



Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb



Investigation of nonlinear I – V behavior of CNTs filled polymer composites

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ARTICLE INFO

Article history:

Received 5 October 2015

Received in revised form

18 December 2015

Accepted 6 January 2016

Available online xxx

Keywords:

Carbon nanotubes

Nonlinear current–voltage behavior

Hopping effect

Joule-heating

ABSTRACT

Nonlinear current–voltage (I – V) behavior is a typical feature of polymeric composites containing conductor or semiconductor fillers, which are desired to handle the transient voltage and electrostatic discharge (ESD) of microelectronic devices. In this paper, the mechanism of nonlinear behavior of carbon nanotubes (CNTs) filled polymer composites in the applied electric field was explored. The I – V curves of the composites exhibited three regions. The variation of current at low voltages (region I) is linear. Under relatively higher voltages (region II), the variation is nonlinear and grows rapidly with voltage. As the voltage is further increased, the I – V curve is still non-linear (region III), but the growth rate is significantly slowed down. The I – V characteristics in the above three regions were analyzed systematically based on the calculation of the electrons hopping from the conduction band of CNTs to epoxy, the induced current under electric field, as well as Joule-heating and tunneling effect.

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1. Introduction

With the rapid development of electronic devices, functions of the IC (integrated circuit) system become increasingly powerful. Meanwhile, in order to reduce power consumption and prolong the service life of the devices, the semiconductor components and IC systems should operate at low voltages [1]. Therefore, the over-voltage protection is undoubtedly important to guarantee the reliability of the devices. Requirements of multifunction and miniaturization of the devices drive the development of system-in-package and component embedding technology [2–4]. It is an effective way to improve system integration by embedding elements inside the IC package substrate. The traditional circuit protection components made of ceramics such as ZnO varistors are not compatible with the printed circuit board (PCB) processing technology. Polymeric composites containing conductor or semiconductor fillers have attracted increasing attention in recent years owing to their flexibility and tailorable properties [2], which have become a primary choice to be integrated in the organic substrate to handle the transient voltage and electrostatic discharge (ESD)

[5]. The material should have a nonlinear voltage characteristic, which behaves like an insulator (dielectric) during normal circuit operation and becomes conductive when voltage surpasses a pre-defined threshold. The material becomes an insulator again after the voltage drops back below the threshold to normal operation level.

Nonlinear current–voltage (I – V) behavior is a typical feature of inhomogeneous systems containing conductive particles or clusters [6–10]. The nonlinear random resistor network (NLRN) model and dynamic random resistor network (DRRN) model, were proposed by Gefen et al. [8,9] to explain the deviation of I – V curves from linear characteristics. The first model assumes that the conducting backbone consists of microscopic components and the current–voltage characteristics of each such component contain a small nonlinear contribution. The second model assumes that in the presence of a sufficiently strong local field a non-conducting channel may become conducting. However, neither of the above models can explain why the channel is turned off at a low voltage and turned on at a high one, or why some channels are nonlinear, while others are linear. A number of studies have been conducted to understand tunneling effects in composites [11]. For example, Sheng [10] has investigated the electrical conduction of disordered materials and proposed a fluctuation-induced tunneling mechanism, in which the thermally activated voltage fluctuation across

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the insulating gaps played an important role in determining the field dependence of the conductivity. Tunneling effect is suitable to explain materials with lower nonlinear coefficient such as less than three [12], but failed to interpret those with high nonlinearity. To analyze a prominent nonlinear I – V behavior, the contribution from electrons with energy higher than the barrier should also be taken into account, as well as the effects of Joule-heating occurring in insulating barriers which however, have been seldom discussed. Therefore, the mechanism of the nonlinear behavior in the inhomogeneous systems, especially the conductor/polymer composites, needs further clarification.

Carbon nanotubes (CNTs) have been used as fillers in polymer composite systems to improve the material properties, such as mechanical [13,14], electrical [15,16] and thermal [17] performance. Compared with the nanoparticles, the high aspect ratio of CNTs enables the formation of electrical conducting paths in the polymer matrix at a very small percolation concentration [18] and has prominent nonlinear voltage characteristics [6]. The mechanism of nonlinear I – V characteristic of CNTs composites has not been fully explored.

In this study, the nonlinear voltage characteristics and the mechanism of carbon nanotubes filled epoxy (CNTs/epoxy) were investigated. With the increase of applied voltages, the I – V curve of the composites exhibited three regions with different nonlinear coefficients. The phenomena were analyzed systematically using a new method based on the calculation of the electrons which hopped from the conduction band of CNTs to epoxy, resulting in current under electric field. The Joule-heating and tunneling effects on the current were also discussed. A rectangular potential barrier model [10,11,19] was used to analyze the mechanism of nonlinear voltage characteristics of the CNTs-epoxy-CNTs unit and further the entire composite material. It has been found that hopping effect and tunneling effect were the main causes of the non-linear voltage characteristics of the composites under relatively lower voltages. As the voltage reaches a critical level, the hopping current tended to be nearly saturated and tunneling current will gradually disappear. Meanwhile, the effect of Joule heating on currents is substantial at high voltages, leading to weak nonlinear behavior.

2. Experimental

2.1. Materials

The polymer matrix was difunctional epoxy resin, (Epikote 828, supplied by Shell Chemical Co.). The curing agent was EMI-2,4 from Aladdin Industrial Corporation. Butanone from Shanghai Chemical Reagent Co., Ltd. Ling was used as solvent. CNTs used here were multiwalled carbon nanotubes purchased from Shenzhen Nanotech Port which were grown by a chemical vapor deposition (CVD) method. Their diameters were around 20–40 nm with the lengths above 5 μ m.

2.2. Preparation of CNTs/epoxy composite films

The CNTs were dispersed in the epoxy by ball milling with butanone as dilute solvent. A series of CNTs/epoxy nanocomposites were prepared with the CNTs loading varied from 1 to 7 wt%. The base polymer formulation was prepared by mixing epoxy and EMI-2,4 with a weight ratio of 100:4. The CNTs/epoxy/EMI-2,4 slurry was prepared using a solution blending and the film was obtained through a bar coating method. The process involved (a) milling epoxy, butanone and CNTs in a planetary ball mill for 24 h, (b) adding EMI-2,4 (which was 4% by weight of epoxy) to the mixture and continuing milling for 30 min, (c) coating the slurry on copper foil, (d) curing the film at 65 °C for 1 h, and 160 °C for 2 h in sequence

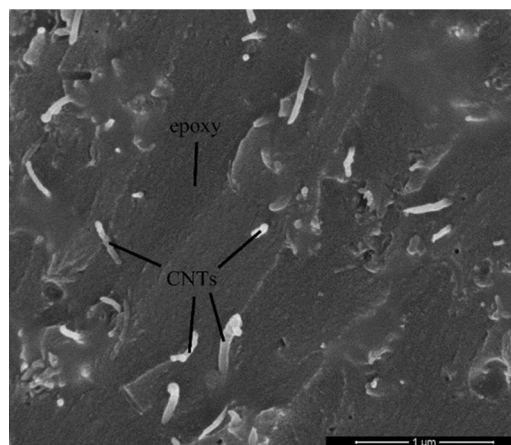


Fig. 1. SEM image of the fractured surface of the CNTs/epoxy composite with 5 wt% CNTs loading.

and (e) cooling to room temperature. A silver paint was applied on top of the film as the other electrode. The thickness of the film was around 20 μ m.

2.3. Characterization and instruments

The morphology of the fractured surface was examined using a scanning electron microscope (FEI Nova NanoSEM450). Raman spectra of CNTs and CNTs/epoxy composites were obtained by using a LabRAM ARAMIS Raman confocal microscope (HORIBA Jobin Yvon) with a 632.8 nm laser irradiation. The I – V curves and variation of current during applied voltage pulses were obtained using Keithley 4200-SCS Semiconductor Characterization System. For each sample, at least three points were measured to ensure repeatability. Effects of temperature on electrical conductivity were investigated via Keithley2410 Source Measure Unit connected with a THMS 600 Temperature Controlled stage and a T95-Linkpad Temperature programmer (Linkam Scientific Instruments) in a temperature range from 20 °C to 203 °C.

3. Results and discussion

3.1. Microstructure

Microstructure of the fractured surface of 5 wt% CNTs/epoxy composites is shown in Fig. 1. CNTs are randomly and well dispersed in the epoxy matrix, most of which are not in contact with each other directly but with an insulating epoxy resin layer in-between.

3.2. Raman spectroscopy

The resonant Raman-scattering technique is a powerful tool for characterizing CNTs [20,21]. Raman spectroscopy has been previously used to elucidate the aggregation state of CNTs [22]. By measuring the spectral shift of particular Raman peaks for CNTs and CNTs/epoxy composites, it is possible to obtain a qualitative analysis of the extent of CNTs/epoxy interactions and dispersion [20]. The Raman spectra of the CNTs and 5 wt% CNTs/epoxy composite is shown in Fig. 2. For the initial CNTs, peaks at around 1323, 1578 and 3650 cm^{-1} were detected, corresponding to the D, G and G' bands, respectively. The Raman spectra of the CNTs/epoxy composites feature a shift of the G band frequency by 34 cm^{-1} with respect to that of the initial CNTs (Fig. 2(a)). A shift in frequency is also observed for the D-band. The degree of the shift depends on whether the nanotubes are separated or are in contact with each

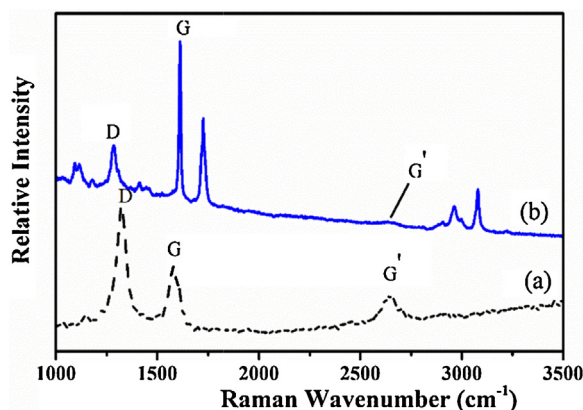


Fig. 2. Raman spectrographs of (a) initial CNTs and (b) 5 wt% CNTs/epoxy composite. The 632.8 nm HeNe laser line was used for excitation.

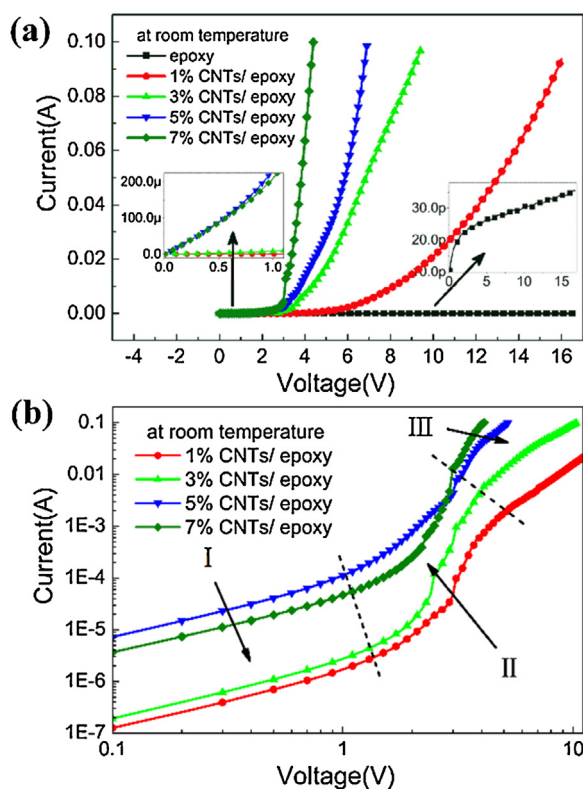


Fig. 3. *I*–*V* curves of the CNTs/epoxy composites under the direct-current voltage at room temperature: (a) in normal scale; (b) in log–log scale.

other [20]. Therefore, the above results indicate that CNTs had been dispersed in the epoxy without contacting with each other.

3.3. *I*–*V* curves of the CNTs/epoxy composites

Fig. 3 shows the *I*–*V* curves of CNTs/epoxy composites with varied CNTs concentrations measured under direct-current voltage at room temperature. As shown in Fig. 3(a), the current in the epoxy is small under the applied voltages and shows no apparent nonlinear effect. In contrast, the CNTs/epoxy composites exhibit Ohmic behavior at low voltages and with the increase of applied voltages, the *I*–*V* curves tend to be nonlinear. Generally speaking, the current in the composites increases with CNTs content under the same applied voltage, except a slight abnormal phenomenon of 7 wt% CNTs/epoxy at low voltages, which may be related to

Table 1

The nonlinear coefficients of CNTs/epoxy composites with varied CNTs loading.

Nonlinear coefficients	Region I	Region II	Region III
1% CNTs/epoxy	1.12	6.13	3.24
3% CNTs/epoxy	1.23	8.00	2.80
5% CNTs/epoxy	1.08	4.47	3.87
7% CNTs/epoxy	1.14	16.77	6.15

the inhomogeneous dispersion of CNTs when its loading is high. CNTs composites exhibit highly nonlinear current–voltage (*I*–*V*) characteristics above a threshold voltage. Since the range showing the highly non-Ohmic property is wide, the *I*–*V* characteristics are expressed logarithmically and are classified into three segments, as shown in Fig. 3(b).

The nonlinear coefficient α can be calculated by fitting $\log I$ versus $\log V$. α is determined by taking the ratio of $\log[I_2/I_1]$ to $\log[V_2/V_1]$, namely $\alpha = (\log I_2 - \log I_1) / (\log V_2 - \log V_1)$ where I_1 and I_2 are the currents under the voltages of V_1 and V_2 respectively [23]. Table 1 shows the nonlinear coefficients of all CNTs/epoxy composites in the three segments which are achieved by piecewise linear fitting with Origin software. In region I (in low electric field) the conduction current changes linearly with voltage, which follows the Ohm's law. In region II, a small increase in the voltage results in a sharp increase of the current. For example, for the 3 wt% CNTs/epoxy composite, when the applied voltage is lower than 1 V, the *I*–*V* curve shows Ohmic behavior. As the voltage is increased to 3 V, the current increases fast and the curve tends to be nonlinear with the nonlinear coefficient of 8.00. However, when the voltage exceeds a critical value of 4 V, the curve remains nonlinear, but the variation of current with the voltage becomes slow and the nonlinear coefficient decreases to 2.80.

3.4. Mechanism of the *I*–*V* nonlinear behavior

Electron hopping and tunneling conduction have been identified as the primary conduction mechanism in some systems, e.g., in the amorphous regions of insulating polyethylene [24,25]. Feng and Jiang [25] reported that the conductivity of CNTs/polymer composites is mainly attributed to nanoscale electron hopping (or quantum tunneling) mechanisms. The CNTs/epoxy composites are composed of many CNTs-epoxy-CNTs structural units. In order to understand the nonlinear voltage behavior of the composites, we firstly focus on the mechanism of nonlinear voltage characteristics of the CNTs-epoxy-CNTs structural unit. Fig. 4(a) and (b) illustrate rectangular potential barrier [10,11,18] of the CNTs-epoxy-CNTs structural unit, in which the energy of potential barrier is $E_b + E_c$ and V is the applied voltage between carbon nanotubes. The early theoretical studies of the electronic properties of CNTs predicted that CNTs could be either metallic or semiconducting depending on their structural parameters [26]. Semiconducting properties of multi-walled carbon nanotubes (MWCNTs) were observed by Hasanien et al. [27]. The band structure and density of states of carbon nanotubes were studied by Kwon et al. [28]. Electrons with varied energy are distributed in the conduction band of CNTs which is illustrated in Fig. 3(c) [29]. It is assumed that to hop into epoxy the electrons should have an energy higher than that of potential barrier. The shaded area is the concentration of electrons which can hop into epoxy.

Generally, the concentration of electrons which can hop from the conduction band of CNTs to epoxy is given by Eq. (1) [29].

$$n_b = \int_{E_b+E_c}^{+\infty} D_e(E) f_e(E) dE \quad (1)$$

where E_b is the height of potential barrier and $E_b + E_c$ the energy of potential barrier.

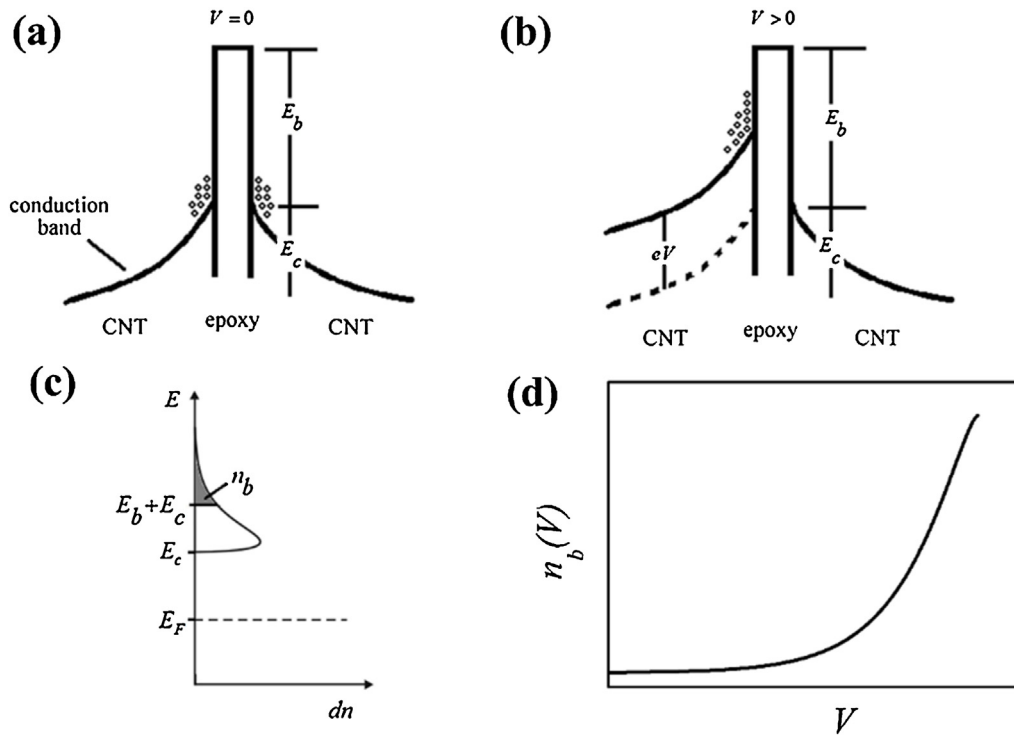


Fig. 4. Rectangular potential barrier in the CNTs-epoxy-CNTs structural unit for: (a) $V=0$; (b) $V>0$; (c) distribution of the electron concentration with energy; (d) electron concentration plotted against the applied voltage V with mathematical simulation.

The density of states in the conduction band is given (for $E > E_c$) as

$$D_e(E) = \frac{1}{2\pi^2} \frac{(2m_e)^{3/2}}{\hbar^3} (E - E_c)^{1/2} \quad (2)$$

where E_c denotes the energy of the bottom of the conduction band, m_e is effective masses and \hbar Planck constant.

In thermodynamic equilibrium, the distribution function for electrons is given by the Fermi-Dirac distribution, but the high-energy tail of the Fermi distribution, i.e. for $E - E_F \gg k_0T$, can be approximated by the Boltzmann distribution:

$$f_e(E) \cong \exp\left(-\frac{E - E_F}{k_0T}\right) \quad (3)$$

where k_0 denotes the Boltzmann constant, T is the temperature and E_F is the Fermi level.

When applying voltage V , the concentration of electrons which can hop from the conduction band of CNTs to epoxy is given by

$$n_b = \int_{E_b+E_c}^{+\infty} D_e(E - eV) f_e(E - eV) dE \quad (4)$$

Coordinate transformation $E' = E - eV$, so

$$\begin{aligned} n_b &= \int_{E_b+E_c-eV}^{+\infty} D_e(E) f_e(E) dE \\ &= \int_{E_b+E_c-eV}^{+\infty} \frac{1}{2\pi^2} \frac{(2m_e)^{3/2}}{\hbar^3} \exp\left(-\frac{E - E_F}{k_0T}\right) (E - E_c)^{1/2} dE \end{aligned} \quad (5)$$

when $V \leq E_b/e$, by introducing a variable $x = (E - E_c)/(k_0T)$, Equation (5) can be written as:

$$\begin{aligned} n_b &= \frac{1}{2\pi^2} \frac{(2m_e)^{3/2}}{\hbar^3} (k_0T)^{3/2} \exp\left(-\frac{E_c - E_F}{k_0T}\right) \\ &\times \int_{x'}^{+\infty} (x)^{1/2} \exp(-x) dx \end{aligned} \quad (6)$$

For the evaluation of the above term, we assign

$$x' = \frac{(E_b - eV)}{k_0T}$$

And apply

$$\begin{aligned} \int_{x'}^{+\infty} (x)^{1/2} \exp(-x) dx &= -(x)^{1/2} \exp(-x) \Big|_{x'}^{+\infty} \\ &+ \frac{1}{2} \int_{x'}^{+\infty} (x)^{-1/2} \exp(-x) dx \end{aligned}$$

So

$$\begin{aligned} n_b &= \frac{1}{2\pi^2} \frac{(2m_e)^{3/2}}{\hbar^3} (k_0T)^{3/2} \exp\left(-\frac{E_c - E_F}{k_0T}\right) \left[\left(\frac{E_b - eV}{k_0T}\right)^{1/2} \right. \\ &\times \exp\left(\frac{eV - E_b}{k_0T}\right) + \frac{1}{2} \int_{(E_b - eV)/k_0T}^{+\infty} (x)^{-1/2} \exp(-x) dx \Big] \end{aligned} \quad (7)$$

When the applied voltage is relatively low, the integral of this second term can be ignored, and then

$$\begin{aligned} n_b &= \frac{1}{2\pi^2} \frac{(2m_e)^{3/2}}{\hbar^3} (k_0T)^{3/2} \left(\frac{E_b - eV}{k_0T}\right)^{1/2} \\ &\times \exp\left(\frac{eV - (E_b + E_c - E_F)}{k_0T}\right) \end{aligned} \quad (8)$$

At relatively lower voltages, $E_b \gg eV$, So $(E_b - eV/k_0T)^{1/2} \sim (E_b/k_0T)^{1/2}$

$$n_b = n_0 \exp\left(\frac{eV}{k_0T}\right) \quad (9)$$

Where

$$n_0 = \frac{1}{2\pi^2} \frac{(2m_e)^{3/2}}{\hbar^3} k_0T (E_b)^{1/2} \exp\left(-\frac{E_c + E_b - E_F}{k_0T}\right)$$

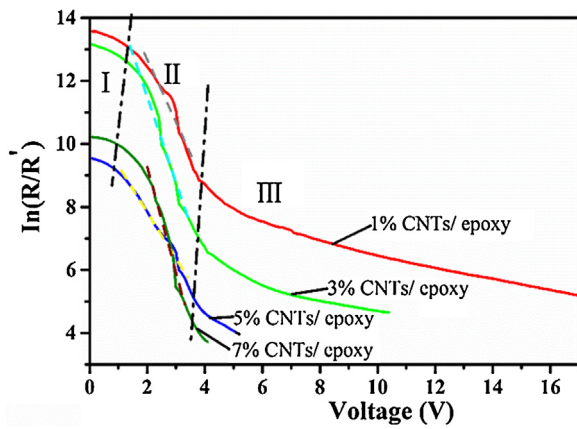


Fig. 5. $\ln(R/R')$ – V characteristics for the CNTs/epoxy composites with varied CNTs loading.

The variation of electron concentration with applied voltage was simulated with Eq. (5), as shown in Fig. 4(d), which indicates that the electron concentration increases exponentially with voltage.

The current of the CNTs-epoxy-CNTs structural unit is mainly determined by the current in the insulating epoxy layer in-between CNTs, which is given by Eq. (10) [29]

$$j_e = \frac{e\mu_e n_b V}{W} \quad (10)$$

where j_e represents current density, μ_e is carrier mobility, W is the distance between carbon nanotubes and V is the voltage between carbon nanotubes.

Therefore, under relatively low voltages, the variation of current with the voltage is nonlinear and grows rapidly with voltage, which results in high nonlinear coefficient: $j_e = V/R_0 \exp(eV/k_0T)$. R_0 is a constant. Simmons [12] reported that at relatively low voltages, the electrons with energy below that of potential barrier can pass through the barrier, resulting tunneling current. The variation of tunneling current at low voltages is linear. Under relatively higher voltages, the variation is nonlinear as expressed by $j_e = \beta(V + \gamma V^3)$, where β and γ are constants, respectively. Combining the hopping effect and tunneling effect, the current is given by Eq. (11).

$$j_e = AV + BV^3 + CV \exp\left(\frac{eV}{k_0T}\right) \quad (11)$$

where A , B and C are constants. Under very low voltages, the variation of current with voltages is linear: $j_e = (A + C)V$; under relatively higher voltages, the first two terms are much smaller than the third term and can be ignored. The variation of current with the voltage is nonlinear and grows rapidly with voltage: $j_e = CV \exp(eV/k_0T)$

$$\frac{\ln R}{R'} = \ln\left(\frac{V}{j_e R'}\right) = \ln(CR') - \left(\frac{e}{k_0T}\right)V \quad (12)$$

Fig. 5 illustrates $\ln(R/R')$ – V characteristics for all composites where R' is 1Ω . In the Ohmic region I, all the curves of $\ln(R/R')$ versus V approach a horizontal asymptote. In the higher voltage region II, the dashed lines were achieved by piecewise linear fitting with Origin software and coincides with the experimental curves respectively. This implied that the experimental data of $\ln(R/R')$ is consistent with the form of Eq. (12), which varies greatly and linearly with the voltage. Under further increased voltages, it is clear that the concentration of electrons (n_b) is independent of voltage when the voltage exceeds a critical value of $V \geq E_b/e$. This means that all of the electrons in CNTs conduction band have hopped into epoxy and the hopping effect tends to get saturated. As a result, the variation of the hopping current with voltage should tend to be linear and tunneling current will gradually disappear. However, the

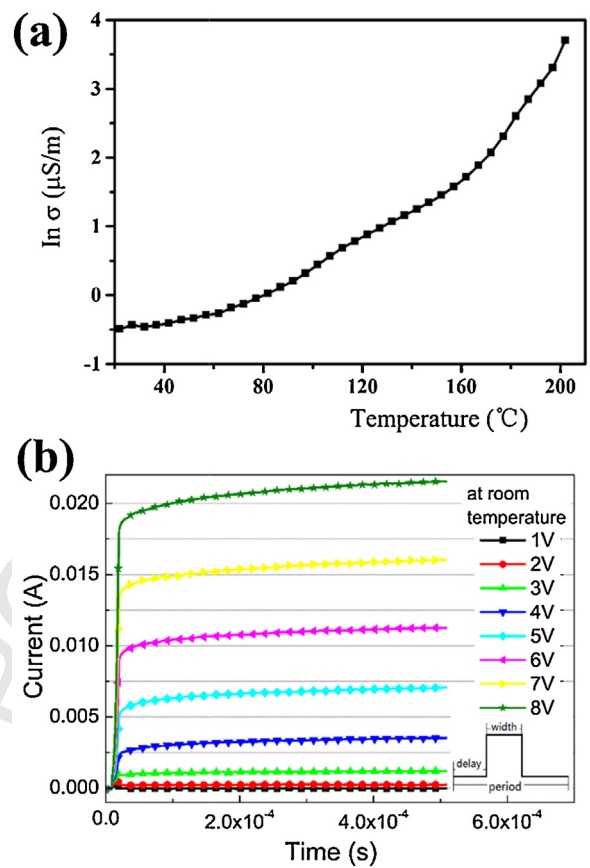


Fig. 6. (a) Temperature dependence of the conductivity (σ) for 3% CNTs/epoxy composites; (b) variation of current during applied voltage pulses for 3% CNTs/epoxy composite at room temperature. The voltage ranges from 1 V to 8 V, the pulse delay is 10 μ s, the pulse period is 1 ms and the pulse width is 500 μ s.

I – V behavior of the composite is still nonlinear, although the nonlinear coefficient decreases in region III. The above results indicate that hopping effect and tunneling effect are not sufficient to well explain the nonlinear phenomena of CNTs/polymer composites at high applied voltages, and the Joule heating effect will be discussed in the following section.

3.5. Joule heating effect

The influence of Joule heating on the nonlinear voltage characteristics was studied in a single crystal [30,31]. Wang et al. [30] reported that Joule heating effect played an important role in the observed nonlinear I – V behavior in a single crystal. For the CNT/polymer composites, the conductance increases with temperature as shown in Fig. 6(a). If the higher voltage is maintained, the heat generated by Joule-current will tend to accumulate and causes the rise of the temperature of the composites. The increase of temperature will further enhance the conductivity, which then causes the increase of current [32]. Therefore, it is necessary to investigate the influence of Joule heating on the nonlinear voltage characteristics for CNTs/epoxy composites.

The current variation during one applied voltage pulse is shown in Fig. 6(b). The voltage ranges from 1 V to 8 V, the pulse delay is 10 μ s, the pulse period is 1 ms and the pulse width is 500 μ s. The measured current remains constant with time when the applied pulse voltage is below 3 V. In contrast, the current exhibits an apparent increase with time when the pulse voltage is above 4 V. The rise of current could be due to accumulated Joule heating. This implies

that the effect of Joule heating on currents is substantial and the current increases obviously when the applied voltage is high. Under lower voltages, the flattop with time implies that the self-heating effect can be ignored.

As shown in Fig. 3b, for the 3 wt% CNTs/epoxy composite, when the applied voltage is lower than 3 V, the influence of Joule heat on the current is very small and can be ignored. The I – V curve shows Ohmic behavior at lower voltages and the curve tends to be non-linear as the voltage is increased, indicating that hopping effect and tunneling effect are the main causes of the non-linear voltage characteristics of CNTs composites.

As the voltage exceeds a critical value, the hopping effect tends to get saturated and tunneling current will disappear. Based on that, the I – V curve of composites should become linear. However, the effect of Joule heating on currents is substantial at high voltages. The higher the voltage is applied, the more thermal energy ($Q = IVt$, where t is the time) will be generated and cause the rise of the temperature and hence the increase of conductivity and current. As a result, the curve remains nonlinear but the nonlinear coefficient decreases in region III under high voltages.

4. Conclusions

In conclusion, the I – V behavior of CNTs/epoxy composites was investigated. It was observed that when the applied voltage was low, the composites showed Ohmic behavior. When the applied voltage was increased, the curves tended to be nonlinear. By theoretical calculation, the electron concentration hopping from the conduction band of CNTs to epoxy increased quickly with voltages and induced hopping current under electric field. Analysis indicated that hopping effect and tunneling effect were the main causes of the strong non-linear voltage characteristics in the composites under the increased applied voltages. Consequently, as the voltage was further increased, the hopping current tended to be nearly saturated and tunneling current could gradually disappear. Meanwhile, however, the effect of Joule heating on currents was substantial at high voltages, resulting in a nonlinear behavior but with relatively low coefficient. Thus under tunneling, hopping effect, and Joule heating, the I – V curve of the CNTs/epoxy composites displayed three regions: the current changes linearly with voltage at low voltages which became substantially non-linear under increased voltages and the growth trend became slow as the voltage reached a critical value.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No.51377157), the Guangdong Innovative Research Team Program (No.2011D052) and Shenzhen Peacock Plan for Innovative Research Team (KYPT20121228160843692).

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