Mechanisms of charge transport and resistive switching in composite films of semiconducting polymers with nanoparticles of graphene and graphene oxide

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Abstract. We have investigated the effect of the resistive switching in the composite films based on polyfunctional polymers – PVK, PFD and PVC mixed with particles of Gr and GO with the concentration of ~ 1 - 3 wt.%. We have developed the solution processed hybrid memory structures based on PVK and GO particles composite films. The effect of the resistive switching in Al/PVK(PFD; PVC):Gr(GO)/ITO/PET structures manifests itself as a sharp change of the electrical resistance from a low-conducting state to a relatively high-conducting state when applying a bias to Al–ITO electrodes of ~ 0.2–0.4 V. It has been established that a sharp conductivity jump characterized by S-shaped current-voltage curves and the presence of their hysteresis occurs upon applying a voltage pulse to the Au/PVK(PFD; PVC):Gr(GO)/ITO/PET structures, with the switching time in the range from 1 to 30 μs. The mechanism of resistive switching associated with the processes of capture and accumulation of charge carriers by Gr(GO) particles introduced into the matrixes of the PVK polymer due to the reduction/oxidation processes. The possible mechanisms of energy transfer between organic and inorganic components in PVK(PFD; PVC):GO(Gr) films causes increase mobility are discussed. Incorporating of Gr (GO) particles into the polymer matrix is a promising route to enhance the performance of hybrid memory structures, as well as it is an effective medium for memory cells.

1. Introduction

Hybrid (organic–inorganic) nanocomposite materials are currently of great interest due to the prospects of their use as nonvolatile memory devices because of their high operation speed, high-density data storage, low power consumption, and low cost. Therefore they exhibit significant advantages over inorganic memory materials in the fabrication of volatile and nonvolatile memory devices [1-3]. Such polymeric and hybrid materials exhibit easy processability, good flexibility, high mechanical strength, and good scalability. They require very simple solution processes such as spin coating, dip coating and inkjet printing, which can be carried out at low cost and further are applied for high density memory devices.

In recent years, of particular interest is the use of new hybrid materials based on graphene (Gr) as OFETs and nonvolatile memory devices, in particular, composites based on Gr particles and particles of graphene oxide (GO) enclosed in a polymer matrix. Owing to the unique properties of Gr, such as high charge carrier mobility, high thermal conductivity, and the possibility of the effective transport of
charge carriers, including the ballistic transport at room temperature [4,5], it is a promising material for optoelectronics. Graphene flakes, being an effective medium for the accumulation of charge carriers, are considered as a promising material for hybrid (polymer–Gr particles) non-volatile WORM memory cells based on the effects of resistive switching. A similar role is played by GO particles with the best solubility in polymer matrices as compared to Gr particles [3].

In this paper we have investigated the effect of the resistive switching in the composite films based on polyfunctional polymers – PVK, PFD and PVC mixed with particles of Gr and GO with the concentration of ~ 1 - 3 wt. %

The effect of resistive switching in Al/PVK(PFD; PVC):Gr(GO)/ITO/PET structures at applying biases to Al–ITO electrodes ~ 0.2–0.4 V is investigated. The observed conductivity jump is accompanied by the appearance of S-shaped current–voltage–characteristics and the presence of hysteresis. The switching time, t, in such structures is in the range from 1 to 30 μs. The mechanism of resistive switching associated with the processes of capture and accumulation of charge carriers by Gr(GO) particles introduced into the matrixes of the PVK polymer due to the reduction/oxidation processes.

2. Experimental

We investigated the electrical and optical properties of composite films based on soluble in organic solvents multifunctional polymers: poly(9-vinylcarbazole) – PVK - (C₁₃H₁₁N)n, average molecular weight Mₙ ~ 1.1 × 10⁶, band gap E₉ ~ 3.6 eV; poly(9,9-di-n-dodecylfluorenyl-2,7-diyi) – PFD, (C₁₀H₄B(O₃)n, Mₙ is about 5.18 × 10², and E₉ is about 3.36 eV; polyvinyl chloride – PVC (C₂H₂Cl)n, Mₙ is in the range from 4 × 10⁴ to 1.45 × 10⁶, and E₉ is about 4.86 eV; and their composites with Gr particles from 200 to 300 nm in diameter (high temperature reduced graphene - HTRG) and GO particles from 400 to 500 nm in diameter. The concentration of Gr and GO particles in the polymer matrix of PVK was varied in the range of 1–3 wt. %. The PVK, PFD polymers and ITO/PET substrates used in our study were purchased from Sigma-Aldrich, PVC was purchased from FGUP VNIISV (Tver) and then used without further treatment. The Gr and GO flakes were purchased from AkKoLab (Moscow, Russia) and were used without further modification.

Polymers were dissolved in chloroform, which was also used for the preparation of a colloidal solution of Gr and GO particles. The solutions were mixed and sonicated (Bandelin Sonopuls HD 2070, f ~ 20 kHz) for 3 - 5 min. The obtained 20% solution of polymers with Gr (or GO) particles in chloroform was applied to flexible PET substrates with ITO (In₂O₃/SnO₂) conducting layer, ITO/PET (the surface resistivity of the ITO layer was ~ 60 Ω/cm²) by spin coating at 2500–3000 rpm, followed by drying at ~ 80°C for 20 min under nitrogen atmosphere. The current–voltage (I-Vs) characteristics of the composite films for memory cells were measured under direct current at 300 K in a sandwich geometry after thermal evaporation of Al electrode on top of the PVK(PFD, PVC):Gr(GO)/ITO/PET structure using an automated measurement setup based on a Keithley 6487 picoammeter in the voltage range from -5 to +5 V. The typical structure of a Al/PVK(PFD, PVC):Gr(GO)/ITO/PET samples for I-V measurements is shown in figure 2(a). The I-Vs of PVK(PFD, PVC):GO-based films were measured in vacuum (3·10⁻³ torr) in the dark at 300 K using a holder of liquid N₂ cryostat and a dc electronic computer controlled measuring system with a Keithley 6487 picoammeter/voltage source and AKIP-1124 programmable voltage source. The voltages were varied between - 15 V and + 15 V in variable steps.

Current–voltage characteristics of the composite films in the pulse mode were measured on a unit with a PCG10A current generator at 300 K. A voltage pulse from the generator was sent to the sample and serially connected load impedance. The ITO layer served as a lower electrode and the gold clamping contact with the area, S ~ 10⁻⁴ cm², as an upper electrode. A triangular pulse with duration of 2 ms was used; the maximum current value was 100 μA, and a clock-frequency period of 4 μs was chosen. The voltage was measured using a PS500 dual channel oscilloscope. The electric current

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\begin{align*}
\mu_2 \text{ ms was used; the maximum current value} & = 100 \mu A, \text{ and a clock-frequency period} = 4 \mu s \text{ was chosen. The voltage was measured using a PS500 dual channel oscilloscope. The electric current }
\end{align*}
\]
strength was determined from the voltage drop at the load and the voltage on the sample from a difference between the input voltage, \( U_0 \), and the voltage at the load.

3. Results and discussion

The above described PVK:Gr(GO) composite films were used in our study of the resistive switching effect which can be utilized for designing of nonvolatile WORM memory. The structure of the studied samples is shown in figure 1.

![Figure 1. The structure of the Al/PVK:Gr(GO)/ITO/PET samples for I-Vs measurements.](image)

The typical experimental I-Vs of these structures are presented in figure 2 and inset (a) in figure 2. As it evident from figure 2, the memory effect for the Al/PVK(PFD, PVC):Gr(GO)/ITO/PET films consists of in switching the conductivity of the composite structure from the low conducting to high conducting state under applying a bias to Al - ITO electrodes of \( \sim 0.1 - 0.4 \) V, which corresponds to the electric field strength \( E \sim 3 - 4 \times 10^4 \) V/cm. As can be seen from inset b) in figure 2, the I-Vs of the samples follow a linear law in both the initial and final states and the ratio of the final electric current density to the initial current through the sample \( \left( \frac{j_2}{j_1} \right) \) varies in the range of \( \sim 2 - 450 \). We have obtained similar results for several other samples of the PVK:Gr(GO) composite films with concentrations of Gr and GO particles in the range of \( 1-3 \) wt. % as well as for some other polymer matrixes mixed with Gr or GO particles [6]. It is important to note that the switching voltage in the Al/PVK:Gr(GO)/ITO/PET structures proved to be considerably less than the threshold voltage obtained for the polymer–nanoparticle and polymer - Gr composites by other authors [7]. For all the studied samples, the switching effect occurs with a sharp (by one to two orders of magnitude) increase in the current through the structure, which indicates a transition from the “off” state to the “on” state (process of “writing”). The sample remains in the “on” state in the reverse scanning of the voltage, as well as in multiple scanning both at a positive bias and at a negative bias applied to the electrodes. In some cases, we observed the effect of reverse switching of the Al/PVK:Gr(GO)/ITO/PET thin films to a relatively low conducting state. The analysis of I-Vs of the Al/PVK:Gr(GO)/ITO/PET structures, in a log–log scale (see inset b) in figure 2) reveal the fact that the slopes of the I-Vs are close to unity in both the low conducting and high conducting states when Gr and GO particles are embedded in the PVK matrices. This indicates that the composite films have the ohmic conductivity following the law \( I(V) = \alpha V \) in both states. The absence of I-Vs of the shape \( I(V) \sim \beta V^2 \), which is typical of the mechanism of space charge limited currents, can indicate that this mechanism is not responsible for the observed resistive switching effect at a relatively low (less than \( \sim 1 \) V) biases.

Current-voltage characteristics of the PVK:Gr, PFD:Gr, and PVC:GO composite films by using a pulsed bias are given in figures 3(a) and 3(b). As is seen from figure 3, the I-V curves for all the investigated samples have S-shapes after increasing the voltage. The transition from the LC to HC state occurs at the threshold voltages, \( U_T \), which are different in magnitude for different types of polymer films; moreover, a sharp voltage drop on the samples without significant changes in the electric current flowing through them is observed in all the cases, which can be explained by the
current crowding effect. As follows from the given results, the threshold switching voltages, UT, for the PVK:Gr, PFD:Gr, and PVC:GO composite films are about 3 to 3.5, 7 to 8, and 15 to 16 V, respectively. The resistivity of the films after the switching is changed by an order of magnitude, i.e., the resistivity state is in the range from 200 to 500 kΩ and in the HC state from 20 to 40 kΩ. As a rule, the samples do not return to the LC state after reducing the voltage, but remain in the HC state.

Figure 2. I-Vs of the composite film Al/PVK:Gr/ITO/PET demonstrating the effect of current switching at low voltages; insets: a) I-Vs of Al/PVK:GO/ITO/PET film; b) I-Vs of Al/PVK:Gr/ITO/PET film on a log-log scale.

As is seen from figure 3, the current-voltage characteristic of the PVK:Gr film in the HC state shows a superlinear dependence unlike the I-V curves of the PFD:Gr and PVC:GO films, which are linear. The electric current changes upon the switching are about 0.2 μA for the PFD:Gr sample and about 5 μA for the PVC:GO sample, whereas the electric current change in the PVK:Gr film is zero (within the measurement accuracy). The observed differences perhaps are possibly connected with different switching times of the samples that are about 20, 30, and 4 μs for the PFD:Gr, PVC:GO, and PVK:Gr films, respectively. In particular, the switching time of the PVK:Gr film for the selected clock frequency period equal to 1 μs was estimated at about 1 μs (perhaps less than a few hundreds of nanoseconds). Repeated pulses of the same or opposite polarity sent to the samples do not lead to switching back to the LC state.

Instabilities with S-shaped I–V curves observed in the PVK:Gr and other films resemble the switching effects in chalcogenide glass semiconductors (CGSs) by their characteristics. These kinds of switching effects have been also observed in a series of composite films on the basis of polymers containing inorganic Si [8] and ZnO [9] particles. According to the model described in [9], the electric current instability effect in the case of CGS is caused by the electrothermal phenomena occurring in films under strong electric fields. For the generation of an instability in the form of the S-shaped I–V curve, the positive feedback should be established between the processes of heating and increasing the electric current strength in the material with an activation-type temperature dependence of the conductivity, σ, expressed by the following formula:

\[\sigma(T) = \sigma_0 \exp(-\Delta E/kT)\]  \hspace{1cm} (1)

where \(\Delta E\) is the activation energy of the conductivity, and \(k\) is the Boltzmann constant. Since the electric current flow leads to heating of the sample, an increase in the temperature in the presence of
the semiconducting dependence, $\sigma(T)$, in the form of Eq. (1) causes an increase in the conductivity, which in turn leads to a further increase in the current strength. The positive feedback effect and temperature rise are finished upon reaching the temperature, $T_n$, at which $(\Delta E/kT_n) = 1$, determined by the phase transition temperature in semiconductor–metal structures. These kinds of processes are typical for some types of CGSs, in which the glass-crystal phase transition occurs near the area of current crowding upon reaching the crystallization temperature; furthermore, the conductivity in the indicated area is switched by several orders of magnitude, i.e., from the LC (glass) state to the HC state (crystal) [9].

**Figure 3.** The I–V curves of the (a) Au/PVK:Gr/ITO/PET and (b) Au/PFD:Gr/ITO/PET composite films upon applying a triangular pulse to the ITO–Au electrodes. Current–voltage characteristics of the Au/PVC:GO/ITO/PET film upon applying a triangular pulse to the ITO–Au electrodes are shown in the insertion.

It should be noted that the mechanisms of current crowding in the other inorganic semiconductors, giving rise to S-shaped I–V curves, were fully described in [10]. To some extent, the electrothermal switching mechanism may be responsible for the S-shaped form of I–V curves in the studied films on the basis of polymer composites containing Gr and GO particles. However, one should take into account the peculiarities of thermomechanical and electrical properties of polymers in this case, as well as the occurrence of redox processes on the Gr and GO particles embedded into the polymer matrix. Mechanical features of polymers include their ability to stay in the vitreous, superelastic, or viscous-flow states. An increase in the conductivity with an increase in the temperature, described by Eq. (1), is typical for a glassy (amorphous) polymer phase. The transition of a polymer into a superelastic state, in which the electrical conductivity does not dependent on the temperature and remains constant, occurs upon reaching the glass transition temperature, $T_g$. At the melting temperature, $T_f$, a polymer experiences a phase transition to the viscous-flow state, in which an increase in the conductivity with an increase in the temperature is also observed [8]. For the starting PVK and PVC polymers, the glass transition and melting temperatures are the following: $T_g$ is about 200 and 80°C, and $T_f$ is about 290 and 270°C, respectively; at the same time, the $T_g$ and $T_f$ values can vary by 20 to 30°C depending on the film thickness and the chemical composition of the polymers. As was shown for CGSs in [9], the S-shaped I–V curves and switching effect at temperatures above 300 K might be caused by the current crowding effect over the sample. One can assume that a polymer in the area of current crowding experiences a phase transition to the viscous-flow state at the temperatures $T > T_f$. At the same time, there is no degradation of the polymer in the indicated area, since its supramolecular structure changes at high temperatures without breaking the molecular structure due to reducing the viscosity coefficient by several orders of magnitude. After cooling the
area of current crowding, the electrical resistivity of the sample may decrease by an order of magnitude. If the temperature of the area of current crowding was in the range $T_g < T < T_f$, i.e., within the superelastic phase, in which the electrical conductivity does not depend on the temperature, then the polymer would return to its initial LC state after cooling, and the HC state would not persist after removing the electric displacement field from the sample.

The considered effect of resistive switching in the Al/PVK:Gr(GO)/ITO/PET composite films makes it possible to create solution processible, i.e. compatible with the technology of flexible organic printing electronics, WORM memory cells based on such composites with electrical recording of information.

4. Conclusions
The effect of the resistive switching in the composite films based on PVK mixed with particles of Gr and GO with the concentration of $\sim 1 - 3 \text{ wt.}\%$ is investigated. The solution processed hybrid memory structures based on PVK and GO particles composite films are developed. It was shown that the effect of the resistive switching in Al/PVK(PFD; PVC):Gr(GO)/ITO/PET structures manifests itself as a sharp change of the electrical resistance from a low-conducting state to a relatively high-conducting state when applying a bias to Al–ITO electrodes of $\sim 0.2–0.4 \text{ V}$. The reversible switching of the source-drain current, $I_{sd}$, is also found at positive and negative $V_{sd}$. We suggest that the mechanism of resistive switching associated with the processes of capture and accumulation of charge carriers by Gr(GO) particles introduced into the matrix of the PVK polymer due to the reduction/oxidation processes. The mechanism of energy transfer between organic and inorganic components in PVK(PFD; PVC):GO(Gr) films may causes the increase mobility. One may conclude that incorporating of Gr (GO) particles into the polymer matrix is a promising route to enhance the performance of hybrid memory cells.

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