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Electrical sensing properties of silica aerogel thin films to humidity

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Abstract

Mesoporous silica aerogel thin films have been fabricated by dip coating of sol–gel derived silica colloid on gold electrode-patterned alumina substrates followed by supercritical drying. They were evaluated as the sensor elements at relative humidity 20–90% and temperature 15–35 °C under an electrical field of frequency 1–100 kHz. Film thickness and pore structure were two main parameters that determined the sensor performance. The film with a greater thickness showed a stronger dielectric characteristic when moisture abounded, and presented a smaller hysteresis loop and a higher recovery rate, due to the large size of pore throats. As the film thickness decreased, at low humidity the surface conductivity enhanced and the response rate increased. The silica aerogel based humidity sensor can be modeled as an equivalent electrical circuit composed of a resistor and a capacitor in parallel, and is driven by ionic conduction with charged proton carriers.

Keywords: Ceramics; Electrical properties and measurements; Sensors

1. Introduction

Silica aerogels are mesoporous materials with cross-linked nanoparticle network structures. They have received great interests in applications of catalyst support, adsorbent, electronic insulator, and kinetic energy absorber [1], because of unique textural properties such as large pore volume of 3–9 cm^3/g, pore size of 1–100 nm, high surface area up to 1000 m^2/g, and bulk density of 3–500 kg/m^3 [2]. Pertinent alcogels are derived by sol–gel chemistry, and supercritical drying helps to produce high porosity by preserving the gel skeleton with minimal shrinkage from capillary stress; otherwise, the gel would shrink in volume to form low porosity xerogels after ambient solvent evaporation. Hydroxyl groups on the aerogel silica surface provide a main source for hydrophilic capability to interact with foreign molecules, and the active sites have been found to remain very strong even after heated to 700 °C or exposure to water vapor [3]. Adsorptive properties of silica-based aerogels to water and hydrocarbons are reported in several studies [4–6].

Another new field for silica aerogels is the use as sensor elements in the form of porous thin films. By taking an advantage of inherent hydrophilicity to water molecules, silica-based humidity sensors generate responses of surface conductance under an electrical field. In the low humidity environment, protons released from surface hydroxyls hop from site to site along with the silica surface or hydrate with adjacent water molecules to form H_3O^+ ions as charge carriers [7]. At high relative humidity (RH), water molecules inside the capillary pores cluster to form a continuous layer where the transfer of protons dominates [7]. The sensing response is dependent upon the pore geometry of silica [8]. Large mesopores provide favorable diffusion accessibility for free molecules to move reversibly from the external environment to the pore interior. Accordingly, silica aerogel thin films are potentially viable for being employed in chemical sensors, but this is rarely uncovered in the literature.

Fabrication of thin films is critical for the determination of electrical device performance, especially when they are applied to an integrated device industry. Sol–gel processing has been well recognized to offer an economical technology for ceramics film deposition, because it allows the preparation of high-purity materials on rough substrates in their final film shapes by either dip- or spin-coating [9]. A recent example is that aerogel silica films are used as microelectronic devices in the field of microelectromechanical systems by taking a favor of their good mechanical property [10]. To better control film microstructure, the good viscoelastic fluidity of a silica sol has to be achieved prior to coating, and the control is governed by hydrolysis and

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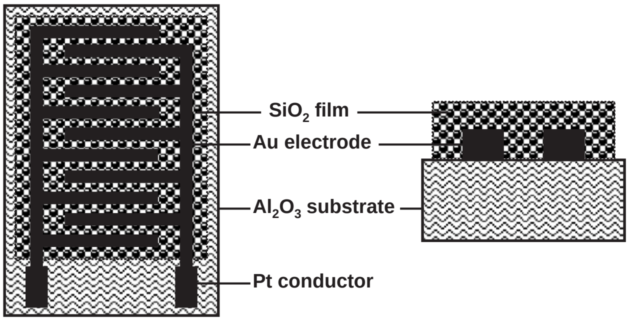

Fig. 1. A schematic diagram for the comb-like silica film sensor device (left: top view; right: side view).

condensation reactions of silicon alkoxide precursors by sol–gel chemistry [11]. Generally, catalysts from acid to base are chosen to accelerate the creation of silanols and siloxane bonds, and the degree of chemical transformation between the two affects the final sol viscosity. Further, increasing the cross-linking extent in the silica matrix helps to stiffen silica skeleton with a high elastic modulus [12]. This wet chemical approach provides promising potential in the fabrication and miniaturization of integrated thin films of chemical sensors.

The study presents new results for structural and electrical sensing properties of aerogel silica thin films after being deposited on gold electrode-patterned alumina substrates. Variation of the viscoelastic behavior with time is related to a continuity change of the gel network and a cross-linking degree of the particles in sol [13]. Many of our efforts have been put to make stable homogeneous viscous silica sols and to determine a viscosity range suitable for dip coating. The selection of a proper film thickness is of great importance for a humidity sensor, because it may affect the adsorptive capacity of the film to water moisture. A good correlation between film thickness and sensor response has been proposed for discussion below.

2. Experimental

2.1. Silica film preparation

The silica sol used in the work was synthesized with two-step acid-base-catalyzed hydrolysis of tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS, Fluka, 99%) dissolved in the solvent of 2-propanol (C_3H_7OH, Tedia, 99.6%). The corresponding sol–gel reactions are described as follows.

Hydrolysis of TEOS by water: (general form)

$$Si(OC_2H_5)_4 + xH_2O \leftrightarrow Si(OH)_x(OC_2H_5)_{4-x} + xC_2H_5OH \qquad (1)$$

Condensation of two silicic acids:

$$\equiv Si - OH + HO - Si \equiv \leftrightarrow \equiv Si - O - Si \equiv + H_2O \qquad (2)$$

Condensation of silicic acid with ethoxy of TEOS incompletely hydrolyzed:

$$\equiv Si - OC_2H_5 + HO - Si \equiv \leftrightarrow \equiv Si - O - Si \equiv + C_2H_5OH \qquad (3)$$

Esterification of silicic acid by 2-propanol (solvent):

$$\equiv Si - OH + CH_3CH(OH)CH_3 \leftrightarrow \equiv Si - OCH(CH_3)_2 + H_2O \qquad (4)$$

The silicon precursor, TEOS, was mixed with 2-propanol (molar ratio 1 : 5) at room temperature, and the stirring at 100 rpm (round per minute) was maintained for an hour. In the first step, an aqueous solution of hydrochloric acid diluted with triply deionized water was added to the alcoholic TEOS solution for hydrolysis and mixed for 15 min at room temperature, and a pH value of 0.5 was obtained for the hydrolyzing solution (molar ratio $TEOS : H_2O : HCl = 1 : 2 : 9 \times 10^{-4}$). In the second step, addition of an aqueous solution of ammonium hydroxide (prepared based on molar ratio $H_2O : NH_4OH : TEOS = 2 : 4 \times 10^{-3} : 1$) then followed for condensation reactions, and a weak acidic solution of pH 6.5 was formed. After another agitation for 30 min, the viscosity of the final silica sol was measured with time by a viscometer (Brookfield, Model LVT).

The silica sol at a selected viscosity was deposited on a clean alumina substrate (96% α-Al_2O_3, 10 × 5 mm) with comb-shaped gold electrodes (Fig. 1) by dipping at a rate of 0.5 cm/s. Alumina mean roughness and grain size are 200–300 nm and 1–6 μm, respectively, measured by an atomic force microscope (Digital Instruments, Nanoscope III). Five paired gold electrodes on the alumina substrate are made by a screen-printing technology, and each single electrode is 2.95 μm thick and 252.3 μm wide, measured by a metallurgical microscope (Olympus, Model BX51). The silica-layered composite device was subjected to supercritical drying in an autoclave for solvent removal. The sealed reactor was supplied with dry nitrogen gas at 10 bar and then slowly heated at 1–2 °C/min until the temperature and pressure reached a supercritical state (255 °C and 85 bar typical) over the critical point of 2-propanol (235 °C and 47.6 bar). The liquid contained in the vessel was slowly released to ambient pressure, and the entire depressurization took about 4 h. The obtained silica films were thermally treated at 500 °C for 2 h, and then kept aged for 12 h in clean humid air (60% RH). Silica xerogel films were also prepared by solvent evaporation drying at the atmospheric condition, which took about 120 h. The preparation parameters of coating viscosity and drying are summarized in Table 1.

2.2. Sensor test

The silica sensor device for evaluation was inserted into a connecting board, and the set was then placed inside a

Table 1
Preparation conditions and thickness measurements of silica films

Sample I.D.	Coating viscosity[a] (cP)	Drying process	Film thickness[b] (nm)
AG12	12	Supercritical	114
AG15	15	Supercritical	172
XG12	12	Ambient	–
XG15	15	Ambient	–

[a] Unit conversion: 1 cp (centipoises) = 10^{-3} Pa s.
[b] Measured by SEM for the sample after calcined at 500 °C.