Available online at www.sciencedirect.com
ScienceDirect
Applied Surface Science 254 (2007) 473–479
applied surface science
www.elsevier.com/locate/apsusc

Structural study of nanoporous ultra low-*k* dielectrics using complementary techniques: Ellipsometric porosimetry, X-ray reflectivity and grazing incidence small-angle X-ray scattering

V. Jousseaume [a,1], G. Rolland [a,2], D. Babonneau [b,3], J.-P. Simon [c,*]

[a] *CEA-DRT-LETI–CEA/GRE, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France*
[b] *Laboratoire de Métallurgie Physique, UMR 6630 CNRS, Poitiers, BP30179, 86960 Futuroscope Cedex, France*
[c] *CNRS/INPG/UJFGrenoble-SIMAP, B75, 38402 St Martin d'Hères, France*

Received 14 February 2007; received in revised form 13 June 2007; accepted 14 June 2007
Available online 28 June 2007

Abstract

This paper is focused on nanoporous methylsilsesquioxane deposited using a polymer approach and shows the complementarities of three experimental techniques: ellipsometric porosimetry (EP), X-ray reflectivity (XRR), and grazing incidence small-angle X-ray scattering (GISAXS). XRR and EP confirm that the pore volume fraction is larger for smaller dielectric constants. EP and GISAXS find mean pore sizes independent of the porosity, in the range 3–4 nm as diameter. GISAXS is the only technique that can estimate the porosity isotropy. Finally, the impact of integration processes such as surface plasma treatment, etching or stripping on the porosity is evaluated: the porosity remains unchanged except in the superficial layer where an increase of the pore size (or of the roughness) is observed.

PACS : 61.10.e; 61.18.j; 61.72.Dd; 61.82.Ms; 68.55.a

Keywords: Porous ultra low *k* dielectrics; Materials for microelectronics; Structural determination; GISAXS; XRR; Ellipsometric porosimetry

1. Introduction

Considerable attention has been focused on the replacement of silicon dioxide, the traditional interconnect dielectric material, with new materials having a lower dielectric constant (k) to reduce the capacitive delay and the power consumption. It is generally agreed that decreasing the dielectric constant below 2.5 is possible only by incorporation of voids in an insulating matrix [1–3]. Among all ultra low k (ULK), SiOCH based materials are the most mature material for a potential integration. The introduction of porosity in a SiOCH insulating matrix can be obtained by different techniques. For spin coated layers, the main ways reported in the literature are through sol-gel processes [1,3,4 and references cited therein] or by using porogen approach (using a mixture of a matrix and a sacrificial material called porogen) [3,4 and references cited therein, 5,6]. In both techniques, the deposition step is followed by a thermal treatment, sometimes UV assisted or electron-beam assisted. In the case of the porogen approach, which can also be performed by using plasma enhanced chemical vapour deposition, the sacrificial material is thermally decomposable and its decomposition allows the formation of voids in the insulating matrix. An alternative is to use a solution of partially cross-linked silsesquioxane oligomers with terminal silicon atoms carrying a hydroxyl group. This silanol can condense during curing to give a three-dimensional cross-linked network. The molecular structure and the porosity can be controlled by adjusting the content of functional end group, Si–OH and the ratio of cage to network structure [7–9 and references cited therein].

An ideal porous material would consist of a network of closed, small pores with narrow size distribution. However, when the porosity is above the percolation threshold, pores are

* Corresponding author. Tel.: +33 4 76 82 66 13; fax: +33 4 76 82 66 44.
E-mail addresses: vincent.jousseaume@cea.fr (V. Jousseaume), guy.rolland@cea.fr (G. Rolland), david.babonneau@univ-poitiers.fr (D. Babonneau), jean-paul.simon@ltpcm.inpg.fr (J.P. Simon).
[1] Tel.: +33 4 38 78 95 22; fax: +33 4 38 78 54 59.
[2] Tel.: +33 4 38 78 31 43.
[3] Tel.: +33 5 49 49 67 25; fax: +33 5 49 49 66 92.

0169-4332/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2007.06.043

interconnected. Characterization and understanding of pore size and interconnectivity are important to optimize the design of porous material. The structural characterizations of such type of porous dielectrics are few. X-ray reflectivity (XRR), which gives the global electronic density (skeleton plus pores) through the determination of the critical angle, allows the volume fraction of the pores to be evaluated if the skeleton composition and density is known. Moreover, from the periodicity of the Kiessing's fringes, the layer thickness can be evaluated and from their damping the interfacial roughness. Ellipsometric porosimetry (EP) is based on the adsorption and condensation of organic vapours in the pores and the determination of the adsorbate amount based on measurement of refractive index changes [10]. This technique allows the mean pore diameter to be determined and the pores size distribution in the case of connected pores. To better characterize sizes and patterns of the pores, transmission electron microscopy (TEM) and small-angle scattering (SAS) are complementary: TEM micrographs would image voids if the thinning of slices did not deformed this weak structure. On the other hand, SAS (X-rays or neutrons) techniques are well known methods to characterize nano-objects (1–100 nm), and are generally used in transmission. The wafer should be thinned from the back-side down to 0.05 mm giving an overall transmission ~0.4, so that the signal of ULK thin films is found too weak, even with a synchrotron source. Alternatively, in the grazing incidence geometry (GISAXS), the signal is multiplied by a factor of ~200 for a grazing angle $\alpha_i = 0.3^\circ$ above the critical angle for total reflection of Si, $\alpha_{c\text{-}Si} = 0.22^\circ$ at 8 keV. The GISAXS technique is in rapid expansion following the one of nanotechnologies. They tackle different fields in hard condensed matter such as superficial dots (metallic or quantum dots) [11,12], implanted defects such as He bubbles for silicium purification [13,14] or co-deposited nitride-metal layers for their optical and magnetic properties [15,16]. The structural information's by GISAXS on ULK films is exploding, as witnessed by the numerous contributions on GISAXS in the last "SAS2006" conference proceedings [17]. The most complete GISAXS study on porous MSQ films using dendritic spheres as porogens has been given by Ree's group [3,18]: they always obtained abrupt interfaces and they discussed the pores size and size distribution with respect to the void volume fraction.

The aim of this paper is to highlight the pertinence of EP, XRR and GISAXS for the characterization of ULK thin film porosity. After a description of the experimental methods based on the full characterisation of an ULK film with $k = 2.2$ (Section 2), the presentation and discussion of the results will cover the influence of the porosity increase on the pore size and the impact of microelectronic processes (adhesion plasma, etching, stripping, pore sealing) on the pore pattern, shape and volume fraction (Section 3).

2. Experimental techniques

2.1. Deposition of ULK films

For the material deposition, a solution of partially cross linked silsesquioxane oligomers was used. Terminal silicon atoms carry a hydroxyl group which can condense during curing to give a three-dimensional cross linked network. The molecular structure can be controlled by adjusting the content of functional end group, Si–OH and the ratio of cage to network structure [7]. In this work, different solutions (in propylene glycol methyl ether acetate) were spin coated on a 200 mm silicon substrate by conventional spin-coating on a TEL Mark 8 track. After baking at low temperature (<300 °C) to evaporate the solvent, spin-coated films of thickness lower than 400 nm were then thermally cured in a furnace at a temperature range of 400–450 °C for 30 min. The thermal annealing causes a film thickness decrease of about 5% due to material crosslinking, structural rearrangements and nanopores forming in the case of porous films. Depending on the chemical composition of the solution, materials with k values in the range 2.0–3.0 were successfully deposited.

2.2. Ellipsometric porosimetry

The experimental process for ethanol sorption was as follow: the samples were introduced into a vacuum cell on a visible spectroscopic ellipsometer for optical measurements at an incidence angle of 75°. Prior to ethanol introduction, the cell was pumped down to 10^{-6} Torr in order to empty the pores in the samples. The ethanol pressure was then increased until saturation to measure the adsorption branch and finally decreased to obtain the desorption one. At each step of the sorption process the ellipsometric parameters ($\tan \Psi$, $\cos \Delta$) were measured in the range of 0.3–0.8 μm. Ellipsometric parameters were adjusted by assuming a one-layer model. Refractive index (at 633 nm) as a function of the relative pressure of ethanol is deduced from the ellipsometric data fitting. The different stages of solvent condensation in the pores of a sample are usually described by dividing the isotherm sorption curve in four main domains (Fig. 1a). At very low relative pressure, the filling of the micropores (pores smaller than 2 nm) and the first condensation layer on the walls of the mesopores (pores between 2 and 50 nm) takes place. The next stage, which occurs until the relative pressure corresponding to the beginning of the hysteresis loop is attained, represents the multilayer coverage part, where the thickness of the layer condensed on the pores walls increases progressively with the pressure. The hysteresis region corresponds to the abrupt filling of the mesopores by capillary condensation: the sharper the slope, the narrower the distribution. The near horizontal plateau at higher relative pressure assures that there is no larger mesopores to be filled. The pore distribution (Fig. 1b) can be obtained from these isotherms by using the Kelvin theory [10]. Results obtained for the ULK film with $k = 2.2$ are summarized in Table 1.

Let us point out the nature of uncertainties for further discussion: the volume fraction is obtained by a mixing law taking the bulk silica refractive index for the skeleton one. In this case, the estimated volume fractions are probably over evaluated.

2.3. X-ray reflectivity

X-ray reflectivity was performed to determine the critical angle $\alpha_{c\text{-}ULK}$ and the thickness t of the ULK films. XRR