Aerogels for Electronics

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ABSTRACT

In addition to their other exceptional properties, aerogels also exhibit unusual dielectric and electronic properties due to their nano-sized structures and high porosities. For example, aerogels have the lowest dielectric constants measured for a solid material (having values approaching 1.0); they have exceptionally high dielectric resistivities and strengths (i.e., ability to insulate very high voltages); they exhibit low dielectric loss at microwave frequencies; and some aerogels are electrically conductive and photoconductive. These properties are being exploited to provide the next generation of materials for energy storage, low power consumption, and ultra-fast electronics. We are working toward adapting these unusual materials for microelectronic applications, particularly, making thin aerogel films for dielectric substrates and for energy storage devices such as supercapacitors. Measurements are presented in this paper for the dielectric and electronic properties of aerogels, including the dielectric constant, loss factor, dielectric and electrical conductivity, volume resistivity, and dielectric strength. We also describe methods to form and characterize thin aerogel films which are being developed for numerous electronic applications. Finally, some of the electronic applications proposed for aerogels are presented. Commercialization of aerogels for electronics must await further feasibility, prototype development, and cost studies, but they are one of the key materials and are sure to have a major impact on future electronics.

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INTRODUCTION

Aerogels are very high porosity materials made by sol-gel chemistry and dried using special conditions to preserve the tenuous solid network [1,2]. The microstructure of the aerogels consists of particles and pores which are only fractions of the wavelength of visible light in size. Such structure is unique among common materials and many extraordinary properties result from it. For example, aerogels are known to exhibit the lowest thermal conductivity, sound velocity, and refractive index, of any bulk solid material [3]. The microstructure and the very high porosity of aerogels are also responsible for exceptional dielectric properties and electronic behavior. The dielectric properties of aerogels are affected by the large volume fraction of trapped gas in the pores and the high concentration of adsorbed molecules on the abundant internal surfaces. This has been confirmed by measurements of the linear change of the dielectric properties with aerogel density, and the large effect on these properties attributed to adsorbed water [4,5]. The electrical conductivity of the dielectric aerogels is predictably low because the tenuous solid structure provides poor conduction paths and few charge carriers. The volume resistivity is expected to be high for the same reason. The dielectric strength of aerogels is also expected to be high due to the high volume resistivity and because the nano-sized pores confine the charge carriers to spaces that are about the same size as the mean-free-path for collisions. These properties show that aerogels are unusual dielectric materials and suggest that they can be used for many interesting applications which will be discussed in this paper. Some aerogels can be transformed into carbon aerogels which are electrically conductive. This property and the very large surface area available within them, make these particular aerogels especially useful for energy storage devices like capacitors and batteries.

The formation of thin aerogel films is a necessary step toward many electronic applications. We have developed methods to form aerogel films having thicknesses from 1 to 20 microns and we have successfully deposited metallized patterns on them. The characterization of the dielectric properties of such thin aerogel films has been challenging, although we have been able to apply optical techniques which allow the determination of some electronic properties. This paper presents measurement and development results for aerogels, and it also describes potential and anticipated applications of aerogel dielectrics and conductive aerogels.
MEASUREMENTS OF DIELECTRIC PROPERTIES

**Dielectric Permittivity**

Few measurements of the permittivity of aerogels have been made to date, but collectively, they cover a wide frequency range from 50 Hz to 40 GHz and demonstrate the low values expected for such highly porous materials. Measurements of the real (dielectric constant) and imaginary (loss factor) parts of the complex permittivity were reported by da Silva, et al. [4] for silica aerogels for frequencies between 50 and $10^5$ Hz, and for temperatures of 1.6K to 300K. Hrubesh, et al. [5] have measured permittivities for both the silica and organic aerogels, at microwave frequencies (i.e., 2 to 40 GHz) and at 298K.

At LLNL, the measurements of the dielectric properties were made at microwave frequencies using a cavity perturbation method. This method allows a sensitive measurement of changes in the resonant conditions of a dielectric filled microwave resonator. Such changes can be directly related to the real and imaginary parts of the relative permittivity of the dielectric. All measurements were made at 298K on aerogel samples which were either equilibrated at atmospheric conditions (as prepared), or were heated at 700K under a vacuum for 10 hours to remove adsorbed water (baked). A plot of the dielectric constants of silica aerogel measured at microwave frequencies, is shown in fig. 1 for the density range from 0.01 to 0.6 g/cc. It is seen that the dielectric constant ($\kappa'$) varies linearly with density ($\rho$) over this density range. A least squares fit of the data gives $\kappa' - 1 = 1.60 \rho$ for the as prepared aerogels, and $\kappa' - 1 = 1.48 \rho$ for the baked aerogels. The difference in the slopes between the 'as prepared' and 'baked' samples is attributed to dispersion of the microwave radiation by interactions with polar molecules (mostly water and hydroxyls) on the internal surfaces of the aerogels. This effect contributes significantly (~7% for silica) to the dielectric constant of aerogels. The surface water affects the loss tangent more than the dielectric constant as seen in fig. 2. The data for the loss tangent fits the relations, $\tan \delta = 0.172 \rho$ for the 'as prepared' aerogels, and $\tan \delta = 0.004 \rho$ for the 'baked' aerogels. The effect of water contributes ~70% of the loss tangent in silica aerogel. The dielectric properties have also been measured at LLNL for the purely organic aerogels, and the properties for those aerogels have also been determined to be linearly related to the densities.

It is notable that the dielectric constant for any silica aerogel having a density less than 0.6 g/cc, is less than the dielectric constant of teflon (~2.0) which is the most common low dielectric material in current use. We measured a dielectric constant of 1.008 for a silica
aerogel having a density of 0.008 g/cc. This is believed to be the lowest dielectric constant ever measured for a bulk solid material.

Three other properties of aerogels are important for applications of dielectrics in electronics; 1) sufficiently high thermal conductivity for heat dissipation, 2) a thermal expansion which closely matches the substrate to reduce chances for stress induced cracks, and 3) sufficient shear and compressive strength to support multiple layers. While aerogels are most notable for their exceptional thermal insulation property and are normally not considered as effective thermal conductors, the higher density silica aerogels (e.g., ρ>0.5 g/cc) are actually better thermal conductors than many polymer films used for low dielectrics. The measured coefficient for thermal expansion of silica aerogel is 3 × 10⁻⁵ cm/cm for the temperature range 275-323K. This value is similar to that for fused silica, suggesting that silica aerogel should be thermally compatible with the glassy substrates or coatings used in electronics packaging. Lastly, the shear strength has not been adequately measured for any aerogels to date. However, the compressive strength of aerogel has been measured and is strongly dependent on the density. The strength of aerogels for electronics applications should be an issue only for the lowest densities (i.e., ρ<0.05 g/cc).

**Dielectric Conductivity and Volume Resistivity**

The dielectric conductivity (σ) of aerogels is obtained from our microwave measurements by using the relation [7];

\[
\sigma = 5.5 \times 10^{-13} \epsilon' \tan \delta f \text{ (ohm-cm)},
\]

where \(\epsilon'\) and \(\tan \delta\) are the dielectric constant and the loss tangent, respectively, and \(f\) is the frequency. For the 'baked' silica aerogel with a density of 0.1 g/cc, the dielectric conductivity ranges from 1.1 × 10⁻⁴ to 8.1 × 10⁻⁶ Ω⁻¹cm⁻¹ in the frequency range from 3 to 40 GHz. The typical volume resistivity for 'baked' silica aerogels (i.e., 2πf/s) with the same density is 4.1 × 10¹⁵ Ω cm. Comparative values of dielectric conductivity for the 'as prepared' organic aerogel with a density of 0.1 g/cc are 2.6 × 10⁻⁴ to 1.9 × 10⁻⁵ Ω⁻¹cm⁻¹, and 4.5 × 10¹⁴ Ω cm, for the typical volume resistivity. These values of volume resistivities for aerogels are comparable with the best of the polymer insulating materials (e.g., polytetrafluoroethylene and polyethylene) [8]. Aerogels should therefore be expected to exhibit very good dielectric strengths against high voltage breakdown.

**Dielectric Strength**

The dielectric strength of silica aerogels is higher than expected for a material that is so porous. This is likely attributable to the fact that pores in air-filled aerogels are of the
same order of size as the mean distance for collisions of electrons. Thus, electrons in aerogel pores tend to collide with the solid before gaining sufficient kinetic energy to ionize upon impact. We have measured the dielectric strength of air-filled silica aerogels at 300K. These measurements were made at 60 Hz on silica aerogels having different thicknesses. Breakdown voltages were registered for different thicknesses of silica aerogel. The average dielectric strength from these data is 128 kV/cm and it was determined to be essentially independent of the aerogel density. Measurements were only made on 'as prepared' aerogels; further measurements will be done to determine the effect of adsorbed water on the dielectric strength of silica aerogel. Higher values of dielectric strength are expected for 'baked' aerogels, but even the value reported here for silica aerogel is higher than for most ceramics (e.g., alumina is 110 kV/cm), though it is less than for pure polymers (e.g., 160 to 500 kV/cm) [9]. Aerogels should be effective, very lightweight insulators for high voltage applications, especially in vacuum applications.

THIN FILM AEROGEL PROCESSING

Sol-gel processes have been well developed, especially during the past decade or so, to produce advanced glasses, glass-ceramics, and ceramics, in thin films for electronics. There are several books and articles which describe the advantages and details of sol-gel films for electronic applications [10,11,12]. The formation of thin aerogel films might seem rather straightforward because of the considerable success in applying sol-gel coatings to surfaces, however, the rapid evaporation of solvent that accompanies the deposition processes causes the sols to form compact films as drying occurs, rather than forming a more porous gel. Therefore, special considerations and methods are needed to successfully form highly porous gels and dry them to make low density aerogels. Very little work has been reported for processing porous sol-gel films where the films are to remain porous for their application. Here we describe the special conditions and requirements which are needed to make highly porous aerogel films which exhibit low dielectric properties.

Most of the methods already developed for applying sol-gel thin films and coatings (e.g., dipping, spinning, spraying, etc.) generally apply to making true aerogel films. However, all of these methods have the common requirement that the gel must be formed under conditions in which the rate of evaporation is limited, both during and after the gel formation. To facilitate this we perform the coating processes within an enclosure that is maintained saturated with the vapor of the working solvent. The enclosure atmosphere also contains a partial pressure of ammonium hydroxide which helps to catalyze the gelation of
the films. The most common aerogel films are silica, but we have also demonstrated our method with other metal oxides for which hydrolysis/condensation of the metal alkoxide is the predominant chemistry (e.g., zirconia, alumina, and tantala.) Generally, depending on the desired porosity of the final aerogel, we used two methods to prepare the precursor solution for the process. For gel porosities >95% we used the two-step, partial hydrolysis/condensation chemistry reported previously for silica aerogels [13]. For gels with other porosities, we prepared a single-step base-catalysed hydrolysis solution according to the typical method for silica as follows: mix tetramethoxysilane (TMOS), water, methyl alcohol, and ammonium hydroxide, in a molar ratio of 1:2:4:0.01. An additional amount of alcohol is added to this mixture to establish the ultimate porosity of the gel. The methods used to make thin aerogel films depend on the thickness desired and whether or not the film is to be bonded to a surface. In the following we discuss the various processing steps and procedures to form thin aerogel films on substrate materials for electronics.

Surface Preparation

From experience we found that most of the metal oxide gels adhere to glass or oxidized surfaces (probably through metal-oxide-metal bonds) but gels did not stick well to unprepared metal surfaces. Bonding to all oxidized surfaces was enhanced by etching the surface with a mild alkaline solution (e.g., KOH), then rinsing with alcohol immediately prior to film deposition. For the opposite case of non-bonding we treated the surfaces with a methylated silicate compound that serves as a release agent.

Spin, Dip, and Spray Coatings

Spin coating is essentially the same as that used to spin glass coatings for electronic applications, except that it is performed with the spin apparatus entirely within an enclosure that has a solvent saturated atmosphere. Film thicknesses are typically less than two micrometers. Special modifications were performed on the apparatus to prevent the possibility of an explosive hazard. Typical substrates are Pyrex glass slides and silicon wafers up to 3" diameter. The procedure for forming films is to meter a droplet of precursor solution onto the spinning substrate while its spin rate is increasing up to a maximum speed of 1850 RPM. The spinner is immediately turned off and stopped with a brake, so that the sample is subject to minimal loss of solvent during gelation. Typically, the gel will form within a few minutes, after which the substrate is manually removed from
the spin apparatus and immersed in solvent. The substrates with films are stored submersed in solvent until ready for supercritical drying.

Dip coating is the simplest of the coating processes, but it is used only when all surfaces of a substrate material are to be coated. With this method, film thicknesses less than a few micrometers are obtainable depending on the viscosity of the precursor and the withdrawal rate. In our work, the precise thickness was not an important parameter, so the dipping and withdrawing procedure was performed manually without concern for controlling the rates. Typical substrates were Pyrex glass slides of various sizes. These were simply dipped into the prepared precursor solution, withdrawn, then placed edgewise and vertical in a holder which is located within the enclosure. The time necessary for a gel film to form was found by trial to be only a few minutes. After the film is gelled, the entire holder containing the slides is immersed in a beaker of solvent and it remains surrounded by liquid until ready for supercritical drying.

Spray coating has been used to put thicker single layer coatings on substrates like glass and silicon wafers. Films as thick as 80 micrometers have been achieved by this method. An aspirator is used to spray the precursor solution directly onto the substrate which is supported in a nearly vertical position within the enclosure. Excess solution drains by gravity, leaving a thick film which gels within a few minutes. These films have a varying thickness due to the draining, but the surface of the gel is smooth and continuous. After gelation, the substrate is manually immersed in solvent until ready for supercritical drying.

Supercritical Drying

All of the prepared gels were converted to aerogels using supercritical drying methods in order to prevent densification of the films. Either direct supercritical extraction (SCE) of the solvent was done at high temperature or an alternate low temperature extraction of carbon dioxide was performed after exchange of the original solvent. The method of drying chosen depended on the temperature stability of the substrate material. Gels on glass substrates were generally compatible with high temperature SCE whereas silicon wafers required a protective coating of silicon dioxide to survive the high temperature SCE of solvents. The procedure for direct SCE is to place the glass container holding the submersed (or encapsulated) samples directly into an autoclave. The autoclave is filled with additional solvent (usually, alcohol) and sealed. The temperature of the autoclave is raised at a rate of 0.3°C/min. while the pressure increases to about 120 bars and excess pressure above that is released. After the temperature reaches about 280°C, the
pressure is released from the vessel at a controlled rate of 0.3 bar/min. until a pressure of about 1.5 bar is reached. The autoclave is then purged with air as the vessel cools. This cycle typically takes 24 hours. Alternatively, a similar cycle is performed at temperatures less than 45°C after the solvent in the gel-film is first exchanged with liquid carbon dioxide. The exchange time to remove solvent from the thin films less than 50 micrometers thick was typically 2 hours.

Metallization

Metallization of the aerogel was done by vapor or sputter deposition directly onto the as-prepared aerogel film surfaces. For some cases, low resolution patterning was achieved by depositing the metal through an appropriate mask. Photoresist patterning techniques were applied only after the aerogel surface was coated with approximately 1000Å of polymer to seal the pores of the aerogel.

Film Characterization

The morphology of the films and the film-substrate interface regions may be examined using a high resolution scanning electron microscope (SEM). The film thicknesses are measured using a stylus type profilometer. Film adherence on glass and silicon wafers are qualitatively determined using a tape stick test with Scotch® tape.

Refractive indexes of films were measured using an ellipsometer. This instrument will measure either the refractive index or the thickness of a thin dielectric layer if the other is known. The thickness measured by a profilometer is entered as input to the ellipsometer to calculate the refractive index of a film. Generally, it is difficult to apply this technique because the surface reflectivity of aerogels is typically less than 1% at a wavelength of 632.8nm. However, sufficient reflectivity is usually obtained at shallow angles of incidence. Other physical properties of the aerogel films were determined from this measurement as follows:

The film densities were determined from the measurement of the optical refractive index, n, using the relation, \( \rho = \frac{(n-1)}{.209} \), reported by Henning and Svensson for silica aerogels [14]. The dielectric constant and the porosity of the films were determined indirectly from the density, after measurement of the optical refractive index. The porosity is determined from the relation: \( \Pi = 1 - \frac{\rho}{\rho_s} \) where \( \rho_s \) is the density of the solid. So for silica aerogel, with \( \rho_s = 2.19 \ g/cc \), \( \Pi = [(1.458 - n) / .458] \) is the percent porosity.
Similarly, the dielectric constants for the silica aerogel films or sheets were determined after measurement of the optical refractive index using: \( \kappa' = 1 + 1.6 \rho \) [15], so \( \kappa = 1 + 7.7 (n-1) \).

Results

Using the methods described, we have successfully fabricated thin, flat, uniform silica aerogel films, having various porosities, with measured thicknesses from less than 1 to 20 micrometers on glass and silicon wafer substrates. The adherence of the films to the substrates has been qualitatively determined by a tape stick test. Generally, good film adherence was obtained for all aerogels with a porosity less than about 86% and mixed results were observed for porosities between 86% and 95%. For porosities >95%, the results were invalid because the aerogel is too weak to survive the application of the tape. These films have been examined using SEM to verify their aerogel microstructure.

We have measured the refractive indexes of deposited films and we have calculated their bulk densities to confirm that they are aerogels having densities in the range from about 0.04 - 0.46 g/cc, and porosities in the range from 77% to 98%. We have also calculated the dielectric constants of these films based on the measured refractive indexes. The dielectric constants span the range from about 1.06 to 1.7.

We developed processes to seal, pattern, and metallize thin aerogel films. An example of a high resolution pattern of gold metal on an aerogel film is shown in figure 3. This pattern of 4 micrometer wide strips was achieved using polymer coating and photoresist techniques. We have also sputtered thin (< 0.5 micrometer) metal layers directly onto the aerogel surfaces and electroplated thicker (> 1.0 micrometer) layers on the sputtered layers.

APPLICATIONS

In addition to their exceptional dielectric properties, aerogels exhibit other complementary properties for electronics such as low thermal expansion and adequate thermal conductivity and mechanical strength. Aerogels provide a unique set of properties and attributes to meet specifications for electronic applications. We list here some of the numerous applications for aerogels as dielectrics, some of which are under current development.
Aerogel Films

Thin aerogel films (≈2 micrometers) are formed on silicon wafers to provide a low dielectric constant substrate to reduce capacitance in integrated circuits. The dielectric constant for all aerogels is less than 2.0 and its value depends on the porosity, a controllable parameter for aerogel films. Dielectric constants of the aerogels well below 2.0 will enable significant improvements in the speed of integrated circuits. Thick organic aerogel films (≈0.5 millimeter) are formed by spray coating, dried by supercritical conditions, then pyrolyzed to carbon aerogel films for use in aerocapacitors. These devices can provide specific capacitances in excess of 45 Farads per gram of material [16].

Applications for the thin film dielectrics include: microwave striplines, microwave circuits such as used in radars and communications, low capacitance chip connectors, high-speed electronic conductors for both ultra large scale integrated circuits and for interconnections between computer chips, high-speed Gallium Arsenide test chips and associated electronic packages, extremely lightweight electronic packages, power transmission high voltage insulators, and spacers for electrodes in vacuum tubes.

Bulk Dielectrics

Aerogels, as bulk materials, are also useful for electronic and electrical applications, particularly where they provide effectively air-like properties of lightweight and high electrical insulation. Applications for the bulk dielectrics include; air-like suspension of microwave circuits, co-axial cable insulation, power transmission high voltage insulators, and microwave antenna.

Other Applications

Other applications in the microelectronics and electro-optics industries include low dielectric constant insulators for high-speed electronic conductors in large scale integrated circuits, for interconnections between computer chips, and as ultra-fast light modulators. Also, the conductive carbon aerogels, filled with electrolite fluids are useful for electrodes in supercapacitors and as batteries.
CONCLUSIONS

Aerogels exhibit very low dielectric permittivities as expected for such highly porous materials. However, the high porosity and high surface area also contribute to significant changes in the dielectric properties from adsorbed molecular species. This effect must be accounted for when considering electronic applications of the aerogels. The dielectric permittivities of aerogels are found to be linearly related to the density. This indicates that the properties are dominated by the trapped gas in the aerogels rather than by the solid matrix. The results presented here provide empirical relations for predicting the magnitude of the dielectric properties when the aerogel density or porosity is known.

It is possible and practical to form highly porous, true aerogel films on substrates using a variety of common deposition methods, if care is taken to slow evaporation of solvents during gelation, and if supercritically dried to preserve their tenuous structure. The aerogel films are good quality, bond well to the substrates, and are strong enough to survive other processing steps used to prepare them for specific applications. The exceptional dielectric properties of aerogels coupled with the ability to produce either bulk materials or thin films, suggest their use in many electronic applications. Already, aerogels are being developed for use in supercapacitors, microwave devices, and electronic packaging.

This paper provides information about the electronic properties of aerogels, discusses why they are exceptional, and offers a variety of applications for the use of aerogels in electronics. The author hopes this information will serve to stimulate commercial interest in these amazing and unusual materials called aerogels. While aerogels have many properties desireable for the electronic applications, further development is needed to determine their compatability with circuit processing and to determine manufacturing costs. Commercialization of aerogel dielectrics must await further feasibility, developmental, and cost studies, but they are expected to have a major impact on future electronics [17]. The commercialization of aerogels for supercapacitors is already underway through a spin-off company from LLNL.
References:

Figure 1. Plot of the dielectric constant of silica aerogel versus density, for moisture laden and dry samples, showing about 7% increase due to adsorbed water.
Figure 2. Plot of the loss tangent (at microwave frequencies) of silica aerogel versus density, for moisture laden and dry samples, showing about 70% increase due to adsorbed water.
Figure 3. Photograph of 4 micrometer wide gold metal strips patterned on a thin silica aerogel film (= 1.3μm) which is on a silicon wafer. This pattern was produced by photoresist processing after the aerogel was first coated with about 100nm thick polymer which remains after the process.