

Microstructure development of mesoporous silica thin films with pore channels aligned perpendicularly to electrode surfaces and application to proton conducting composite electrolyte membranes

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Abstract

We investigated a novel preparation technique of a proton conducting inorganic composite thin membrane consisting of an oxyacid salt proton conductor, CsHSO₄, and a mesoporous SiO₂ thin film that has highly oriented mesopores. The mesoporous SiO₂ thin films were prepared through the removal of the Fe component from Fe–Si–O precursor thin films synthesized by sputter deposition. In this study, we focused on the SEM observation of growth structures of Fe–Si–O precursor thin films and the resultant mesoporous SiO₂ thin films. The relationship between the deposition parameters (working gas pressure and target component) and the growth structures of the thin films is discussed. The obtained mesoporous SiO₂ thin films showed pore channels aligned perpendicularly to electrode surfaces when relevant deposition parameters were applied. A CsHSO₄/SiO₂ composite thin membrane was prepared by the impregnation of a CsHSO₄ aqueous solution into the mesopores of a SiO₂ thin film. The proton conductivity of the CsHSO₄/SiO₂ composite thin membrane was examined with respect to the difference between proton conduction in the composite thin membrane and that in neat CsHSO₄, which suggests that mesopores of a SiO₂ thin film play an important role in the enhancement of proton conductivity, especially in the low-temperature region between 60 and 140 °C.

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1. Introduction

Mesoscopic space provides many chemical and physical functions. Mesoporous silica in particular has potential applications to catalysis, separation technologies and electronic devices [1–5]. With respect to ionic conduction, mesopores also play an important role in enhancement of ionic conductivity. It has been reported that some ion conducting materials (H⁺, Ag⁺ and Li⁺ conductors) caged in insulating chemically inert mesoporous materials or powder matrices show enhanced ionic conductivity [6–16]. Mesoporous silica is therefore a prospective framework material for electrolyte membranes of energy devices such as solid electrolyte fuel cells, capacitors and secondary batteries.

In the present work, we report a novel preparation technique of mesoporous silica thin films on various substrates such as silica, glassy carbon and silicon, by using radio frequency (rf)

sputter deposition. The application of this technique to proton conducting composite electrolyte membranes was also developed. It is interesting to note that the present synthesized silica thin films have mesopores oriented perpendicularly to a substrate surface. Although mesoporous silica films having mesopores oriented parallel to a substrate surface have been reported by several researchers [17,18], there have been few previous studies on mesoporous silica films with mesopores oriented perpendicularly to a substrate surface [19,20]. Kondoh et al. report mesoporous silica films with one-dimensional through channels perpendicular to the surface of a silica substrate [19]. They prepared Fe–Si–O amorphous precursor films on silica substrates, and the precursor films were first annealed under oxidizing conditions at 600 °C and then decomposed to a regular array of needle-like hematite (Fe₂O₃) surrounded by a silica matrix (eutectic decomposition method). Mesoporous silica films were successfully obtained by chemical etching of hematite. However, the above method is not suitable for our aims because it includes an oxidation process; mesoporous silica films on electron-conducting materials like carbon are necessary for applications to energy

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devices and such materials are decomposed or oxidized in the oxidation process. In our preliminary experiments, we noticed that a silica film having mesopores oriented perpendicularly to a substrate could be obtained from Fe–Si–O precursor films without an oxidation process. In the present study, this new method of preparation of mesoporous silica films was investigated and the microstructure of the films was examined. Specifically, scanning electron microscopic (SEM) observations of the morphology of Fe–Si–O precursor films and mesoporous silica films were carried out in detail. The advantage of the present method is the expandability of its applications. This method makes it possible to prepare perpendicularly oriented mesoporous silica films on given substrates with the desired amount of porosity.

Next, a proton conducting composite thin film was prepared, which consists of the mesoporous silica thin film and oxyacid salt (CsHSO_4). CsHSO_4 shows a superionic phase transition, which means that the conductivity steeply increases by four orders of magnitude at 141 °C and reaches 10^{-2} S/cm, being accompanied with structural transformation (monoclinic phase \rightarrow tetragonal phase) and disordering of a hydrogen bond network [21–27]. In previous works, we studied the proton conductivity of $\text{CsHSO}_4/\text{SiO}_2$ composite electrolytes [8–10]. The conductivity of CsHSO_4 below its superionic phase transition temperature has been found to increase significantly in mesoporous silica matrices [7–10]. At temperatures below the superionic phase transition temperature (141 °C), the conductivity of the composite is larger by over three orders of magnitude than that of neat CsHSO_4 [8,9], i.e. the superionic phase of CsHSO_4 was maintained in mesoporous silica matrices below its phase transition temperature. Proton conduction of structurally disordered CsHSO_4 in mesoporous silica matrices contributes to the enhancement of conductivity [6–10]. Given the potential applications of proton conducting composite electrolytes to energy devices such as solid electrolyte fuel cells and capacitors, the development of a fabrication technique for composite thin membranes is of great importance.

The present work represents the first steps in the development of porous silica thin films with a highly oriented microstructure on electron-conducting substrates and their applications to proton conducting composite electrolyte membranes. In this study, we focused on SEM observation of the growth structures of Fe–Si–O precursor thin films and mesoporous SiO_2 thin films. We discuss the relationship between sputtering conditions and the microstructures of the thin films through SEM observations. The proton conductivity of a $\text{CsHSO}_4/\text{SiO}_2$ composite thin membrane was also evaluated.

2. Experimental

Fe–Si–O thin films were deposited on substrates using an rf magnetron sputterer. Mesoporous silica thin films were then obtained by removing the Fe components from the Fe–Si–O thin films in an HCl solution (template method). The desired amounts of FeO powder (Sigma–Aldrich Co., USA, purity > 99.9%, 10 mesh) and SiO_2 powder (Sigma–Aldrich, purity > 99.6%, 325 mesh) were first mixed in an agate mortar, and the FeO– SiO_2 powdered mixture was then pressed and set in a quartz plate to

be used as a target. Next, Fe–Si–O thin films were deposited under Ar-flow conditions (purity > 99.99%) using the rf magnetron sputterer. Glassy carbon (Tokai Carbon Co., Ltd., Tokyo, Japan), n-type silicon (Nilaco Co., Tokyo, Japan) and silica glass sheets were used as substrates. The base pressure of the chamber was below 1×10^{-6} Torr. The influence of Ar pressure and the molar ratio of the FeO– SiO_2 target on film structural properties were investigated; Ar pressure conditions were changed between 5×10^{-3} and 8×10^{-2} Torr, and the various molar ratios of the FeO– SiO_2 targets, FeO: $\text{SiO}_2 = 2:1, 3:1, 4:1$ and $5:1$, were examined. The target power density was fixed at 5 W cm^{-2} . Substrate temperature was not controlled during deposition. The obtained Fe–Si–O thin films were characterized by X-ray diffraction (XRD) (Rigaku Rint 2500VHF), field emission scanning electron microscopy (FE-SEM) (Hitachi S-4200 and S-900), and X-ray photoelectron spectroscopy (Physical Electronics Quantum 2000). The deposition rate was determined from the thickness of the obtained Fe–Si–O thin films. Finally, the Fe components, which served as a template in the mesoporous silica thin film, were removed by wet etching in an HCl aqueous solution (HCl conc. 18 wt.%) for approximately 30 min to obtain mesoporous silica thin films. After the wet etching, the resultant samples were placed in methanol, and dried at approximately 5–10 °C. This procedure enabled us to obtain crack-free films on substrates. The microstructures of the mesoporous silica thin films were observed by FE-SEM, and components in the thin films were examined by SEM-energy dispersive X-ray (EDX) analysis (Horiba EMAX-7000).

A $\text{CsHSO}_4/\text{SiO}_2$ composite electrolyte thin film was prepared by the impregnation method, in which a CsHSO_4 aqueous solution is impregnated into the mesopores of a silica thin film. The mesoporous silica thin film was set in a CsHSO_4 aqueous solution (20 wt.%) for over 30 min under reduced pressure. The film was then drawn out of the solution and was dried, first at room temperature, and then at 50 °C for 3 h in air, after which it was maintained at 90 °C for 12 h in air. The typical size of the obtained $\text{CsHSO}_4/\text{SiO}_2$ composite thin film was $5 \text{ mm} \times 5 \text{ mm} \times 2 \mu\text{m}$ thickness. A $\text{CsHSO}_4/\text{SiO}_2$ composite thin film prepared on an n-type silicon substrate was used for conductivity measurements. An Au electrode was attached on one side of the $\text{CsHSO}_4/\text{SiO}_2$ composite thin film by Au vapor deposition (electrode size: ca. $4 \text{ mm} \times 4 \text{ mm}$). Thus, the $\text{CsHSO}_4/\text{SiO}_2$ composite thin film was sandwiched between the Au electrode and the n-type silicon substrate. Finally, the resultant sample was placed between thin Au sheets to collect electronic signals.

A polycrystalline CsHSO_4 pellet was used as a reference for conductivity measurement. Polycrystalline CsHSO_4 was obtained by the evaporation of an aqueous solution containing equimolar amounts of Cs_2SO_4 (Soekawa Chemical Co., Tokyo, Japan, purity > 99%) and H_2SO_4 (Wako Pure Chemical Industries, Ltd., Osaka, Japan) at 80 °C for 1 day. The powdered sample of CsHSO_4 was prepared by grinding in an agate mortar for 30 min. The formation of single-phase CsHSO_4 was confirmed by powder XRD measurement. The powdered sample was heated at 170 °C for 1 h in air, and then pressed at 3 t/cm^2 to form a pellet (diameter, 10 mm; thickness, ca. 1 mm). The

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