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

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Elsevier use only: Received date here; revised date here; accepted date here

Abstract

Neutron and X-ray reflectivity have been measured for a silicon-gel-derived porous thin film, deposited on an oxide silicon wafer. The complementary neutron and X-ray reflectivity 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 X-ray and neutron reflectivity as a contrast to study the three-phase porous thin films. © 2001 Elsevier Science. All rights reserved

Keywords: X-ray reflectivity; neutron reflectivity; porous thin film, contrast vairation

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 interlayer 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 and neutron reflectivity 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 neutron and X-ray reflectivity (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, the critical wavevector transfer of the films for total neutron or X-ray reflection Q_c usually is small, especially for neutrons (~0.005 Å^{-1}). High resolution reflectivity is therefore advantageous in the studies of porous films. In

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this report, we discuss the strategy of using neutron and X-ray reflectivity 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 scattering-length-density (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

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

where p is the volume ratio of phase 2 with a 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 scattering-length-density ρ_{1r}, can be examined by the contrast S of the two Q_c values of the film measured for neutron and X-ray reflectivity, namely,

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

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, the density of the skeleton is not necessarily identical to the dense, nonporous 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, 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, neutron reflectivity can provide an additional contrast to solve the skeleton density, open pore volume fraction p_1, and sealed pore volume fraction p_2. Three contrast conditions will be needed to solve the three parameters. For instance, X-ray reflectivity for an as-prepared porous film and the film with solvent in the open pores, together with neutron reflectivity for the later case. The three conditions can be expressed as:

$$Q_{c,x}^2 = 16\pi(1-p_1-p_2)\rho_{1,x}$$
$$\text{or } Q_{c,n}^2 = 16\pi(1-p_1-p_2)\rho_{1,n}, \quad \text{(XR or XN)} \quad (3\text{-}1)$$

$$Q^s_{c,x}{}^2 = 16\pi[(1-p_1-p_2)\rho_{1,x} + p_1\rho_{s,x}], \text{ (XR with solvent)} \quad (3\text{-}2)$$

$$Q^s_{c,n}{}^2 = 16\pi[(1-p_1-p_2)\rho_{1,n} + p_1\rho_{s,n}]. \text{ (NR with solvent)} \quad (3\text{-}3)$$

Note, while Eq. (3-2) and (3-3) are necessary, Eq. (3-1) can be either from XR or NR, since these two are linear proportional and represent the same relation. Of course, there is no loss to have 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(001) 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 backscattering 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 forwards scattering of α particles [6].

X-ray reflectivity 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 (NSRRC). 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×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-3M 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 X-ray reflectivity of the xerogel film, with the two clear maxima at $Q_{c,x}$ = 0.0145±0.0003 $Å^{-1}$ and $Q'_{c,x}$ = 0.030 $Å^{-1}$ identified, respectively, for the total external reflection of the xerogel film and the SiO_2 overlayer on Si wafer. For $Q \le 0.0145$ $Å^{-1}$, 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 $\Delta Q \sim 0.001$ $Å^{-1}$ 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, the neutron reflectivity data for the same film (Fig. 1) demonstrate two similar maxima at $Q_{c,n}$ = 0.0047±0.0003 $Å^{-1}$ and $Q'_{c,n}$ = 0.0130 $Å^{-1}$ as those observed in the X-ray data. Oscillations with a ΔQ-spacing

resembling to 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.

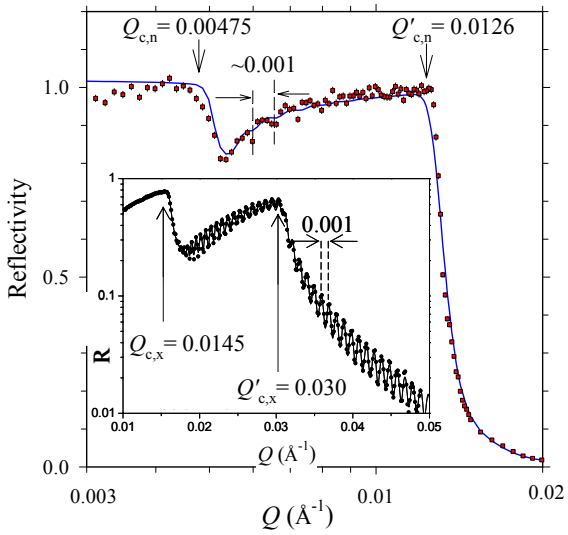

Fig. 1. Neutron and X-ray (inset) reflectivity data for a xerogel film. In the inset, the X-ray reflectivity data exhibit clearer oscillation characteristics than that in neutron reflectivity data between the two intensity maximum, due to a better contrast of the film with air and the SiO_2 layer for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

From the 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 fm and $b_{i,n}$ = 15.77 fm of the SiO_2 layer. On the other hand, the S value 3.1±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 fm) in the xerogel composition. Using Eq. (2) with the measured S value, we have 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±0.03 g/cm^3 for the porous xerogel layer (i.e. $d = (1\text{-}p)d_w$ with the density of xerogel skeleton d_w) using Eq. (1). A linear X-ray absorption coefficient μ = 14.3 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 Å^{-1}, we can estimate the xerogel film thickness t ~ 4600 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 the data fitting (curves shown in Fig. 1) for a consistent model of the scattering-length-density 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 neutron reflectivity profile reasonably well with similar structural parameters as those obtained in the X-ray case (see Fig. 1).

5. Conclusions.

Using X-ray and neutron reflectivity as a contrast variation in the study of a xerogel film, we have model-independently deduced certain structural parameters of the film. Especially, the 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.

Acknowledgements.

We thank Drs. C. Jin and T.-M. Lu for providing the sample. The NR measurements were performed with the approval of the Neutron Scattering Program Advisory Committee (Proposal No. 4610). This research was partially supported by the NSC under the grant No. NSC-93-2112-M-213-011.

References

[1] C. Jin, S. List, and E. Zielinski, Mat. Res. Soc. Proc. 511 (1998) 213.
[2] L.G. Parratt, Phys. Rev. 95 (1954) 359.
[3] J. Als-Nielsen, D. Jacquemain, K. Kjaer, F. Leveiller, M. Lahav and L. Leiserowitz: Phys. Rep. 246 (1994) 251.
[4] K. Maexa, M. R. Baklanov, D. Shamiryan, F. Iacopi, S. H. Brongersma, Z. S. Yanovitskaya, J. Appl. Phys. 93 (2003) 8793.
[5] W.-L. Wu, W. E.Wallace, E. K. Lin, G. W. Lynn, J. Appl. Phys. 87 (2000) 1193.
[6] W.-L. Wu, E. K. Lin, C. Jin, J. T. Wetzel, Mat. Res. Soc. Symp. Proc. 612 (2000) D5.22.2.
[7] C.-H. Hsu, H.-Y. Lee, K. S. Liang, U. Jeng, D. Windover, T.-M. Lu, C. Jin, Mat. Res. Soc. Symp. Proc. 612 (2000) D5.23.1.
[8] C.-H. Hsu, U. Jeng, H.-Y. Lee, C.-M. Huang, K. S. Liang, D. Windover, T.-M. Lu, C. Jin, Thin Solid Films, 472 (2005) 323.