Flake-Filled Barrier Membrane Made by Photo Lithography

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Membranes with impermeable flakes can find applications as barriers for solutes like HCl, KOH and oxygen. The flakes can be mica, clay or other impermeable materials. Flakes can reduce the mass transport through the membrane ten times or more if they are aligned parallel to the membrane surface. However, theories about the permeation through flake-filled barrier membrane are not fully tested because the size, alignment and exfoliation of the flakes in the polymer matrix are not easy to control [1-5]. To overcome this, we have made flake-filled barrier membrane by photolithography. We can then control the size and shape of the flakes, as well as their distribution in the matrix. Our preliminary studies of the permeability of these composites are described here.

Membrane Preparation

The polymer we are using is poly(dimethyl siloxane) (PDMS, Sylgard® 184, Dow Corning, weight ratio elastomer to curing agent 10:1). There are several advantages of choosing PDMS as the polymer matrix. PDMS is easy to process into thin films. It is stable during photolithography, even when in contact with different solvents and high temperatures. PDMS also has a large permeability, which allows quick experiments. However, PDMS has one significant disadvantage: the surface energy of cured PDMS is low, which inhibits other material attaching to its surface.

We make a composite film as shown in Figure 1. Hexane is mixed with PDMS to decrease the viscosity, and the solution is spin-coated on silica wafers. The speed, 5000rpm for 30 seconds, makes about a 10 um film. The polymer film is cured at 150 ºC for 15 minutes. We next give the PDMS an oxygen plasma treatment to make its surface hydrophilic. We then spin-coat the positive photoresist (Shipley's 1813) on the treated polymer films at 2000rpm for 30 seconds. The coated wafers are baked on a hotplate at 105 ºC for two minutes.

We next expose the photoresist. A mask which silhouettes the desired geometries is prepared. A contact mask aligner is used to expose UV light on the surface of the wafer and transfer the pattern from the mask onto the photoresist. After the photoresist is developed in its developer (H_2O:351, 5:1) for one minute, the mask pattern is on the PDMS surface. The wafers are then treated with the oxygen plasma, and put into an electron beam evaporator to deposit 0.5-1um titanium. The wafers are soaked into acetone to dissolve the remaining photoresist, and an ultrasonic bath is used to improve the lift-off. The result is one well patterned titanium flake layer on the PDMS surface. We repeat the previous procedure until the number of layers desired is of achieved.

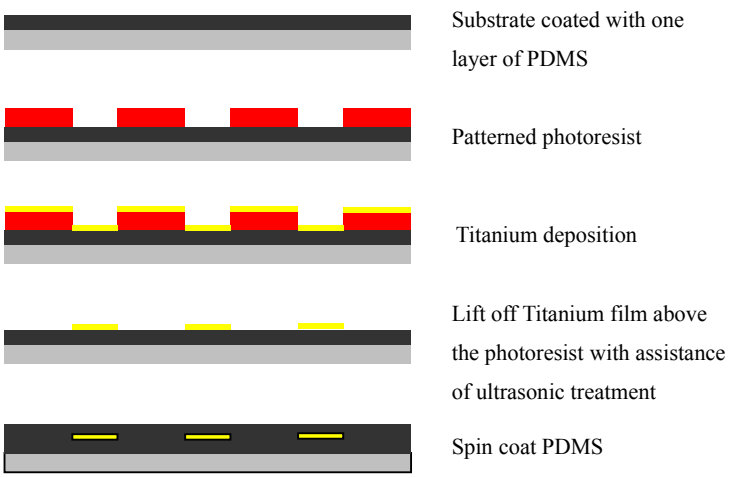

Figure 1. Scheme for the fabrication of composite membrane

We made three different shapes of the titanium flakes: ribbons, squares and hexagons. Examples are shown in Figure 2. Theses samples are described using the parameters shown in Figure 3. The composite is topped with a film of pure polymer of thickness l_0. Under that, there are one or more layers of flakes of thickness a, separated by pure polymer of thickness b. The gap between flakes is $2s$. For squares, those parameters are sufficient. For ribbons, the distance W is essentially infinite. For hexagons, $2d$ is defined as the length of two parallel sides. We prepared nine different samples of all geometries. For every different shape of flakes, we have 1) $2d$ =200um, $2s$ =40um (200x200x40); 2) $2d$ =200, $2s$ =10 (200x200x10); and 3) $2d$ =100, $2s$ =5 (100x100x5).

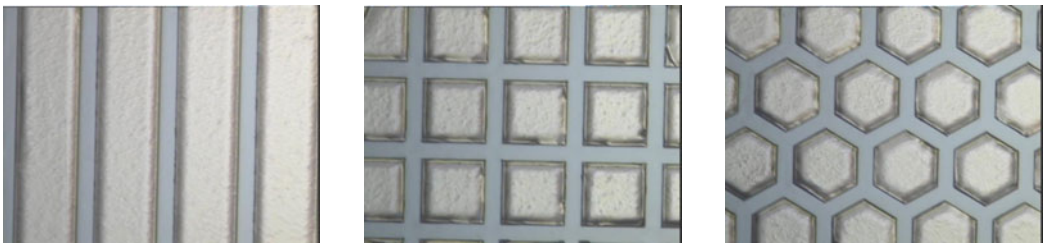

Figure 2 Different shapes of flakes (200x200x40)

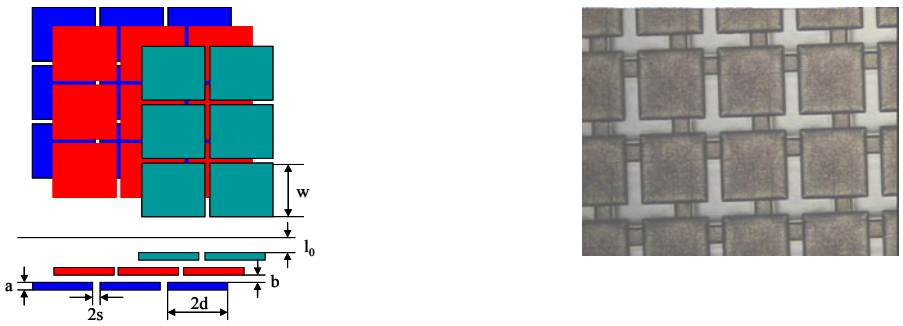

Figure 3. Dimensions of composite with square flakes

Permeability Measurements

Experimental flux measurements are made with the diaphragm cell shown in Figure 4. The cell uses a membrane of area of 1.03 cm^2 clamped between compartments of 22.1 and 11.7 cm^3. A brass plug is sometimes added to reduce the volume of the receiving compartment and thus allow a shorter experiment. In a typical experiment, both compartments were first filled with 200 kPa helium. After an hour, both compartments were refreshed with more of the same gas. Then an additional 200 kPa of helium was added to the larger (donating) compartment, and the pressure difference between the compartments was measured with two pressure transducers as a function of time. The permeability P was calculated from these differences by means of the equation [6]

$$P = \frac{\ell}{At\left(\frac{1}{V'} + \frac{1}{V''}\right)} \ln \frac{\Delta p_o}{\Delta p} \qquad (1)$$

where Δp_0 and Δp are the pressure differences initially and at time t, respectively; and V' and V'' are the volumes of the two compartments.

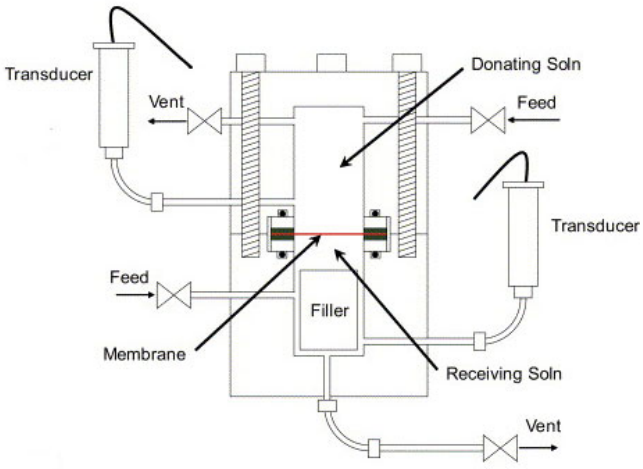

Figure 4. Diaphragm cells for gas permeation

Figure 5 shows typical permeation data for pure PDMS and for PDMS with one or three layers of 200x200x40um square flakes. The pressure change of the downstream side is much slower for PDMS with three layers of flakes than the pure PDMS and the composite with only one layer of flakes. Because the slope of these data is proportional to the permeability (Equation 1), the composite with three layers of flakes has the smallest permeability.

The diffusion resistance across a unit area of membrane without flakes is:

$$\frac{Dc_{10}}{J_0} = \frac{l}{dw} \tag{2}$$

These results are exemplified by the black line in Figure 5.

For the composite with only one layer of flakes, there have more resistances adding into the structure:

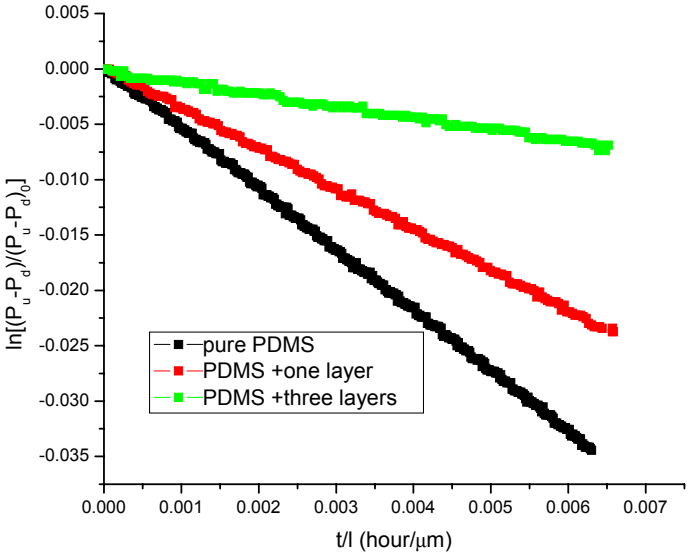

Figure 5. Typical gas permeation data

$$\left[\frac{\text{total}}{\text{resistance}}\right] = \left[\frac{\text{resistance}}{\text{of top and bottom layer}}\right] + \left[\frac{\text{resistance}}{\text{necking into and out of slit}}\right] + \left[\frac{\text{resistance}}{\text{of slits}}\right] \tag{3}$$

We can estimate the resistance of the composite relative to that of the flake-free film as [5]

$$\frac{J_0}{J} = \frac{l_0}{l} + \frac{d\ln\left(\frac{2W}{s}\right)}{2\pi l} + \frac{Nad}{2sl} \tag{4}$$

where N is the number of the flake layers. The results are represented by the red line in Figure 5. One layer of flakes does not cause a tortuous path (a wiggle).

For the composite with three layers of flakes, there is resistance due to wiggling:

$$\left[\frac{\text{total}}{\text{resistance}}\right]=\left[\frac{\text{resistance}}{\text{of top and bottom layer}}\right]+\left[\frac{\text{resistance}}{\text{necking into and out of slit}}\right]+\left[\frac{\text{resistance}}{\text{of slits}}\right]+\left[\frac{\text{wiggling}}{\text{resistance}}\right] \quad (5)$$

The resistance of the composite relative to that of the flake-free film becomes [5]:

$$\frac{J_0}{J}=\frac{l_0}{l}+\frac{d\ln\left(\frac{2W}{s}\right)}{2\pi l}+\frac{Nad}{2sl}+\frac{(N-1)d^2}{bl} \quad (6)$$

These results are exemplified by the green line in Figure 5. We choose to fabricate composite with only three layers of flake is because they are the least number to fully cover the area (i.e. to form a full wiggle). For ribbon shape flakes, we only need two layers but for hexagonally shaped flakes, we also three layers. Other measurements show that wiggles dominate this reduction. However, the decrease in the permeability observed here is smaller than what we expect from Equation (6), possibly because of the weak adhesion between PDMS and titanium.

References

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