Effect of sintering temperature on varistor and dielectric properties of Si–polymer composite films

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A B S T R A C T

Silicon–polyaniline–polyethylene composite films were prepared through hot pressing at a pressure of 60 MPa and different temperatures and their current–voltage characteristics were investigated. Results show that these films have varistor behavior and can be used to protect circuits from 64 V up to 80 V overvoltages. In addition, it is found that the varistor breakdown voltage decreases by increasing sintering temperature while the corresponding nonlinear coefficient increases. Dielectric properties of the films vary as a function of frequency in such a way that, at low frequencies, capacitance, relative permittivity and loss coefficient of the samples, as well as their fluctuations, are high. By increasing frequency, both dielectric properties of the films and their reduction rate decrease. On the other hand, by increasing sintering temperature, capacitance and relative permittivity of the varistors tend to increase at a constant frequency whereas their loss coefficient decreases.

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1. Introduction

Zinc oxide (ZnO) varistors are semiconducting ceramic devices, produced by sintering ZnO powder containing additives of small amount with varistor former, enhancer, and stabilizer. The voltage–current properties of these devices exhibited markedly nonlinear properties [1,2]. To date, SnO2 and TiO2 based ceramic varistors have also proved very attractive [3]. Varistors possess excellent surge withstanding capability because, unlike Zener diode which operates through a single junction, they are multi-junction devices [4,5]. Furthermore, their special electrical properties are supposed to be dominated by grain–boundary interface state [6]. Nowadays, as scaling down of semiconductor devices has rapidly progressed, there is a high demand for manufacturing low-voltage varistors. Therefore, new varistors are made of a low-band gap semiconductor, Gallium arsenide as filler and polymers, polyaniline and polyethylene as matrix [7–9]. In addition, due to its interesting electrical properties as well as its low cost, compared with Gallium arsenide, silicon can be another choice to make low-voltage composite varistors. Silicon is a hard, relatively inert tetravalent metalloid which is very brittle in crystalline form and has a marked metallic luster. Unique properties of silicon make it an especially important choice in micro- and nanoelectronic industry. It forms the backbone of modern microelectronics. It is noteworthy that silicon is also widely used in optoelectronics because of its 1.12 eV indirect band gap.

Recently, conjugated polymers have attracted more attention due to their wide potential applications [10–14], which arise from their unique electrical, optical and mechanical properties [15–21]. Among these conjugated polymers special attention has been paid to doped polyaniline, as well as its de-doped state, on the account of its low production cost and good environmental stability.
In the past, principal industrial applications focused on the doped form of the polymer with the purpose of achieving the highest possible conductivity [26]. Nowadays researchers’ interests are also directed towards de-doped form of polyaniline (PANI), which exhibits semiconducting properties [27]. Surprisingly, few aging studies have been carried out on de-doped polyaniline [28–30]. One of the key problems related to potential applications of the electro-active polymers, however, is their poor processability and poor mechanical properties. The most promising approach to the solution of these problems is to prepare composite materials using conventional thermoplastic polymers [31]. Due to its excellent thermal and electrical insulation properties, high resistance to chemicals, good mechanical and optical properties, and ease of fabrication, polyethylene (PE) is one of the most widely used thermoplastics [32,33]. Among all types of PEs, high density polyethylene (HDPE) is a commonly used thermoplastic with a high degree of crystalline structure [34–36]. On the account of its competitive market price [37] and energy consumption for processing, HDPE resin is ideal for many applications such as bags, bottles, films, and pipes [34,38].

To use a varistor as a voltage protector, a capacitor should be constructed. For this purpose each varistor disk should be invested by two copper, silver or aluminum electrodes, which construct the capacitor. Hence investigating dielectric properties of the sandwiched material is necessary to comprehend their electrophysical properties [39–45].

This paper deals with the details which pertain to the influence of sintering temperature on the varistor and dielectric properties of silicon–polymer composite films. Polymer matrix consists of a conductive and a thermoplastic polymer, polyaniline and polyethylene respectively. The present study will help provide more insight and rationalize the dielectric and varistor behavior of these Si–polymer composite films.

2. Material and methods

The raw chemicals, i.e., pure de-doped polyaniline, high density polyethylene and high purity silicon crystals, were ground and sifted using a No. 200-mesh sieve to guarantee that the size of chosen particles is less than 70 μm. Since varistor property is strongly affected by the amount of compounds as well as sintering condition, a well-behaved composite Si–polymer sample was prepared by picking up 70 wt%, 15 wt% and 15 wt% of Si, PANI and PE, respectively [46]. Selected amounts of materials were mixed in a ball mill for 5 h to obtain a uniformly mixed powder. Finally, the powder was hot-pressed into disks of 10 mm in diameter and 250 μm in thickness at 60 MPa and five different temperatures, i.e., 30 °C, 60 °C, 90 °C, 120 °C and 130 °C. It is noteworthy that when sintering temperature is increased more than 130 °C, PE starts to melt. As a result, not only the form of the films but also their physical properties will be spoiled. Eventually after checking under an MBC-9 microscope, made by Russia, for their observable qualities such as uniform thickness and lack of any cracks, the films were used to study frequency-dependent behaviors. In order to measure dielectric properties, each disk was invested by two copper electrodes whose useful area was 19.625 mm². Then circulating current was measured by applying voltage between the two electrodes. Applied voltage has been provided by a GPR-100H05D power supply, and circulating current has been measured by an ADM-552R multi meter. Capacitance of the resulted capacitors and their loss coefficient were measured using a KC 605 LCR meter, made by Japan. During these measurements, frequency ranged from 1 kHz to 5 MHz. Ultimately, dielectric constants of films at the selected frequency range were calculated.

3. Results and discussion

Studied I–V characteristic of Si–PANI–PE composite film sintered at 30 °C displays that this composite is a nonlinear resistor and that three regions are recognizable on the curve (Fig. 1):

- a. pre breakdown zone with electrical resistance of about 23 kΩ;
- b. nonlinear zone in which the electrical conductivity of the sample abruptly changes from a low value to a high one;
- c. upturn zone with electrical resistance of about 90 Ω.

Within these regions, leakage current increases about 2000 times. Therefore, the sample can be a varistor with a breakdown voltage which is lower than those of similar ZnO-based varistors [47] but whose leakage current is higher. Varistor behavior could be interpreted from grains and grain boundaries similar to what is done in the ZnO-based varistor case [48]. The difference is that in present varistors, silicon has lower indirect band gap (1.12 eV at 300 K); furthermore, the phase between grains is made of metal oxides. The other important consideration is that in this case grain boundary conductivity is strictly dependent on PANI percentage in composite varistor since PANI has relatively high conductance (10⁻⁶ Ω⁻¹ m⁻¹) compared to PE, which is a complete insulator [8]. As a result, silicon–polymer composite varistors are suggested
to be used as device protectors against low overvoltages. This is where ZnO-based varistors fail to function. Due to high leakage current, the system must have thermal evacuation capability. Increasing sintering temperature up to 130 °C leads to lower breakdown voltages as well as higher leakage currents while nonlinear behaviors of samples are preserved (Fig. 2a).

As sintering temperature increases, PE particles become flexible and mix homogeneously with PANI particles as a result of high molecular movement as well as high diffusion at high temperatures. Therefore the grain boundary phase becomes more homogeneous, which results in more conductivity. This causes leakage current to increase because PANI semiconducting particles have spread among the completely insulating PE particles; it also strengthens the probability of charge carriers tunneling through this homogeneous matrix. At more than 130 °C, PE melts and destroys the structure and nonlinear behavior of the samples. While melting, polyethylene completely sheathes polyaniline and silicon particles [49]; hence the phase between Si grains becomes completely insulated, which disturbs the varistor nonlinear behavior and therefore causes its I–V characteristic to become linear (Fig. 2b).

Nonlinear coefficient $\alpha$ is defined by

$$I = KV^\alpha$$

Nonlinear coefficient varies from 4.39 to 4.94 as sintering temperature increases from 30 °C to130 °C (Table 1).

From the C–f diagram of each sample, it is obvious that at low frequencies, both capacitance and its fluctuation are high in such a way that any increase in frequency leads to rapid capacitance decrease (Fig. 3a). More increase in frequency results in low capacitance reduction rate. It is to be noted that capacitance is almost constant at frequencies higher than 500 kHz (Fig. 3b). Comparing C–f diagrams of different samples displays that by increasing sintering temperature, capacitance tends to increase at a constant frequency. As mentioned previously, increasing sintering temperature leads to higher conductivity of the samples; this higher conductivity, in turn, causes their capacitance to increase. When the step of frequency increment is too short, a non-uniformity is observed in C–f diagrams of all samples at the frequency of $\sim 100$ kHz.

To illustrate this non-uniformity C–f characteristics of three pure PANI, PE and Si disks, which are prepared at a pressure of 60 MPa and a temperature of 130 °C, have been separately studied (Fig. 4). A glance at Fig. 4a–c displays that C–f diagram of pure Si disk changes in a uniform manner at low frequencies and becomes almost smooth at high frequencies; C–f diagrams of both PE and PANI show non-uniformity at the frequency of $\sim 100$ kHz. It is interesting that although this non-uniformity exists in a wide range of conductive and thermoplastic polymers, no report has yet been released concerning it. Such a behavior may be due to the rearrangement of dipole moments through polymer chain and resonance which is a response to frequency change. Therefore, the non-uniformity of C–f diagrams of the samples can be related to their polymer matrix i.e. silicon filler has no role in it. More study about this phenomenon, which is beyond the goal of this research, may result in interesting explanations and further applications.

Fig. 5 shows the relative permittivity of samples as a function of frequency, which is typically denoted as $K$ and defined as

$$K = \varepsilon(\omega)/\varepsilon_0,$$

where $\varepsilon(\omega)$ is the complex frequency-dependent absolute permittivity of the material, and $\varepsilon_0$ is the vacuum permittivity. Relative permittivity of samples can be calculated approximately from the C–f diagrams as well as the definition of the capacitance of a parallel-plate capacitor:

$$C = K\varepsilon_0A/d,$$

### Table 1

Main parameters of the composite varistors.

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Breakdown voltage (V)</th>
<th>Nonlinear coefficient</th>
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<tr>
<td>30</td>
<td>80</td>
<td>4.39</td>
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<tr>
<td>60</td>
<td>75</td>
<td>4.47</td>
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<td>90</td>
<td>70</td>
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<tr>
<td>120</td>
<td>68</td>
<td>4.74</td>
</tr>
<tr>
<td>130</td>
<td>64</td>
<td>4.94</td>
</tr>
</tbody>
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Fig. 2. a) I–V characteristics of Si–polymer composite films sintered at different temperatures b) I–V characteristics of the sample sintered at 150 °C.
where $A$ is the area of copper electrodes and $d$ is thickness of the sample. Regarding Fig. 5a it can be concluded that any increase in frequency results in relative permittivity reduction at low frequencies except at the frequency of $\sim 100$ kHz which, as mentioned before, is due to the nonlinearity of the capacitance at this frequency. Relative permittivity reduction rate reduces by increasing frequency and the diagram becomes almost flat at high frequencies (Fig. 5b). Moreover, increasing sintering temperature causes relative permittivity to increase at a constant frequency.
Dielectric loss quantifies a dielectric material’s inherent dissipation of electromagnetic energy into, e.g., heat. It can be parameterized in terms of either the loss angle $\delta$ or the corresponding loss coefficient ($D = \tan \delta$). Both refer to the phasor in the complex plane whose real and imaginary parts are, respectively, the resistive (lossy) component of an electromagnetic field and its reactive (lossless) counterpart. Loss coefficient is defined as

$$ D = 1/\tan \theta, $$

where $\theta$ is the phase angle. According to Fig. 6a, by increasing the frequency, the loss coefficient of each sample decreases; this is while polymer-related non-uniformity is observed again at the frequency of $\sim 100$ kHz. Besides, the rate of the decrease is high at low frequencies and the diagram becomes almost flat at high frequencies (Fig. 6b). Fig. 6 also displays that, at low frequencies, by increasing sintering temperature, loss coefficients of the samples decrease at a constant frequency. This behavior is disturbed as frequency increases beyond 100 kHz. Hence increasing sintering temperature can be a positive factor in reducing the inherent dissipation of electromagnetic energy of a varistor at frequencies lower than 100 kHz.

4. Conclusion

Changing sintering temperature affects properties of Si–PANI–PE composite varistors; its increment leads to decrease in their breakdown voltage and simultaneous increase in their nonlinear coefficient and leakage current. Based on varistor function, devices with high nonlinearity coefficients ($\alpha$) and low breakdown voltages are useful in protecting sensitive electrical circuits from overvoltages. On the other hand, increasing sintering temperature results in high capacitance and relative permittivity when the films are subjected to frequency changes. Also, low dielectric loss coefficient is obtained at higher sintering temperatures at frequencies lower than 100 kHz. As a result, the best synthesis temperature must be selected according to application conditions.

References
