Comparative Study of Porous SOG Films with Different Non-destructive Instrumentation

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Abstract

Porosity and pore size of siloxane-based porous spin-on-glass (SOG) thin films are comparatively studied with different non-destructive methods and also with reference nitrogen porosimetry. The pore size and its spread are found to increase with increasing porosity, or with decreasing dielectric constant.

Introduction

The use of porous dielectric films is of considerable interest in the ULSI technology to near the ultimate dielectric constant of unity (1–3). Silica-based SOG films have been thought to be the most feasible because of their potential compatibility with conventional Si technology and also because of the high thermal and mechanical stability of the siloxane network. Pore size and its distribution are crucial properties of porous materials. The maximum pore size must be sufficiently smaller than the minimum feature size of device components. Mechanical strength, electrical and thermal stability, and thermal conductivity have a close relationship with the structure of the SOG backbone. Characterization of pore size helps to have better understanding of the backbone structure and to improve these properties.

There are many established methods for determining the pore size and pore size distribution (PSD) of porous media, such as mercury porosimetry and sorption porosimetry. These methods are based on the permeation of a probe substance -usually liquid or gas - into the pores. Since thin films have too small total pore volume and surface area, the traditional porosimetries are hardly applicable to thin films. Recently, advanced non-destructive methods, such as ellipsometric porosimetry (EP) (4), small-angle neutron scattering spectroscopy (SANS) combined with specular X-ray reflectivity (SXR) (5), positronium annihilation lifetime spectroscopy (PALS) (6), have been successfully applied to determining the pore size and PSD of thin porous films. Although these new techniques are based on different physico-chemical principles, few systematic studies have been so far reported on crossover experiments using the same specimens.

In this paper, we report EP, SANS/SXR, PALS and conventional N_2 (BJH) porosimetry results obtained comparatively from the same set of low-k porous SOG films. Different types of SOG having different porosity and composition are used in order to perform reliable experiments and to study the effect of porosity on pore size and PSD.

Results and discussions

Hydrogen and methyl-siloxane-based porous SOGs, synthesized by CCIC (IPS) and Dow Corning (XLK) are formed on Si wafers. Details about this type of SOG are documented elsewhere (7,8). Table I summarizes film properties used in this work. The dielectric constants are 1.8-2.5. The wafers are divided into pieces and are subjected to different instrumental analyses of pore size. Four different methods are used in the round robin experiments. Two of them are sorption porosimetry (EP (4) and BJH porosimetry (9)) and the others are radiation beam-based (SANS/SXR (5) and PALS (6)). Bulk specimens are used only in the BJH porosimetry - i.e., it is film-destructive.

Table I. Properties of the films measured on-site.

Sample	Refr. index (633 nm)	Thickness (A)	K
RR18	1.198	2549	1.8
RR20	1.223	4029	2.0
RR22	1.257	4172	2.2
RR25	1.317	3973	2.5

The results are summarized in Table II and Fig.1. The porosity is determined in the EP and SANS/SXR experiments, and the film thickness is determined using EP and SXR. Characteristic pore size has practically the same meaning as pore diameter defined in conventional porosimetry. The primary parameter measured in the sorption method is the amount of adsorbed substance. The PSD is determined from capillary and layer condensation theories of gaseous adsorptive (9). EP is based on *in-situ* ellipsometric measurement arranged to detect a small

change of optical parameters upon sorption - toluene in our case. Average pore diameters for specimens RR18-RR25 are shown in Table II.

Table II. Summary of PSD analysis.

Sample	Characteristic Pore Size (A)			
	EP	BJH	SANS/SXR	PALS
RR18	84±2	70	62±8	82±9
RR20	90±3	92	61±6	73±5
RR22	57±2	63	50±4	57±2
RR25	31±4	33	27±3	39±2
Sample	Porosity (%)		Thickness (nm)	
	EP	SANS/XR	EP	SXR
RR18	53±4	37±7	265±1	265±1
RR20	45±2	33±6	418±1	424±1
RR22	39±4	26±5	427±1	424±1
RR25	26±4	20±7	410±1	427±1

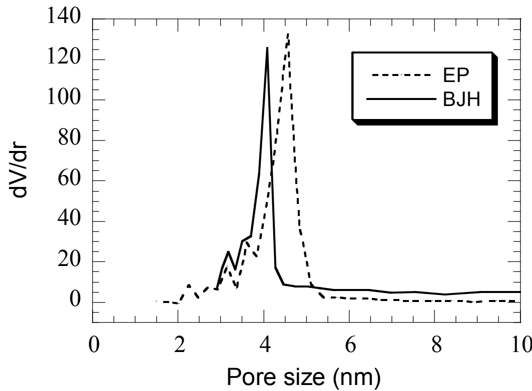

Fig.1. Characteristic pore size of XLK 2.0 measured by EP and BJH porosimetry (10). PALS pore size is 4.4 nm.

The trend is the average pore diameter increases as k decreases. However, specimen RR18 has an exceptionally smaller pore size than RR20. The BJH porosimetry, being regarded as a standard technique for porosity characterization (Quantachrome Autosorb-6 sorption analyzer). The average pore diameter obtained show good agreement with the EP data, including the inversion of pore diameters of RR18 and RR20. Cumulative pore volumes are 0.98, 0.88, 0.70, and 0.35 (ml/g) for RR18, RR20, RR22 and RR25, respectively, which shows consistent agreement with the change of k. Because the adsorptive vapor is not accessible to closed pores, traditional ways of the N_2 sorption porosimetry is not capable of detecting inaccessible (closed) pores. A unique feature of the EP is that the amount of the closed pore can be determined with a multiangular and/or spectroscopic ellipsometry arrangement where a dielectric model that the film consists of solid part +open porosity filled with adsorptive +closed pore is assumed. It is found that the pore connectivity, the ratio of open porosity to total porosity increases from 86% (RR25) to 97%(RR18), as k decreases. The determined full porosity (Table II) is seen to consistently increase as k decreases.

In the radiation beam-based porosimetry techniques - SANS/SXR and PALS - the signal from the specimen is analyzed. The primary beam interacts with pores and/or wall material and bears the information of pore structure. The pore size is extracted from the recorded signal, assuming pore geometry and physical interaction between the beam and pore. In SANS/SXR experiments, Rutherford Backscattering Spectrometry (RBS) and Forward Recoil Elastic Scattering (FRES) are also employed, and film thickness, wall density, overall film density, porosity, average pore chord length (pore size), and elemental composition are characterized.

In SANS, the absolute scattered neutron intensity, I, plotted against the scattering vector (q) where $q = (4\pi/\lambda)\sin(\theta/2)$ and θ is the scattering angle from the incident beam path and λ is the neutron wavelength (6 A). For these samples, the scattering data from each sample are well described by the random two-phase model of Debye. Quantitative analyses are made in the following way (5). From the SANS experiments, parameter, which involves the porosity and wall density, is determined, assuming a random two-phase (void +solid) structure. The film thickness and overall electron density are evaluated by the SXR measurements and are combined with the film composition data obtained by RBS and FRES so that the overall film density is determined. Since the overall film density is also a function of the porosity and wall density, these values are independently obtained using the parameter. The results are shown in Table II. It is obvious that the average pore size increases with increasing porosity. These pore size values are similar to those obtained from the sorption porosimetry measurements. It is also seen that the average film density decreases with increasing porosity (1.082, 0.939, 0.833,and 0.727 (g/cm^3) for RR25, RR22, RR20 and RR18, respectively). Film thickness data calculated from SXR are in good agreement with the data from EP, where the difference is within 4%.

In using PALS, films are irradiated with a focused positron beam. Positron forms positronium -the electron-positron bound state - that is trapped in the pores where its natural lifetime of 142 ns is reduced by annihilation during collisions with the pore surfaces. Thus, the reduced lifetime can be correlated with pore size. Positronium lifetime histograms are recorded, and the lifetime distribution curves are obtained with a fitting program specified for this purpose. The distribution curves are transformed into pore

size data, using pore geometries of three-dimensional cubes or two-dimensional infinitely long squared channels (6). It is noted that the discrepancy between the two models is found not very significant. The PALS data shown in Table II are deduced using an infinitely long square channel pore model, where the pore size is the side length corresponding to a tubular pore diameter. The pore size increases with decreasing k, and the values are very similar to those obtained by other techniques. In all four films the pores are found to be nominally fully interconnected.

A crucial issue of this study is to demonstrate specific tendencies and characteristics of the pore data of each method. The instrumental ways employed in this study are based on different physico-chemical principles. The primary experimental parameters acquired during measurements are not pore size itself. In order to determine the pore size and porosity, it is necessary to transform the raw data by assuming an appropriate model that takes into account pore structure and pore-probe interaction. That is, the results can be highly model dependent. Sorption porosimetry reflects pore surface geometry and SANS reflects spatial density of scattering bodies, either voids or particles. PALS is more related to the volume of void elements. For these reasons, we must emphasize that perfect agreement cannot be obtained. Besides the above points, it can be safely said that successful agreement is obtained.

The difference in pore size between the results is not significant. The dependence of porosity on k is reasonable. It is also found that the spread of pore size increases with average pore size. This phenomenon is a general feature of the SOG films (11) and we observed it in different types of low-k SOG films (Fig.2).

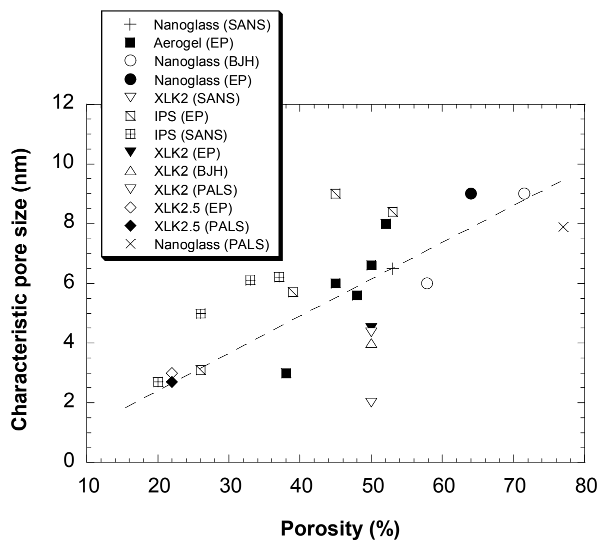

Fig.2. Dependence of pore size of different SOG films on film porosity.

To investigate the dependence of the pore parameters on porosity is, in fact, another point of this work. Porosity is more or less predictable from k. However, the pore size and PSD cannot be uniquely determined by k. The consistency between porosity, pore size, its spread, and k is observed regardless of experimental methods. Therefore, it can be concluded that the porosity can be used as a representative measure of PSD, more specifically, average pore size. We speculate that this is a common feature of silica-based porous SOG thin films synthesized through sol-gel technique. There is seen, however, small inconsistency in the data of RR18 and RR20. Both EP and BJH data show that RR18 has a smaller pore size than RR20.The SANS/SXR data show that these specimens have almost identical pore size. However, specimen R18 has the largest pore size in the PALS analysis. This discrepancy may reflect the limitation of pore analysis techniques when pore size and/or PSD is large. Authors are now in the process of collecting more data of various porous thin films synthesized by different methods. Some of them will be presented at the conference.

Summary

EP, BJH, SANS/SXR, and PALS are comparatively used to evaluate pore size and porosity of siloxane-based SOG thin films having different k values (k =1.8 - 2.5). The porosity and pore size data show good agreement regardless of the instrumental ways. The pore size and its spread are found to increase with increasing porosity, or with decreasing k. From a methodology point of view, we conclude that any methods employed in this study are appropriate for characterizing pore.

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