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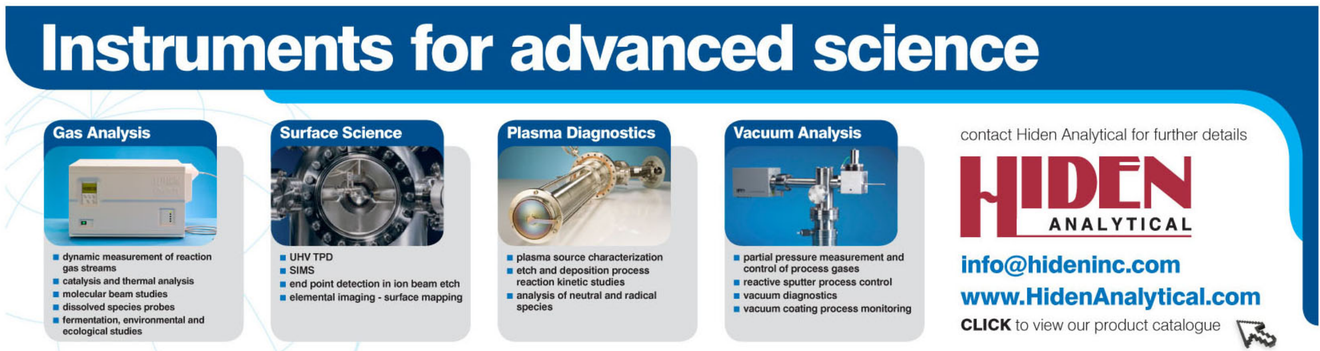

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Porous TEM windows fabrication using CsCl self-assembly

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Thin non-porous silicon nitride membrane has been used for transmission electron microscopy (TEM) "windows" due to its transparency to high-energy electrons. However, to completely eliminate the background scattering, a porous membrane is desirable. Here the authors report the fabrication of porous silicon nitride membranes by CsCl self-assembly to form hemispherical islands, followed by "image reversal" via drying etching and liftoff steps. Through controlling the evaporated CsCl film thickness, the exposure time of the film in air, and the relative humidity of air, the authors were able to fabricate porous silicon nitride membranes with pore diameter and interpore spacing of order 100 nm. The pore diameter could be further shrunk by coating a conformal film onto the porous membrane. In addition, conductive porous TEM windows can be achieved by simply skipping the final metal removal step. Such a porous membrane would also find applications in separation or filtration of macromolecules or nanoparticles. © *2012 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4751550]

I. INTRODUCTION

Thin silicon nitride membrane has been used for transmission electron microscopy (TEM) "windows" due to its relatively high transparency to high-energy electrons.[1,2] It is carbon-free, resistant to most chemicals, and stable at very high temperature (up to $\sim$1000 °C), so one can synthesis nanomaterial that involves high temperature and/or very harsh chemical conditions (such as Piranha treatment with a heated mixture of H_2SO_4 and H_2O_2) directly on them for TEM analysis. However, though silicon nitride is a relatively weak electron scattering material due to its low density and low equivalent atomic number, a very thin (well below 50 nm thick) membrane is needed to achieve atomic resolution as the electron beam broadening due to elastic scattering is proportional to $T^{2/3}$ (T is the membrane thickness).[3] But such a thin membrane is very brittle, particularly when the membrane size is large (in mm range), which is more convenient for TEM analysis. Therefore, to completely eliminate the background scattering, porous TEM windows etched in a thick and thus mechanically stable membrane are desirable.

Microscale porous silicon nitride membrane TEM windows with pore sizes of several micrometers fabricated by photolithography and etching is commercially available. For nanoscale porous membrane, though it has been fabricated using focused ion beam (FIB) milling for the application of extraordinary optical transmission devices[4] and electron beam lithography (EBL),[5] FIB and EBL are both too slow for practical applications. On the other hand, the high throughput nanoimprint lithography cannot be used to pattern the membrane because it will break the fragile membrane easily. Previously porous silicon membranes have been fabricated by rapid thermal annealing of a thin (15-nm-thick) amorphous silicon film that leads to spontaneous formation of voids as nanocrystals nucleate and grow.[6] Though sub-50 nm pores can be achieved readily using this method, the membrane has to be very thin for the self-formation of nanopores, which affects its mechanical strength. Pores in silicon nitride can also be created by irradiating the nitride film by accelerated heavy ions (e.g., Bi and Xe) with GeV energy that lead to the formation of damaged tracks, and subsequent chemical etching of the irrigated sample using hot H_3PO_4.[7] The number of the pores per unit area and the pore diameter can be very well controlled in this method, yet the access to the GeV heavy ion facility is very limited and only pores with conical shapes (i.e., tapered sidewall) can be formed.

In this work, we report the fabrication of nanoporous silicon nitride membrane by self-assembly of evaporated CsCl thin film[8] followed by an "image reversal" pattern transfer process that converts the protruded dot pattern into a recessed hole pattern. As a lithography tool, CsCl self-assembly has been employed to fabricate protruded nanopillars by etching into the substrate material using the self-assembled CsCl islands as mask, which can be used to form superhydrophobic surface for microfluidic devices, or antireflective surface for improved light collection in solar cells.[9,10] The film self-assembles to form isolated hemisphere because CsCl is soluble in the layer of absorbed water. In the process, the smaller radius islands will be more soluble than larger ones as described by the Hulett equation ($\ln[c_s(r)/c_s(\infty)] = 2\gamma v/kTr$, c_s is the saturation solubility, γ is the interfacial tension, and v is the volume of a molecule);[11] thus, they will disappear by completely dissolving in the adsorbed water, and the film will become more discontinuous. Drying off the adsorbed water layer (e.g., by putting the film in a vacuum chamber of a reactive ion etcher) will result in CsCl islands with smooth surface and usually spherical shape. As no time-consuming top–down nanolithography is involved, this method is of low cost and high throughput where an entire wafer (contains some 700 TEM windows for a 4 in. wafer) can be patterned at a time. The lack of periodicity and long-range ordering is not a concern for TEM windows.

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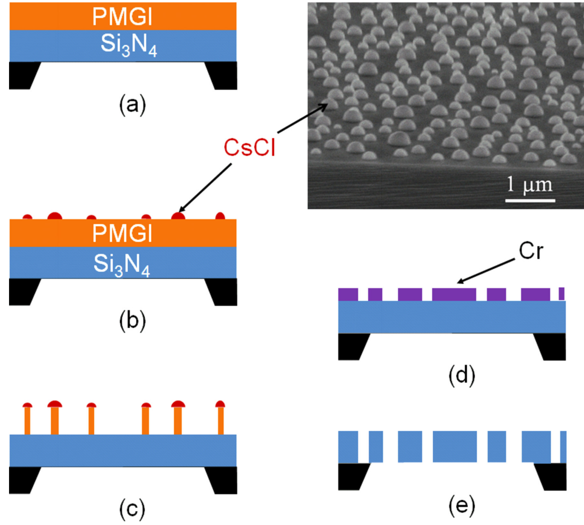

FIG. 1. (Color online) Schematic of porous membrane fabrication process. (a) Spin-coat PMGI film onto Si_3N_4 membrane. (b) Thermally evaporate CsCl film and allow it to self-assemble in the presence of moisture. (c) RIE PMGI to obtain undercut profile. (d) Evaporate Cr layer and lift it off. (e) RIE silicon nitride and (optional) remove Cr to form porous membrane.

Using the same pattern transfer process as described below, nanosphere lithography preferably with sphere size shrinking by oxygen plasma etching,[12] which is also a gentle and high throughput process, could also be employed to pattern nanoporous silicon nitride membrane; but we believe the current process offers better control. In addition to TEM windows, porous membrane would also find applications in separation or filtration of small and macromolecules or nanoparticles based on size, electric charge, or hydrophobicity;[7,13–15] as well as in the synthesis of nanoparticles where the dissolved particle material flows through the nanoporous membrane into the receiver solution for which the material become insoluble.[16]

II. EXPERIMENT

The porous silicon nitride membranes were fabricated in two stages: the fabrication of nitride membrane with area of order millimeter square and the creation of pores through the membrane.

A. Silicon nitride membrane fabrication

Four inch 0.3 mm thick double-side polished silicon wafers were first coated with 200 nm thick low-stress silicon nitride film by low pressure chemical vapor deposition (LPCVD) using the micro- and nanofabrication facility at INRS (Varennes, Quebec). The backside of the nitride was then patterned by standard photolithography and reactive ion etching (RIE). As it was found that the positive photoresist, here Shipley S1805, did not adhere well to the nitride film, a layer of anti-reflection coating (ARC, XHiRC-16 from Brewer Science) was first coated as an adhesion layer. Next, the Si in

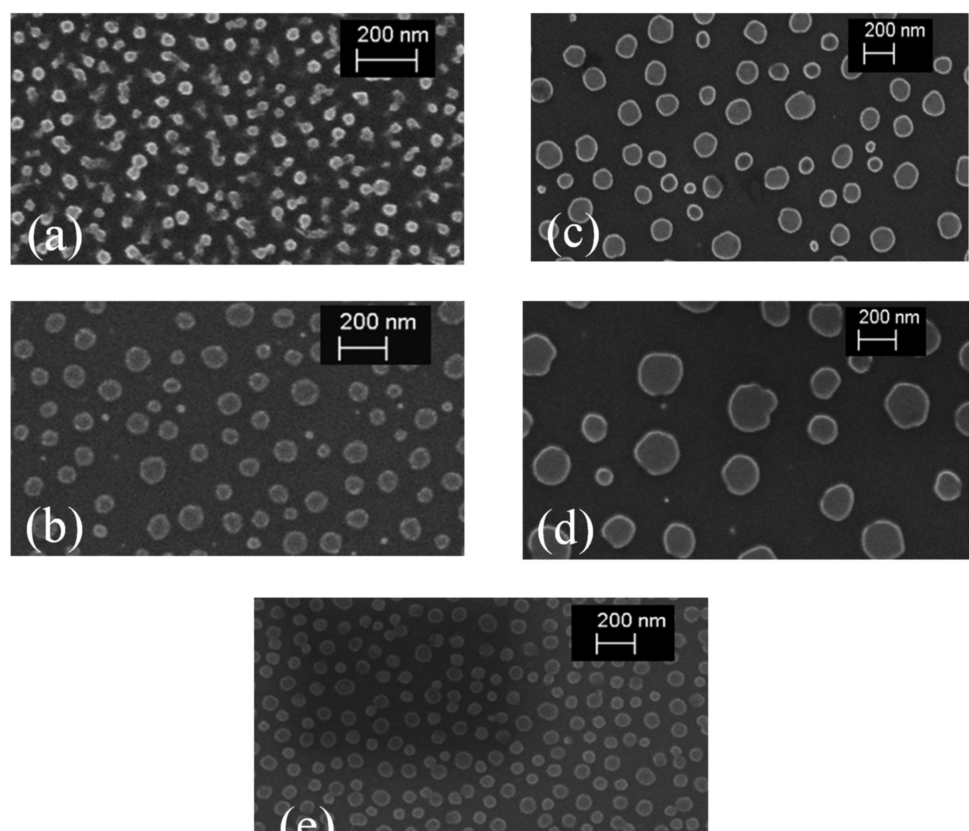

FIG. 2. SEM images of silicon pillar patterns transferred by RIE from CsCl islands that are self-assembled on PMGI/Si substrate at various CsCl film thickness, relative humidity (RH), and time. (a) 15 nm CsCl, 45% RH, 1 h; (b) 15 nm CsCl, 45% RH, 2 h; (c) 3 nm CsCl, 45% RH, 24 h; (d) 5 nm CsCl, 45% RH, 24 h; (e) 5 nm CsCl, 15% RH, 24 h.

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the areas not protected by the nitride film was etched using a 25% KOH solution heated to ∼80 °C for 1–2 h to reach the nitride film on the front side, leading to the formation of nitride membrane supported by silicon at four sides.

B. Porous membrane fabrication

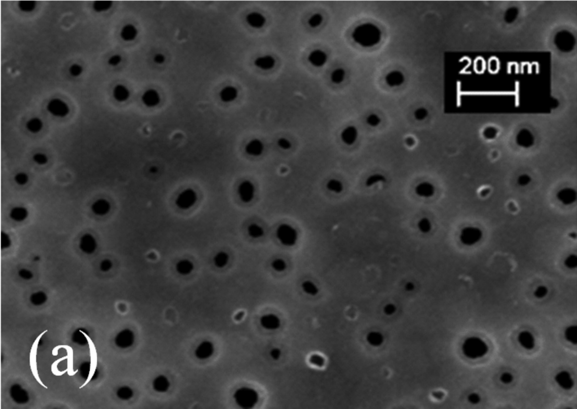
Since the self-assembly of CsCl film leads to a protruded dot pattern, an "image reversal" process is needed to convert it into recessed hole pattern in the nitride film. Starting from a (nonporous) Si_3N_4 membrane, the fabrication process of the porous membrane is illustrated in Fig. 1. First, the wafer with hundreds of membrane areas was treated with O_2 plasma to provide good adhesion for the subsequent layer. Next, a liftoff layer of polydimethyl glutarimide (PMGI) was spin-coated onto the membrane [Fig. 1(a)] and baked at 150 °C for 2 min. A layer of CsCl was then thermally evaporated onto the PMGI using an Intlvac Thermal Evaporator. At this point, the samples were exposed to moisture to allow hemispherical CsCl islands to form by self-assembly [Fig. 1(b)]. This pattern was then transferred into PMGI using O_2 RIE with over etch to obtain an undercut profile for easy liftoff [Fig. 1(c)]. A subsequent Cr layer was deposited using electron beam evaporation and lifted off using AZ 300 MIF developer that dissolves PMGI [Fig. 1(d)]. Finally, the resulted hole pattern in Cr was transferred into the nitride membrane by RIE using CF_4 gas, followed by the removal of Cr using wet etching [Fig. 1(e)]. A conductive support is often desirable in order to minimize the charging effect during TEM analysis, which can be achieved readily by skipping the final Cr removal step.

III. RESULTS AND DISCUSSION

The size and spacing of the CsCl hemispherical islands formed by self-assembly are controlled by the thickness of the CsCl film, the relative humidity (RH) of the air, the time of exposure in air, and the surface energy of the sublayer. A systematic study of the self-assembly process can be found in Ref. 8. Increases in the CsCl thickness, exposure time, and RH results in an increase in the diameter of the hemispherical islands formed. As well, exposing CsCl to higher RH for longer time leads to an increase in the average inter-island spacing.

Figure 2 demonstrates the effects of varying exposure times, CsCl thicknesses, and relative humidity on island size. Here, the CsCl films were deposited on PMGI/Si substrate. After the appropriate exposure time was reached, the samples were etched using O_2 gas followed by CF_4 gas to transfer the CsCl island pattern into PGMI and then into Si. The island pattern is thus "frozen," preventing further evolution due to additional exposure to moisture prior to SEM imaging. In one experiment, 15 nm CsCl (nominal thickness for the rough film) was deposited and exposed at 45% RH for 1 h [Fig. 2(a)] and 2 h [Fig. 2(b)]. As expected, the sample with 2 h exposure showed a greater island diameter and separation than the sample with 1 h exposure. Figures 2(c) and 2(d) illustrates the effect of varying CsCl thicknesses; here very thin CsCl film of 3 and 5 nm were deposited and exposed at 45% RH for a long period of time (24 h). The sample with 5 nm CsCl initial thickness showed larger islands and separation than the sample with 3 nm CsCl thickness. Higher humidity also led to larger islands and separation, as shown in Figs. 2(d) and 2(e) for 5 nm CsCl with 24 h exposure time at 45% and 15% relative humidity.

Figure 3 shows the SEM image of the completed nanoporous membrane. In Fig. 3(a), 3 nm of CsCl film self-assembled at 45% RH for 24 h to obtain pore diameters of around 80 nm and interpore distances of ∼80 nm. Since silicon nitride is an insulating material, the Cr layer could be retained in order to provide the conductivity that is critical for TEM analysis. Some pores were missing due to the collapse or bending of PMGI pillars having smaller diameters and thus higher aspect ratio, which led to unsuccessful Cr liftoff. This would not greatly affect the application of the porous membrane as TEM windows. If preferable, smaller pores can be realized by shrinking the pores using a range of methods, including coating a conformal film onto the porous membrane by atomic layer deposition (ALD) or initiated chemical vapor deposition (iCVD),[15] and rapid thermal carbonization of acetylene.[17] On the other hand, larger pores can be obtained by depositing thicker CsCl film, exposing the film to higher relative humidity and/or for longer time, as shown in Fig. 3(b). Here 10 nm CsCl was deposited, and subsequently exposed to 68% RH for 24 h, resulting in pores with diameter and interpore distance both



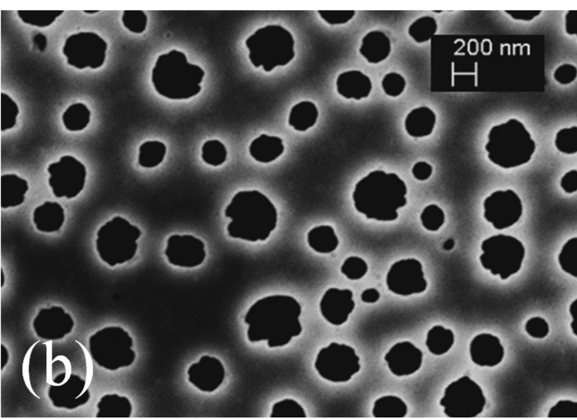


Fig. 3. SEM images of nanoporous silicon nitride membrane patterned by CsCl self-assembly. (a) 3 nm CsCl, 45% RH, 24 h; (b) 10 nm CsCl, 68% RH, 24 h.

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roughly 200 nm; and as expected, there is no missing pores because the thick PGMI pillars were mechanically stable against collapse or bending.

IV. CONCLUSIONS

In this work, we have successfully demonstrated the use of CsCl self-assembly in the fabrication of porous silicon nitride membranes for the application as TEM windows. This low cost method is effective for patterning the fragile membranes. By controlling the CsCl thickness, the exposure time, and relative humidity, we were able to fabricate porous silicon nitride membranes with pore diameter and interpore spacing of order 100 nm. Several approaches are suggested to shrink the pores when desirable. In addition, conductive porous TEM windows can be achieved by simply skipping the final metal mask removal step.

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