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Low dielectric constant porous BN/SiCO made by pyrolysis of filled gels

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Abstract

BN/SiCO composite ceramics having a dielectric constant, ε_r, as low as 1.9 have been made by pyrolysis of filled gels at temperature $\geq$1000 °C. Such a low value of ε_r is supposed to be due to a combination of factors: the low ε_r of BN and of SiCO itself and the high amount of residual porosity present in the samples. The porous microstructure – and the related dielectric properties – obtained at 1000 °C show a very good stability up to 1400 °C. This result has been ascribed to the high viscosity of the SiCO glass and to the platelet shape particles of BN. Both factors hinder the sintering and prevent the closure of the pores.

Keywords: Precursors-organic; Sol–gel processes; Dielectric properties; Porosity; Silicon oxycarbides

1. Introduction

There is an increasing interest to develop low dielectric constant and low loss materials that can operate in the GHz range for wireless telecommunication systems.[1] One of these new materials are SiCO glasses that have a dielectric constant, ε_r of 3–3.5. In comparison silica has $\varepsilon_r = 3.9$.[2,3] The low ε_r values of the SiCO are believed to arise from the substitution of some of the polar Si–O bonds in the silica network by more covalent Si–C bonds.[4] Porous solids are another class of materials with a potential for decreasing the dielectric constant.[5] In the present paper these two approaches are combined. Porosity in SiCO is induced by using platelet shapes particles of BN as fillers during the processing of SiCO from gels.

Silicon oxycarbide glasses can be synthesized by pyrolysis of gel-derived siloxane networks.[6] Accordingly, SiCO glasses belong to the broader family of polymer derived ceramics, PDCs.[7] The volatile products released during the polymer-to-ceramic transformation, leave a transient porosity which usually closes up near 800 °C.[8] A way to stabilize the porosity is to load the gel network with a filler. The filler constrains the sintering of the pores which otherwise starts to occur from 800 °C.[9]

Here we present the results of the synthesis, the microstructure and the dielectric characterization of a SiCO glass loaded with BN powders. BN has been chosen because it combines low ε_r with good thermal conductivity. Good thermal conductivity is desirable in the materials for microelectronic components.

2. Experimental

2.1. Synthesis of the filled gels

Methyltriethoxysilane, MTES (ABCR, Karlsruhe, Germany) was used as the starting silicon alkoxide to obtain, through hydrolysis and condensation (sol–gel process) the hybrid methylsilsequioxane network, which is the precursor for the SiCO glass. Platelet-like, hexagonal BN powders, 99.5% pure with grain size lower than 1 μm (B-1084 Cerac Inc., USA) were used as fillers.

The flow chart of the synthesis is reported in Fig. 1. The proper amount of BN powder (Table 1) was loaded into 10 ml of the liquid MTES to form the starting suspension. 11.5 ml of ethanol per 10 ml of MTES were added to help the dispersion of the BN particles. The suspension was refluxed overnight at 70 °C. Next the temperature was raised to 90 °C and acidic water (HCl, pH 1) was added to promote the hydrolysis of the alkoxide. A H_2O/MTES molar ratio of 3 was used. After about 2 h the

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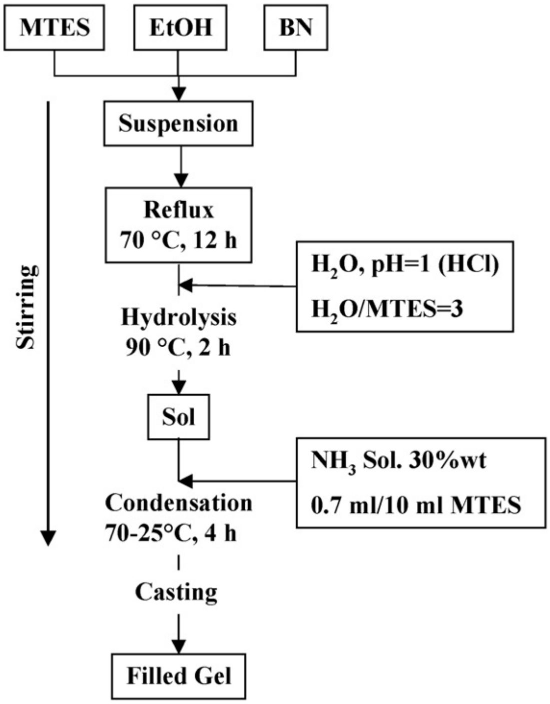

Fig. 1. Flow chart for the production of the h-BN filled gels.

suspension had cooled down to 70 °C and, at that point, 0.7 ml of a 30 wt% ammonia solution was added to start the condensation. At this point the flask was taken out from the oil bath, allowed to cool down to room temperature, and stirred for 4 h. This BN-suspension was poured into plastic test tubes. It gelled in about 2 h.

Three compositions with different amounts of BN were prepared. Filled gels having a nominal $100 \times V_{BN}/(V_{BN}+V_{gel})$ ratio of 38, 48 and 58% were synthesized. The amounts of filler (Table 1) have been estimated assuming that MTES leads to a fully condensed gel network with composition $CH_3SiO_{1.5}$ and density of 1.2 g/cm^3. The density of h-BN was assumed to be 2.25 g/cm^3. Note that the volume fraction of filler estimated above refers only to the condensed phases of the filled gels; it does not include the open porosity which is also present in the samples.

The filled gels were finally dried for 1 week at room temperature and then for 1 more week at 60 °C. Rods 3–4 cm long and 5–10 mm of diameter were obtained. These samples were cut into discs 5–10 mm thick ready for pyrolysis.

Table 1
Grams of BN powders used for the synthesis of the filled gels starting from 10 ml of silicon alkoxide

h-BN	
vol%	g/10 ml of MTES
38	3.93
48	5.86
58	8.90

2.2. Pyrolysis of the filled gels

Samples of the filled gels were converted into the SiCO-based ceramics by a pyrolysis process in controlled atmosphere (flowing Ar, 100 ml/min) at 1000, 1200 and 1400 °C using a graphite furnace (Astro, Thermal Technology, USA). The disc samples were placed into a graphite crucible and were heated at 3 °C/min up to the maximum temperature for 1 h and then they were cooled down at 5 °C/min. For each sample the weight loss and the shrinkage associated with this pyrolysis treatment was recorded.

2.3. Characterization of the ceramic samples

Density and porosity were measured by the Archimedes method using distilled water as infiltrating liquid. Ceramic samples were first dried at 150 °C for one night and then immersed in distilled water for 12 h before density measurements.

Phase analysis was carried out by X-ray diffraction of specimens pyrolyzed to different temperatures. A Rigaku DB Max III diffractometer operating at 40 kV and 30 mA, with Cu Kα radiation was used. Data collection was carried out from $2\Theta = 10–110°$ with a step of 0.05° and an acquisition time of 3 s. SEM investigation of either fracture or polished surfaces was carried out using a JEOL JSM 5500 equipment.

Dielectric constant, ε_r, and dielectric loss, tan (δ) were measured by the cavity resonator method, using a network analyzer (model Hp 8510B) with a cylindrical cavity of 20 mm in diameter operating at 10 GHz.

3. Results and discussion

3.1. Characterization of the filled gels

The homogeneous distribution of the inorganic powders in the gel samples was checked by SEM. All the investigated samples showed a uniform distribution of the filler particles in the hybrid gel matrix in agreement with the earlier results from our laboratory with other fillers.[10,11] To further rule out the possibility of sedimentation of the filler before gelation, the densities of the discs obtained from the bottom and from the top of the original gel rods were measured and compared. The same value was found showing that the distribution of the filler particles along the height of the samples was homogeneous.

3.2. Microstructure

The weight losses experienced during pyrolysis (up to 1000 °C) for the specimens are reported in Table 2. The weight change is associated with the evolution of CH_4, H_2 and small siloxane molecules.[12] Note that weight loss decreases with the amount of BN (Fig. 2); this is explained by the lower amount of gel present in these samples, assuming that BN serves as an inert filler, that is, it does not influence the pyrolysis process of the preceramic network.

The shrinkage associated with the pyrolysis process decreases by increasing the filler load suggesting that the sam-

Table 2
Experimental data measured on the BN/SiCO composites as a function of the pyrolysis temperature

Temperature	BN (vol%)		
	38	48	58
1000 °C			
Weight loss ± 1 (%)	6.5	5.8	2.7
Volume shrinkage ± 1 (%)	27.5	19.7	9.1
Density ± 0.02 (g/cm^3)	1.30	1.11	0.70
Porosity ± 1 (%)	33.0	48.7	54.0
Dielectric constant	4.2	2.7	1.9
tan (δ)	2.70×10^{-3}	5.2×10^{-3}	4.8×10^{-3}
1200 °C			
Weight loss (%)	7.5	6.7	4.0
Volume shrinkage (%)	29.5	21.4	7.1
Density (g/cm^3)	1.36	1.29	0.71
Porosity (%)	32.9	46.1	60.9
Dielectric constant	4.1	2.7	1.9
tan (δ)	1.50×10^{-3}	2.5×10^{-3}	5.2×10^{-3}
1400 °C			
Weight loss (%)	11.1	14.7	13.0
Volume shrinkage (%)	27.9	22.1	9.3
Density (g/cm^3)	1.32	1.18	0.61
Porosity (%)	37.2	47.0	58.1
Dielectric constant	4.0	2.7	1.8
tan (δ)	3.80×10^{-3}	6.2×10^{-3}	5.1×10^{-3}

ples become more porous. Indeed, the open porosity increases with the BN content, as shown in Fig. 2 and Table 2. Open porosity of the ceramic samples at 1000 °C ranges from 33% up to 54% for the composition with 38 and 58 vol% of BN, respectively. Similar porosity values were measured for SiCO-based ceramics with other inert fillers, such as Al_2O_3, at the same loading content.[9]

All the diffraction peaks found in the XRD spectra recorded on the BN–SiCO samples pyrolyzed at the various temperatures (not shown here) can be assigned to BN.[13] Peaks corresponding to any crystalline form of silica were not found. Accordingly, up to 1400 °C the samples can be described as a composite consisting of a mixture of un-reacted BN and a SiCO glass.

SEM pictures of the microstructure of the BN–SiCO ceramics reported in Fig. 3 confirm the formation of highly porous microstructures. The platelet-like h-BN grains are bonded together by the SiCO glass. Despite the high amount of porosity (up to ca. 60% for the sample with the 58 vol% of BN) the pyrolyzed samples were mechanically strong enough to be handled with care.

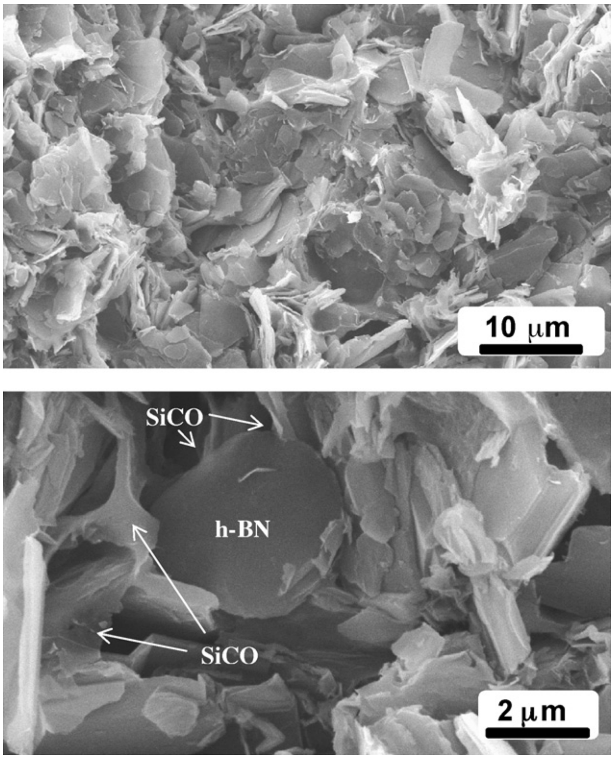

Fig. 3. Typical microstructure of the BN/SiCO samples (fracture surface). This particular sample has 48 vol% BN and was pyrolyzed at 1000 °C. Note the high amount of porosity and the SiCO glass bonding the BN platelets.

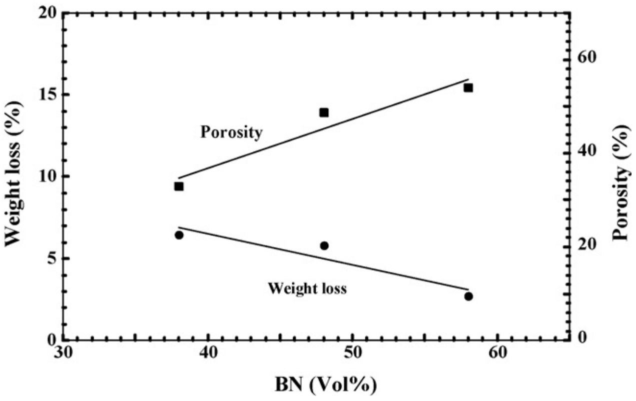

Fig. 2. Weight loss and open porosity measured of the ceramic specimens pyrolyzed at 1000 °C.

3.3. Dielectric properties

The dielectric constant, ε_r, and the losses, tan (δ) measured on the samples pyrolyzed at 1000 °C are reported in Table 2 and presented in Fig. 4. ε_r decreases with increasing filler content. Samples with 58 vol% BN have a value as low as 1.9. Such low values of the dielectric constant may be due to three factors: (i)

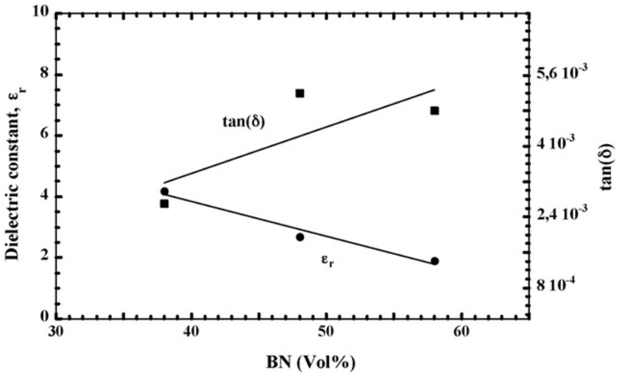

Fig. 4. Dielectric constant, ε_r, and tan (δ) measured on the BN/SiCO samples pyrolyzed at 1000 °C.

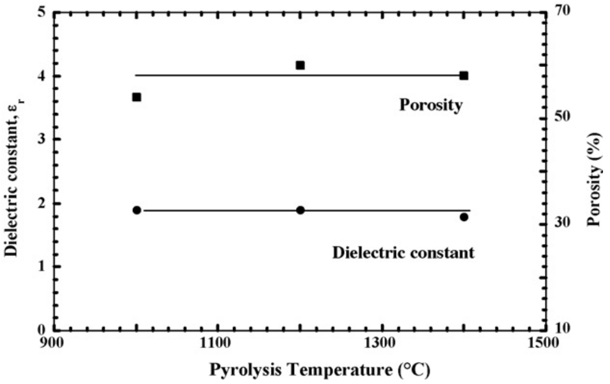

Fig. 5. Dielectric constant, ε_r, and porosity (%) measured on the 58 vol% BN/SiCO samples pyrolyzed at 1000, 1200 and 1400 °C.

the presence of BN which itself has a low dielectric constant ($\varepsilon_r = 4.4$), (ii) the presence of the silicon oxycarbide matrix which is expected to have ε_r in the range 3–3.5 and (iii) the presence of a high amount of porosity. In view of the strong correlation between the increase in porosity and the decrease in the ε_r, we may conclude that the main microstructural parameter affecting the dielectric constant is the porosity of the samples. Indeed, the estimation of the dielectric constant for the 58 vol% BN sample according to the Clausius–Mossotti model[14] gives a value in the range 1.8–2, in good agreement with the experimental value. The BN–SiCO composites show also low values of tan (δ) in the range of 2.7×10^{-3} to 5.2×10^{-3}. The dielectric constant value of 1.9 and the low value of the loss tangent means that BN–SiCO composites are highly promising candidates for new low-K materials.

3.4. *High temperature evolution*

The properties of the samples pyrolyzed at 1000, 1200 and 1400 °C (Table 2) provide information on the thermal stability of the BN–SiCO composite. The weight loss increases, mainly, from 1200 to 1400 °C suggesting that above 1200 °C the silicon oxycarbide glass further loses some volatile species, which is well known in the literature.[15] However, the weight loss does not appear to cause any measurable change in the microstructure or the dielectric properties of the samples. Indeed, the density, porosity, and shrinkage of the samples are all stable up to 1400 °C. The dielectric properties also do not change as shown in Fig. 5: the ε_r values measured on the sample containing 58 vol% of BN and pyrolyzed at 1000, 1200 and 1400 °C remain constant in this temperature range. The very good high temperature stability of the microstructure and therefore of the dielectric properties is an outstanding advantage of the BN–SiCO materials over different low-K porous materials, such as, for example, porous SiO_2. The sintering process which is active in silica glass starting from the glass transition temperature ($T_g = 1150$ °C) closes up the pores and results into an increase of ε_r up to 3.9. The higher viscosity of SiCO compared to silica[16] combined with the platelet-like morphology of h-BN particles, prevents sintering even at temperatures exceeding 1350 °C and stabilizes the porous structure.

4. Conclusions

Ceramic BN/SiCO composites with ε_r as low as 1.9 have been produced through pyrolysis of filled gels at temperature between 1000 and 1400 °C. XRD study showed only the presence of h-BN without any crystalline silica phase revealing that the samples were composed, even up to the maximum temperature (1400 °C) of a mixture of un-reacted BN and a SiCO glass. Porosity up to 58% has been measured for the samples with the highest filler content. The combination of high porosity values with the low dielectric constant of the constituents (BN and SiCO) leads to values of ε_r as low as 1.9 and tan (δ) in the range of 2.7×10^{-3} to 5.2×10^{-3}. The microstructure of the BN/SiCO composites is stable up to 1400 °C and consequently the excellent dielectric properties measured at 1000 °C are preserved even after the high temperature annealing. All these results suggest that the BN/SiCO composites made by pyrolysis of filled gels are highly promising candidates for new low-K materials.

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