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DIELECTRIC PROPERTIES AND ELECTRONIC APPLICATIONS OF AEROGELS

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Dielectric Properties and Electronic Applications of Aerogels

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ABSTRACT

Among their other exceptional properties, aerogels also exhibit unusual dielectric properties due to their nano-sized structures and high porosities. For example, our measurements of the dielectric constants and loss tangents for several aerogel varieties at microwave frequencies show that they both vary linearly with the aerogel density, indicating that the dielectric behavior of aerogels is more gas-like than solid-like. We have also measured the dielectric strength of silica aerogels and find that they are better than ceramics for high voltage insulation. The low dielectric constants and loss tangents of aerogels, along with their controllable thermal expansion properties, make them desirable materials for use as thin films in high speed integrated digital and microwave circuitry.

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I. Introduction

Aerogels are high porosity materials made by sol-gel chemistry and dried using supercritical fluid conditions to preserve the tenuous solid network [1,2]. The nanostructure of aerogels consists of particles and pores which are only fractions of the wavelength of visible light in size. This 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 nanostructure and the very high porosity in aerogels is also responsible for exceptional dielectric properties and electronic behavior. The dielectric properties of aerogels are dominated by the large volume fraction of trapped gas in the pores and the high concentration of adsorbed molecules on the abundant 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 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.

The formation of thin aerogel films is a necessary step toward many electronic applications that require very low dielectric properties. We have developed methods to form aerogel films having thicknesses from 1 to 100 microns by spinning and by capillary flow. Characterizing these thin films has been difficult but we describe one successful method.

In this paper we present our measurements of some of the dielectric properties of aerogels, including the dielectric constant, loss factor, dielectric 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, we will describe some of the electronic applications proposed for aerogels, utilizing their exceptional dielectric properties.

II. Dielectric permittivity measurements

Only a 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.

The measurements by da Silva, et.al. were made using parallel plate configurations and a capacitance bridge. They showed that for silica aerogels, the dielectric constant is nearly constant for temperatures between 80 and 300K whereas, the loss tangent (i.e. loss factor / dielectric constant) decreases with temperature over the same range. Both the dielectric constant and loss tangent change sharply for temperatures less than 80K, similar to the effect observed in amorphous fused silica. The dielectric constant data, plotted as a function of density (or porosity), are considerably scattered and do not fit any particular model very well.

Our 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 frquencies, are shown in Fig.1 for the density range from 0.01 to 0.6 g/cc. It is seen that the dielectric constant (κ') varies linearly with density (ρ) 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. Here, 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.

It is noted that the dielectric constant for any silica aerogel with a density <0.6 g/cc, is less than the dielectric constant of teflon 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.

Plots for the dielectric constant and loss tangent versus density are shown for organic aerogels in Fig.3 and Fig.4 respectively. As is the case with the silica aerogel, the dielectric constants and loss tangents for the organic aerogels are linearly related to their densities. The data in Fig.3 give the following relations: $\kappa' - 1 = 1.75\ \rho$ for resorcinol-formaldehyde (RF) aerogels, and $\kappa' - 1 = 1.83\ \rho$ for melamine-formaldehyde (MF) aerogels. The data in Fig.4 gives the following relations: $\tan\delta = 0.010\ \rho$ for RF aerogels, and $\tan\delta = 0.023\ \rho$ for MF aerogels. The effect of surface adsorbed molecules on the dielectric properties of the organic aerogels was not determined because they decompose at the temperatures necessary to sufficiently dry them.

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^{-6} 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, but qualitatively, it is known to be weak in tension. However, the compressive strength of aerogels is a strong function of the density, and the strength of aerogels for electronics applications should be an issue only for the lowest densities (i.e., ρ<0.02 g/cc). The variation of both the dielectric constant and the compressive modulus with density are shown for silica aerogels in Fig. 5.

III. Dielectric conductivity and volume resistivity

The dielectric conductivity (σ) of aerogels is obtained from our microwave measurements by using the relation[7]; $\sigma = 5.5 \times 10^{-13}\ \kappa' \tan\delta\ f$ (ohm-cm), where κ' 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 $8.1 \times 10^{-6}\ \Omega^{-1}cm^{-1}$ in the frequency range from 3 to 40 GHz. The typical volume resistivity for 'baked' silica aerogels (i.e., $2\pi f/s$) with the same density is $4.1 \times 10^{15}\ \Omega$ 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 $1.9 \times 10^{-5}\ \Omega^{-1}cm^{-1}$, and $4.5 \times 10^{14}\ \Omega$ 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., poly-tetrafluoroethylene and polyethylene) [8]. Aerogels should therefore be expected to exhibit very good dielectric strengths against high voltage breakdown.

IV. Dielectric strength measurements

Aerogels exhibit higher dielectric strengths than expected for porous materials. This is probably, at least in part, attributable to the pore sizes in air-filled aerogels being of the same order as the mean free path for electron collisions. 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 breakdown voltage versus thickness is shown in Fig.6 for silica aerogels. 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.

V. Thin film dielectrics

The formation of thin aerogel films might seem rather straightforward because of the considerable successful work reported by many workers to apply sol-gel coatings to surfaces [10]. 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 form low density aerogels.

We are developing processes to seal, pattern, and metallize both bulk and thin film aerogels. We have successfully fabricated thin film silica aerogels of thicknesses from 1 micron to 100 microns, and we are measuring the electrical and mechanical properties of these thin aerogel films. Qualitative tests show that the aerogels can be sealed from subsequent semiconductor process liquids so that conventional photoresist techniques can be used to pattern the aerogels. We also have for the first time patterned aerogels with plasma-etching techniques. We have sputtered thin (< 0.5 micron) metal layers onto the aerogel surfaces and electroplated thicker (> 1.0 micron) layers. We have patterned metal conductors on top of the thin film aerogels on silicon substrates.

Silica thin film aerogels are made using a silica solution (with a consistency of oil) to which water, a solvent, and a basic catalyst are added, forming a gel [11]. The ungelled solution is spun onto a silicon wafer in a manner similar to that used to spin on conventional photoresists in semiconductor processing. The solution is allowed to gel in an environment designed to limit evaporative drying. The resulting layers can be made to given thicknesses. The laboratory scale process takes only a few hours, while other methods can take days.

It has been difficult to determine the very low dielectric constants for the thin aerogel films. To measure such low dielectric constants by capacitance techniques with precision, requires inordinately large electrode areas. In an alternative approach, we have successfully measured the refractive index of silica aerogel films using ellipsometry. We first measure the refractive index to determine the film density from the empirical relation, $\rho = (n-1)/.21$, and then the dielectric constant is calculated from the appropriate relation between the dielectric constant and density, given above in section III.

VI. 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.

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

Applications for the bulk dielectrics include;

- air-like suspension of microwave circuits
- co-axial cable insulation

Applications for the dielectric strength include:

- power transmission high voltage insulators
- spacers for electrodes in vacuum tubes

VII. Conclusions

To summarize, 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 is known.

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 microwave dielectric applications and for electronic packaging applications.

References:

1) R.P. Iler, The Chemistry of Silica, (J. Wiley and Sons, N.Y., 1979), pp.537-539.
2) J. Fricke, "Aerogels," Sci. Am. 256, 92 (1988).
3) J. Fricke and A. Emmerling, "Aerogels - Preparation, Properties, Applications," in Chemistry, Spectroscopy, and Applications of Sol-Gel Glasses, eds. R. Reisfeld and C.K. Jorgensen, (Springer Series on Structure and Bonding, Vol. 77, Springer-Verlag, Heidelberg, Germany, 1991), p.37.
4) A. da Silva, P. Donoso, and M.A. Aegerter, "Properties of water adsorbed in porous silica aerogels," J. Non-Cryst. Solids 145, 168-174 (1992).
5) L.W. Hrubesh, L.E. Keene, and V.R. Latorre, "Dielectric properties of aerogels," J. Mater. Res. 8 (7), 101 (1993).
6) A. da Silva, D. I. dos Santos, and M.A. Aegerter, "Dielectric response of silica aerogels," J. Non-Cryst. Solids 96, 1159-1166 (1987).
7) A.R. von Hippel, Dielectric and Waves, (J. Wiley and Sons, N.Y., 1954), p. 28.
8) D.W. Van Krevelen, Properties of Polymers, (Elsevier, N.Y., 1990), pp. 330-333.
9) R.A. Flinn and P.K. Trojan, Engineering Materials and Their Applications, (Houghton Mifflin Co., Boston, 1981), pp. 614-615.
10) D.R. Ulrich, "Chemical processing of ceramics," Chem. & Eng. News, Jan. (1990) pp. 28-40.
11) T.M. Tillotson, L.W. Hrubesh, and I.M. Thomas, in: Better Ceramics through Chemistry III, ed. C.J. Brinker, D.E. Clark, and D.R. Ulrich, Mater. Res. Soc. Proc. 121 (1988) 685.

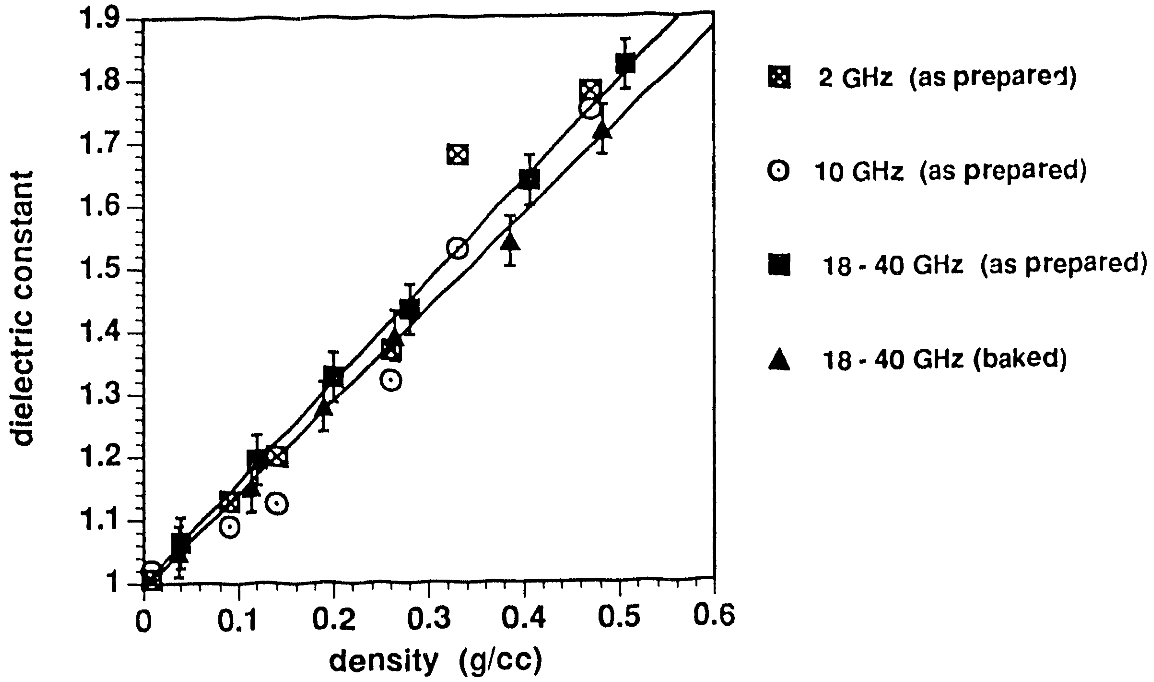

Figure 1. Plot of dielectric constant for 'as prepared' and 'baked' silica aerogel versus density.

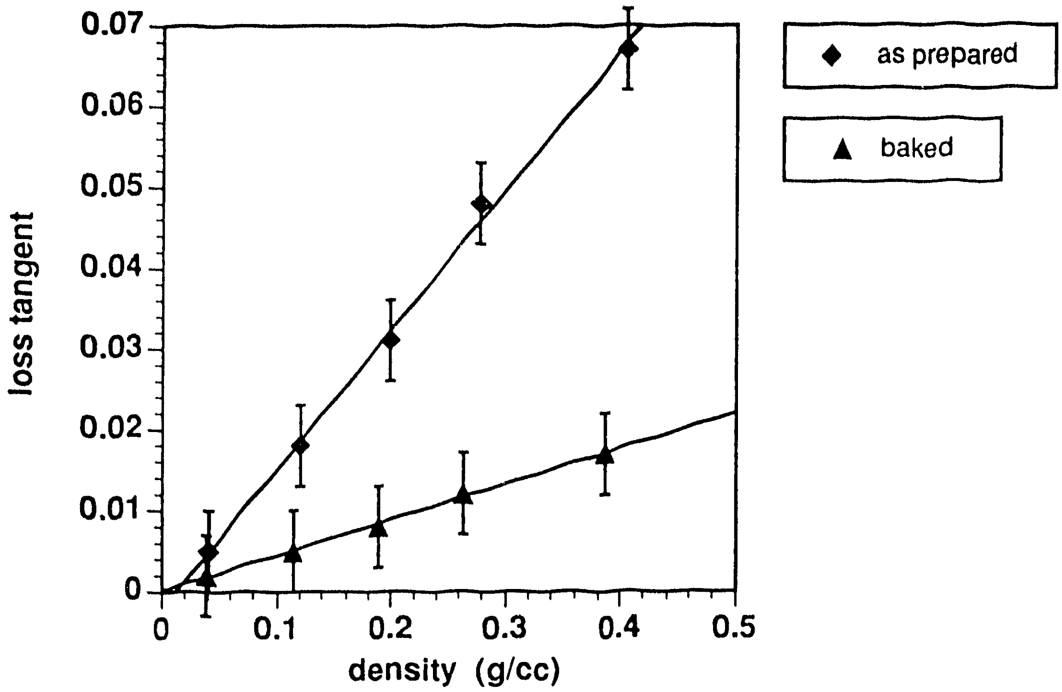

Figure 2. Plot of loss tangent for 'as prepared' and 'baked' silica aerogel versus density.

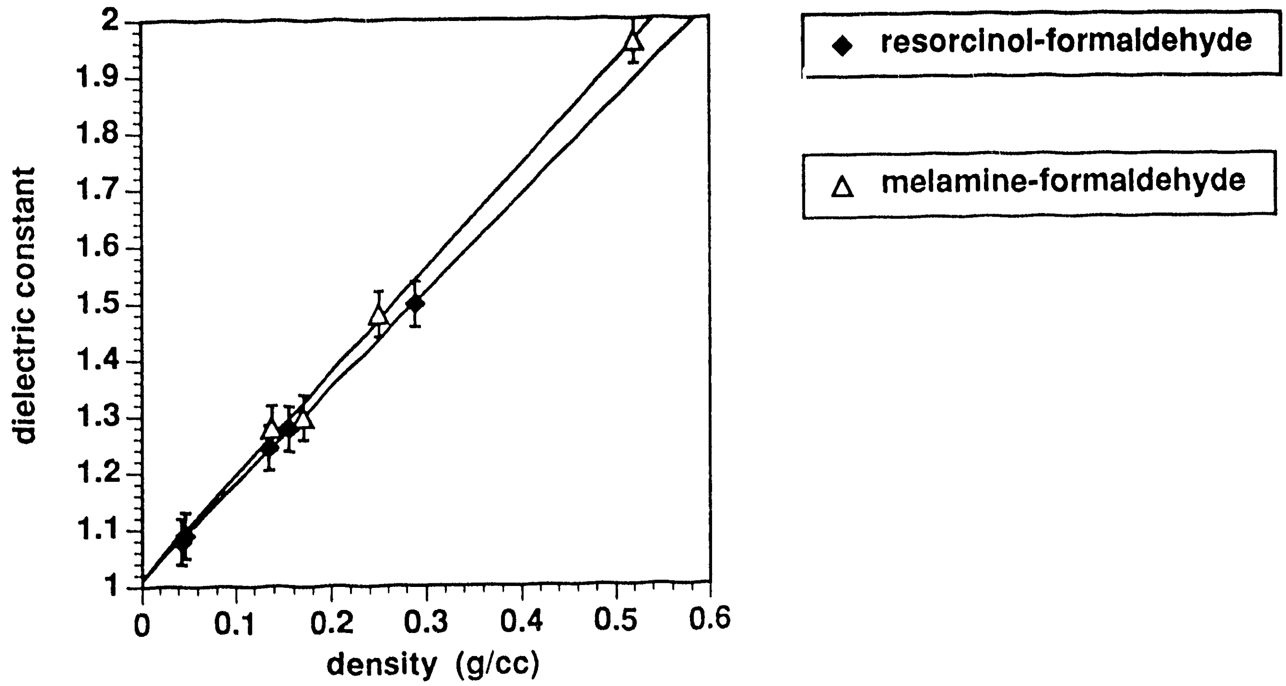

Figure 3. Plot of the dielectric constant for organic aerogels versus density.

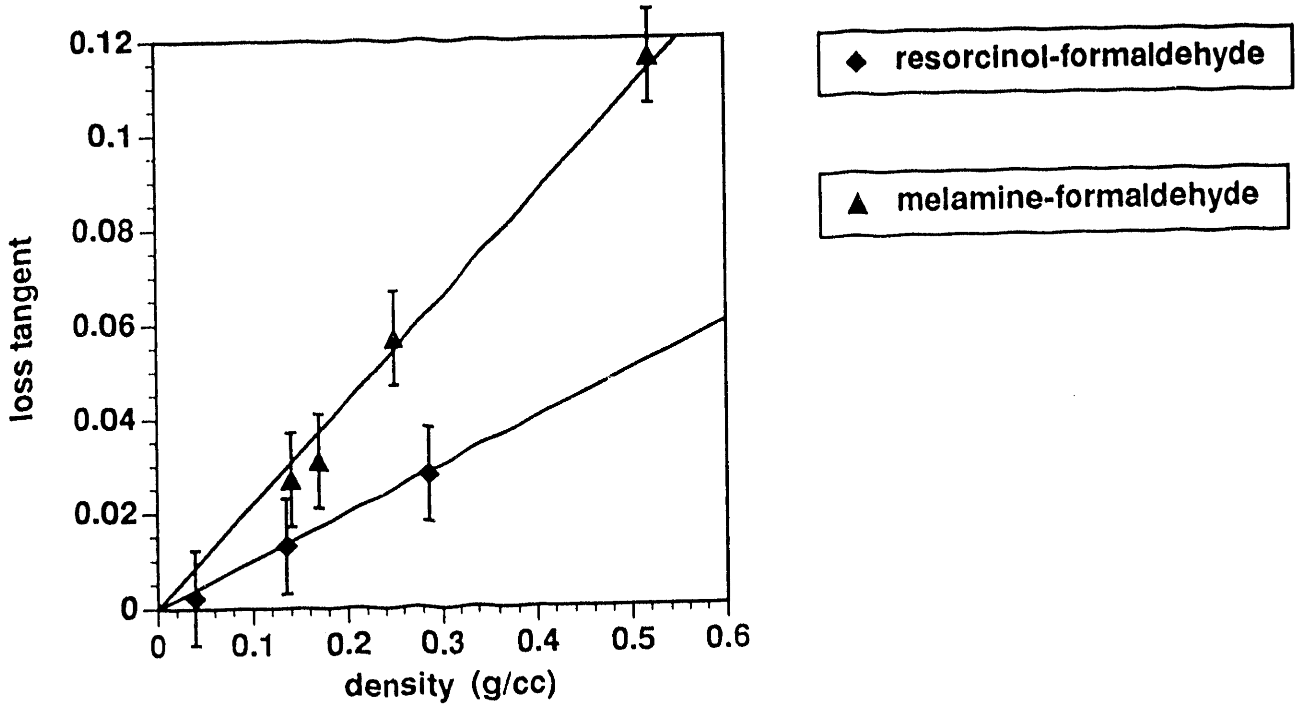

Figure 4. Plot of the loss tangent for organic aerogels versus density.

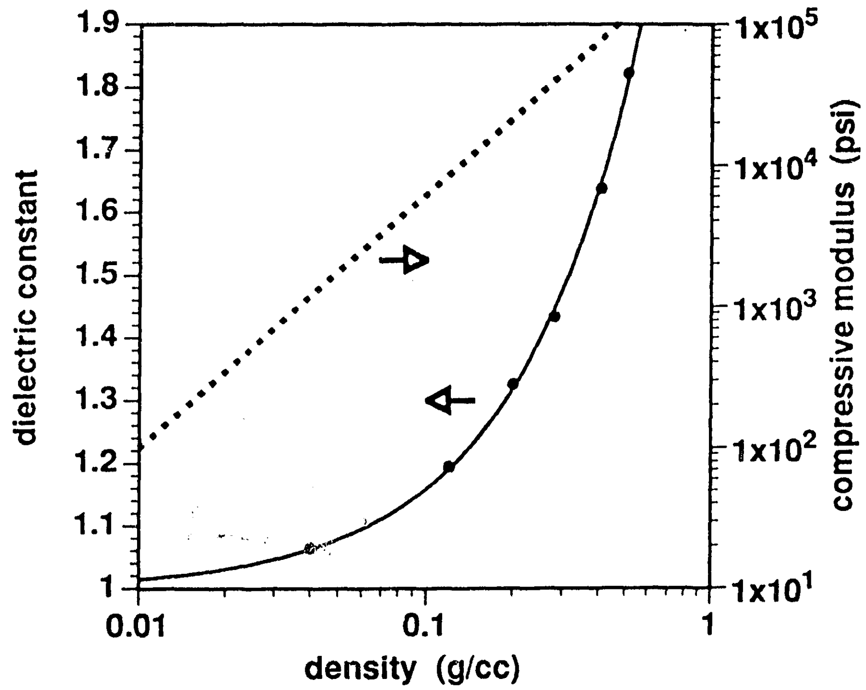

Figure 5. Dielectric constant and modulus vs density for silica aerogel.

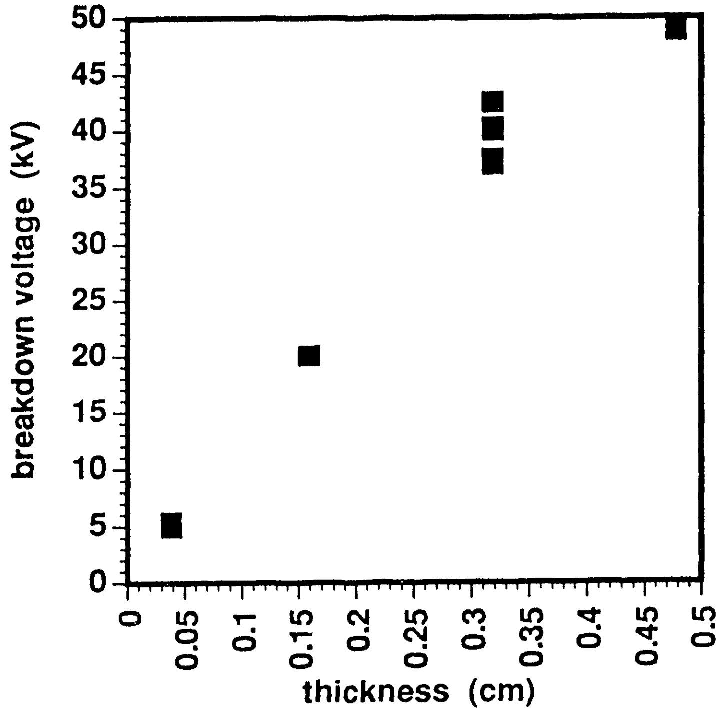

Figure 6. Breakdown voltage for various thicknesses of silica aerogel. The average dielectric strength for the silica aerogels is 128 kV/cm.

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