



Characterization of spin-on zeolite films prepared from Silicalite-1 nanoparticle suspensions

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ABSTRACT

Spin-on porous films were prepared on silicon wafers using Silicalite-1 nanozeolite suspensions crystallized from clear solution. The content and size of Silicalite-1 nanocrystals and of residual ~2–4 nm nanoparticles in the starting suspensions were varied by varying the crystallization time. The films were characterized using scanning electron microscopy, X-ray diffraction, spectroscopic ellipsometry, atomic force microscopy, Fourier transform infrared spectroscopy, ellipsometric porosimetry, impedance analysis and nanoindentation. All the properties of spin-on Silicalite-1 films strongly depended on the composition of the Silicalite-1 suspensions spun onto the support. With increasing Silicalite-1 nanocrystal content, crystallinity, hydrophobicity and porosity increased, while elastic modulus, homogeneity, roughness, and dielectric constant decreased. Their implementation in on-chip interconnects is discussed.

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1. Introduction

The dielectric constant (*k* value) is a critical parameter in micro and nanoelectronics and needs to be minimized for future down-scaled technology. The classic interlayer dielectric (ILD) material in on-chip interconnects is non-porous silica having a *k* value of ~4. Increasing the porosity in a material is one possible strategy to achieve a low *k* value. Among other materials porous organosilicate SiCOH glasses have been studied for this purpose [1,2]. Thanks to their organic moieties and porosity, these materials have reasonably low dielectric constants (*k* ~ 2, 3). However, they show poor mechanical properties limiting their implementation in the technically demanding environment of on-chip interconnects [1,2]. As an alternative, pure-silica zeolites have been proposed because their porous crystalline nature offers both a stiffer skeleton and the porosity needed to obtain a lower dielectric constant [3–6]. Synthesis methods of films containing pure-silica zeolite MFI (i.e., Silicalite-1) crystals include in-situ crystallization, [7] vapor-phase synthesis, [8] dip-coating, [9] and spin coating [3–5,10,11]. The latter technique offers advantages in scalability to large supports like silicon wafers [4,12]. A typical Silicalite-1 precursor suspension for spin coating contains Silicalite-1 nanocrystals of 40–80 nm and residual silica [4,5]. Beside potential application in

on-chip interconnects zeolite films also are promising for further applications in fields of traditional zeolite utilization such as molecular separation processes, [13] chemical synthesis, [14] and sensors [15].

In earlier research, the pore size distribution of spin-on Silicalite-1 films was estimated by means of nitrogen adsorption porosimetry on powdery Silicalite-1 products processed in a similar way as the films [4,5,16]. Nitrogen adsorption isotherms typically comprise a low pressure uptake ($P/P_0 < 0.1$) and a high pressure uptake ($P/P_0 = 0.85-1$) with hysteresis extending to the relative pressure range 0.40–0.50. The uptake at low pressures is attributed to Silicalite-1 micropores (~6 Å). Hysteresis is ascribed to capillary desorption from a meniscus formed in pores with diameters of 2.6–4 nm estimated using Barrett–Joyner–Halenda (BJH) method. However, comparison between nitrogen and argon adsorptions has shown that there is no capillary desorption but cavitation desorption [17]. The porosity of actual spin-on Silicalite-1 films has been investigated using ellipsometric porosimetry (EP) [17]. Those investigations have revealed the presence of voids of a few tens of nanometers wide. Moreover, the number and width of interstitial voids increases with the crystallization time of the Silicalite-1 suspension. This phenomenon has been explained based on the composition of the suspensions used for spin coating [17]. After short crystallization times, the content of Silicalite-1 nanocrystals is low. Silica is mainly present as colloidal precursors of ~2–4 nm and some silicate oligomers [18–26]. Upon prolongation

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of the crystallization the content of precursor silica decreases in favor of Silicalite-1 nanocrystals [17,25]. When using well crystallized suspensions, the quantity of precursor silica does no longer suffice to fill the interstitial nanocrystals void volumes and large voids remain in the films [17].

In this paper, we provide an extensive characterization of spin-on Silicalite-1 films prepared from suspensions with different crystallization times to reveal the influence of the Silicalite-1 content of the films on key properties for the application in on-chip interconnects. We characterized the porosity via ellipsometric porosimetry with toluene probe molecule. Structural and morphological characterization was done via X-ray diffraction, atomic force and scanning electron microscopy, spectroscopic ellipsometry and nanoindentation. The hydrophobicity was evaluated using Fourier transform infrared spectroscopy, ellipsometric porosimetry with water adsorbate, and impedance analysis.

2. Experimental

2.1. Film preparation

Spin-on Silicalite-1 films were synthesized following a recipe described by Wang et al. [4]. Clear Silicalite-1 synthesis solution was prepared by mixing tetraethyl orthosilicate (TEOS, 98%, Acros), tetra-n-propylammonium hydroxide (TPAOH, 40%, Alfa-Aesar), double deionized water and ethanol in a ratio after hydrolysis of the TEOS of 25 Si: 9 TPAOH: 360 water: 200 ethanol. The resulting clear solution was stirred for 3 days at room temperature in a closed autoclavable polypropylene bottle. The aged solutions then were heated to 80 °C and kept at this crystallization temperature for different times between 3 and 5 days. The resulting suspensions contained both Silicalite-1 nanocrystals next to residual colloidal Silicalite-1 precursors and oligomers. These suspensions were quenched, centrifuged at 5000 rpm for 30 min, and filtered through 200 nm PTFE filters to remove possible dust and occasional large crystallites (>200 nm). Composition and particle distribution in the filtered solutions did not change in any significant amount. Films were deposited on 2×2 cm² pieces of Si-p and Si-n⁺⁺ wafers. The latter only were used for impedance measurements. The deposition was carried out by fully wetting the Si pieces with suspension and successively spinning up to 3300 rpm. This velocity was achieved with an acceleration of 1300 rpm/s and was kept for 30 s. The films were dried overnight at 80 °C before calcination on preheated plates at 450 °C in air. The temperature in the films reached 425 °C and was kept constant for 3 h.

2.2. Characterization of Silicalite-1 suspensions

Particle-size analysis on prepared suspensions was carried out by dynamic light scattering (DLS) on an ALV-NIBS high performance particle sizer, and corrected for variation in viscosity measured with a viscometer AMVn Anton Paar. To quantify the Silicalite-1 nanocrystal content in the prepared suspensions, these were rapidly diluted with doubly deionized water ($\times 5$) and immediately centrifuged at 18000 rpm for 2.5 h at 20 °C. DLS analysis ensured this procedure removed the majority of the nanocrystallites from the suspension. The sedimented nanocrystals were recovered in ethanol, calcined in air at 600 °C for 5 h, and weighed. The supernatant liquid was desiccated, calcined, and weighed under identical conditions. Then, the nanocrystal weight percent was calculated on silica basis. X-ray diffraction (XRD) patterns of the dried and calcined residues of the spin-on suspensions used in the films deposition were measured on a STOE Stadip diffractometer (transmission, Cu K_{α1}).

2.3. Characterization of structural and morphological properties of spin-on Silicalite-1 films

Views of top and cross-section of Silicalite-1 films were obtained by scanning electron microscopy (SEM, W-filament, Philips X-30, 5 kV). Atomic force microscopy (AFM) was performed probing an area 5×5 μm² in size. Spectroscopic ellipsometry (SE) in the visible region 350–850 nm (Sentech SE801) was used to measure the refractive index in vacuo of dried films and thickness. Toluene adsorption isotherms were obtained by monitoring the ellipsometric angles Ψ and Δ at 633 nm wavelength during an adsorption and desorption cycle at 20 °C (ellipsometric porosimetry, EP). Two models were used for the pore size distribution analysis on toluene adsorption isotherms. For pore size larger than 2.2 nm the model was based on Kelvin equation and for pore size smaller than 2.2 nm the model was based on Dubinin–Raduskevitch theory. Further details of the calculation of the isotherms and the pore size distribution were previously published [27–29]. The elastic modulus and hardness was measured by nanoindentation (NI) in continuous stiffness measurement with a Berkovich tip for the 400–500 nm films. Poisson's ratio used was approximated to that of fused silica (0.18).

2.4. Characterization of physico-chemical properties of spin-on Silicalite-1 films

X-ray diffraction (XRD) patterns of the calcined spin-on Silicalite-1 films were measured on a Siemens D5000 (reflection, Cu K_{α1}). The silicate cross-linking and hydroxyl content in the films were probed by Fourier transform infrared spectroscopy (FT IR, Biorad FTS-40) in nitrogen atmosphere. Measurements averaged over 64 scans were collected in the region 4000–400 cm⁻¹ with 4 cm⁻¹ resolution. Spectra were normalized by the Si–O–Si anti-symmetric stretching integrated in the region 1000–1300 cm⁻¹. Water adsorption isotherms at 20 °C were obtained by EP (water-EP) with the already mentioned system. Further details of this measurement for water probe can be found elsewhere [30]. The average contact angle (CA) of 1 μl drops of double deionized water on the film surface was determined from the drop images by fitting the curvature with the Young–Laplace equation. The dielectric constant (k) of the calcined films was measured at 100 kHz in MIS type capacitors (Metal–Insulator–Semiconductor) obtained by deposition of Al dots on top of the films. An impedance analyzer (HP4284A-LCR meter) was used to measure the capacitance in those MIS capacitors. The following formula was used:

$$k = Ct\epsilon_0^{-1}A_m^{-1} \quad (1)$$

in which t is the thickness of the dielectric film (measured by SE), A_m the Al dot area, and ϵ_0 the permittivity of vacuum. The capacitance measurements were collected after the films were dried in nitrogen atmosphere at 150 °C for 3 h.

3. Results

3.1. Characteristics of Silicalite-1 suspensions (DLS and XRD)

Table 1 shows the characteristics of the Silicalite-1 suspensions at different crystallization times. The nanocrystals' size and content increased with the crystallization time. The residual silica content decreased accordingly. The average nanocrystal size roughly was between 40 and 70 nm in a content between 6 and 63 wt.%. Addition of extra ethanol to the synthesis (cf. experimental section) extended the nucleation step and slowed down the crystal growth step [31,32]. It resulted in even smaller and more uniform nanocrystals.

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