High Temperature Dielectric Properties of Polyimide/Boron Nitride Nanocomposites : Nanoparticle Size and Filler Content Effects

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Abstract: **An interesting way to improve high temperature polyimides (PI) electrical properties by filling it with boron nitride nanoparticles (BN) is proposed in this study. The filler content (from 0 to 60 vol.%) and the average diameter size (35 nm and 120 nm) of these nanoparticles have been varied. The preparation of the patented PI/BN nanocomposite films was performed following an optimized process in order to obtain a good dispersion of the nanoparticles in the films. The nanocomposite films were electrically characterized in the range 200-350 °C. In the case where the nanoparticles had the smallest size, the DC conductivity and leakage currents decreased from 4 to 6 orders of magnitude when the PI/BN films were compared to the neat PI films. The improvement of this property was obtained by a small amount of nanoparticles (1.6 vol.%). Results also show an increase in the dielectric strength of 1 MV/cm for a filler content of 42 vol.%. In the case where the nanoparticles had a larger size, a small improvement was seen on the DC conductivity and leakage currents. In contrast, the breakdown field was lower than the one of the neat PI, due to aggregate formation within the films.**

I. INTRODUCTION

In recent years, thermally conducting but electrically insulating materials attracted more and more attention because high thermal conductivity, low dielectric constant and high electrical resistance are needed for fast signal propagation. Polyimides (PI) are a class of high performance polymers that have excellent thermal, mechanical, electrical and chemical properties. They are widely used as electrical insulating coating films (~10 µm) in microelectronics and power electronics, as buffer coating, interlayer insulation, wafer-scale package or component passivation. However, the dielectric properties of PI degrade at high temperatures (> 200 °C), making it a semi-insulating material, exhibiting high dielectric losses at low frequency and low dielectric strength in such a high temperature range [1-5]. For this reason the use of PI may become limited for the new high temperature operating wide bandgap semiconductor devices. In order to improve the electrical properties of PI, some electrical insulating ceramic fillers, such as alumina, silica, aluminum nitride …, were used to obtain PI based composites. Nevertheless, up to now, very few studies have been led on PI nanocomposites [6-11]. Moreover, all of them were studied at room (or near) temperature and they do not show a true improvement of electrical properties. The poor electrical properties obtained were related to the poor quality of the nanoparticles dispersion in the matrix and the presence of agglomerates in the film.

In this study, two different grades of boron nitride (BN) nanoparticles having different size and shape were used to fill the PI matrix. Particular caution has been made on the fabrication process optimization resulting in a better quality dispersion of nanoparticles and limiting the presence of agglomerates wich was recently patented [13]. The electrical properties of the different films of PI and PI nanocomposites were studied, as presented and discussed here after.

II. EXPERIMENTAL PART

A. Materials and synthesis of PI/BN nanocomposites

The polyimide host matrix used in this study is synthesized from biphenyltetracarboxilic dianhydride (BPDA) and *p*–phenylene diamine (PDA) precursor monomers. The BPDA/PDA polyimide has a density of 1.48 g/cm^3. The two monomers are dissolved in *N*-methyl-pyrrolidone (NMP) solvent to form a polyamic acid (PAA) liquid precursor solution of 120 poises of viscosity at 25 °C.

Two kinds of BN nanoparticles are considered in this study. The first one presents a hexagonal form (*h*-BN) with an average size of 120 nm (measured by dynamic light scattering) and a volume density of 2.3 g/cm^3. The second one exhibits a wurtzite structure (*w*-BN) with an average size and a volume density of 40 nm and 1.95 g/cm^3 respectively. Figure 1 presents TEM images of both BN nanoparticles used in this study.

The nanocomposite materials and their related elaboration process have been optimized and recently patented by the authors [13]. The BN nanoparticles have been dispersed into PI precursors dissolved in NMP solvent by sonication. With the optimized process, a good electrophoretic stability of the BN nanofillers in the precursor solution (high ζ -potential) has been obtained. The solution has been centrifuged to eliminate the rest of agglomerates. The obtained PAA/BN nanodispersed solutions have been deposited on stainless steel substrates (33×33 mm^2) by spincoating at 3000 rpm during 30 s.

Substrates were preliminary cleaned and treated using an adhesion promoter solution. Then, after the coatings, the solvent evaporation and the polymerization have been performed through consecutive curing of the nanocomposite films at 100 °C for 1 min, 175 °C for 3 min, 200 °C for 20 min and 400 °C for 1h in nitrogen gas. Gold circular upper electrodes of 5 mm and 600 µm in diameter were evaporated in vacuum onto the PI and PI nanocomposite surface in order to achieve the SS–PI/BN–Au structures for electrical measurements. Final volume filler contents have been measured by He pycnometry and from 2 vol.% to 30 vol.% for PI/h-BN (120 nm), and from 1.6 vol.% to 60 vol.% for PI/w-BN (40 nm). Thicknesses of the films were in the range 3 to 5 μ m.

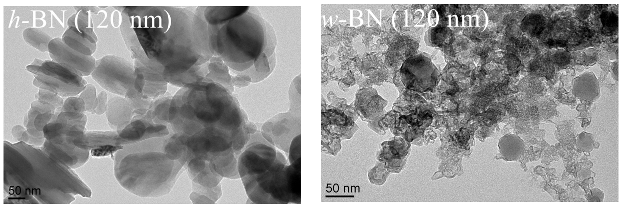

Figure 1: TEM images of h-BN (120 nm) and w-BN (40 nm) nanoparticles.

B. *Measurements*

Dielectric breakdown field measurements have been performed using a dc voltage ramp supplied by a 3.5 kV FUG voltage source connected to the sample through a probe station using HV insulated needles fixed to precision xyz-micropositioners S725 from Microworld. Prior to the measurements, the needles have been disposed on the top of the electrodes with a high precision using a stereo microscope. The dc voltage rising was controlled using a software program and was set to 80 V.s^{-1}. The breakdown field was identified when the voltage source switched into current source supplying a shortcircuit current set to 20 mA. The maximum voltage supplied was also recorded using a voltmeter connected to the source *via* a HV probe and was considered as the breakdown voltage. Measurements followed the D149-97a ASTM norm related to the breakdown of solid dielectric materials [12]. High temperature measurements have been performed between 200 and 350 °C (± 1 °C checked with a thermocouple on the sample surface) thanks to a regulated Signatone heating chuck in an air-closed cell (i.e. homemade closed cell with a transparent glass upper face for no fresh air exchange with the environment). The heating rise rate was of 5 °C.min^{-1}.

Leakage current have been measured using the same probe station used to measure the breakdown field. The sample was connected to a Keithley 2410 having an ammeter with 10 pA resolution. Measurements were achieved by applying a large range of electric fields (0.1-1.5 MV/cm) for 1000 s. The temperature was varied from 200 to 350 °C. Each measurement was carried out on a new electrode that has never been polarized before.

The dielectric properties have been measured by broadband dielectric spectroscopy using a Novocontrol Alpha-A spectrometer. Measurements have been performed under a nitrogen gas flow in a range starting from 20 to 350 °C by step of 10 °C. The frequency ranged from 0.1 Hz to 1 MHz. The data have been obtained in the form of the dielectric complex permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' and ε'' are respectively the permittivity and the dielectric loss index, and $i = \sqrt{-1}$. The low frequency DC conductivity values (σ_{DC}) have been obtained from the AC conductivity (σ_{AC}) measurements at 0.1 Hz given by [13]:

$$\sigma_{AC}(\omega) = \omega\varepsilon_0\varepsilon''(\omega) = \sigma_{DC} + A\omega^{\mathrm{n}} \qquad (1)$$

where ε_0 is the vacuum permittivity, A is a temperature dependent parameter and s is the exponent of the “universal” power-law.

III. RESULTS AND DISCUSSION

Figure 2 shows TEM images of PI/h-BN (30 vol.%) and PI/w-BN (42.1 vol.%). One can observe in the first image that the nanoparticles (h-BN) are not well dispersed in the film nanocomposites at high volume contents. Aggregate in the order of 500 nm are observed. This can be explained by the large nanoparticle size and their shape. On the contrary, the nanoparticles having the smallest sizes (w-BN) are well dispersed. The maximum of the aggregate size seen in these films are in the order of 200 nm.

Figure 3 shows the temperature dependence of the DC conductivity σ_{DC}, presented in Arrhenius plot, of the neat PI, of PI/h-BN and PI/w-BN for low and high volume contents. The results show a slight improvement for this properties when PI is filled at low volume content oh h-BN nanoparticles. On the contrary, and for similar volume content, a strong improvement (2-3 orders of magnitude) has been obtained when filling PI with the smallest w-BN nanoparticles. On the other hand, when the volume content is increased, 1 and 2-4 orders of magnitude of improvement are obtained when PI is filled with h-BN and w-BN respectively.

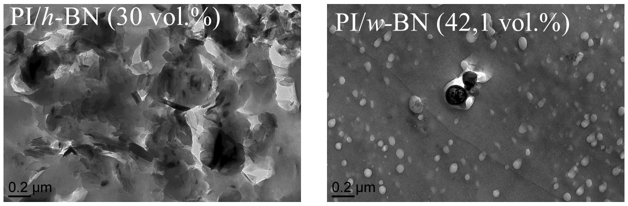

Figure 2: TEM images of PI/h-BN (30 vol.%) and PI/w-BN (42,1 vol.%) nanocomposite films.

The activation energy of the conduction phenomenon E_a was calculated using the Arrhenius equation, given by:

$$\sigma_{DC}(T) = \sigma_0 exp\left(-\frac{E_a}{k_B T}\right) \qquad (2)$$

where σ_0 is the conductivity at an infinite temperature, T is the temperature and k_B is Boltzmann’s constant.

The value of E_a for the neat PI is 2.13 eV. This value is in agreement with ionic conduction reported in PI materials [5]. In the case of PI/h-BN at low and high volume content, E_a remains close to the one of the neat PI with values of 2.2 eV. This means that the ionic conduction has been slightly affected by the presence of the h-BN nanoparticles. On the contrary, E_a has been strongly decreased in the case of PI/w-BN. This means that a significant modification occurs in the involved electrical conduction mechanism with a strong reduction of the ionic motions in the PI bulk. The small size of w-BN nanofillers, related to the development of a large interaction surfaces (i.e. interphase/interface zone) with PI, could be at the origin of this improvement.

Figure 4 shows the leakage current for neat PI and PI/*w*-BN (40 nm) for different volume contents at 300 °C and 1 MV/cm. There are 2 phenomena on the leakage current results for neat PI. A peak is observed <1 s and is related to the ionic conduction movement within these materials. The increase and saturation obtained at 90 s is related to the electron injection that is coming from the SS electrode. The injection phenomenon is activated when the electric field becomes high at the electrodes due to the ion displacement and blocking at the electrode. After 90 s, the leakage current becomes constant at 4×10^{-4} A.

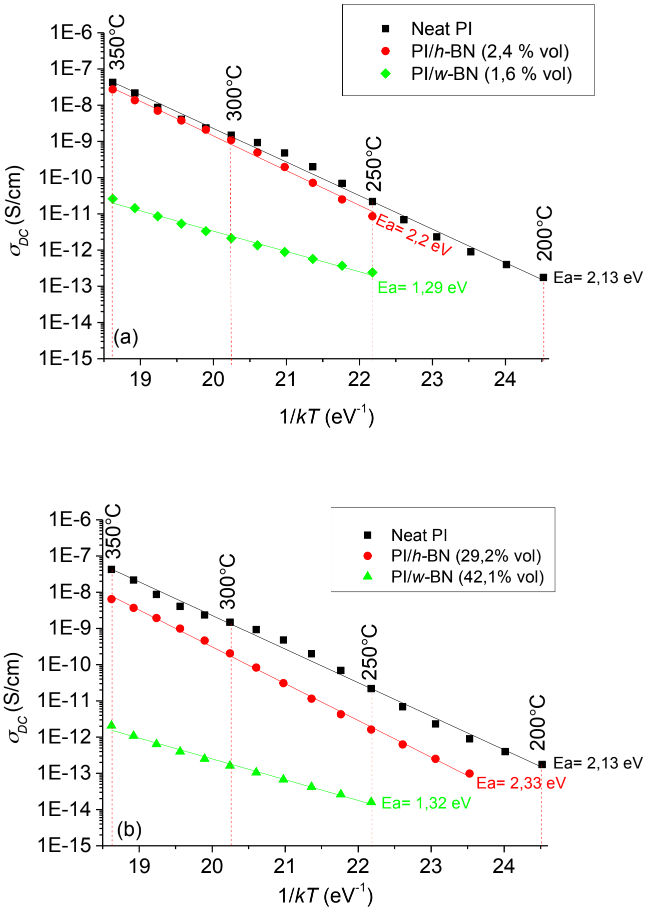

Figure 3: Temperature dependence of the DC conductivity of neat PI, PI/*h*-BN (120 nm) and PI/*w*-BN (40 nm) at low (a) and high (b) volume content.

In case of PI/*w*-BN, no anormal phenomena in the conduction current measurement is obtained. This means that the ionic conduction has been limited due to the *w*-BN nanoparticles. In addition, no volume content effect is observed, indeed the best optimum is obtained as soon as 1.6 vol.%. This means that the quantity of nanoparticles for this volume content was enough to block the ions present in the PI films.

Figure 5 shows the leakage currents for neat PI, PI/*h*-BN (120 nm) for different volume contents and PI/*w*-BN (40 nm-1.6 vol.%) at 300 °C and for 1 MV/cm supplied electric field. One can observe that 2.4 vol.% of *h*-BN has slightly affected the ion conduction in the films. This volume content is not enough to block all the ions that contribute to the conduction phenomenon (presence of shifted peaks).

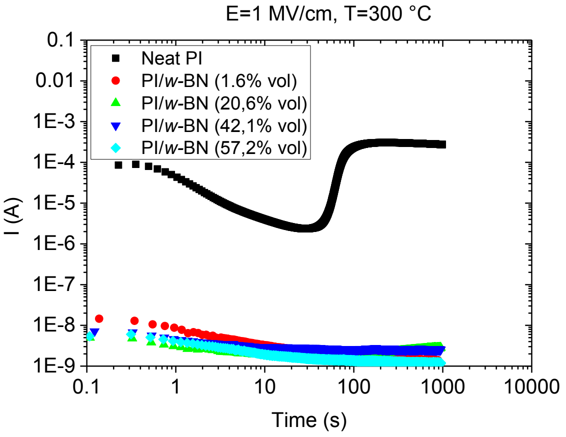

Figure 4: Leakage currents for neat PI and PI/*w*-BN (40 nm) for different volume contents at 300 °C and 1 MV/cm.

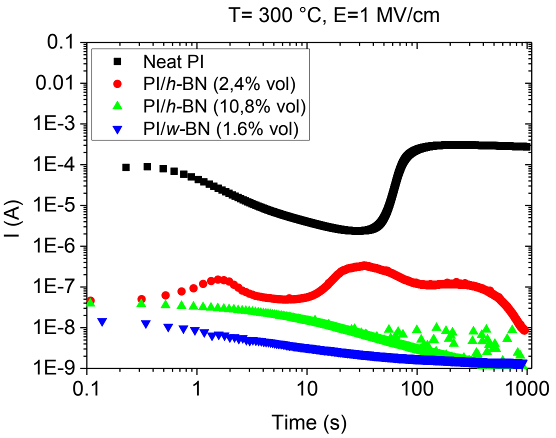

Figure 5: Leakage currents for PI neat, PI/*h*-BN (120 nm) for different volume contents and PI/*w*-BN (40 nm-1.6 vol.%) at 300 °C and 1 MV/cm.

On the contrary, 10.8 vol.% of *h*-BN is enough to obtain similar results that those obtained when PI was filled with 1.6 vol.% of *w*-BN. These results can be explained by the fact that the small size of nanoparticles results in a large interaction zone with PI comparing to the big size of nanoparticles.

Figure 6 shows the temperature dependence of the breakdown field for the neat PI and PI/*w*-BN (40 nm) for different filler contents.

One can observe that the breakdown field for the neat PI decreases from 4.1 MV/cm at 200 °C to 1.8 MV/cm at 350 °C. When PI was filled with *w*-BN, and for a volume content ≤ 42.1 vol.% the breakdown field increases comparing to the neat PI. If PI is filled with a higher volume content, the breakdown field decreases again.

This means that at high volume contents, it is difficult to well disperse the nanoparticles, and the agglomerates become the weak point of the material, then the breakdown field decreases. When PI is filled with the *h*-BN nanoparticles and at high volume content (29.2 vol.%) (cf. Figure 7), the breakdown field was degraded.

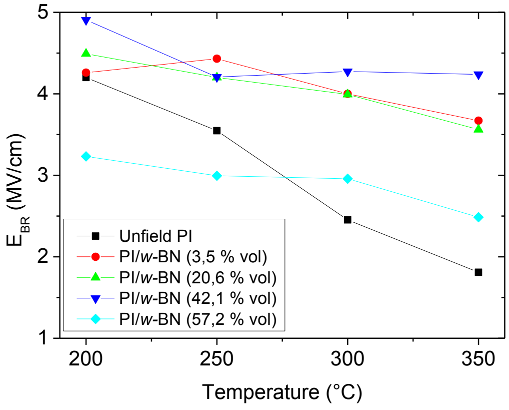

Figure 6: Temperature dependence of the breakdown field for the neat PI and PI/*w*-BN (40 nm) for different filler contents.

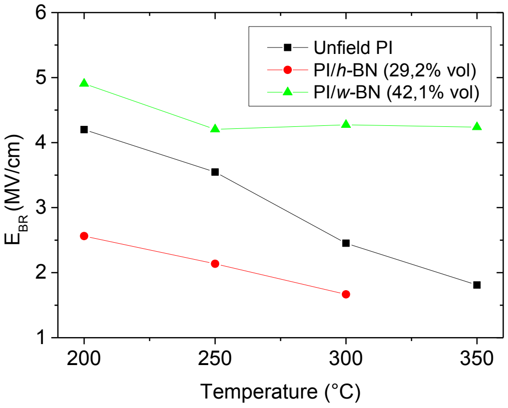

Figure 7: Temperature dependence of the breakdown field for the neat PI, the PI/*h*-BN (120nm- 29.2 vol.%) and the PI/*w*-BN (40 nm-42.1 vol.%).

IV. CONCLUSION

In this paper, the dielectric properties of two kinds of PI/BN nanocomposites with different nanofiller sizes have been investigated at low and high volume content and in high temperature (up to 350 °C). The important role of the BN nanofiller size in the reduction of the electrical conductivity, of the current conduction, and in the improvement of the breakdown field, is highlighted. The preparation of the PI/BN nanocomposite films is performed following an optimized process in order to obtain a good dispersion of the nanoparticles in the films. Nanocomposite films were electrically characterized in the range 200-350 °C. In the case where the nanoparticles have the smallest size, the results show that the DC conductivity and leakage currents decreased from 4 to 6 orders of magnitude when the loaded films were compared to the unfilled films. The improvement of this property was obtained with a small amount of nanoparticles (1.6 vol.%). Results also show an increase in the dielectric strength of 2.5 MV/cm for a loading content of 42 vol.%. In the case where the nanoparticles have a larger size, a small improvement is seen on the DC conductivity and leakage currents. On the contrary, the breakdown field is lower than the one of the neat PI, due to aggregate formation within the films. Particularly, a significative improvement is achieved when filling the PI with *w*-BN (40 nm). The electrical conduction of neat PI is controlled by macroscopic motions of ions occurring in the bulk, which induces important electron injection from the cathode. BN nanofillers block the ions motions in the nanocomposites film reducing their effects on DC conductivity.

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