

# **Microporous Silica Coatings on Mesoporous SiO<sub>2</sub>: Membranes for High Temperature Gas Separation Applications.**

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## **Abstract**

In this work, composite asymmetric membranes are prepared by magnetron sputtering deposition (MS), and atmospheric pressure plasma enhanced chemical vapour deposition (APPECVD) of silica films onto flat mesoporous SiO<sub>2</sub>. The deposition conditions for both coating types were systematically controlled to determine their effect on the deposited coating architecture (morphology, porosity and thickness) and stoichiometry using scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), ellipsometry, X-ray diffraction (XRD) and optical profilometry. These methods were used to provide an accurate depiction of the membrane coating physical and chemical properties. In addition, permeation measurements were made on all membranes in order to assess their perm-selectivity and suitability for membrane applications. APPECVD coatings showed promising permselectivity values with an average pore size of 0.42 nm. The coatings were found to be mechanically stable up to 400<sup>0</sup>C and showed good adhesion properties.

## **Introduction**

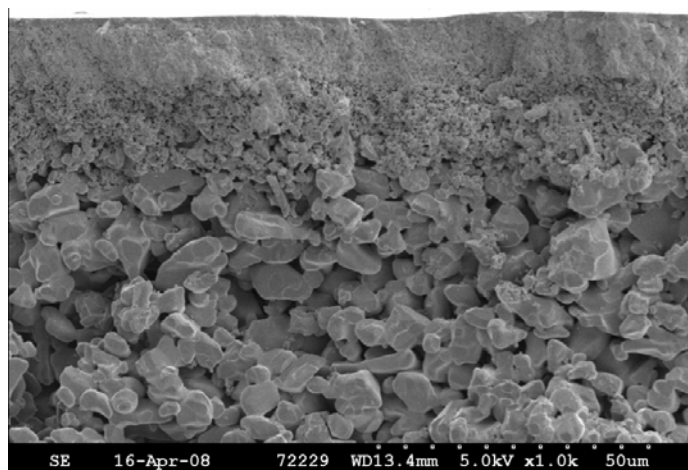
High atmospheric CO<sub>2</sub> concentrations resulting, in large part, from fossil fuel combustion, are now considered directly responsible for increasing global temperatures [1]. A cost-effective means of separating CO<sub>2</sub> from hot exhaust gases however, represents a major scientific challenge. In addition to the demanding hot exhaust gas environment, there is also the very significant problem of the small differences in molecular size between CO<sub>2</sub> and N<sub>2</sub> (3.3 and 3.7 Å, respectively) [2].

Recent theoretical and experimental studies have demonstrated promising permselectivity results for porous inorganic composite membranes (Fig. 1) fabricated through the chemical vapour deposition (CVD) of ultra-thin layer (≈5–25 nm), microporous, dense films onto carrier mesoporous substrate materials [2, 3]. However, films produced by conventional thermal CVD methods exhibit significant variability in the quality of the controlling deposits, particularly deposition density, which is key to CO<sub>2</sub> separation efficiencies. Plasma-based deposition processes could provide significantly better control of coating properties, including film thickness, density, and, indeed, film chemistry, and therefore offer the potential of fabricating improved membranes.

## **Experimental methods**

## Support materials

$\alpha$ -Al<sub>2</sub>O<sub>3</sub> (with average pore size of 3  $\mu$ m) discs were used as membrane supports. These 1 mm thick discs had a 0.5  $\mu$ m thick top layer of SiO<sub>2</sub> with a pore size of 1 nm. Fig. 1 shows an SEM image of the SiO<sub>2</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composite support.



**Fig. 1:** SEM cross-sectional image of SiO<sub>2</sub>/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> composite support.

## Magnetron sputtering deposition

SiO<sub>x</sub> coatings were deposited onto the composite ceramic supports by magnetron sputtering using a Teer Coatings UDP450 closed field unbalanced magnetron sputtering system. In this deposition process, a high energy argon plasma is controlled and regulated using an Advanced Energy MDX magnetron drive power supply, the output of which is regulated via a Sparc Le V DC pulsing unit. The argon plasma is used to systematically bombard a silicon target in the presence of oxygen to form a silicon oxide coating. The range of deposition parameters are listed in Table 1.

**Table 1:** Processing parameters - Magnetron Sputtering Deposition

<b>Processing parameter</b>	
Coating thickness (nm)	100
Target Current (amp)	1.0
Flow rate of oxygen (SCCM)	3.0
Working pressure (mbar)	$1 \times 10^{-3}$
Pulsed DC duty factor (%)	64
Distance between target and substrate	10cm – 17cm

## **Atmospheric pressure plasma enhanced chemical vapor deposition**

SiO<sub>x</sub> coatings were deposited onto SiO<sub>2</sub> supports by atmospheric pressure chemical vapor deposition (APPECVD) using a Dow Corning Plasma Stream™ system. In this deposition process, a liquid precursor tetraethylorthosilicate (TEOS) is nebulised inside a helium plasma. The processing parameters used during deposition are listed in Table 2.

**Table 2:** Processing parameters – Atmospheric Pressure PECVD

<b>Processing parameter</b>	
Precursor	TEOS
Precursor flow rate (SCCM)	0.01
Coating thickness (nm)	100
Height between substrate & nozzle (mm)	2 - 20mm

## **Results**

### **Gas separation**

Gas permeation measurements were carried out at room temperature using a specially constructed membrane test apparatus. Ideal gas selectivity was determined by administering a fixed concentration of permeating gas upstream of the membrane and measuring the differential pressure across the membrane over a period of 1 minute. Prior to permeance measurements, the membranes were heat treated at 400°C in order to remove all adsorbed material from the membrane micropores. Each of the coatings on the membranes evaluated in this study had a thickness of 100 nm. The thicknesses were determined using both ellipsometry and atomic force microscopy measurements.

Membranes fabricated by magnetron sputtering yielded lower He permeance and He/N<sub>2</sub> selectivity compared with those deposited by APPECVD (Table 3). This may suggest that the coating densities achieved with magnetron sputtering are higher and the low selectivity may suggest non-homogeneous pore size particularly at grain boundaries. The APPECVD technique yielded the highest overall membrane He/N<sub>2</sub> selectivity of 55. The permeances and selectivities listed in Table 3 are referring to those of the actual coating. Calculation of the coating permeance is based on Eqn. 1 where P<sub>mem</sub>, P<sub>sup</sub> and P<sub>coat</sub> are the permeances of the membrane, support and coating respectively. For this equation to be valid it is assumed that the support membrane undergoes no change in thickness, pore size, porosity or tortuosity during the deposition of the selective coating.

$$\frac{1}{P_{mem}} = \frac{1}{P_{sup}} + \frac{1}{P_{coat}} \quad \text{Eqn. 1}$$

**Table 3:** Ideal He/N<sub>2</sub> selectivities for silica coatings deposited by APPECVD and magnetron

sputtering (1nm SiO<sub>2</sub> support)

Deposition method	He/N <sub>2</sub> selectivity	He Permeance x 10 <sup>8</sup> Mol M <sup>-2</sup> S <sup>-1</sup> Pa <sup>-1</sup>	Approx pore size (nm)
APPECVD	83	5.55	0.42
Magnetron Sputtering	5.4	0.85	0.8

### Scanning Electron Microscopy images

The SEM images (Fig. 2.) clearly show a more homogenously dense coating exhibited by APPECVD. An issue with these coatings however, is the presence of powder particles which are co-deposited with the coating (Fig. 2b). The presence of powder on the coating surface is undesirable as it leads to lower coating density as well as higher surface roughness.

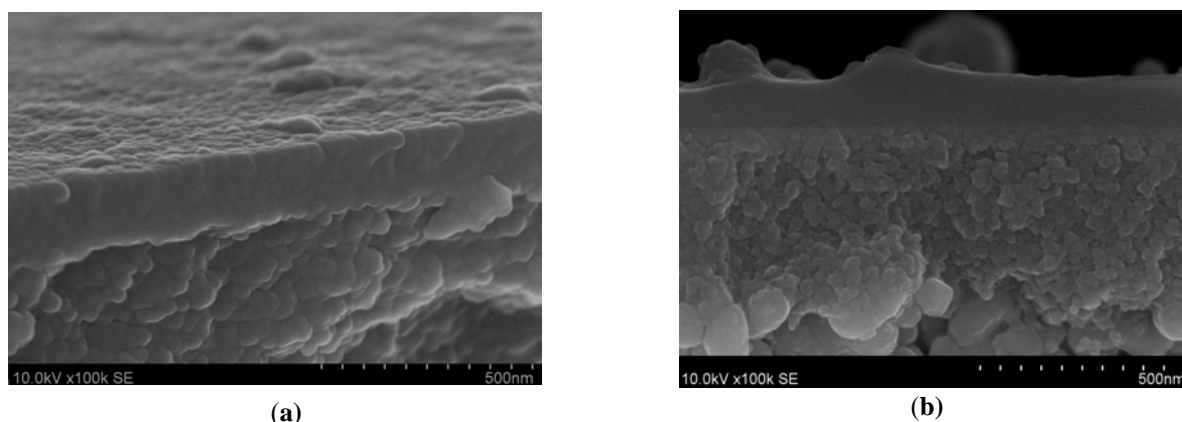
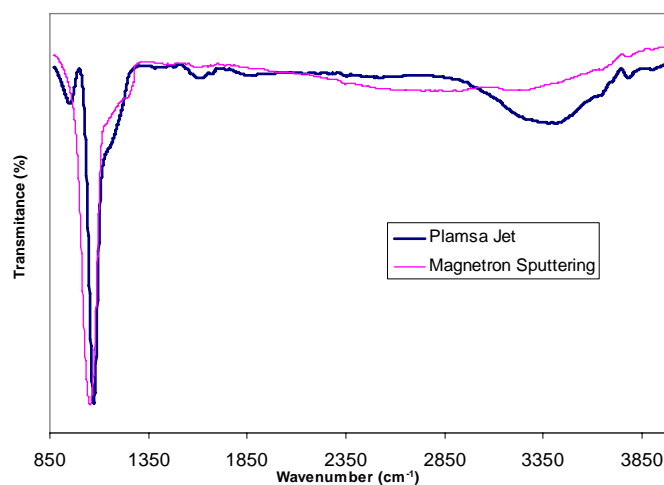


Fig. 2: Cross-sectional views of selective membrane structure produced by a) magnetron sputtering and b) APPECVD of silica onto microporous SiO<sub>2</sub> support.

Note: the denser structure observed in b.

### FTIR spectra

Fourier transform infra red spectroscopy was used to examine coating chemical functionality. A comparison between two types of SiO<sub>x</sub> coatings of the same thickness but deposited by APPECVD and magnetron sputtering is given in Fig. 4. Both spectra show the presence of SiO<sub>x</sub> in the form of Si-O-Si stretching peak at 1045cm<sup>-1</sup>. The APPECVD APPLD deposited coating however also exhibits -OH and weak -C peaks at 3400 and 1600 cm<sup>-1</sup> respectively. For high temperature membrane separation, the incorporation of carbon into the coating may be unfavourable as it could burn out to leave void spaces open for non-selective gas flow.



**Fig. 4:** FTIR spectra of SiO<sub>x</sub> coatings deposited by APPECVD and Magnetron sputtering

SiOH is present as powder on the coating surface and is undesirable as it leads to lower coating density as well as high surface roughness. The presence of carbon groups is also not favourable as carbon is removed at high temperature thus leaving void spaces open for non-selective gas flow.

## Conclusion

SiO<sub>2</sub> films were deposited onto porous SiO<sub>2</sub> and ZrO<sub>2</sub> support membranes by APPECVD and magnetron sputtering. These methods were optimised to accurately control coating thickness and chemistry. The corresponding permeance of N<sub>2</sub> and He was measured at room temperature for both deposition methods. Magnetron sputtering coatings exhibited higher levels of SiO<sub>x</sub> however their columnar structure and grain boundaries led to poor separation efficiency. The denser and more homogenous APPECVD coatings show promising permselectivity values with an average pore size of 0.42 nm. However, the presence of low concentrations of carbon may adversely affect their suitability for high temperature separations. The coatings were found to be mechanically stable up to 400°C.

## Acknowledgements

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## References

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