Nanochannel Glass Replica Membranes

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The preparation of thin metallic membranes containing uniform, patterned voids with diameters as small as 40 nanometers and packing densities greater than 3×10^9 voids per square centimeter is described. These membranes, made of platinum, gold, tungsten, and molybdenum, have been fabricated by thin-film deposition with nanochannel glass wafers as substrates. The membranes are well suited for use as masks in substrate patterning applications such as ion implantation, reactive ion etching, and materials deposition. Results are presented on their use in the parallel patterning of silicon by direct materials deposition with features in the 100-nanometer size regime.

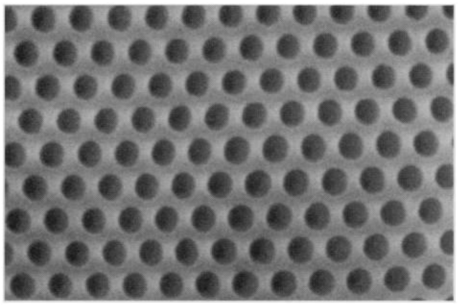

Fig. 1. SEM micrograph of a polished and etched NCG wafer with 240-nm voids arranged in a hexagonal-close-packing arrangement. The section shown is 4.6 μm wide.

The scientific and technological interest in materials engineered on a nanometer scale is widespread, impacting research and development in many disciplines. These materials have found use in electronic and optical devices (*1*), filtration (*2*), and biomedical applications (*3*, *4*). In addition, these materials provide an opportunity to study quantum effects not observed in bulk materials.

In this report we describe the fabrication and patterning applications of nanochannel glass replica membranes. These membranes, prepared thus far from refractory and noble metals, are thin films that contain uniform, nanometer-scale voids, the sizes, positions, geometric patterns, and packing densities of which may be controlled to a high degree. In addition, the thicknesses of the membranes, and thus the aspect ratios of the voids, may also be controlled. These properties make nanochannel glass replica membranes somewhat different than polymeric track-etch membranes and porous alumina membranes, which have been used in replication studies (*5*), as hosts for the fabrication of other materials (*3*, *6*), and as electrochemically switchable filters (*7*). Currently, we have prepared tungsten, molybdenum, platinum, and gold membranes with void diameters as small as 40 nm at packing densities greater than 3×10^9 voids per square centimeter. The aspect ratios of the voids present in these membranes have ranged from 0.06 to approximately 2, reflecting our primary interest in low–aspect-ratio masks for patterning applications.

The processes used in the preparation of these membranes, however, are not limited to the materials nor the aspect ratios listed above. In principle, membranes with larger aspect ratios may be prepared, and other materials that can be deposited by physical vapor deposition may be used, provided the resulting membranes possess the necessary robust character and chemical stability to withstand the processing conditions encountered. Our success in preparing tungsten, molybdenum, platinum, and gold membranes suggests the likelihood of extending the types of materials used to include other metals and potentially glasses and ceramics. As a demonstration of their use in patterning applications, we have used platinum membranes as masks for patterned materials deposition onto silicon with features in the 100-nm size regime.

As the name implies, nanochannel glass replica membranes are films that are prepared from nanochannel glass (NCG), a recently developed material containing patterned arrays of parallel uniform voids (*8*). The NCG material is fabricated by a draw process similar to that used in the preparation of optical fibers and microchannel plates (*9*). In the work reported here, the void pattern is that of a regular hexagonal array. The preparation of the NCG material begins by placing an acid-etchable glass rod into an inert glass tube and drawing the pair at elevated temperature into fibers. These fibers are then packed together in a hexagonal close-packed arrangement forming a bundle with an overall hexagonal shape. The bundle is then drawn along its length at elevated temperature, reducing its cross-sectional area and fusing the individual glass fibers together while maintaining the geometric regularity of the pattern. These resulting fibers are then repacked and redrawn, and the process is repeated until the desired packing density and element size is achieved. The material is then wafered, polished, and etched in an appropriate acid solution, leaving voids where the acid-etchable glass was initially present. More details on the fabrication process may be found in the original paper (*8*). In addition, other packing schemes may be used to produce more complex void patterns. The end result is a highly uniform, patterned glass material, such as that shown in the scanning electron microscopy (SEM) micrograph of Fig. 1. This hexagonally patterned NCG wafer with voids 240 nm in diameter contains a packing density greater than 8×10^8 voids per square centimeter. Currently, NCG materials have been fabricated with voids as small as 17 nm and packing densities greater than 10^{11} voids per square centimeter. The samples used in this work contained about 6×10^6 voids.

The lateral dimensions of the NCG materials prepared thus far are on the order of millimeters. However, larger sample dimensions can be attained by one additional bundling step followed by a fusion process. In principle, NCG materials prepared in this manner can be made several inches in diameter.

For applications requiring patterned membranes with high aspect ratios, the NCG wafers themselves may be mechanically polished and used. However, it is impractical to polish these wafers thin enough for use as low–aspect-ratio pattern masks with voids in the 100-nm regime or below. Instead, we have made thin-film replicas of the NCG wafers using the wafers as patterned substrates. We begin by depositing a thin-film bilayer onto the surface of a polished NCG wafer in which the voids have been exposed by chemical etching. Deposition techniques such as sputtering, thermal evaporation, or electron-beam evaporation may be used. The thin-film layer in contact with the NCG wafer is an easily dissolved buffer material, and the outer thin-film layer is the NCG replica membrane. By slowly immersing the coated wafer into a chemical solution that rapidly dissolves the buffer layer, the membrane is released and is supported by the surface tension of the solution (Fig. 2). Appropriate choices for the buffer-layer material and the chemical solution depend on the choice of the membrane material. In preparing membranes of platinum, gold, tungsten, and molybdenum, we have used aluminum buffer layers, which quickly dissolve in hot sodium hydroxide solutions. Once released, the membrane may be lifted from the surface of the solution with a glass slide and floated onto the surface of a deionized water bath for rinsing. We typically repeat the rinse process several times before placing the membranes on substrates. This replication process does not

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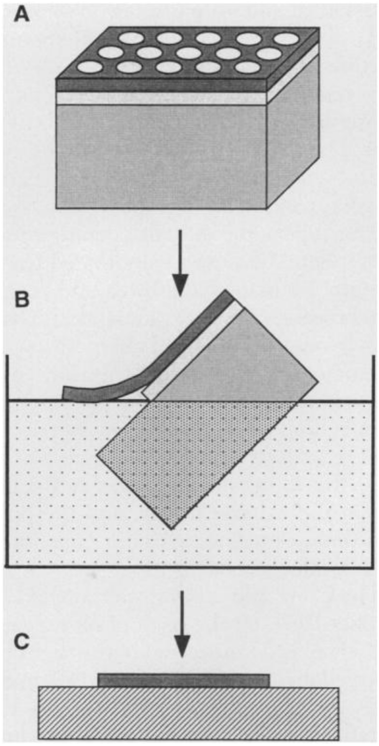

Fig. 2. Schematic of the preparation of the NCG replica membranes. (**A**) An easily dissolved buffer layer and a desired membrane layer are deposited onto the surface of the NCG wafer. (**B**) The membrane is released by dissolving the buffer layer in a chemical solution. (**C**) After rinsing, the membrane may be placed on a substrate or support structure for characterization or use.

destroy the NCG wafers, and they may be repolished and reused.

As an illustration of this process, we fabricated a hexagonally patterned platinum replica membrane 75 nm in thickness with voids 40 nm in diameter. We prepared this membrane by mechanically polishing the surface of an NCG wafer 0.9 mm in diameter using progressively finer diamond powders to a final particle size of 0.25 μm. After polishing, the wafer was briefly acid etched, exposing the voids to a depth of about 1.5 μm, and was then coated with 90 nm of aluminum followed by 75 nm of platinum by planar magnetron sputtering in argon gas. The sample was then slowly immersed in a solution of 3 g of sodium hydroxide in 15 ml of deionized water at a temperature of 60°C, quickly dissolving the aluminum and releasing the platinum replica membrane. The membrane was rinsed in deionized water and picked up with a 1000-mesh copper grid for SEM characterization (Fig. 3). The membrane has an aspect ratio slightly less than 2 and a packing density greater than 3×10^9 voids per square centimeter.

The replica membrane shown in Fig. 3 was prepared from an NCG wafer with voids 130 nm in diameter, which are considerably larger than the voids present in the membrane itself. This reduction in the void diameter is a result of the sputtering process. By the nature of the process, sputtered atoms arrive at the substrate (NCG wafer) with a variety of trajectories. Those atoms with tangential trajectories naturally tend to close the openings present in the NCG wafer. This effect can be controlled to a certain degree with the use of collimating apertures placed above the wafers and by adjusting the pressure of the argon gas to change the mean free path between argon atoms. The effect can also be minimized by adjusting the gas pressure to ensure that the mean free path between the argon atoms is larger than the dimensions of the collimating apertures.

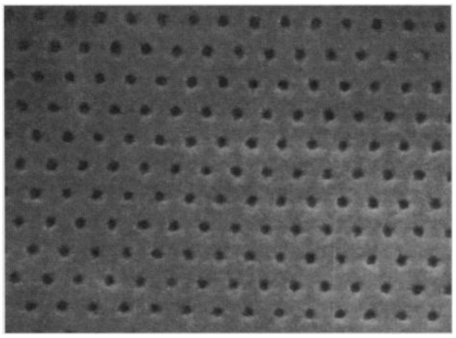

Fig. 3. SEM micrograph of a platinum replica membrane with 40-nm voids and a thickness of 75 nm supported by a 1000-mesh copper grid. The section shown is 2.3 μm wide.

To illustrate the use of these membranes in substrate patterning, we prepared a platinum replica membrane 110 nm in thickness with voids 115 nm in diameter for use as a deposition mask. The membrane was prepared from an NCG wafer 1.65 mm in diameter with voids 240 nm in diameter. After polishing and etching, the NCG wafer was sputter coated with 100 nm of aluminum followed by 110 nm of platinum. The membrane was released from the wafer and rinsed, and was then lifted from the rinse bath with a silicon (110) substrate and allowed to dry. After sputtering 30 nm of platinum onto the substrate, the replica membrane was removed with adhesive tape, leaving an array of platinum dots on the surface of the silicon substrate (Fig. 4). We have carried out similar experiments resulting in the patterned deposition of tungsten, molybdenum, gold, and nickel on various substrates and have found that these membranes maintain their pattern integrity at the elevated substrate temperatures encountered under normal sputtering conditions. This stability is a benefit compared to conventional resists used in lithographic processes, which can suffer pattern degradation under the deposition of refractory materials.

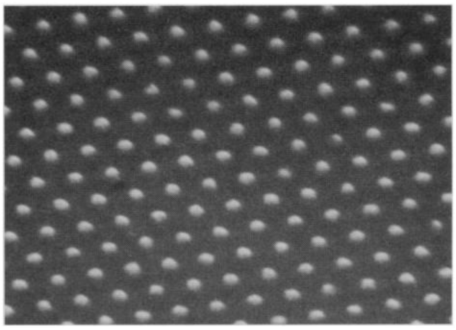

Fig. 4. SEM micrograph of a platinum dot array on a silicon (110) substrate prepared with a platinum replica membrane as a deposition mask. The substrate is tilted at 45°, and the section shown is 4.6 μm wide.

These NCG replica membranes have desirable characteristics with regard to their preparation and their use in substrate patterning. First, the polishing and deposition processes involved in the preparation of these membranes allow relatively large quantities to be produced simultaneously. Also, no serial lithographic techniques are used to define the individual void features present in a given membrane. In addition, because no resists are used in preparing NCG replica membranes, fewer steps are required overall. Another benefit is flexibility in the choice of the materials used, which we believe can be extended to include various metals and potentially glasses and ceramics. Such flexibility in materials choice is desirable in order to tailor the properties of these membranes for various uses. The tungsten, molybdenum, platinum, and gold membranes prepared thus far illustrate properties such as high-temperature stability, good chemical resistance, and high mass density, making them well suited for use as materials-deposition masks, reactive-ion-etching masks, and ion-implantation masks. We believe they will be useful in the parallel patterning of semiconductor materials with features of 40 nm and below, a size regime of interest for studying quantum confinement effects.

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Emission Measurements of the Concorde Supersonic Aircraft in the Lower Stratosphere

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Emission indices of reactive gases and particles were determined from measurements in the exhaust plume of a Concorde aircraft cruising at supersonic speeds in the stratosphere. Values for NO_x (sum of NO and NO_2) agree well with ground-based estimates. Measurements of NO_x and HO_x indicate a limited role for nitric acid in the plume. The large number of submicrometer particles measured implies efficient conversion of fuel sulfur to sulfuric acid in the engine or at emission. A new fleet of supersonic aircraft with similar particle emissions would significantly increase stratospheric aerosol surface areas and may increase ozone loss above that expected for NO_x emissions alone.

Emissions from aircraft include many species that play a role in atmospheric chemical and radiative processes (*1*). Programs in the United States and other countries are under way to evaluate the effects of expanding the number of high-speed civil transport (HSCT) aircraft that operate in the stratosphere (*2, 3*). In addition to the severe technical challenges that must be addressed, significant environmental issues related to the role of exhaust emissions in climate and global change must also be addressed before such a fleet can be considered viable (*4*). The emission requirements imposed on new engines will largely depend on the environmental consequences attributed to the emissions.

The HSCT aircraft will emit reactive nitrogen, NO_y, in the form of NO_x at altitudes in the lower stratosphere between 16 and 23 km while operating at speeds of Mach 1.6 to 3.2, respectively. The NO_x participates directly and indirectly in catalytic cycles that destroy O_3 in the lower stratosphere (*5*). However, the sensitivity of O_3 loss to NO_x emissions is reduced in atmospheric models when heterogeneous reactions on background sulfate aerosol particles are included (*6–8*), because the NO_x fraction of NO_y is reduced through more effective conversion to HNO_3 (*9*). One current estimate is that the emission from a fleet of 500 HSCT aircraft operating in the year 2015 at Mach 2.4 (20 km) would change column O_3 by less than 1% between 40° and 50°N if the emission index (EI) for NO_x is 15 g of NO_x per kilogram of fuel or less (*7*). Losses increase if either the EI for NO_x or the flight altitude are increased. However, these calculations currently do not include the effects of the emission of sulfate particles.

To date, no direct EI measurements for reactive nitrogen species or particles have been reported for a supersonic aircraft operating in the stratosphere. Instead, EI values for NO_x are derived from ground-based engine measurements (*10, 11*). Particle emission parameters are not well characterized for supersonic aircraft operating in the stratosphere, because ground-based tests do not fully simulate the growth and coagulation processes in the plume that change particle number, size, and composition after the engine exhaust enters the surrounding atmosphere. We present here measurements made behind the Concorde aircraft and use them to address NO_x and particle emission rates, the formation of nitric and sulfuric acid in the exhaust plume, and the potential consequences of particle emission for O_3 loss calculations.

The Concorde exhaust was sampled on 8 October 1994, off the coast of New Zealand (Fig. 1). A 320-km section of the flight path traversed by the Concorde in 10 min at Mach 2 was sampled by the NASA ER-2 aircraft in three 30-min segments, during which the ER-2 moved back and forth across the path at different altitudes. The plume was encountered at least 11 times during this period (Fig. 2). The gas and particle instruments on board the ER-2 are well suited to analyze aircraft exhaust: all have a sampling rate of 0.3 Hz or higher and have demonstrated precision and accuracy in measurements in the background atmosphere (*12*) (Table 1). A CO_2 measurement in the plume provided the dilution factor because CO_2 can be directly related to fuel use from the stoichiometry of combustion. This dilution factor allows measurements of other species to be expressed as EIs. The reactive nitrogen instrument provided separate measurements of NO (the primary nitrogen emission), the secondary product NO_2, and NO_y; NO_y is the reservoir of reactive nitrogen species

$$NO_y = NO + NO_2 + HNO_3 + 2N_2O_5 + ClONO_2 + HO_2NO_2 + CH_3C(O)O_2NO_2(PAN) + \ldots \quad (1)$$

(PAN, peroxyacetyl nitrate) measured through catalytic conversion to NO and detection of NO using chemiluminescence. With a measure of NO and NO_y, the conversion of NO to higher oxides can be monitored in the plume. Other gaseous combustion products include H_2O, also directly related to the quantity of fuel burned, and CO, which is related to the efficiency of combustion. We used N_2O as a reference to the background atmosphere because it is a long-lived species in the stratosphere and significant N_2O production is not expected in the engine (*11, 13*). Measurements of

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