.

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$0.0003\,\text{Å}^{-1}$ and $Q'_{c,x} = 0.030\,\text{Å}^{-1}$ identified, respectively, for the total external reflection of the xerogel film and the SiO_2 overlayer on Si wafer. For $Q \leqslant 0.0145\,\text{Å}^{-1}$, the reflectivity is not unity due to the finite sample size, which cannot intercept the full beam at the small incidence. Pronounced oscillations with a period $\Delta Q \sim 0.001\,\text{Å}^{-1}$ are observed and attributed to Kiessig fringes originating from the xerogel film. A thickness of 6200 Å for the film can be estimated from the oscillation period using $2\pi/\Delta Q$. On the other hand, NR data for the same film (Fig. 1) demonstrate two similar maxima at $Q_{c,n} = 0.0047 \pm 0.0003\,\text{Å}^{-1}$ and $Q'_{c,n} = 0.0130 \pm 0.0003\,\text{Å}^{-1}$ as those observed in X-ray data. Oscillations with a ΔQ-spacing resembling that in X-ray data are barely discernable in the Q region between the two Q_c of the xerogel and the SiO_2 layers.

From XR and NR data, the contrast $S = Q'_{c,x}/Q'_{c,n}$ deduced for the SiO_2 layer of the film is 2.31 ± 0.07, which matches well with the value 2.32 calculated using Eq. (2) with $b_{i,x} = 84.84\,\text{fm}$ and $b_{i,n} = 15.77\,\text{fm}$ of the SiO_2 layer. On the other hand, $S = 3.1 \pm 0.1 (= Q_{c,x}/Q_{c,n})$ deduced for the xerogel film deviates significantly from the value 2.2 calculated using the composition $SiO_{2.2}C_{0.6}$ measured from RBS. This discrepancy implies the possible existence of hydrogen in the film, as discussed previously [6]. To have a consistent S value for the xerogel layer, we have to include a hydrogen content (of a negative $b_H = -3.739\,\text{fm}$) in the xerogel composition. Using Eq. (2) with the measured S value, we deduced a composition $SiO_{2.2}C_{0.6}H_{2.5}$ for the xerogel film. With the H-included composition of the xerogel layer and the $Q_{c,x}$ measured, we also calculate a mean density of $d = 0.47 \pm 0.03\,\text{g/cm}^3$ for the porous xerogel layer (i.e., $d = (1-p)d_w$, where d_w is the density of xerogel skeleton) using Eq. (1). A linear X-ray absorption coefficient $\mu = 14.3\,\text{cm}^{-1}$ of the film for 1.55 Å X-rays can be derived using the mean density and the composition. From μ and the reflectivity 0.7 at $Q'_{c,x} = 0.03\,\text{Å}$, we can estimate the xerogel film thickness $t \sim 4600\,\text{Å}$ using $R = \exp(-\mu l)$, with the path length of X-rays inside the xerogel film $l = 8\pi t/(Q\lambda)$. The model-independent structural parameters estimated, although not with high accuracy, serve a good reference in data fitting (curves shown in Fig. 1) for a consistent model of the SLD profile of the film [8]. On the other hand, neutron incoherent scattering by hydrogen in the xerogel film dominates the neutron intensity loss in the dip region between the two critical Q_c values. Taking into account the incoherent scattering effect, we can also model the NR profile reasonably well with similar structural parameters as those obtained in the X-ray case (see Fig. 1).

5. Conclusions

Using XR and NR as a contrast variation in the study of a xerogel film, we have model-independently deduced certain structural parameters of the film. Especially, neutron data in this study, being more sensitive to hydrogen than X-rays, are advantageous in the determination of hydrogen content of the xerogel film.

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