



## Development of P-Doped SiO<sub>2</sub> as Proton Exchange Membrane for Microfuel Cells

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Phosphorus-doped silicon dioxide (PSG) thin films with improved ionic conductivity were deposited via plasma-enhanced chemical vapor deposition for application as a thin-film proton exchange membrane (PEM) in microfabricated fuel cells. More than three orders of magnitude improvement in the ionic conductivity is obtained by P doping of low-temperature deposited SiO<sub>2</sub>. The area resistance of 3 μm thick film of PSG is comparable to a 200 μm thick film of Nafion. Application of these PSG films as PEM in microfuel cells yielded more than one order of magnitude improvement in power density compared to low-temperature, undoped SiO<sub>2</sub> membranes.

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Fabrication of microfuel cells on Si substrates using a complementary metal oxide semiconductor (CMOS) compatible process flow is of interest because it provides a method for fabricating self-powered electronic components. In addition, several emerging fields such as microelectromechanical systems (MEMS) and microfluidic devices will also benefit from the availability of on-chip power sources. The ability to cofabricate the power source on the same substrate as the electronic circuit offers many advantages, including reduction in size and weight, improved signal integrity because of fewer interconnects, increased processing efficiency due to cofabrication of components, and lower cost due to fewer components. In recent years, there have been few reports in the literature dealing with fabrication of micropower sources for electronic devices with small power requirements.<sup>1-3</sup> Microfabrication of direct methanol fuel cells (DMFC) on Si substrates using sacrificial polymers to create air channels for the flow of hydrogen or methanol fuels has been recently reported,<sup>4</sup> and an output power density of ~4 μW/cm<sup>2</sup> at room temperature has been obtained. At higher temperature (e.g., 60°C), the power density was increased to 26 μW/cm<sup>2</sup>. The most critical components in the microfuel cells are the anode and cathode catalyst layers and the proton exchange membrane (PEM). State-of-the-art macrofuel cells use a thick film paste of Pt–Ru as the catalyst layer and a machine-extruded film of 100s of micrometers in thickness of perfluorinated polymer with side chains terminating in sulfonic acid moieties (e.g., Nafion) as the PEM. These polymers exhibit excellent ionic conductivity (ca. 10<sup>-2</sup> S/cm) as well as high mechanical strength and chemical stability.<sup>5</sup> Recently, a microfabricated fuel cell was reported<sup>4</sup> with sputtered anode and cathode catalysts, and low-temperature plasma-enhanced chemical vapor deposition (PECVD) deposited SiO<sub>2</sub> as the PEM. The reason for replacing Nafion with low-temperature SiO<sub>2</sub> as the PEM was the incompatibility of Nafion (greater than 100 μm thick) with the thin-film integrated processing sequence. The ionic conductivity of low-temperature SiO<sub>2</sub> was of the order of 10<sup>-5</sup> to 10<sup>-7</sup> S/cm, which is three to five orders of magnitude lower than that of Nafion, and is very sensitive to the deposition temperature.<sup>6</sup> Some of the conductivity decrease was compensated by decreasing the thickness of the PEM by a factor of nearly 100. The low-temperature SiO<sub>2</sub> membrane, therefore, is the major performance-limiting factor in the microfuel cells. Clearly, development of a thin-film PEM with improved ionic conductivity and compatibility with the CMOS processing sequence is desirable

for microfabrication of fuel cells on Si substrates.

Alkaline-earth-metal-doped phosphate glasses (P<sub>2</sub>O<sub>5</sub>) are well known for their high ionic conductivity.<sup>7,8</sup> The mobility of protons in P<sub>2</sub>O<sub>5</sub> doped with alkaline earth metals such as Be, Mg, Ca, Sr, Ba, La, etc., has been reported to be up to 10<sup>8</sup> times higher than in the silica glass (SiO<sub>2</sub>).<sup>9</sup> The reason for this high mobility of protons in P<sub>2</sub>O<sub>5</sub> glasses is the reduction in the strength of O–H bonding in these glasses compared to that in SiO<sub>2</sub>. This is due to hydrogen bonding between the hydroxyl groups that are attached to a network-forming cation (X) such as Si<sup>4+</sup> or P<sup>5+</sup> and a counter oxygen (X–O–H··O–X). The extent of this reduction in the O–H bonding strength due to formation of the hydrogen bond is much higher in phosphate glasses compared to silicate glasses, giving them a higher ionic conductivity. The strength of hydrogen bonding also depends on the oxygen bonding, which is weaker in the case where a bridging oxygen exists (X–O–X) compared to the case where the oxygen is nonbridging (X–O<sup>-</sup>).<sup>10</sup> The type of network-modifying cations also modifies the hydrogen bond strength, allowing further improvement in the ionic conductivity through substitution of the network-forming cation with other elements, such as alkaline earth metals as mentioned before, which improve the ionic conductivity by up to eight orders of magnitude.<sup>9</sup> In this study, we have improved the ionic conductivity of the low-temperature PECVD SiO<sub>2</sub> through substitutional doping with phosphorus. We have been able to obtain three to four orders of magnitude higher ionic conductivity in the phosphorus-doped SiO<sub>2</sub> (PSG) compared to undoped glass under optimized growth conditions. Consequently, the microfuel cells fabricated using PSG as the PEM have shown more than one order of magnitude higher current density than undoped SiO<sub>2</sub> membranes.

### Experimental

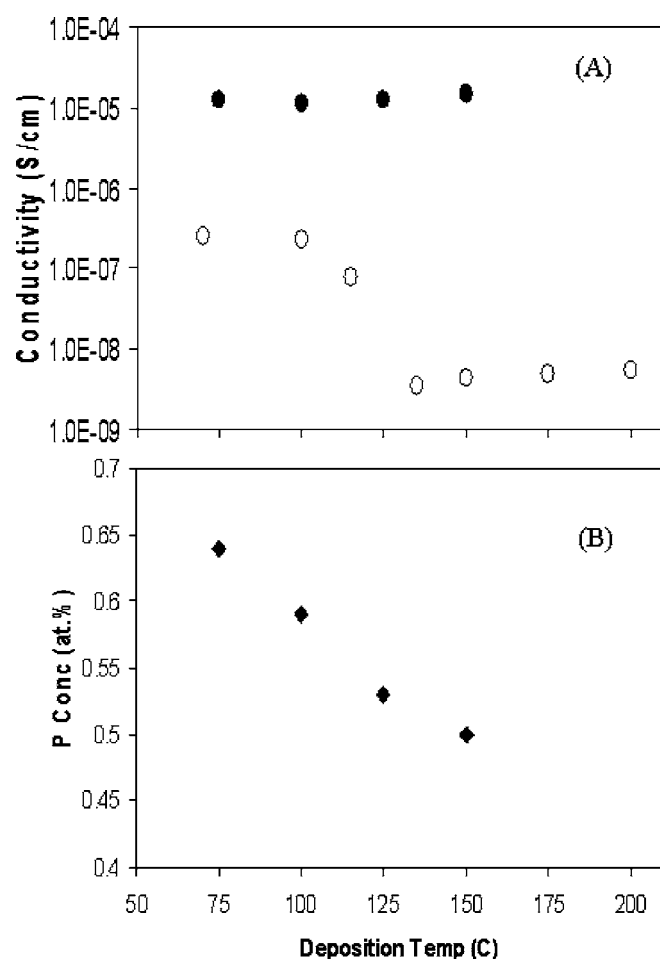
Undoped SiO<sub>2</sub> films were deposited on crystalline Si substrates in a Unaxis rf PECVD system using a semiconductor grade gas mixture of SiH<sub>4</sub> (5% SiH<sub>4</sub> in He) and N<sub>2</sub>O. The PSG films used a mixture of SiH<sub>4</sub> and 0.3% PH<sub>3</sub> as the feed gas. Other baseline deposition parameters were substrate temperature 100°C, deposition pressure 600 mTorr, rf power 400 W, N<sub>2</sub>O gas flow rate 450 sccm, and SiH<sub>4</sub> gas flow rate (with or without premixed PH<sub>3</sub>) 200 sccm. The ionic conductivity of PSG films was optimized by varying the above deposition parameters from their baseline values.

The chemical composition (phosphorus concentration in the film) and local bonding environments of Si, O, and P were studied with X-ray photoelectron spectroscopy (XPS) while the ionic conductivity was measured by impedance spectroscopy. The thickness of the films deposited on bare Si substrates for XPS measurements was 2–3 μm, measured with an alpha-step profilometer. For the electrochemical impedance spectroscopy measurements, Al-coated Si substrates were used. The XPS spectra were recorded using a Perkin Elmer XPS system (model PHI 1600). The ionic conductivity of the

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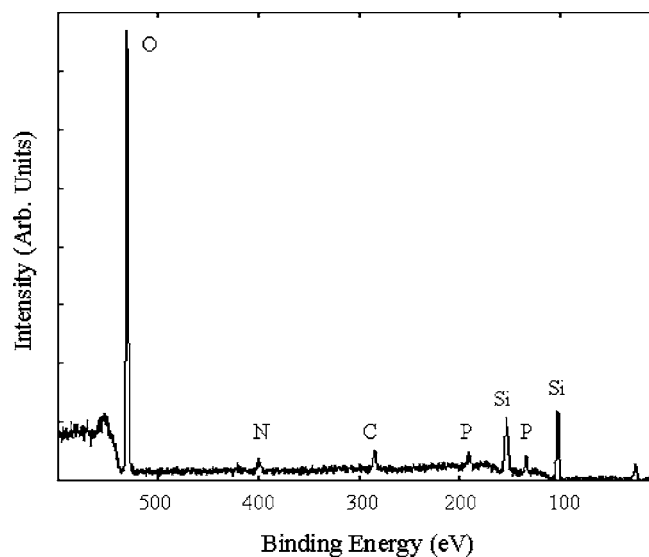


**Figure 1.** Variations in (A) ionic conductivity of P-doped (●) and undoped (○) SiO<sub>2</sub> films and (B) P concentration with deposition temperature.

films was measured by impedance spectroscopy using EG&G PAR STAT 2263 electrochemical system with a mercury probe. The frequency range for impedance measurement was from 100 mHz to 1 MHz, with an ac signal amplitude of 10 mV. These measurements were carried out at room temperature at the relative humidity of 22%, using a four-probe measurement. Fuel cells were fabricated on Si substrates using the sacrificial polymer process, which is described in detail in our previous publication.<sup>4</sup> Thickness of the PSG and undoped SiO<sub>2</sub> PEM in the fuel cells was 3 μm. Humidified hydrogen at an inlet pressure of 1 psig was used as the fuel.

### Results and Discussion

The ionic conductivity of low-temperature-deposited undoped SiO<sub>2</sub> is known to depend on the deposition temperature to a great extent, decreasing rapidly with increasing temperature above 100°C.<sup>6</sup> Figure 1 shows the variation in ionic conductivity and P concentration in PSG films with an increase in deposition temperature from 75 to 150°C. For comparison, the ionic conductivity of undoped SiO<sub>2</sub> as a function of deposition temperature is also plotted in Fig. 1. Figure 1A shows that the conductivity of undoped SiO<sub>2</sub> decreases rapidly by about two orders of magnitude from 10<sup>-7</sup> to 10<sup>-9</sup> S/cm with the increase in deposition temperature from 100 to 130°C. However, the conductivity of PSG is higher by almost two orders of magnitude compared to undoped SiO<sub>2</sub>. Also, the conductivity of P-doped glass is nearly independent of the deposition temperature. Interestingly, the conductivity of PSG remains nearly independent of the deposition temperature despite the reduc-



**Figure 2.** Typical XPS survey scan spectrum of a PSG film.

tion in its P content from 0.64 atom % at 75°C to 0.5 atom % at 150°C, as can be seen in Fig. 1B. This behavior underscores the hypothesis that ionic conductivity in doped glasses is controlled more by the structural intermediate range order than the dopant concentration itself, as mentioned earlier. Further, this result is important for the application of PSG films as PEM in microfuel cells because depositing the glass at high-temperature is more desirable than at low-temperature owing to its higher mechanical strength and density, resulting in lower fuel crossover. The highest ionic conductivity obtained under baseline growth conditions (given in the Experimental section) at 100°C was  $1.1 \times 10^{-5}$  S/cm. The water content of these films has not been determined yet, but is expected to be greater than 5 wt % based on previous results reported in the literature.<sup>6</sup> The growth rate of these PSG films was 20–25 Å/s without a systematic dependence on the deposition temperature. The growth rate of the undoped SiO<sub>2</sub> films was 12–13 Å/s under otherwise identical growth conditions. Thus, in addition to the higher ionic conductivity, the PSG also has a higher deposition rate by almost a factor of two, which is beneficial for high fabrication throughput.

Further optimization of the growth parameters yielded PSG films with ionic conductivity as high as  $1.2 \times 10^{-4}$  S/cm, an order of magnitude improvement over the baseline growth conditions. This optimized ionic conductivity in PSG obtained here is two orders of magnitude lower than that of Nafion. Since the glass thickness is also two orders of magnitude less than Nafion when used as a PEM, the two will have comparable area-conductivity values (S/cm<sup>2</sup>). (Area-conductivity is the figure of merit for membrane resistance and is the conductivity divided by thickness or resistance times area.) The optimized growth conditions included a reduced N<sub>2</sub>O flow rate of 80 sccm (from 450 sccm in baseline conditions) and reduced pressure of 200 mTorr (from 600 mTorr in baseline conditions).

A typical XPS survey scan spectrum for PSG film grown at 100°C is presented in Fig. 2. In addition to the expected Si, O, and P peaks, small amounts of C and N are present as impurities, due presumably to the cross-contamination of the deposition chamber. The overall chemical composition of the films was Si 29–30 atom %, O 69–70 atom %, and P 0.5–0.7 atom %. The Si/O ratio in the

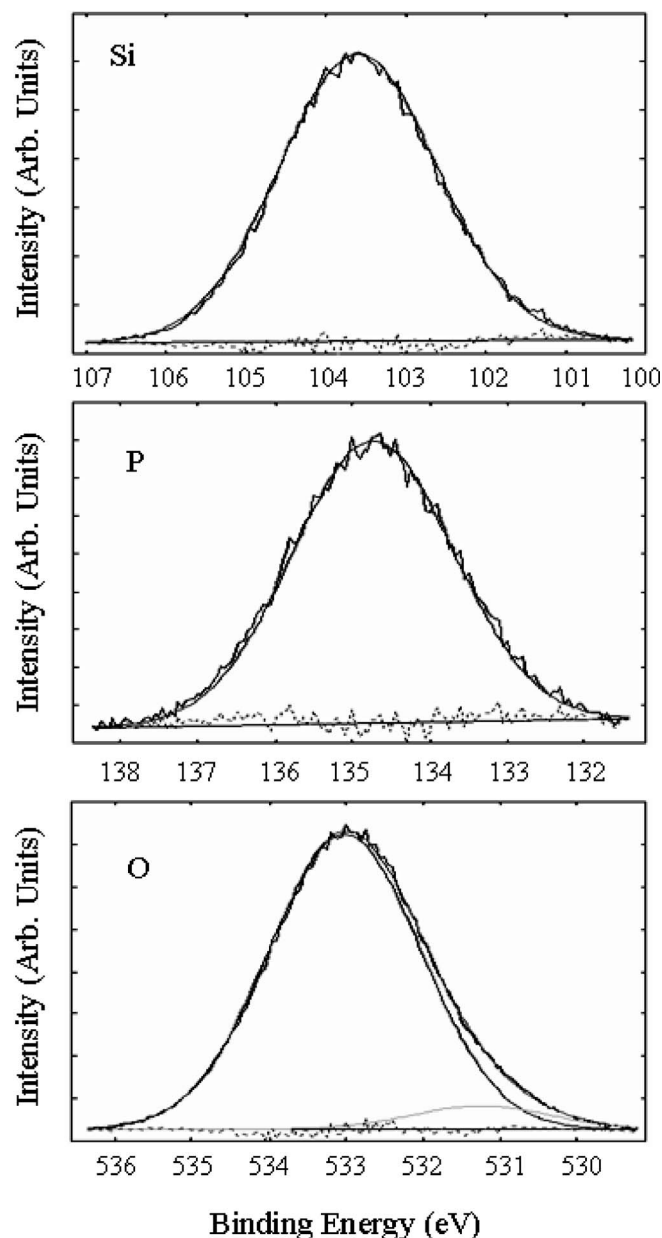


Figure 3. Core level XPS spectra of Si, P, and O peaks for PSG film.

films was found to be nearly independent of the deposition temperature, while the P concentration decreases with the increase in deposition temperature (see Fig. 1B). The local bonding configurations of Si, O, and P were studied from their respective core level photoelectron peaks, which are presented in Fig. 3. The Si 2p peak can be seen to be fitted adequately with a single Gaussian peak centered at 103.6 eV, indicating that Si is present in the Si–O bonding only. The absence of a contribution at 99.3 eV confirms that no Si–Si bonding is present. The P 2p photoelectron peak can also be fitted adequately with a single Gaussian peak centered at 134.8 eV, again indicating that P is present in the P–O bonding only, and that P is indeed present in the substitutional state. The O 1s peak, on the other hand, displays two components at 531.2 and 533.1 eV, corresponding to O–P and O–Si bonding, respectively. Consistent with this result, the relative fraction of the 531.2 eV component in the O peak that corresponds to the O–P bonding is also found to be directly proportional to the P concentration in the film. Thus, the core level photo-

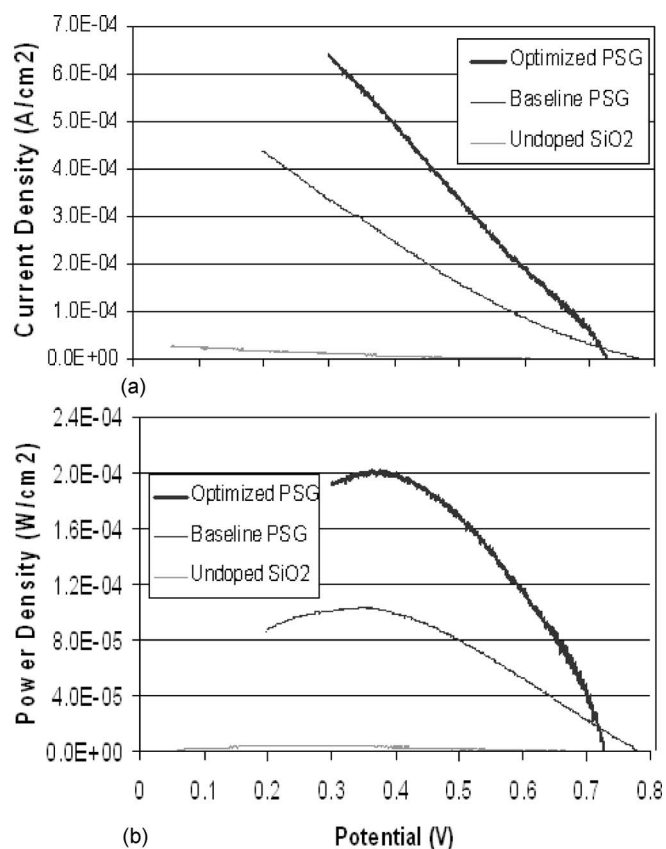


Figure 4. Room temperature  $I$ - $V$  and power characteristics of fuel cells with undoped  $\text{SiO}_2$  and two different PSG PEMs.

electron spectra in Fig. 3 show that the PSG films grown in this study are chemically homogeneous and maintain stoichiometry even at low deposition temperatures.

Microfuel cells were fabricated on Si substrates incorporating 3  $\mu\text{m}$  thick PSG films as the proton exchange membrane. The typical room temperature  $I$ - $V$  characteristics of two cells with humidified hydrogen fuel, one with the membrane deposited at the baseline conditions, and another with the membrane deposited at optimized growth conditions, are shown in Fig. 4a. For comparison, the room temperature  $I$ - $V$  characteristics of a similar cell but with an undoped  $\text{SiO}_2$  membrane are also shown. The fuel cell with an undoped  $\text{SiO}_2$  membrane shows an open circuit voltage (OCV) of 670 mV and the highest current density of 27  $\mu\text{A}/\text{cm}^2$  at 60 mV. The fuel cell with a PSG membrane deposited at baseline conditions (as given in the Experimental section) that yielded ionic conductivity of  $1.1 \times 10^{-5}$  S/cm, on the other hand, shows an OCV of 780 mV and a current density of 437  $\mu\text{A}/\text{cm}^2$  at 200 mV. Thus, substitutional doping of  $\text{SiO}_2$  with P under otherwise identical deposition conditions improved the OCV by more than 100 mV as well as improving the current density. The fuel cell with the PSG membrane deposited under optimized growth conditions (lower  $\text{N}_2\text{O}$  flow rate and lower deposition pressure than the baseline conditions) yielded a film with higher ionic conductivity of  $1.2 \times 10^{-4}$  S/cm, which further improved the current density by a factor of two. There was a slight reduction in the OCV, which will be investigated in future work. The power density curves of these three cells are compared in Fig. 4b. The cell with undoped  $\text{SiO}_2$  membrane yielded a power density of 3.9  $\mu\text{W}/\text{cm}^2$ , the cell with baseline PSG membrane had a power density of 104  $\mu\text{W}/\text{cm}^2$ , and the cell with PSG grown under optimized conditions had a power density of 200  $\mu\text{W}/\text{cm}^2$ ,

an improvement of a factor of 50 over undoped SiO<sub>2</sub> membrane. In order to test their lifetime, these cells have been operated at 0.4 to 0.6 V for longer than hundreds of hours. The cells with a single-layer PSG membrane were found to be stable (no decrease in current density) for a few tens of hours. On the other hand, fuel cells with a composite membrane (a thin layer of Nafion over the PSG membrane) were found to be stable for several hundreds of hours. A detailed study of the fuel cell performance with single and composite membranes, temperature, fuel, membrane thickness, and aging is currently underway and will be the subject of a future publication.

### Conclusions

Phosphorus-doped SiO<sub>2</sub> films deposited by PECVD at low temperatures are shown to display higher ionic conductivity by three to four orders of magnitude compared to the undoped SiO<sub>2</sub> films. Furthermore, the ionic conductivity of PSG is almost independent of the deposition temperature, making them suitable candidates for micro-fabricated fuel cells. Microfuel cells fabricated incorporating the PSG films as the proton exchange membrane have been shown to yield power density as high as 200 μW/cm<sup>2</sup> at room temperature,

compared to only 4 μW/cm<sup>2</sup> yielded by the undoped SiO<sub>2</sub> membrane cells.

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### References

1. S. J. Lee, A. Chang-Chien, S. W. Cha, R. O'Hayre, Y. I. Park, Y. Saito, and F. B. Prinz, *J. Power Sources*, **122**, 410 (2002).
2. M. Hayase, T. Kawase, and T. Hatsuzawa, *Electrochem. Solid-State Lett.*, **7**, A231 (2004).
3. J. Yu, P. Chenga, Z. Maa, and B. Yi, *J. Power Sources*, **124**, 40 (2003).
4. C. Moore, J. Li, and P. Kohl, *J. Electrochem. Soc.*, **152**, A1606 (2005).
5. S. Slade, S. A. Campbell, T. R. Ralph, and F. C. Walsh, *J. Electrochem. Soc.*, **149**, 1556 (2002).
6. M. F. Ceiler, Jr., P. A. Kohl, and S. A. Bidstrup, *J. Electrochem. Soc.*, **142**, 2067 (1995).
7. Y. Abe, H. Shimakawa, and L. L. Hench, *J. Non-Cryst. Solids*, **51**, 357 (1982).
8. M. D. Ingram, *Phys. Chem. Glasses*, **28**, 215 (1987).
9. Y. Abe, H. Hosona, and Y. Ohta, *Phys. Rev. B*, **38**, 10166 (1988).
10. H. Scholze, *Glastech. Ber.*, **32**, 81 (1959).