

Improved Reproducibility in Porous Silica Sol-Gel Processing

Using Tertiary Butanol Solvent

A. Rissanen, M. Blomberg and H. Kattelus

MICRONOVA Centre for Micro- and Nanotechnology, VTT Information Technology
P.O. Box 1208, FIN-02044 VTT, Espoo, Finland, Anna.Rissanen@vtt.fi

ABSTRACT

Silica aerogels and xerogels are porous materials, which possess many exceptional properties. The research for the use of aerogel thin films in MEMS applications, such as humidity sensors, biosensors and calorimetric devices, is still at an early stage. Therefore the aerogel thin film process development is prerequisite. Previously, highly volatile liquids like ethanol or isopropanol (IPA) have been used for the solvent in the traditional two-step acid-base sol-gel process, which may deteriorate the reproducibility of the process. In this paper, a novel method to produce porous films with improved reproducibility is presented. It is also demonstrated that aerogel films act as a source for particles during the supercritical drying process. Aerogel patterning with lithography and plasma etching is investigated.

Keywords: sol-gel, aerogel, xerogel, TBA, porous film patterning

1 INTRODUCTION

Aerogels are extremely porous materials, which consist of nanometer-size pores and particles. They are made using sol-gel chemistry to obtain gels consisting of a solid silica part and a liquid solvent part. The gel can be dried by removing the solvent from the pores so that the solid matrix does not collapse, creating a highly porous material.

Usually the sol consists of tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS), alcohol, water and a base/acid catalyst. The sol turns into a gel through hydrolysis and condensation reactions. The solid silica network needs time to become stronger in a process called aging. After this, the gel can be dried to form a porous silica film.

The highest porosities can be obtained by supercritical drying. The solvent liquid in the pores is exchanged with liquid CO₂. When CO₂ is evaporated the pores will not collapse due to the lack of surface tension. If other drying methods are used, like conventional evaporation by heating, the pores will lose some of their size and the obtained material is called xerogel.

The porous silica materials possess many exceptional properties: they have a very low dielectric constant, an adjustable refractive index, low thermal conductivity, low density and a high surface area. The properties of the film can be modified by tailoring the sol-gel process. Because of these unique properties, a lot of research has been done concerning the applications of these porous materials in IC industry and optical devices. However the research for the use of aerogel thin films in MEMS applications, such as humidity sensors, biosensors and calorimetric devices, is still at an early stage. In order to be used as a part of a MEMS process, the film preparation must be well repeatable.

2 EXPERIMENTAL

2.1 Film Preparation

In this work, films were synthesized using a two-step acid-base sol-gel process using tertiary butanol (TBA) as the solvent. The sol composition used in the hydrolyzation step was TEOS:TBA:H₂O:HCl = 1: 3: 2: 7.3 x 10⁻⁴ in molar ratio. Films were also prepared using several variations of the traditional two-step acid-base sol-gel process [1-3] using IPA as the solvent.

Film preparation process is presented in Figure 1. The solution was hydrolyzed at 60 °C for 1.5 hours. This stock solution was stored below room temperature and before the use it was heated to 30 °C. To catalyze the condensation reaction, 0.6 ml of 0.5 M NH₄OH and 0.4-0.6 ml of DI water was added to 10 ml of the warm stock solution. The gelation time was 11-13 minutes.

The solution was spun on Si substrates in a solvent saturated atmosphere in the optimized viscosity range at $t < 0.4 t_{gel}$. Spinning was conducted at 2000 – 3000 rpm for 10 s. After coating, 5 ml of IPA was pipetted onto the substrates through the lid of the spinner to prevent evaporation and the wafers were transferred to petri dish for aging. The films were aged using IPA/ ammonia solution (pH 10) from 18 h to 4 d. The solvent was changed to isopropanol and removed with CO₂ supercritical drying.

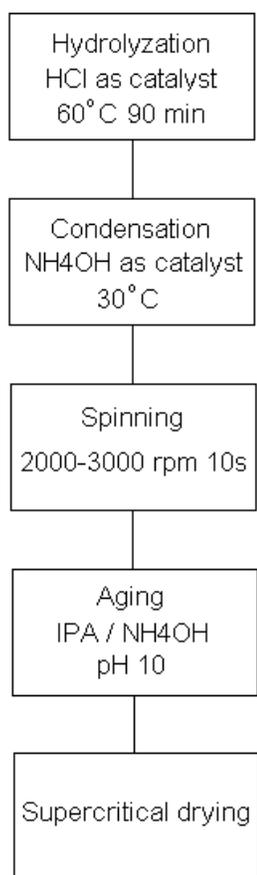


Figure 1: Process flow of silica aerogel film preparation.

2.2 Characterization

Films were characterized with ellipsometry, SEM (see Fig. 2 and Fig. 3) and RBS measurements. The changes in the film properties during lithography and plasma etching in RIE with CF_4 were monitored. IC compatibility of aerogel films was evaluated by detecting particles transferred over a blanket silicon reference sample during supercritical drying.

Film porosity was determined from refractive index measurements and RBS. The density and porosity (P) can be determined from the refractive index n using the empirical equation [4, 5]:

$$P = \frac{1.458 - n}{0.458} \quad (1)$$

The density and porosity of the films were also determined using Rutherford backscattering spectrometry (RBS) with collimated 2 MeV He^+ ions. The areal density value (number of atoms per unit area of film) can be determined from the spectra by calculating the energy gap between the leading and trailing edges of the signals related to each element. The density of the film can be calculated

by dividing the total areal mass by the thickness (d) of the film.

IC compatibility of aerogel films was evaluated by detecting particles created during supercritical drying in Tousimis automegasamdri -915B. This was done by processing two wafers in Tousimis, one blank one (wafer #1) by itself and another blank wafer (wafer #2) with a test wafer coated with aerogel, and comparing the particle counts on these two blank wafers with light point defect counter and PC- based software (VTTWAFER) [6]. Tousimis is not an IC clean instrument, but the difference in the particle counts gives an estimate of how many particles are produced by the aerogel film.

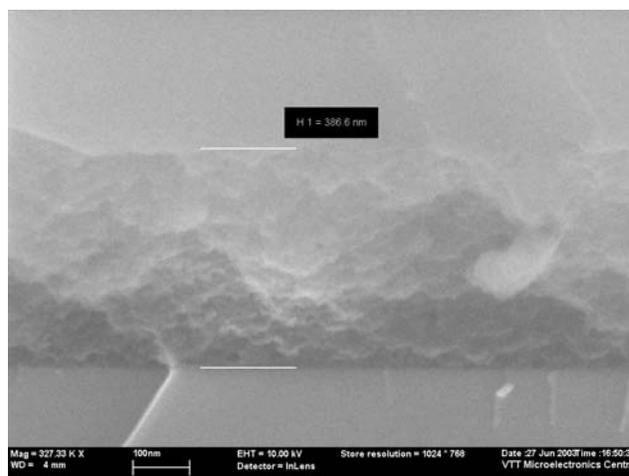


Figure 2: SEM cross section image of a 387 nm-thick aerogel film.

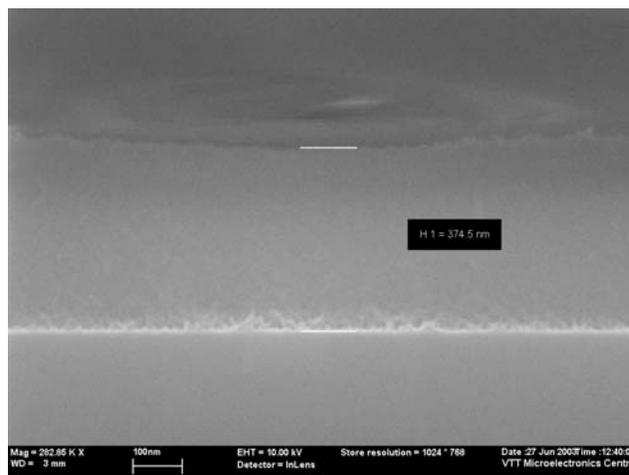


Figure 3: SEM cross section image of 375 nm-thick aerogel film.

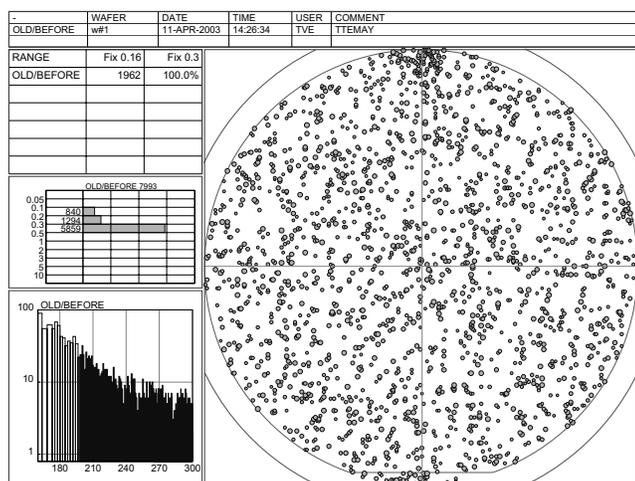


Figure 4: Particles sized 160-300nm on wafer #1.

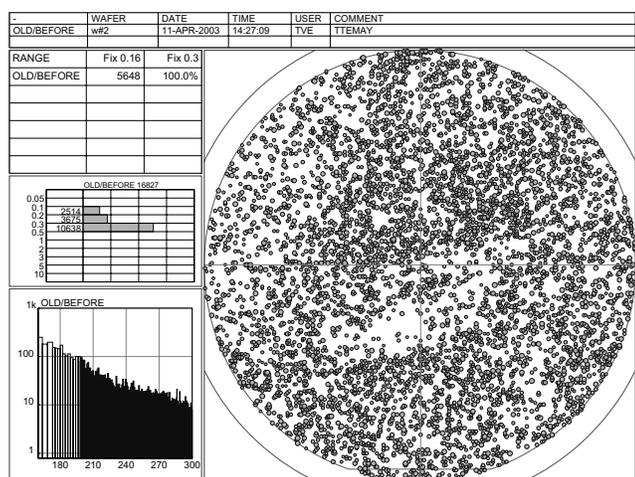


Figure 5: Particles sized 160-300nm on wafer #2.

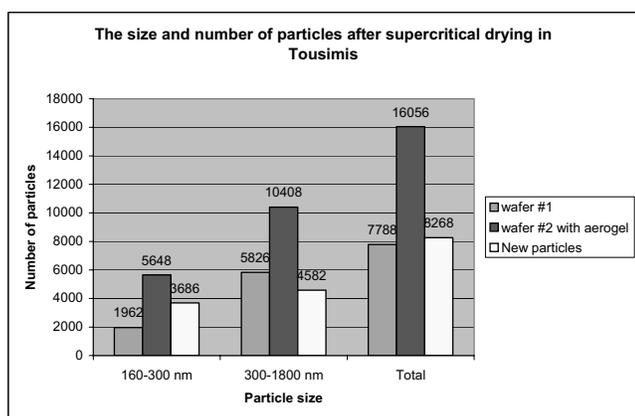


Figure 6: The particle counts on wafers processed with and without an aerogel-coated wafer.

2.3 Patterning

The wafers were primed in HMDS vapor at 115 °C for 30 minutes. Photoresist EZ5214 was manually spun on at 5000 rpm for 35 s. The samples were then prebaked at 90 °C for 1 min on a hot plate.

UV exposure was done with SUSS Mask Aligner MA 6 with a resolution mask. The exposure time was 5 s. The wafers were developed using a mixture of developer AZ351 and DI water (1: 3.5). The developing time ranged from 35 s to 70 s. All the aerogel films remained undamaged during lithography. The films did not suffer from the liquid contact during photoresist development and movement during the development had no effect.

The samples were etched with CF₄ in RIE (reactive ion etching) Electrotech under following conditions:

- Pressure = 20 mTorr
- CF₄ flow rate = 20 sccm
- P (RF) = 100 W
- Time = 2 – 6 min

After etching the photoresist was stripped with O₂ plasma in RIE under the following conditions:

- Pressure = 125 mTorr
- O₂ flow rate = 40 sccm
- P (RF) = 150 W
- Time = 3.5 – 10 min

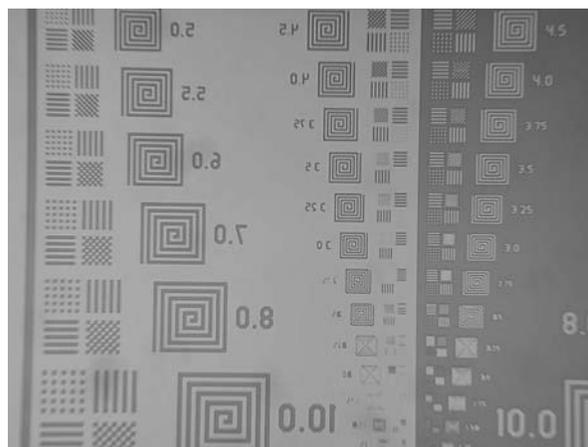


Figure 7: Patterned aerogel test structures.

From Figure 7 it can be seen that it is easier to pattern a hole and trenches into the film than form dots and lines of the film. In the latter case adhesion problems may occur.

3 RESULTS AND DISCUSSION

Films were prepared using several variations of the two-step acid-base sol-gel process to produce films with porosity in the range between 60-80%. It was observed that films made with high volatility solvents like IPA were subject to serious reproducibility problems caused by evaporation during spinning.

The desired porosity and reproducibility were obtained by using tert-butanol (TBA) as a solvent instead of ethanol or IPA. Tert-butanol is a low-volatility solvent and has previously been used in film synthesis through sublimation [7] because of its high freezing point (25.6 °C). Excess amount of TBA during freeze-drying causes film cracking [7], so to obtain the best reproducibility, which is required for MEMS/IC- processing, supercritical drying is preferable. The obtained refractive indices were in the range of 1.10-1.18 for the aerogel films and 1.22-1.26 for the xerogel films, depending on the aging time. The porosities for the aerogel films were in the range of 60% to 78% and for xerogel films in the range of 43% to 52%. The values obtained from the RBS measurements showed a slightly higher value for the porosities than the values obtained indirectly from the refractive indices.

Films made with TBA showed a greatly improved reproducibility since solvent evaporation during processing was significantly decreased. Process reproducibility is important when planning to use aerogel films as a part of commercial MEMS structures for example as semipermeable etching layers or as the active film in humidity sensors. With long device processes, the aerogel coating quite often may take place as one of the last steps and if the coating process is not stable, failing to obtain the desired porosity can be quite expensive.

Aerogel films still have obstacles in becoming a part of commercial products because of the particle problem demonstrated in this work. From Figures 4 and 5 and the summary in Figure 6 it can be seen that the particle counts are much higher on wafer #2, which was processed together with the aerogel wafer. Small particles (160-300 nm) were increased by 3686 particles and big particles (300-1800 nm) were increased by 4582 particles. Introducing a source of thousands of particles to an IC process is not acceptable. In MEMS processing the particles are not necessarily as bad as a problem, especially if the film is deposited at a later stage in the processing chain. However if particles are introduced to the process at an early stage, that can lead to problems in such steps as structure releasing. Other layers such as photoresist might be useful in inhibiting the particles from the aerogel layer to spread in other processing steps.

Aerogel film patterning has previously been demonstrated with surfactant templated films [8], but based

on our work patterning sol-gel-based films seems to be more challenging. We found that the porosity suffered somewhat during patterning, especially with films using IPA as the solvent. Films made with TBA showed also in this respect to be superior; they had lower refractive indices after patterning than the films made with IPA. Photoresist trapped in the pores showed also to be a problem with some of the films.

It was also demonstrated that aerogel films do not adhere to some metals, like Mo-N and aluminum films. In processing this can be solved by depositing an adherence layer. However, this feature can also be used as a benefit to avoid lithography steps and pattern aerogel selectively on areas not covered by the metal film.

4 CONCLUSIONS

It was shown that the reproducibility and the porosity of the films improved using TBA instead of IPA. Porosity was about 76% and refractive index 1.11 for 380 nm thick films. Carbon content was about 12-24 at-% in films prepared with IPA. Particle transfer between wafers during supercritical drying was recorded to be a problem, thousands of added particles were counted on a 100 mm wafer, Table 1. Films were patterned using standard lithography processes, but in some cases the photoresist clogged in the aerogel pores caused problems.

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