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Self-assembled aerogel-like low dielectric constant films

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Abstract

A series of new spin-on nanoporous silica films with controlled porosity and dielectric constants were prepared by evaporation induced self-assembly (EISA) during spin-coating. Starting with a homogeneous solution of soluble silica and surfactant/swelling agent prepared in an alcohol/water solvent, preferential evaporation of alcohol during spin-coating results in the hierarchical self-assembly of surfactants plus swelling agent and soluble silica into a templated microemulsion system. Silicate polymerization followed by removal of surfactant and swelling agents via immediate calcination results in a highly porous silica film of the liquid crystalline assembly with controlled porosity ranging from 50% to 90% and dielectric constant ranging from 1.3 to 2.6. TEM and surface acoustic wave (SAW) techniques were used to characterize the microstructure of the films. The dielectric constant, Young's modulus, and hardness of the final films are also discussed. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The desire for very low dielectric constant materials (<2.5) for use as interlayer dielectrics (ILD) in very large scale integration (VLSI) microelectronic devices has motivated considerable research into porous, spin-on films for new dielectric materials [1–3]. Porous silica films are an attractive candidate for this application [2,3]. Traditional sol-gel approaches to porous films involve spin-coating of oligomeric or polymeric silica sols. Evaporation of solvent drives aggregation and the formation of a highly disordered, often fractal, gel

network. The final porosity of the xerogel film depends on the nature of this gel network and its extent of collapse by capillary stresses developed during the final stage of drying [4]. Supercritical solvent extraction is used to produce silica aerogels with dielectric constants ranging from 1.1 to 1.5 and porosities ranging from 85% to 99% [1].

However, supercritical processing is costly, sometimes dangerous, and not suited for the preparation of thin films needed for future generations of microelectronic chips. As an alternative to supercritical drying, surface silylation agents (e.g., trimethylchlorosilane) have been used to modify the silica framework to form aerogel-like films that exhibit reversible drying shrinkage. However, like bulk aerogels, aerogel-like films have a highly disordered pore network with a very broad pore size distribution and pure mechanical

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properties. Likewise, xerogel films often have average pore sizes of over 10 nm and a broad pore size distribution. Also, the fabrication of aerogels and xerogels requires long processing times, making their implementation in commercial semiconductor applications difficult.

Surfactant templating is a rather recent approach for controlling pore size and porosity in silica coatings, and possesses great promise for fabricating low dielectric constant coatings [5–8]. Surfactant templated mesoporous materials are characterized by a uni-modal pore size distribution controllable in the approximate range of 2–10 nm [7,9,10]. In addition, whereas aerogel and xerogel networks are characterized by pendant branches that do not contribute to mechanical strength, mesoporous frameworks are completely mechanically connected. In this paper, an evaporation-induced surfactant/silica self-assembly process is used to prepare nanoporous silica thin films with controlled porosity. Our strategy is based on the co-assembly of silica and surfactant during spin-coating: Silica condensation freezes the surfactant/silica mesophase; removal of surfactant results in a mesoporous silica film. Addition of co-solvent (oil) results in the formation of a microemulsion, which can template a second class of pores leading to a highly porous silica films with rather narrow pore size distributions.

2. Experimental procedure

Precursor solutions for spin-coating were synthesized by the addition of triblock co-polymers (Pluronic-P123; (ethylene oxide, EO)20 (propylene oxide, PO)70 (E)20, gift from BASF) to an acidic silica sol. The acid concentration used in the acidic silica sol was chosen to minimize the siloxane condensation rate, therefore promoting facile silica surfactant self-assembly during film deposition and patterning. In a typical preparation, TEOS ($\text{Si}(\text{OCH}_2\text{CH}_3)_4$, from Aldrich), ethanol, water and dilute HCl (mole ratios: 1:3.8:1:5 $\times 10^{-5}$) were refluxed at 60°C for 90 min. Swelling agents (oil) including polypropylene glycol (PPO, M.W. 2000) were added in amounts of 0–20% of the total weight of final sol.

Thin films were prepared by spin-coating the sols onto [1 0 0] single crystal silicon wafers or ST-cut piezoelectric crystalline quartz surface acoustic wave (SAW) substrates at a rate of 1000–8000 rpm. The surfactant templates were removed by calcination in air immediately at 600°C. High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2010 TEM, operated at a voltage of 200 KV. The films were subjected to a 1,1,1,3,3,3-hexamethyldisilazane (HMDS) vapor treatment at 160°C after calcination to make the pore surface hydrophobic.

The films deposited on the SAW substrates were used to estimate surface area and pore size. The SAW devices (97 MHz) prepared with Ti-primed Au transducers were designed and fabricated at Sandia National Laboratories [11]. The measurements were conducted at 77 K by measuring the frequency shifts of the SAW device configured as the feedback element of an oscillation circuit during adsorption and desorption of nitrogen. The amount of nitrogen adsorbed as a function of relative pressure was determined from the frequency change, assuming that the SAW frequency is only perturbed by a mass loading variation. Surface areas were estimated by using the Brunauer–Emmet–Teller (BET) equation; pore radii (r) were estimated by modeling the pores as cylinders and calculating the hydraulic radius as $r = 2V/S$, where V is the pore volume and S is the surface area.

Thickness measurements were made using a WVASE 32 ellipsometer. The dielectric constant was measured using a mercury probe approach. The capacitance (C) was obtained with an HP 4275A multi-frequency LCR meter with frequency of 1 MHz and voltage of 0.1 V. Samples were measured for mechanical properties using a Nanoindenter XP machine with a Berk pyramid tip. A constant strain rate was used to a depth of 400 nm. Five indents were taken and averaged for hardness and Young's modulus.

3. Results

Recently, we demonstrated the formation of mesoporous silica films with controlled pore size

and porosity through an evaporation-induced interfacial self-assembly approach [6,7,12–14]. Starting with a homogenous solution containing soluble silica oligomer, surfactant, water, acid, and alcohol, the preferential evaporation of alcohol during film drying drives the local surfactant concentration to exceed the bulk critical micelle concentration, therefore developing micelles and lyotropic silica mesophases. As discussed below we have extended this approach to prepare a series of highly porous silica films. We used microemulsions formed by non-ionic surfactants and co-solvent to template and control the film porosity, thereby controlling the dielectric constant. A potential advantage of using non-ionic block co-polymers as templates is the formation of thicker walls resulting in greater thermal and mechanical stability [10], as well as avoidance of mobile ions that could degrade dielectric performance.

Fig. 1 shows a plan-view TEM image of a calcined thin film deposited on a silicon wafer by using block co-polymer P123 and swelling agent PPO (15 wt%). The film exhibits a uniform microstructure without phase separation. The SAW technique was used to determine the pore microstructures of the final film [11]. Fig. 2 shows the SAW nitrogen sorption isotherms for the corre-

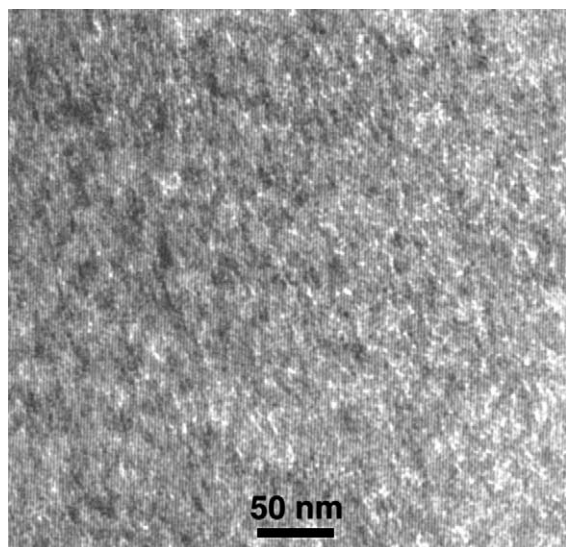


Fig. 1. Plan-view TEM micrograph of microemulsion-templated silica thin film.

sponding film shown in Fig. 1. This illustration is a typical type IV isotherm without any hysteresis and shows a well-defined adsorption/desorption curve between partial pressures, P/P_0 , of 0.2–0.8. The measured BET surface area is about $1033 \text{ m}^2/\text{g}$ and calculated porosity and pore size are 88% and 125 \AA , respectively.

In order to fabricate films with controlled porosity, a series of silica films was prepared using different concentrations of PPO. The porosity/dielectric constant and modulus/hardness are plotted as a function of amount of PPO as shown in Figs. 3 and 4. As the concentration of PPO is increased in the starting sol, the porosity increases while the dielectric constant decreases. The increase in porosity also reduces the mechanical properties of the film as shown in Fig. 4.

4. Discussion

Through combination of traditional sol-gel processing with self-assembly strategies we have established a self-assembly route to the formation of highly porous mesoporous films. Previously we fabricated films of less than 50% porosity by using

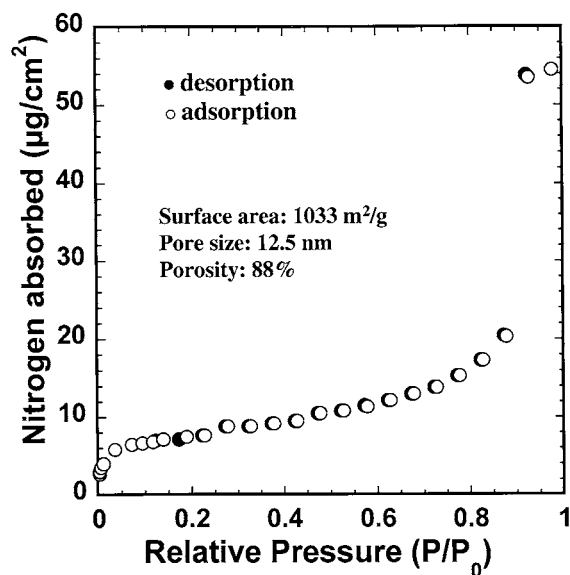


Fig. 2. Nitrogen sorption isotherms of microemulsion-templated silica film.

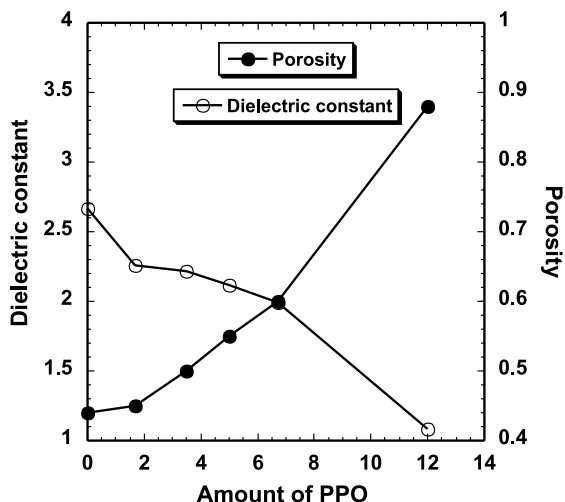


Fig. 3. Porosity and dielectric constants of microemulsion-templated porous silica films as a function of the amount of swelling agent PPO.

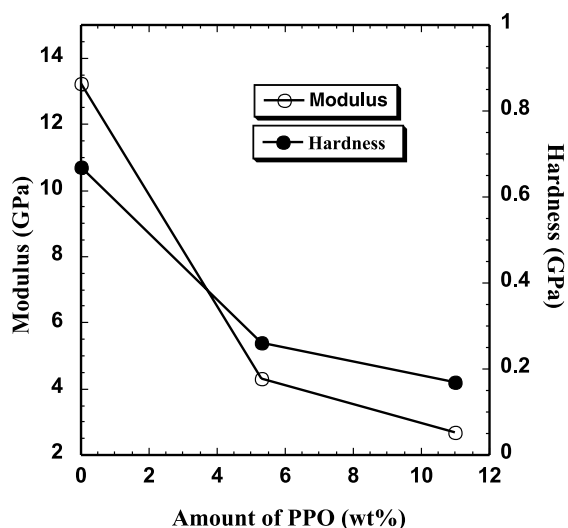


Fig. 4. Modulus and hardness of microemulsion-templated porous silica films as a function of the amount of swelling agent PPO.

pure surfactant without adding swelling agents [7]. In the current system, extra PPO was added as swelling agent to achieve porosity between 50% and 90%. During spin-coating, evaporation of alcohol induces a cooperative assembly of silica, P123, and PPO into a silica/P123/PPO hierarchi-

cally-templated composite film. Instant calcination at 600°C in air, results in a highly porous silica film. The microstructure of the corresponding silica film as shown in the TEM image (Fig. 1) exhibits no phase separation. The lower contrast between the silica film and the carbon skeleton of the TEM grid indicates that the film is highly porous. The contrast pattern of the microstructure has a much finer texture than that of conventional aerogel films.

The film shows type IV nitrogen absorption-desorption isotherms (Fig. 2), characteristic of surfactant templated silica materials. The lack of hysteresis and absence of adsorption above partial pressure of 0.8 indicate a uni-modal pore size distribution.

By using different amounts of swelling agent, a series of films is synthesized with controlled porosity ranging from 50% to 90%, and controlled dielectric constant between 1.3 and 2.6. The resulting porous silica films exhibit much better mechanical properties than conventional silica aerogel films.

5. Conclusion

In summary, we have synthesized a series of highly porous silica thin films with controlled dielectric constants through co-assembly of silica and microemulsion formed by the block co-polymer P123 and swelling agent PPO. A range of dielectric constants from 1.3 to 2.6 was obtained through the addition of different amounts of swelling agent PPO.

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