Photo patternable porous siloxane thin films using cyclodextrins as template materials

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Abstract

Photo patternable cyclic silsesquioxane (mCSSQ) compositions containing heptakis (2,3,6-tri-O-methyl)-β-cyclodextrin (tCD) as a porogen and photo acid generator (PAG) have been prepared, with the goal of achieving a photo resist free porous low dielectric constant precursor. The composition containing triphenylsulfonium based PAG could effectively create a patterned mCSSQ thin film with a resolution approaching \( \sim 2 \) \( \mu \)m. The pore size of the mCSSQ film with PAG was smaller than that without PAG. Furthermore, the pore size distribution of the mCSSQ film with PAG was much narrower than that without PAG. This might be attributed to the disturbance effect of the agglomeration of tCD molecules through pre-vitrification of the matrix at the relatively low curing temperature. The mechanical property and dielectric constant of the photo-definable mCSSQ/tCD/PAG film were comparable to those of the mCSSQ/tCD counterpart.

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1. Introduction

Nano structured materials have been extensively researched for various applications such as catalysts, adsorbents, membranes, sensors, and waveguides [1–4]. In particular, many porous thin films have been demonstrated as low-\( k \) (dielectric constant) materials in large-scale integrated circuits (LSI) to reduce resistance and capacitance delay. Predictions from the semiconductor industry indicate that an inter level metal insulator with a bulk \( k \) below 2.4 will be realized by 2007 [5]. Inevitably nano voids are incorporated into the matrix film to obtain ultra low-\( k \) thin films (\( k<2.4 \)). The nanoporous structures in thin films could be easily prepared with a spin-on composition containing a thermally stable low-\( k \) precursor with a pore generator (porogen), which can be decomposed and volatilized at high temperature to leave pores in the film. Typical examples of porogen are polymeric materials [6–9] or ionic as well as nonionic surfactants [10,11].

The typical dual damascene process for the integration of LSI device consists of a number of processes, including deposition of an insulating layer, photo resist (PR) patterning, PR stripping, etching, ashing, metallization, and chemical mechanical polishing. If the insulating layer were photo-definable, the integration process could be dramatically simplified. Therefore, photo patternable compositions based on the concept of chemical amplification are becoming important in electronic applications. Harkness et al. have reported that photo-definable hydrogen silsesquioxane could be prepared with photo base generator which induces silyl hydride condensation [12,13]. Moreover, several studies have endeavored to pattern nanoporous structures without using the conventional PR process [14–16]. In particular, Doshi et al. introduced optically defined patterning of silica ordered mesoporous film through an evaporation induced self-assembly and the use of a specially designed PAG [16]. Recently, Kim et al. reported a direct photopatterning method to generate patterns of nanoporous poly(methylsilsesquioxane) thin films with relatively large nanopore (>10 nm) by using amphiphilic polymer based porogen and PAG [17].

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The potential of making porous thin films with small nanopore (<2 nm) by using cyclodextrin (CD) as a porogen has been previously demonstrated [18,19]. The CDs are cyclic oligosaccharides consisting of at least six glucopyranose units which are joined together by \((1\rightarrow4)\) linkages. The CD compounds have a three-dimensional structure with maximum diameter varying from 13.7–16.9 Å and have a narrow decomposition window (320–390 °C) as compared with star-shaped poly(caprolactone) based porogen [18,20]. These CDs could be molecularly dispersed in the film, acting like a single nanoparticle in the matrix precursor. They could then create isolated nano-pores via their decomposition in the low concentration of CD molecules, while porogen agglomeration and pore collapse would become severe with increased CD molecule concentration [21]. The interconnected pore structure can be postulated as a worm-like pore shape based on the tendency for CD molecules to linearly interact.

Considering shrinkage of feature size in a LSI device, it is desirable to maintain a pore dimension that is at least one order of magnitude smaller than the feature size in order to ensure chip reliability. In this study, the primary interest was the preparation of a photo patternable porous thin film having a very small pore diameter (<2 nm). Although the concept of direct photopatterning to make a nanoporous film using PAG has been investigated [17], there have been no discussions on the control of the nanopore structure (pore size and pore interconnectivity) of a photo patternable siloxane film. Therefore, the secondary objective of this study was to achieve reduction of pore size and pore interconnection length, which had previously been investigated for high CD concentration (30 wt.% relative to solid content) in a coating solution [21]. To this end, the reduction of the agglomeration of CD molecules was investigated by using a low temperature curing process.

2. Experimental details

2.1. Materials

The porogen material, heptakis (2,3,6-tri-O-methyl)-\(\beta\)-cyclodextrin (tCD), which purchased from CYCLO LAB. Co. was used as-received. The chemical structure of tCD compound is illustrated in Scheme 1. Triphenylsulfonium (TPS) based photoacid generators, triphenylsulfonium trifluoromethane sulfonate (Uray Co.), triphenylsulfonium p-toluenesulfonate (Uray Co.), and triphenylsulfonium 10-camphorsulfonate (Uray Co.), were used as received (see Scheme 1). The Ir complex, bis[2-(4,6-difluorophenyl)pyridinato-N,C2]picolinate iridium (III) (American Dye Source, Inc.) was also used as received.

2.2. Synthesis of modified cyclic silsesquioxane precursors

In this study, MTMS (methyl trimethoxy silane) and TCS (2,4,6,8-tetramethyl-2,4,6,8-tetraakis (trimethoxysilyl)ethyl cyclootetra siloxane) were used as monomers to synthesize the matrix precursor. The modified cyclic silsesquioxane (mCSSQ) precursor was prepared by acid catalyst controlled hydrolytic polycondensation of MTMS and TCS according to the experimental method outlined in our previous report [22]. The reaction scheme is briefly described in Scheme 2. The Si-OH content of the mCSSQ precursor, calculated by \(^1\)H-Nuclear Magnetic Resonance Spectroscopy (Bruker AM300), was 30.2 mol% and the weight average molecular weight \((M_w)\) and

Scheme 1. Abbreviations and chemical structures of tCD porogen and various kinds of PAG in this paper. TPS-TFMS: tCD is a heptakis (2,3,6-tri-O-methyl)-\(\beta\)-cyclodextrin. TPS-TFMS, TPS-PTS, and TPS-CD are Triphenylsulfonium trifluoromethane sulfonate, Triphenylsulfonium p-toluenesulfonate, and Triphenylsulfonium 10-camphorsulfonate, respectively.

Scheme 2. Synthetic procedure of mCSSQ, abbreviations and chemical structures of silicon based monomers.
polydispersity measured by Gel Permeation Chromatography (Waters 2690) were 4194 and 1.82, respectively.

2.3. Preparation of patterned porous thin films

The spin-on coating solutions were prepared by properly mixing the mCSSQ precursor as a matrix with tCD as a porogen (typically 30 wt.% relative to amount of mCSSQ), triphenyl sulfonium based PAG (typically 3 wt.% relative to amount of mCSSQ), and propylene glycol methyl ether acetate (PGMEA) as a solvent. The solution was spin-cast for 30 s at 3000 rpm, onto silicon wafers. The films were then exposed through a photo mask to broadband UV radiation using a UV projector model ORIEL (10.0 mW/cm² at 365 nm). After a post-exposure bake on a hot plate at 120°C for 3 min, the negative patterns were developed by dissolving the non-exposed UV area with PGMEA. All of the experimental steps described were carried out in a yellow room. Patterned porous thin films were then produced by curing the wafers in a cylindrical furnace (Linberg type 55642) at 420°C for 60 min under vacuum.

2.4. Characterization of porous thin films

Cross-section images of the patterned films were investigated by FE-SEM (Field Emission Scanning Electron Microscopy). The SEM images were recorded on a Hitachi S4500 apparatus operating at 5 kV. The surface morphology of the patterned film was inspected by AFM (Atomic Force Microscopy) using a DI3100E (Veeco Metrology Group) equipped with a carbon nano tip. The surface topology of the prepared samples was measured by AFM in tapping mode at a resonance frequency of 297 kHz. The scan size and scan speed were 1 μm² and 1 Hz, respectively. The scanning tip was a carbon nano tube (CNT) tip (HDC-tips type U3S on NCH cantilevers, Nano tools). The length and diameter of the CNT tip is 1.2 μm and 5 nm, respectively.

The film porosity and pore radius distribution (PRD) were analyzed by ellipsometric porosimetry [23]. Ellipsometric porosimetry is a combination of non-intrusive (wave propagation) and intrusive (adsorption) methods. Full porosity is calculated using an Effective Medium Approximation or Lorentz–Lorenz equation, which describes the relation between the optical characteristics and the porosity of the film. Open porosity was calculated from the variation of the refractive index during the absorption and desorption of organic solvents. The relative volume of open and closed pores was calculated by comparing the results obtained with empty and filled pores (before and after adsorption). The pore radius and PRD were calculated from the adsorption and desorption isotherms of the chosen adsorptive (toluene in this particular case) [24]. A more detailed description of the method can be found elsewhere [23–25].

Depth-profiled PALS was used to determine the micropore and mesopore sizes and pore interconnectivity. Details of the PALS setup and measurement methods appear elsewhere [26]. A monoenergetic positron beam implants positrons into the film with a mean implantation depth controlled by the selected beam energy (1–8 keV). Positronium, the bound state of a positron and electron, is formed by electron capture and traps in the void volume of pores. The Ps annihilation lifetime (2–142 ns) is correlated with the pore size using the extended Tao–Eldrup model [27]. PALS spectra with ~10^7 events were acquired at room temperature using a conventional fast lifetime system with a time resolution of ~500 ps and the POSFIT program [28] was used for data fitting.

The refractive index and thickness of the films were measured using a prism coupler (Metricon Co., Prism coupler 2010). The dielectric constant was measured at a frequency of 100 kHz using an impedance analyzer (HP 4284)-equipped probe station with a metal-insulator–metal structure. The hardness (H) and elastic modulus (E) of the thin films were measured using the continuous stiffness measurement of nanoindentation method [29]. In this technique, the force required as a function of indentation depth is recorded while a three-sided Berkovich diamond indenter is pushed into the sample and then withdrawn. In addition, the contact stiffness for all depths is measured by superimposing a small oscillation to the force.
signal at a relatively high frequency (45 Hz). Multiple points (typically 6 points) on each sample were indented and the average hardness and elastic modulus are reported to assure reliability.

3. Results and discussion

The photo patterning process for the nanoporous mCSSQ thin film is illustrated in Scheme 3. The mCSSQ precursor has a relatively high content of silanol group (typically >25 mol% in the total functional group). The high content of silanol groups in the mCSSQ precursor could be used as crosslinking sites in low temperature curing using acid catalyzed condensation, as illustrated in Scheme 4. Therefore, control of the acid generated area on the mCSSQ/tCD/PAG mixture film using UV irradiation on a photo mask can yield a patterned film after post-baking and a simple developing process. The by-product of the reaction would be a small amount of H2O vapor that would vent out from the film during the curing process. Finally, tCD molecules in the patterned film can be eliminated during the high temperature (~400 °C) curing process to generate nano sized pores (<2 nm) in the mCSSQ film.

In this study, we used three kinds of TPS based PAG that release strong sulfonic acid, TPS-TFMS (Triphenylsulfonium trifluoromethane sulfonate), TPS-PTS (Triphenylsulfonium p-toluenesulfonate), and TPS-CS (Triphenylsulfonium 10-camphorsulfonate). The TPS based PAG has been used as a component for KrF PR composition.

The patterning conditions for the mCSSQ/tCD/PAG mixtures dissolved in PGMEA were investigated as shown in Table 1. At a post-curing temperature of 120 °C, a time of 3 min, and 5 wt.% PAG concentration, the thickness of the UV-exposed area approached that of the spin-on deposition area. Therefore, the pattern selectivity of mCSSQ/tCD/PAG mixtures would be roughly attained in these condition. It should be note that we did not perform intensive research to optimize the conditions for patterning in this work.

Various patterned images of line and space etched mCSSQ film are shown in Fig. 1. The patterns were prepared by spin coating a mCSSQ/tCD/PAG mixture film, irradiating the film with broadband UV through a photo mask, postbaking at 120 °C for 3 min, and image developing by washing in PGMEA. The patterned optical images were fairly clear in micrometer dimensions. Line and space patterns having a resolution approaching 2 μm were prepared in the films, as can

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Patterning conditions for the mCSSQ/tCD/PAG mixtures dissolved in PGMEA at a concentration of 30 wt.% solid</th>
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</thead>
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<tr>
<td>Type of PAG</td>
<td>PAG (wt.%%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>–</td>
<td>0.0</td>
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<tr>
<td>TPS-TFMSd</td>
<td>10.0</td>
</tr>
<tr>
<td>TPS-TFMSd</td>
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</tr>
<tr>
<td>TPS-TFMSd</td>
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<tr>
<td>TPS-TFMSd</td>
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<tr>
<td>TPS-PTSd</td>
<td>5.0</td>
</tr>
<tr>
<td>TPS-CSd</td>
<td>5.0</td>
</tr>
</tbody>
</table>

The content of tCD is 30 wt.% relative to mCSSQ matrix. The temperature of post exposure baking is 120 °C.

a T I denotes the thickness after spin-on deposition.
b T II denotes the thickness of UV-unexposed area after post baking and developing.
c T III denotes the thickness of UV-exposed area after post baking and developing.
d TPS-TFMS: Triphenylsulfonium trifluoromethane sulfonate; TPS-PTS: Triphenylsulfonium p-toluenesulfonate; TPS-CS: Triphenylsulfonium 10-camphorsulfonate.

Fig. 1. The pattern images of the porous mCSSQ thin film. (a) Optical image of porous mCSSQ thin film containing fluorescent Ir complex—bis[2-(4,6-difluorophenyl)pyrindinato-N,C2] picolinate iridium (III). White areas correspond to UV-exposed and selectively developed regions. (b) Optical micrograph of UV-exposed and selectively etched porous structured thin film (thickness ~1 μm). (c, d) FE-SEM images of the porous mCSSQ thin film.
be seen in the FE-SEM image (See Fig. 1(d)). The patterns below 2 \( \mu m \) were poorly resolved. Hence, further study is necessary to achieve submicron patterns. These results confirm that mCSSQ/tCD/PAG compositions can be employed as a facile method for photo patterning to micrometer dimensions in the preparation of a porous low-\( k \) thin film. The resolution of the line/space pattern could be improved through optimization of the sensitivity of the photo curable system, the photo masking process, and developing process, including selection of the developing solvent. The one concern in using this approach is to avoid contamination and change in the film roughness due to PAG decomposition. The residue of PAG in the film was almost undetectable by means of Fourier-Transform Infrared Spectroscopy after the hard curing. Moreover, the roughness of the porous mCSSQ films was almost the same, regardless of use of PAG and/or tCD, as shown in Fig. 2. The roughness of the thin film made of mCSSQ/PAG/tCD mixture was only 0.45 nm while that of mCSSQ film was 0.34 nm. This confirms that the proposed PAG system does not deteriorate the properties of the film such as the composition and surface roughness.

The secondary interest of this study was control of the pore size and pore size distribution in a porous thin film. In our previous study, at low concentration, cyclodextrin-based porogen molecules were singly dispersed resulting in isolated pores, while porogen agglomeration and pore collapse became severe with increasing concentration [21]. Furthermore, the porosity increased and PRD became broad with increasing porogen concentration. The onset point of the broadening of PRD was 30 wt.% of tCD porogen relative to the solid content in the coating precursor [21]. Therefore, we selected a porogen concentration of 30 wt.% for making various porous thin films. The order of acidity of TPS based PAGs is TPS-TFMS > TPS-PTS > TPS-CS. Pore diameters of the thin film using PAG were smaller than that of the thin film without using PAG (Table 2).

Table 2

<table>
<thead>
<tr>
<th>Type of PAG</th>
<th>R.I.(^a)</th>
<th>Porosity (%)(^b)</th>
<th>(D_{EP}) (nm)(^b)</th>
<th>(D_{PALS}) (nm)(^c)</th>
<th>Inter. length (nm)(^c)</th>
</tr>
</thead>
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<td>–</td>
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<td>31</td>
<td>2.84</td>
<td>1.80</td>
<td>30</td>
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<tr>
<td>TPS-TFMS(^d)</td>
<td>1.3343</td>
<td>28</td>
<td>1.94</td>
<td>1.59</td>
<td>25</td>
</tr>
<tr>
<td>TPS-PTS(^d)</td>
<td>1.3491</td>
<td>25</td>
<td>1.62</td>
<td>1.44</td>
<td>21</td>
</tr>
<tr>
<td>TPS-CS(^d)</td>
<td>1.3523</td>
<td>25</td>
<td>1.62</td>
<td>1.48</td>
<td>17</td>
</tr>
</tbody>
</table>

\(^a\) Refractive index (\(\lambda\)=632 nm) of thin films measured by Prism Coupler.
\(^b\) Porosity and pore diameter of the films measured by Ellipsometric Porosimetry (the volume of adsorbed toluene normalized to the film volume).
\(^c\) Interconnection length and pore diameter of thin films measured by PALS.
\(^d\) TPS-TFMS: Triphenylsulfonium trifluoromethane sulfonate; TPS-PTS: Triphenylsulfonium p-toluenesulfonate; TPS-CS: Triphenylsulfonium 10-camphorsulfonate.
of the porous thin film decreases with the use of PAG. The reason for the dependency of types of PAG on the variation of pore size and the interconnection length is presently unclear and an investigation into correlations between pore structure and the acidity of PAG is underway. It should be noted that the porosity of porous thin films using PAG was somewhat smaller than that of porous thin film without using PAG. This indicates that the combination of a UV process and PAG may partially destroy the structure of a 3-dimensional CD based porogen. In other words, a small portion of C–O linkages or C–C linkages in the CD would be broken as a result of attack by UV and strong acid. Problems in this system such as porosity reduction could be mitigated by changing various process parameters such as UV dose amount, time, etc. The shape of PRD of the thin film became mono disperse with the use of PAG. It is noteworthy here that the use of PAG results in a unique pore structure as can be seen in Fig. 3. The PAG could accelerate mCSSQ matrix crosslinking at a relatively low cure temperature, and thus the agglomeration of tCD molecules could be disturbed in the hard curing process of the porous thin film.

In order to determine the relationship between the pore structure and film properties, we monitored dielectric constant, modulus, and hardness of porous mCSSQ thin films having different pore structures as summarized in Table 3. We fabricated thick films above 1000 nm in order to eliminate substrate effect in nanoindentation. Value of hardness and modulus of all films were collected at an indentation depth of 100 nm. Mechanical properties of the films were slightly changed with porosity. The change of the dielectric constant with porosity also shows similar behavior. Therefore, the properties of patternable mCSSQ/tCD/PAG films including mechanical properties and dielectric constant, could be sustained as compared with the properties of mCSSQ/tCD.

![Graphs showing pore radius distributions of porous mCSSQ thin films prepared with different PAG](image)

**Fig. 3.** Pore radius distributions of porous mCSSQ thin films prepared with (a) mCSSQ and tCD 30 wt.%; (b) mCSSQ, tCD 30 wt.% and TPS-TFMS 3 wt.%; (c) mCSSQ, tCD 30 wt.% and TPS-PTS 3 wt.%; (d) mCSSQ, tCD 30 wt.% and TPS-CS 3 wt.%.

<table>
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<tr>
<th>Type of PAG</th>
<th>Mechanical property</th>
<th>Electrical property</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>$T$ (nm)</td>
<td>Hardness (GPa)$^a$</td>
</tr>
<tr>
<td>–</td>
<td>1175</td>
<td>0.56</td>
</tr>
<tr>
<td>TPS-TFMS$^c$</td>
<td>1040</td>
<td>0.57</td>
</tr>
<tr>
<td>TPS-PTS$^c$</td>
<td>1198</td>
<td>0.62</td>
</tr>
<tr>
<td>TPS-CS$^c$</td>
<td>1063</td>
<td>0.64</td>
</tr>
</tbody>
</table>

$^a$ Mechanical properties were measured by nanoindentation, and hardness and elastic modulus of all films were collected at an indentation depth of 100 nm. 
$^b$ Measured at 100 kHz.
$^c$ TPS-TFMS: Triphenylsulfonyl trifluoromethane sulfonate; TPS-PTS: Triphenylsulfonyl p-toluenesulfonate; TPS-CS: Triphenylsulfonyl 10-camphorsulfonate.
4. Conclusion

Photo patternable mCSSQ compositions showing a dielectric constant below 2.4 and pattern resolution approaching micrometer scale were realized in the present study. We demonstrated patterned mCSSQ thin film with a resolution approaching $\sim 2\,\mu m$. This simple patterning process for a siloxane based insulator can be easily applied in practical fields, which have a relatively large feature size. Considering the minimum feature size ($\sim 90\,nm$) of recent LSI integration process, however, this approach appears to require considerable improvement via optimization of the photo patterning process parameters. The pore size and the interconnection length of the mCSSQ film with PAG were smaller than those without PAG. Furthermore, the pore radius distribution of the mCSSQ film with PAG was much narrower than that without PAG. Vitrification of the matrix at a relatively low curing temperature effectively reduced the agglomeration of CD molecules, resulting in decreased interconnection length.

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References