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# Sol-Gel Processing of Low Dielectric Constant Nanoporous Silica Thin Films

Deok-Yang Kim[1], Henry Du[1], Suhas Bhandarkar[2], and David W. Johnson, Jr.[3]
[1]Department of Chemical, Biochemical, and Materials Engineering, Stevens Institute of Technology, Hoboken, NJ 07030, U.S.A.
[2]Bell Laboratories, Lucent Technologies, Murray Hill, NJ 07974, U.S.A.
[3]Agere Systems, Murray Hill, NJ 07974, U.S.A.

## ABSTRACT

Tetramethyl ammonium silicate (TMAS) is known as a structuring agent in zeolite synthesis. We report its first use to prepare porous silica films for low k dielectric applications in microelectronics. A solution of TMAS 18.7 wt. % was spin coated on silicon substrates with a 3000 Å thick thermal oxide. The spin coated films were subsequently heat-treated at 450°C to obtain porous silica. The use of TMAS solution without gelation led to films of only moderate porosity value of 10%. The addition of methyl lactate, a gelling agent, significantly increased film porosity and improved the pore size distribution. For example, 50% porosity and uniform pore size distribution (average pore size ~ 40 Å) has been achieved. Dielectric constants (k) of our porous films are as low as 2.5.

## INTRODUCTION

There has been intensive research on low dielectric constant materials for metal-insulator interconnects in integrated circuits. A variety of materials have been explored so far, including polymers [1], inorganic-organic hybrid [2] and porous silica [3-6]. Among those candidates, porous silica is the most promising because it has high tunability of porosity and thermal stability. Tetramethylammonium (TMA) cation salts have been used as common structure-directing agents in the synthesis of zeolite [7]. This quartenary ammonium ion is known to form hydrates in aqueous solution. Water associated with the TMA ion is partially displaced by silicate in the synthesis of zeolite to form precursors for nucleation centers, allowing for the structure-direction to occur. TMA ions have strong affinity to silicate ions, which allows effective screening and dispersing of silicate ions in the solution. Nuclear magnetic resonance study of tetramethyl ammonium silicate (TMAS) has shown that it forms oligomers at high pH [8]. The sol-gel chemistry of TMAS system is much simpler than that of typical TEOS- based recipe because it does not need to use co-solvent (i.e. methanol). The unique feature of TMAS sol-gel process is kinetically controllable gelation with hydrolyzable ester [9]. The addition of ester reduces the pH value down to a level below 10 where gelation takes place in this system. Introduction of positive charge dissipates the space charge on silicate and allows the silica monomers to coalesce under the influence of attractive van der Waals forces. Spin coating has been used to deposit the porous thin silica films on desired substrates. This technique can be easily adapted to a manufacturable process.

## EXPERIMENTS

An aqueous solution consisting of 18.7 wt.% TMAS in water (Aldrich, 99.99+% purity, LOT 06301HU) was used. The ratio between TMA cation to Si atom is 1:2. Silicon wafers with a 3,000 A thermal oxide were used as substrates for spin coating using a Model PC101 spinner by Headway Research, Inc. All the wafers were used as-received without any pretreatment process. Approximately 2 mL of TMAS liquid was dispensed onto the stationary substrate, which was then accelerated to the process speed of interest. The deposition was carried out at spin speeds ranging from 2,000 to 7,000 rpm for 30s during which time most of the water evaporated. Partially gelled silica films were obtained using a similar method. In addition, 0.8 equivalent mol ester (i.e. methyl lactate, 98 wt.%, Aldrich) was introduced to the solution before spin coating. Spin coating did not start until the solution reached the about-to-gel point, approximately 6/7 of its gelation time. After spin deposition, the wafers were heat-treated in a tube furnace at 450 °C for an hour in air to remove any residual solvent and carbon contents.

The thickness and refractive index of the heat-treated porous silica films were measured by a SENTECH SE801 spectroscopic ellipsometer. The ellipsometric data from a 350nm to 800nm was fit to a Cauchy dispersion model. The thickness values of the films were further measured using profilometry. Selected samples were also examined using a LEO 1530 field emission scanning electron microscope (FESEM) in a cross-section geometry. Powder samples of gelled TMAS were prepared for BET measurement. The powder was gelled with methyl lactate and dried quickly using air sprayer on hot plate so as to yield nearly the same evaporation condition as in spin coating. A nitrogen isotherm at 77 K on the powder was conducted with Micromeritics ASAP 2010. A Pt-silica-Pt parallel-plate capacitor structure was fabricated for dielectric measurements. The top and bottom Pt electrodes were electron-beam evaporated and sputter deposited, respectively. Top electrode area was 1.13 $mm^2$. The dielectric constant of the porous films was calculated based on their capacitance values at 1 MHz.

## RESULTS AND DISCUSSION

Fig.1 shows the dependence of thickness on spin speed for TMAS films as well as partially gelled TMAS films. As expected, the thickness of both types of silica films decreases as the spin speed increases due to increased shear forces exerted on the liquid before drying. The partially gelled films are three to four times thicker as compared to the films without the gelling agent. These results can be understood as follows. At the about-to-gel point, the solution containing gelling agent experiences an abrupt increase in viscosity, which better withstands the centrifugal force of spin coating. According to Bornside's model [10], the thickness of spin coated film is roughly proportional to one-third power of viscosity of the fluid used. For example, a tripled film thickness means that the viscosity is increased by $3^3 = 81$ times. This dramatic increase in the viscosity of solution can only be attributed to the process of gelation rather than the shear thickening of the fluid. Shear thickening can at most double the viscosity of the original solution.

Illustrated in Fig. 2 is refractive index versus the spin speed for TMAS only films and partially gelled TMAS films. The refractive index is not a strong function of the spin speed, indicating the insensitivity of the film porosity to the spin speed. The refractive index of the partially gelled films is significantly lower than that of the TMAS films without the gelling agent.

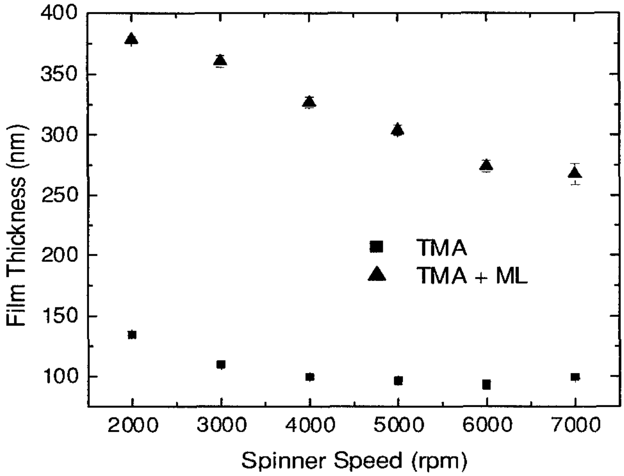

**Figure 1.** Thickness data of TMAS films vs spinner speed

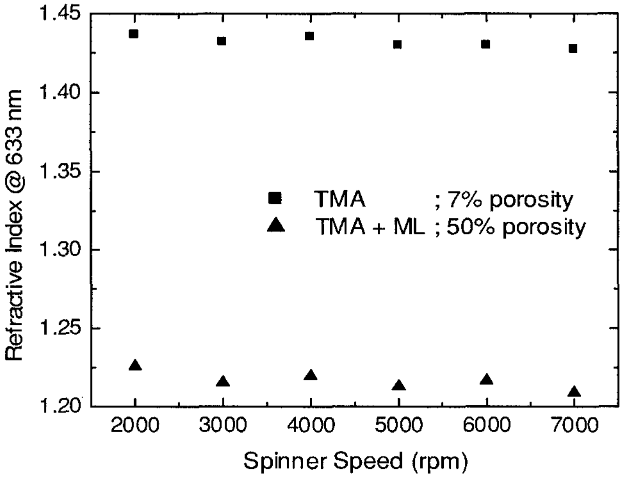

**Figure 2.** Refractive index data of TMAS films vs spinner speed

Bruggemann effective medium layer model [11] based on refractive index data was used to estimate the porosity of these films. Fig. 3 (a) describes the assumption this model makes. It is assumed that the film has small spherical inclusions (in this case, pores filled with air) in silica with a different index of refraction, $n_i$. The fraction of inclusion can thus be calculated using the equation in Fig. 3 (a). Fig. 3 (b) shows that the theoretically calculated curve based on this model fits well with the experimental data of one of the samples. This technique allows us to evaluate the porosity of films indirectly with ease even though we can not get pore size or pore distribution information. TMAS films without gelling agent contain less than 10% porosity whereas partially gelled films have 50% porosity on average. As gelation takes place, the silica network starts cross-linking and pore structure begins to evolve.

Enough time was allowed for partial gelation till about-to-gel point before significant evaporation occurred during spin coating. Therefore, when evaporation takes place in spin coating of these films, the already formed silica network would resist collapsing and pores created during gelation would remain intact. This mechanism is responsible for the higher porosity of partially gelled films. Shown in Fig. 4 is a cross sectional SEM micrograph, which gives the general morphological appearance of partially gelled porous silica thin film. In contrast, TMAS without gelling agent would experience quick evaporation of solvent and precipitate relatively dense silicates on the substrate. Further cross section SEM analysis revealed the existence of cluster-like precipitates in TMA only silicate films.

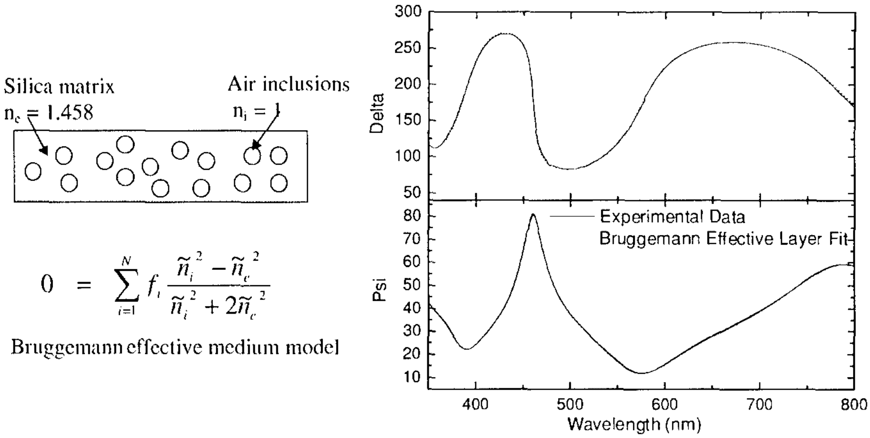

**Figure 3.** (a) Schematic diagram of Bruggemann effective layer model (b) two curves fitting of Psi and Delta values over wavelength range of 350 - 800 nm

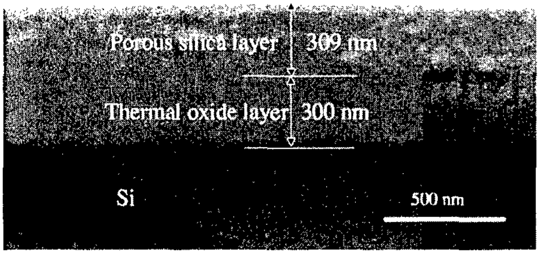

**Figure 4.** Cross sectional SEM of a partially gelled silica film at 4,000 rpm spin

TMAS gel with gelling agent shows a typical adsorption and desorption curve of mesoporous materials (type IV), based on the BET analysis of the corresponding powder samples shown in Fig. 5. The specific surface area of the porous silica is about 790 m$^2$/g. A BJH desorption curve study shows a very narrow pore size distribution of average diameter of ~ 40 Å for this material. Low angle x-ray diffraction experiments did not reveal any evidence of ordered pore structures. Silica films from TMAS with gelling agent are therefore considered to contain randomly distributed ~ 40 Å size pores.

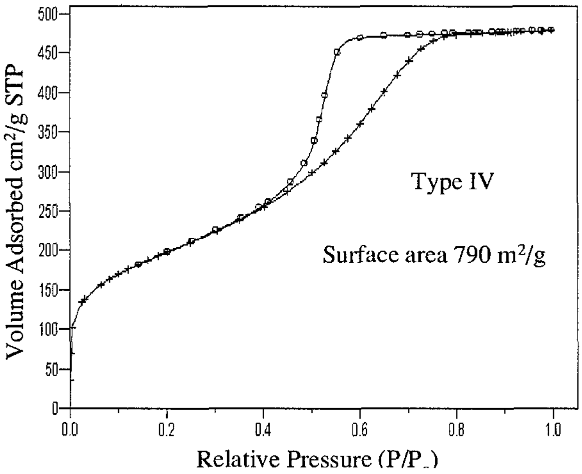

**Figure 5.** $N_2$ isotherm curve by BET measurement

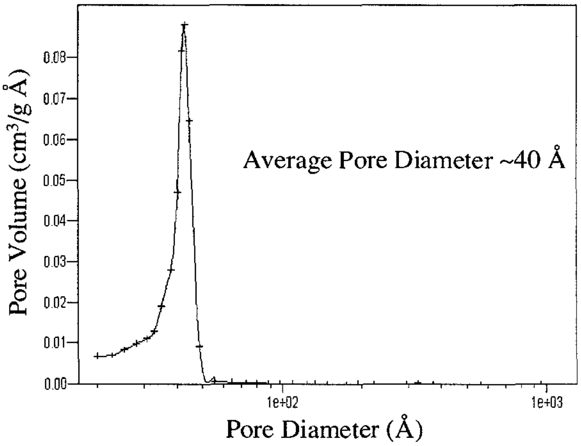

**Figure 6.** BJH desorption curve (pore size distribution) by BET measurement

Accurate dielectric measurements of silica films can be challenging because they are terminated with hydroxyl (-OH) groups and thus highly hydrophilic. Any moisture uptake in the porous thin films would significantly affect the measured values of the dielectric constants. Extra care was therefore taken by immediately storing the porous silica films in a dry nitrogen ambient after the heat treatment, Pt metallization and capacitance measurement. The lowest dielectric constant on 50 % porous TMAS films was 2.5 at 1 MHz.

## CONCLUSION

Two different types of TMAS thin films were fabricated via sol-gel processing. Partially gelled TMAS films have high porosity (~ 50%) and narrow pore size distribution of small pores (~40 Å). These films would be good candidates for low k application with further hydrophobic treatment as well as for host materials of larger pore arrays from surfactants.

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