Current transfer mechanisms in polyvinyl alcohol films with inclusions of multi-walled carbon nanotubes

S V Vasin1*, M S Efimov2, V A Sergeev1,2 and I V Frolov1,2

1 Kotel'nikov Institute of Radio Engineering and Electronics of Russian Academy of Sciences, Ulyanovsk Branch, Ulyanovsk, 432071 Russia
2 Ulyanovsk State Technical University, Ulyanovsk, 432027 Russia

*E-mail: svasin@ulireran.ru

Abstract. Current-voltage and capacitance-voltage characteristics of polyvinyl alcohol (PVA) films with the inclusion of multi-walled carbon nanotubes (MWCNT) deposited on silicon and ITO substrates were experimentally studied. It is shown that such structures demonstrate rectifying properties and their current-voltage characteristics are nonlinear. With direct bias, the structures have a positive temperature coefficient of resistance (TCR). With a reverse bias, the sign of TCR changes from negative to positive. A qualitative analysis of the results based on the tunneling mechanism of current transfer is presented.

1. Introduction

Polymers are well known as structural materials and electrical insulators. However, some polymers exhibit conductive or semiconductor electrical properties, providing the basis for a new approach to electronics, the so-called polymer or organic electronics. The main advantages of polymer electronics compared to traditional ones are the lower cost of manufacturing devices, their flexibility, the use of simpler manufacturing technologies, as well as the possibility of manufacturing large-area products, which is especially true for screens and lighting systems. However, at the present stage of development of organic electronics, it is not without a number of disadvantages, the main of which is the low mobility of charge carriers in traditional semiconductor polymers, which limits the range of operating frequencies.

One of the promising methods for modifying the properties of polymers is the creation of polymer composites based on carbon nanotubes (CNT). The combination of polymer materials and CNT can significantly improve the properties of the original polymers, as well as obtain materials with new, unique mechanical, thermal, electrical or electrochemical properties. This allows both creating new electronic devices and improving the characteristics of existing ones, such as supercapacitors, sensors, organic light-emitting diodes (OLED), solar cells, electromagnetic absorbers, etc. [1-3].

In this work, we studied the effect of multi-walled carbon nanotubes (MWCNT) on the electro-physical parameters of polyvinyl alcohol (PVA) films. PVA is widely used in medicine, fuel cells, optical fiber sensors, humidity sensors, polarizers, and holographic gratings, as well as a dielectric layer material in organic thin-film transistors [4]. This polymer also has excellent adhesion, emulsifying and film-forming properties, high tensile strength and flexibility. All of the above makes PVA one of the best materials as a polymer matrix for creating film nanocomposite structures.
2. Materials and methods

To produce the nanocomposite, a commercially available PVA of the 16/1 label was used. MWCNT were synthesized by the MOCVD method on an experimental laboratory setup developed at the Ulyanovsk State Technical University [5]. The diameter of the MWCNTs was in the range of 40-80 nm. To improve the compatibility of MWCNT with a polymer matrix, MWCNTs were functionalized by grafting on the surface of polar carboxyl groups (COOH) when treated with strong acids.

Initially, a 10% (wt-wt) solution of PVA powder in deionized water was prepared by continuous magnetic stirring for an hour at a temperature of 90 °C. 1% (by weight) of MWCNT were dispersed into the resulting solution by ultrasonic mixing. The speed of drawing the substrate from the solution was selected in the range of 1–5 cm/min. After the coating of the films, the structures were dried at a temperature of 80 °C for an hour. Aluminum contacts were deposited on the surface of the films by vacuum thermal evaporation. Schematic representation of the resulting structures shown in the inset to figure 1. Also, structures on ITO-coated glasses were fabricated in a similar way in order to study in the future the optical properties of nanocomposite films.

To measure the current-voltage (I–V) characteristics, we used a setup based on the APS-7313 programmable power supply and two Tektronix DM4040 precision multimeters in voltage and current measurement mode. High-frequency capacitance-voltage (C–V) characteristics were measured at a frequency of 100 kHz using a Protek 9216A LCR meter. All measurements were made in a chamber with temperature control.

3. Results and discussion

Figures 1 and 2 show C–V and I–V characteristics of Al/PVA/Si and Al/PVA + MWCNT/Si structures. The C–V characteristic of the control Al/PVA/Si structure is typical for the MIS structure. Standard analysis of this characteristic allows us to estimate the thickness of the dielectric film and the density of the fixed charge in the dielectric [6]. The film thickness in our structures varied in the range 500-1000 nm depending on the speed of substrate extraction from the solution. The density of charge traps was of the order of $10^{10}$ cm$^{-2}$ that is a good indicator even for such a traditional dielectric as SiO$_2$. The addition of MWCNT to the PVA leads to a shift in the C–V characteristics toward positive voltage values, which indicates that part of the positive charge is compensated during the formation of the nanocomposite. At the same time, the dependence in the region of negative bias becomes characteristic of the deep depletion mode, which is usually implemented with non-equilibrium depletion of the semiconductor.

![Figure 1](image1.png)

**Figure 1.** Capacitance–voltage characteristics of Al/PVA/Si and Al/PVA+MWCNT/Si structures at a temperature of 293 K.

![Figure 2](image2.png)

**Figure 2.** Current–voltage characteristics of Al/PVA/Si and Al/PVA+MWCNT/Si structures at a temperature of 293 K.
\( I-V \) characteristics of the control Al/PVA/Si structures are linear in the entire range of voltages used and have sufficiently small leakage currents of the order of \( 10^{-6} \) A, which also indicates good dielectric properties of the pure PVA film. At the same time, it is seen (figure 2) that the addition of only 1% MWCNT to the PVA leads to an increase in current by 2 orders of magnitude for reverse bias and 4 orders of magnitude for forward bias. Also \( I-V \) characteristics of the Al/PVA+MWCNT/Si structures become non-linear indicating the presence of current transport mechanisms typical for barrier structures. Experimental dependences for Al/PVA+MWCNT/Si structures are well approximated by the expression for the current–voltage characteristic of a Schottky diode or p-n junction [6]:

\[
I(V) = I_s \left( \exp \left( \frac{qV}{nkT} \right) - 1 \right),
\]

where \( I_s \) is the saturation current, \( q \) - electron charge, \( n \) – ideality factor parameter, \( k \) - Boltzmann constant and \( T \) is the temperature.

![Figure 3. Current–voltage characteristics of Al/PVA/ITO and Al/PVA+MWCNT/ITO structures. The solid line is approximation by expression (2).](image)

Structures made on ITO-coated glass substrates behave in a similar way (figure 3). \( I-V \) characteristics of the control Al/PVA/ITO structures are linear in the entire range of voltages used but the addition of only 1% MWCNT to the PVA leads to an increase in current by 2 orders for reverse and forward biases. Unlike structures on Si substrates, structures on ITO substrates have nearly symmetrical \( I-V \) characteristic at positive and negative bias. In this case the use of a conductive Al and ITO electrodes on the two sides of the PVA+MWCNT films can form two metal–semiconductor junctions equivalent to two back to back Schottky diodes which show a symmetrical behaviour. The equation for the \( I-V \) characteristics of such a structure is given by [7]:

\[
I(V) = \frac{I_{s1}I_{s2} \sinh \left( \frac{qV}{2nkT} \right)}{I_{s1} \exp \left( \frac{qV}{2nkT} \right) + I_{s2} \exp \left( -\frac{qV}{2nkT} \right)},
\]

where 1 and 2 are indexes for two barriers. The line in figure 3 represents a fitting of the experimental dependence with the expression (2). There is a good agreement with the experiment.

Such a large increase in current in both structures under study with the addition of a relatively small number of MWCNT is somewhat unexpected, since the concentrations of MWCNT we use are far from the percolation threshold [8]. It can be assumed that the current transfer mechanism in this case is the tunneling of current carriers between conductive particles (MWCNT in our case). In support of this assumption we can also interpret the type of \( C-V \) characteristics of Al/PVA+MWCNT/Si structures at

3
negative bias. Increased leakage currents prevent the formation of an inverse layer and lead to a monotonic drop in capacity with an increase in reverse bias. This type of $C-V$ characteristic is typical for MIS structures with a tunnel-thin dielectric [9].

Figures 4 and 5 show $I-V$ characteristics of the Al/PVA/Si and Al/PVA+MWCNT/Si structures under forward bias measured at different temperatures. It can be seen that the Al/PVA/Si structures show an increase in current as the temperature increases, while the opposite behavior is typical for the Al/PVA+MWCNT/Si structures. In other words the Al/PVA/Si structures have a negative temperature coefficient of resistance (TCR) and the Al/PVA+MWCNT/Si structures have a positive one.

![Figure 4. I-V characteristics of the Al/PVA/Si structures at a forward bias voltage at various temperatures.](image1)

![Figure 5. I-V characteristics of the Al/PVA+MWCNT/Si structures at a forward bias voltage at various temperatures (the solid lines are the fitting according to (1)).](image2)

Figure 6 shows the temperature dependences of the current of the Al/PVA+MWCNT/Si structures at various forward bias voltages. The current weakly exponentially decreases with increasing temperature. In the case of reverse bias (figure 7), the current-temperature dependence shows an even more complex behavior. The current increases up to temperatures of ~315 K and decreases at higher temperatures.

This behavior can also be explained in the framework of the hopping (or tunnel) current transfer model in composites with inclusions of conducting particles [10]. The probability of such a process is characterized by only two parameters: the height of the energy barrier between the particles $\eta$ and the distance between them $d$:

$$T_N = \exp(-\eta^{1/2}d).$$

(3)

Heating the PVA film leads to its thermal expansion, and, consequently, the distances between the MWCNT also increase. Since the probability of tunneling depends exponentially on the tunneling distance, this expansion leads to an exponential drop in forward current. However, our estimates have shown that taking into account only one thermal expansion of the polymer matrix allows us to achieve agreement with the results of the experiment at values of the linear thermal expansion coefficient $-10^{-4}$ K$^{-1}$, which is an order of magnitude higher than the known values for PVA. The temperature dependence of the height of the energy barrier at the polymer – MWCNT boundary cannot also be ruled out.

Another factor that reduces the conductivity of PVA+MWCNT films with increasing temperature is probably the temperature dependence of the conductivity of the MWCNT themselves. It was shown [11] that arrays of annealed and acid-functionalized MWCNT exhibit metallic properties. A change in temperature in the range from 300K to 373K leads to a 20% change in the resistivity of the MWCNT array, that can also make a significant contribution to the observed dependencies.
Figure 6. Dependences of current $I$ on temperature $T$ of Al/PVA+MWCNT/Si structures at various forward bias voltages (1 – 3 V, 2 – 5 V, 3 – 7 V, 4 – 10 V).

Figure 7. Dependences of current $I$ on temperature $T$ of Al/PVA+MWCNT/Si structures at various reverse bias voltages (1 – 3 V, 2 – 10 V, 3 – 20 V, 4 – 30 V).

In the case of reverse bias voltages, an increase in temperature, probably, primarily leads to an increase in current due to the mechanisms of thermionic or thermal field emission, and only at higher temperatures mechanisms of tunnel transport and reduction of the resistivity of the MWCNT begin to play the role decreasing the reverse current.

In summary, according to the results of experimental studies of the $I$–$V$ and $C$–$V$ characteristics of the PVA films with the inclusion of MWCNT on silicon and ITO substrates, it was found that these structures have a nonlinear character of $I$–$V$ characteristics, a positive TCR at forward bias, and changing sign from negative to positive TCR at reverse bias.

Acknowledgments
This study was performed as part of a state assignment with financial support from the Russian Foundation for Basic Research and the Government of Ulyanovsk Region, Project No. 19-42-730011.

References
[1] Hu N, Karube Y, Arai M, Watanabe T, Yan C, Li Y, Liu Y and Fukunaga H 2010 Carbon 48 680
[2] Sariciftci N S, Smilowitz L, Heeger A J and Wudl F 1992 Science 258 1474
[3] Kraabel B, Lee C H, McBranch D, Moses D, Sariciftci N S and Heeger A J 1993 Chem. Phys. Lett. 213 389
[4] Facchetti A, Yoon M-H and Marks T J 2005 Adv. Mater. 17 1705
[5] Klimov E S, Buzaeva M V, Davydova O A, Makarova I A, Svetukhin V V, Kozlov D V, Pchelintseva E S and Bunakov N A 2014 Russ. J. Appl. Chem. 87 1109
[6] Sze S M 1981 Physics of Semiconductor Devices (New York: Wiley–Interscience)
[7] Chiquito A J, Amorim C A, Berengue O M, Araujo L S, Bernardo E P and Leite E R 2012 J. Phys. Condens. Matter 24 225303
[8] Chebil A, Ben Doudou B, Dridi C and Dammak M 2019 Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 243 125
[9] Dubey P K, Filikov V A and Simmons J G 1976 Thin Solid Films 33 49–63
[10] Ambrosetti G, Balberg I and Grimaldi C 2010 Phys. Rev. B 82 134201
[11] Sergeev V A, Klimov E S and Frolov I V 2019 Tech. Phys. 64 1155–60