

Phosphorus-doped glass proton exchange membranes for low temperature direct methanol fuel cells

Shruti Prakash*, William E. Mustain, SeongHo Park, Paul A. Kohl

Georgia Institute of Technology, School of Chemical and Biomolecular Engineering, Atlanta, GA 30332-0100, United States

Received 17 July 2007; received in revised form 13 September 2007; accepted 14 September 2007

Available online 26 September 2007

Abstract

Phosphorus-doped silicon dioxide thin films were used as ion exchange membranes in low temperature proton exchange membrane fuel cells. Phosphorus-doped silicon dioxide glass (PSG) was deposited via plasma-enhanced chemical vapor deposition (PECVD). The plasma deposition of PSG films allows for low temperature fabrication that is compatible with current microelectronic industrial processing. SiH₄, PH₃ and N₂O were used as the reactant gases. The effect of plasma deposition parameters, substrate temperature, RF power, and chamber pressure, on the ionic conductivity of the PSG films is elucidated. PSG conductivities as high as $2.54 \times 10^{-4} \text{ S cm}^{-1}$ were realized, which is 250 times higher than the conductivity of pure SiO₂ films ($1 \times 10^{-6} \text{ S cm}^{-1}$) under identical deposition conditions. The higher conductivity films were deposited at low temperature, moderate pressure, limited reactant gas flow rate, and high RF power.

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Keywords: Glass; Phosphorus doped; Fuel cell; Methanol; Membrane

1. Introduction

Silicate glasses deposited by plasma-enhanced chemical vapor deposition (PECVD) have traditionally been used as low-loss electrical insulators in microelectronic devices. However, in recent years it has been reported that introducing minority additives into the silicate matrix allows researchers to tune the physical properties of these glasses, making them attractive for a variety of applications. It has been shown that introducing limited amounts of a secondary oxide in the glass can tailor its structure, mechanical strength, and both the electrical and ionic conductivity [1]. One possible application of silicate glasses with increased ionic conductivity is fully inorganic electrolyte materials for low temperature proton exchange membrane fuel cells. Silicate glasses with adequate proton conductivity are ideal because they are inexpensive, reliable, easily fabricated over a wide range of thicknesses and can serve as a methanol barrier layer to lower the fuel crossover rate in direct methanol fuel cells (DMFCs).

Silicate glasses have a tetrahedral structure where defect –OH terminated silicon groups assist in ion transport by providing nano-porous regions that are tens of angstroms in diameter. These imperfections retain the high electrical loss characteristics of the structure, while providing a surface-site ionic pathway along the length of the pores. The ionic conductivity is achieved by liberation of the protons from silanol hydroxyl groups in the glass structure pores [2]. Abe et al. have shown that oxides prepared at low temperature incorporate a large number of hydroxide and water impurities that impart high porosity to the glass as compared to those formed at high temperature [3].

It has been shown that doping of silicate glasses with group V elements, such as phosphorus, increases the conductivity of the silicate glasses. This is accomplished by introducing gaps in the tetrahedral glass network as the requisite Si–O–Si bond formation is sterically hindered and replaced by either –Si–OH or –Si–O–POH surface groups. This increases both the free volume and pore wall surface area, thus increasing the ion-exchange capacity of the prepared glass. It should also be considered that the group V hydroxyl groups have a higher acidity when compared to silanol. This indicates that the associated proton in the P–OH group is more strongly bonded with neighboring water molecules [1], which should increase its mobility.

* Corresponding author. Tel.: +1 404 579 2886; fax: +1 404 894 2866.
E-mail address: shruti.prakash@chbe.gatech.edu (S. Prakash).

Further studies in this area have shown that proton mobility is also a function of the hydrogen bonding that occurs between the hydroxyl groups attached to a network-forming cation ($X = \text{Si}^{4+}$ or P^{5+}) and a hydroxide ion ($X\text{--O--H}\cdots\text{O--X}$) [4,5]. It has been shown that the strength of the hydrogen bond between the hydroxyl groups depends on the type of counter ion it is bonded to. The hydrogen bonding is extremely weak in cases where the counter ion is of the bridging type ($X\text{--O--X}$) compared to those where the counter ion is of the non-bridging type ($X\text{--O}^-$). Uma et al. found that in phosphorus-doped silicate glasses (PSG), the phosphorus is bonded to one bridging and three non-bridging oxygen atoms [6]. It is believed that the increase in non-bridging oxygen bonds increases the ion conduction sites, leading to higher conductivity for phosphorus-doped silicate glasses.

Additional enhancement in the ionic conductivity of silicate glasses occurs by water absorption into the pores. The defect sites located within the glass film provide a high local charge density and electrostatic field, promoting the chemisorption of water molecules that provide a bulk transport mechanism for the charge carrying protons. Therefore, the magnitude of the ionic conductivity in phosphorus-doped silica glasses depends on free volume and pore surface area (for ion transport), chemical structures in the glass (e.g. --Si--OH and --P--OH concentration), intermediate range order and the local bonding environment in the glass network [3,7,8].

It has been well established that high quality phosphorous-doped silicate glasses can be fabricated by melt-quenching techniques. However, the high processing temperature of melt casting makes it incompatible with many microelectronic and electrochemical applications. Also, glasses fabricated by this technique have low proton conductivity, making it undesirable as an electrolyte material [9,10]. Therefore, alternative fabrication methods have been explored in order to deposit the proton-conducting silicate glasses, including sol-gel and plasma-enhanced chemical vapor deposition (PECVD). Sol-gel processes have been commonly used, though they often suffer from low mechanical strength and stability [10–12].

On the other hand, the low temperature, PECVD yield high mechanical strength and stable glasses using a fabrication technique that is compatible with state-of-the-art microelectronic materials and processes. Plasma-deposited oxides can also have higher porosity than high-temperature sol-gel glasses due to increased silanol concentration and water impurities, especially when deposited at low temperature [13], which should provide enhanced ionic conductivity. Furthermore, the PECVD technique provides better control of the surface reactions, adsorbate mobility, and desorption of reaction byproducts by controlling the number of active radicals and ions in the plasma, which may be adjusted by control of several variables, including substrate temperature, chamber pressure, RF power and reactant flow-rate [2].

In this study, we have characterized the ionic conductivity of PECVD, phosphorus-doped silicate glasses by parametrically adjusting the plasma deposition conditions in order to optimize its properties for use as a proton-conductor for low-power DMFCs. It was found that undoped, plasma-deposited

silicon dioxide has an ionic conductivity in the range of $1 \times 10^{-6} \text{ S cm}^{-1}$, which is inadequate for use as a solid electrolyte material in low-power proton exchange membrane (PEM) fuel cells due to resistive losses in the membrane. For example, a low-power fuel cell operating at $100 \mu\text{A}$ and 0.5 V with a $1 \mu\text{m}$ thick silica membrane (1 cm^2 area) would have a 20% resistive energy loss with a $1 \times 10^{-6} \text{ S cm}^{-1}$ membrane. Therefore, the goal of this study is to characterize plasma deposition conditions for the fabrication of phosphorus-doped silicate glasses (PSG) that have higher ionic conductivity such that the fuel cell energy loss is less than 0.1%. For low-power applications, the ionic conductivity should be at least $1 \times 10^{-4} \text{ S cm}^{-1}$, which is two orders of magnitude higher than dense silicate glass. For this purpose, thin-film PSG membranes were prepared on a metallized substrate by reacting silane, phosphine and nitrous oxide. A systematic variation of critical deposition parameters (substrate temperature, RF power, pressure, and gas composition) was performed in order to investigate their effect on the ionic conductivity of PSG films. Additional experiments were carried out in order to compare the performance of passive DMFCs fabricated with PSG-Nafion composite and single-component Nafion membranes.

2. Experimental

Thin films of phosphorous-doped SiO_2 were deposited on (100) n-type silicon substrates. The first step in preparing the silicate glasses involved metallization of the silicon substrate to provide a conductive plane underneath the glass. For this purpose, a thin layer (200 \AA) of aluminum metal was deposited on the substrate by DC sputtering. Oxide deposition was carried out using a Unaxis 78324 RF PECVD (plasma-enhanced chemical vapor deposition) system operating at a frequency of 13.56 MHz. The semiconductor grade reaction precursors were 5% SiH_4 in He, 1% PH_3 in He and pure N_2O . The SiH_4 and PH_3 flow rates were both kept constant at 200 sccm in order to maintain a molar ratio of phosphorus to silicon at 1:5 in the plasma chamber. The N_2O flow rate was set to one of the two values: 80 and 450 sccm.

In this study, three deposition parameters: RF power of plasma, substrate temperature and chamber pressure were investigated. First, the temperature of the metallized silicon substrate was varied from 100 to 200 °C while holding the chamber pressure and RF power constant at 400 mTorr and 400 W, respectively. Next, the RF power was adjusted between 100 and 400 W at constant substrate temperature (100 °C) and chamber pressure (400 mTorr). Finally, the chamber pressure was varied from 400 to 800 mTorr with a substrate temperature of 100 °C and a chamber pressure of 400 mTorr.

The thickness of the deposited phosphorus-doped glass film was typically 2–3 μm for a 30 min deposition time. The resulting thin oxide membranes deposited were amorphous in nature and formed translucent films. The ionic conductivity of the films was measured by ac impedance spectroscopy using a Perkin-Elmer PARSTAT 2263 electrochemical system with a MSI Electronics Model Hg-412 mercury probe. The frequency range of the impedance measurement was 100 mHz to 1 MHz with an ac signal amplitude of 10 mV. Phosphorus concentration in the films

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