Sintering-Oxidation Method to Prepare Self-Supporting Silica Films

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Abstract. In this work, an innovative method of sintering-oxidation has been developed to prepare self-supporting silica films with good flexibility. Polyethylene (PE) film was used as a template, SiC powder and polycarbosilane (PCS) were employed as silicon sources. The surface of the PE films was coated with slurry of SiC powder and hydroxypropyl methylcellulose aqueous solution. After drying, the hexane solution of PCS was sprayed on the slurry. Subsequently, the films were coated with slurry in high-temperature furnace under Ar conditions. After cooling, a white and self-supporting film was prepared. The thickness of the films was 15 µm, and it demonstrated flexibility. The morphology and composition of the film were characterized and the results proved that the films prepared as innovative method described above was pure silica. The formation mechanism and self-supporting mechanism of self-supporting silica films were discussed. The method required no tedious operation or restriction conditions, and is easy and economical. Therefore, the proposed method offers a new way to prepare self-supporting silica films.

Introduction

SiO$_2$ films are widely used in optical applications, microelectronic applications, separation technology, and biotechnology because their excellent properties such as hardness, optical and dielectric properties, wear resistance, and corrosion resistance [1–3]. Currently, the main methods used to prepare SiO$_2$ films include physical vapor deposition [4, 5], chemical vapor deposition [6], thermal oxidation method [7, 8], and sol-gel method [9–13]. However, SiO$_2$ films are prepared by deposition or reaction on the surface of a silicon substrate by using the above methods and cannot be self-supported, which is restrict in application. Self-supporting films are usually prepared as follows. First, each film is synthesized on a special substrate, and then the substrate is removed to obtain a self-supporting film. Hence, self-supporting films are prepared using depositing and stripping techniques. Two main methods are also used to prepare self-supporting thin films [14–18]. First, such films are prepared on a sacrificial layer, which can be readily removed by hydrofluoric acid or organic solvents. In the second method, the films are prepared on a layer which is release agent coated on the substrate. Afterward, the self-supporting films are obtained by dissolving the release agent.

Some efforts have been made to obtain self-supporting SiO$_2$ films, and the main preparation method of these self-supporting silica films is sol-gel method [19–21]. For instance, Y. Si et al [19] have reported silica nanofibrous (SNF) films with ultra-softness and enhanced tensile strength; these SNF films are prepared by...
electrospinning technique with a sol-gel solution containing NaCl. RG Juez et al [20]. have prepared self-supporting mesostructured silica thin film membranes as gateable interconnects for microfluidics via direct coating of thixotropic polymeric sols. Chang Han et al [21]. have prepared self-supporting hybrid silica membranes with 3D large-scale ordered and interconnected pore architectures by filling the organic–inorganic hybrid sol on the template.

In the present work, we developed an innovative method of sintering-oxidation to prepare self-supporting silica films, which is different from existing preparation methods. The morphology and composition of the films were characterized by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Energy Dispersive Spectrometer (EDS) and Fourier Transform Infrared Spectroscopy (FT-IR). The results showed that the prepared films were silica thin films. Therefore, the proposed method offers a new way to prepare self-supporting silica films.

**Experimental**

Scheme 1 shows the schematic of the fabrication of self-supporting SiO$_2$ films. The first step of the experiment was to prepare slurry. Industrial SiC powder (95 wt% purity) with average diameter of 0.8 µm was used as silicon source, and hydroxypropyl methylcellulose (HPMC) was employed as a compound binder. The quantity of the compound binder was 6.7% of the SiC amount. The added water was approximately 67% of the SiC weight. The content of solid phases (SiC) in the compound slurry was about 40%.

Commercial PE films were wrapped on the surface of a SiC ceramic plate (100 mm diameter) that was made in our laboratory. We ensured that the surface of the films was flat and smooth. The slurry was coated on the PE films after being stoved at 100 °C. Up to 5% hexane solution of PCS was sprayed on the films. Afterward, the films were coated with the slurry at 1450 °C for 1 h under Ar conditions in high-temperature furnace. After 1 h of heat preservation at 1450 °C, the high-temperature furnace began to cool. During the cooling process, the temperature decreased to 900 °C, and the outlet of the protective gas Ar was closed and no longer accessible in the high-temperature furnace.

The morphology and microstructure of the films were characterized by SEM (JSM-5510LV, EDAX, America) and TEM (JEM-2100, JEOL Ltd., Japan), and the composition of the film was analyzed by FT-IR (Nicolet 6700, American Thermo Electron) and EDS.

![Scheme 1. Schematic of the fabrication of self-supporting SiO$_2$ films.](image-url)
Results and Discussion

The photographs of the films that we prepared are shown in Figs. 1a and 1b. Translucent white self-supporting films can be observed in Fig. 1. As shown in Fig. 1a, the films were placed on a 14 mm-wide bracket to ensure that the films can be self-supported. Additionally, Fig. 1b shows that the films were bent in the middle of the two strips of tweezers, indicating that the films demonstrated flexibility. The thickness of the self-supporting films was measured in micrometers. The results showed that the thickness was 15 µm.

![Figure 1. Photographs of self-supporting films.](image)

The SEM images of the self-supporting SiO\textsubscript{2} films are shown in Figs. 2a and 2b. Fig. 2a shows one side of the films, and Fig. 2b shows the other side. As shown in the image, one side of the film surface presented fibrous materials, which are woven into the network structure. By contrast, the other side of the surface was relatively flat. Combined with preparation method, the side with fibrous materials was sprayed PCS, and the PCS was cracking into fibrous SiC when sample was heated.

The micro-area in the black box was studied by EDS. The corresponding EDS spectrum of each side was located on the right side of the SEM images. The EDS spectra showed that the films contained two elements, namely, Si and O. The weight percent of Si and O on the first side with fibrous materials was 47.28% and 52.72%, respectively. Correspondingly, the atomic percent was 33.81% and 66.19%. The weight percent of Si and O on the other side was 47.85% and 52.15%, and the atomic percent was 34.33% and 65.67%, respectively. The results showed that the sum of the mass of Si and O on both sides was 100%, and the atomic ratio was 1:2. These findings indicate that the prepared films are SiO\textsubscript{2} films.

![Figure 2. SEM images of two sides (a and b) of the self-supporting SiO\textsubscript{2} films and their corresponding EDS spectra.](image)
The TEM image of the materials of the films was obtained through ultrasonic wave (Fig. 3a), and its corresponding HRTEM image is shown in Fig. 3b. The HRTEM image of the film reveals the clear crystal fringe, and the spacing of the lattice fringe was 0.296 nm. The lattice fringe of the films was consistent with tridymite. This finding further proved that the self-supporting films are SiO$_2$ films.

Fig. 3c shows the TEM image of the fibrous materials in films and its corresponding EDS spectrum. The EDS spectrum shows that the fibrous material contains Cu, C, Si, and O. Hence, Cu came from the copper grid, and the fibrous material mainly consisted of Si and O, with a small amount of C. This result indicates that the fibrous material is SiO$_2$, which contains a small amount of SiC that is not completely oxidized. This finding suggests that the main component of the fibrous material is SiO$_2$, which was oxidized by SiC (produced by decomposition of PCS), thereby preserving the morphology of SiC.

Fig. 4 shows the Schematic of the formation mechanism of the self-supporting SiO$_2$. The formation and self-supporting mechanism of the self-supporting SiO$_2$ films can be inferred that when the temperature reached 1450 °C, the fibrous SiC cracked by PCS and SiC powder was coated on the PE films, which were sintered into the SiC films. After the reaction, the temperature decreased to 900 °C, which was close to the temperature of Ar. No inert gas protection existed in the high-temperature furnace. The SiC films were oxidized to the SiO$_2$ films, thereby preserving the morphology of the SiC films and the fibrous structure supported the films and contributed to their flexibility. Therefore, silica films can be self-supported and can demonstrate flexibility.

The FT-IR spectrum of the self-supporting SiO$_2$ films is shown in Fig. 5. The Si-O-Si bond presents three types of vibration modes, namely, rocking vibration, stretching vibration, and bending vibration. Three distinct absorption peaks can be observed at 1092.73, 795.65, and 473.58 cm$^{-1}$. The absorption peak of 1092.73 cm$^{-1}$ is ascribed to the asymmetric stretching vibration of Si-O bond. The peak at 795.65 cm$^{-1}$ is attributed to the bending vibration absorption peak, and the rocking vibration peak is 473.58 cm$^{-1}$. The most obvious and strongest peak is the stretching vibration peak at 1092.73 cm$^{-1}$.
which indicates that the purity of the SiO$_2$ films is high. A relatively weak absorption peak can also be observed at 1632.25 cm$^{-1}$; this peak corresponds to the H-O-H bending vibration, which might be caused by the absorption of moisture on the surface of the sample.

![Figure 5. FT-IR spectrum of the self-supporting films.](image)

**Conclusions**

In this work, an innovation method of sintering-oxidation was developed to prepare self-supporting silica films. The thickness of the prepared films was 15 µm. These films can be self-supported and can demonstrate good flexibility. SEM, TEM, EDS, and FT-IR characterization results suggest that the films which were prepared by this innovation method were SiO$_2$ films. Therefore, the proposed method offers a new way to prepare self-supporting silica films.

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**References**


