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Electrical Characteristics of the Organic Field Effect Transistors Based on New Organic Semiconducting Compounds

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In present study four newly synthesized organic semiconductor compounds have been used for fabrication of the organic field effect transistors. In all cases p-type channel organic field effect transistors were fabricated. I-V characteristics of the samples were investigated. The highest on/off ratio (up to 180) was observed in the case of the organic field effect transistors fabricated using 4-diphenylaminobenzaldehyde N-methyl-N-phenylhydrazone and 4,4'-diformyltriphenylamine bis(N-2,3-epoxypropyl-N-phenylhydrazone) organic semiconductors. The lowest on/off ratios were observed for organic transistors fabricated using 4-diphenylaminobenzaldehyde N,N-diphenylhydrazone semiconductor.

Keywords: organic field effect transistor, electrical properties, semiconductor organic compounds.

INTRODUCTION

Organic electronics offers very interesting potential advantages over inorganic semiconductor (silicon, GaAs, GaN, SiC etc.) based devices such as ability to process organic material layers at low temperatures over large areas on flexible materials (for example plastic or paper) using cheap technological processes such as spin coating and printing [1]. Therefore, organic semiconductors – the backbone of the organic electronics – became a top of the considerable interest in the last decade [1 – 4]. However, many problems associated with organic semiconductors such as air stability [2] and low charge carrier mobility must be solved [3]. Therefore search of the alternatives for most widely used organic semiconductors such as pentacene is in progress [2].

In present study electrical properties of the four new semiconducting organic compounds were investigated. Electrical characteristics of the new organic semiconductor based field effect transistors have been studied.

EXPERIMENTAL

In present study top-contact configuration of the organic thin film transistors (OTFT) has been used (Fig. 1). n^+GaAs wafers with sintered AuGe-Ni ohmic contacts were used both as readily available substrates and gate electrodes. Afterwards GaAs wafers were degreased in dimethylformamide and acetone. GaAs native oxides were removed by etching in $NH_4OH : H_2O_2 : H_2O$ solution. Then dielectric layer has been deposited by spin coating at 4000 rpm. Photoresist FP-383 was used as a gate dielectric. Thickness of the gate dielectric in all cases was ~200 nm. Sintering of the gate dielectric was finished by 7 min air annealing at 100 °C temperature and 25 min air annealing at 120 °C temperature. Organic semiconductor thin film was deposited by spin coating as well (deposition conditions are presented in Table 1). Formation of the field effect transistor was finished by vacuum evaporation of the source and drain electrodes. 300 nm thickness Au or Cr films were deposited through the mask. Channel length was 100 μm and channel width was 500 μm.

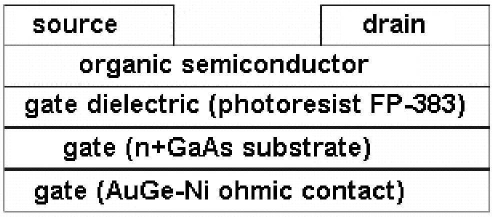

Fig. 1. Structure of the top-contact organic field effect transistor used in present study

Table 1. Parameters of the organic semiconductor thin film deposition process

Organic semicond.	Solvent	Solution formation temp.	Concentr. of the solution (%)	Spin coat. rate (rpm)	Thickn. of the layer (nm)
AT-RB-1	THF*	Room	5	6000	178
AT-RB-2	THF*	Room	5	6000	162
E-139	THF*	Room	3	8000	170
MT-12	THF*	+40 °C	5	6000	168

* THF refers to the tetrahydrofurane

Four organic semiconductors were investigated in the present study:

- Di(2,2-diphenylvinyl)(9-ethyl-3-carbazolyl)amine (further in the present study E-139);
- 4-diphenylaminobenzaldehyde N-methyl-N-phenylhydrazone (further in the present study AT-RB-1);
- 4-diphenylaminobenzaldehyde N,N-diphenylhydrazone (further in the present study AT-RB-2);
- 4,4'-diformyltriphenylamine bis(N-2,3-epoxypropyl-N-phenylhydrazone) (further in the present study MT-12).

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The synthesis and structure of the organic semiconductor MT-12 were reported earlier [5]. The synthesis of AT-RB-1 and AT-RB-2 was described by Nomura et al [6]. The synthesis and characterization of E-139 will be published soon [7].

Thickness of the spin coated organic semiconductor films was measured by a laser ellipsometer Gaertner L115 ($\lambda = 633$ nm). Current-voltage characteristics of the organic field effect transistors were investigated using a picoammeter/voltage source Keithley 6487. All measurements were performed in air.

EXPERIMENTAL RESULTS

The structures of organic semiconductors used in this study are shown below (Fig. 2).

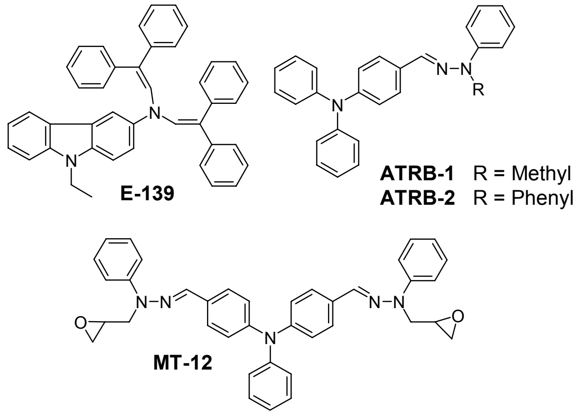

Fig. 2. The structures of the organic semiconductors used in the present study

All these materials form glasses. Their amorphous films can be prepared both by cooling from the melts and by casting or spining of the coating from the solutions.

The thermal and photoelectrical properties of organic semiconductors used in this study have been studied in detail [5 – 7]. The glass transition temperatures of MT-12, AT-RB-1, AT-RB-2, and E-139 were determined to be 65 °C, 30 °C, 50 °C and 104 °C, respectively. Hydrazones and enamine used in this work posses relatively low ionization potentials. For example ionization potentials of E-139 and MT-12 are 5.22 and 5.34 respectively [5, 7]. Hole drift mobilities of the solid solutions of the studied compound in bisphenol Z polycarbonate are given in Table 2.

Table 2. Hole mobility data for molecularly doped polymers containing E-139, MT12, AT-RB-1, AT-RB-2

Layer composition	μ, cm^2/Vs
E-139 + PC-Z (1:1)	$9.0\cdot10^{-5}$ [a)]
MT12 + PC-Z (1:1)	$3.6\cdot10^{-5}$ [a)]
AT-RB-1 + PC-Z (1:1)	$2.5\cdot10^{-6}$ [b)]
AT-RB-2 + PC-Z (1:1)	$5.6\cdot10^{-6}$ [b)]

[a)] defined electric field $6.4\cdot10^5$ V/cm;

[b)] electric field $1\cdot10^5$ V/cm (reported by Shirota et al [6])

Data presented in Table 2 shows that all the studied materials are efficient p-type semiconductors. Molecularly doped polymers containing these compounds show relatively high hole drift mobilities. Charge mobilities in the amorphous layers of pure compounds are usually by 1 – 2 orders of magnitude higher. Therefore it was decided to test such materials in field effect transistors.

Source-drain current-voltage (I-V) characteristics of the transistors fabricated using different organic semiconductors are presented in Fig. 3. It can be seen, that current strength can differ by an order for various semiconductors. The smallest leakage currents were observed for AT-RB-2 semiconductor. In the case of E-139 semiconductor higher currents were observed. The highest currents were measured for the transistor fabricated using MT-12 semiconductor. 4 hour annealing at 40 °C temperature in vacuum (before evaporation of the source and drain electrodes) decreased leakage current of the AT-RB-1 semiconductor based samples. It can be seen, that MT-12 semiconductor based samples are the only samples with regular I-V characteristics without any sudden decrease and increase of the current strength. Leakage current was lower for the samples with Cr electrodes in the case of MT-12 semiconductor and vacuum heated AT-RB-1 semiconductor. In other cases leakage currents were lower for the samples with Au source and drain electrodes.

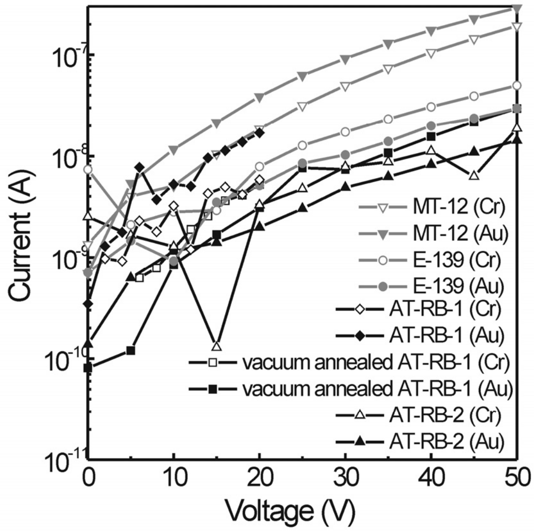

Fig. 3. Source-drain I-V characteristics of the field effect transistors fabricated using different organic semiconductors ($U_{\text{gate}} = 0$ V)

I-V characteristics of the different samples measured between the source and gate electrodes are presented in Fig. 4. It can be seen, that in the case of MT-12 semiconductor both negative and positive voltage induced currents are the highest. Slightly lower negative voltage induced current was observed in the case of the AT-RB-2 semiconductor. While its positive voltage induced currents were the smallest. Vacuum annealing at 40 °C temperature resulted in significant changes of the I-V characteristics of the AT-RB-1 based structure: decrease of both positive and negative voltage induced currents was observed. It can be seen, that all investigated organic semiconductors were p-type: negative voltage (positive source, negative gate) induced currents were slightly higher.

Forward-reverse current ratio was different for the different semiconductors (Fig. 5). In most cases forward current changed its direction only when forward voltage exceeded 10 V – 20 V. While for E-139 semiconductor it was 30 V – 35 V. In the case of the forward and reverse bias induced currents flowing in opposite directions only for E-139 semiconductor based structures forward-reverse current ratio is higher than 20. While in the case of the AT-RB-1 and MT-12 it is less than 10.

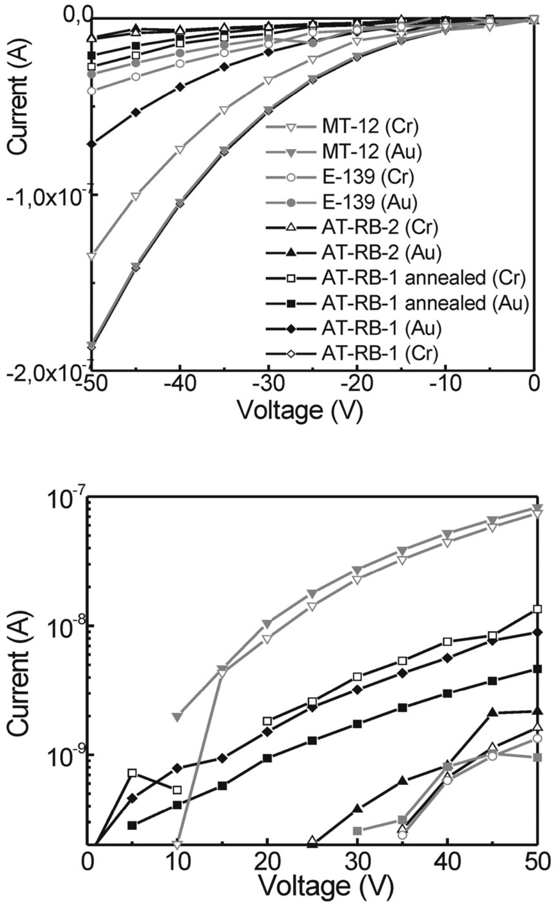

Fig. 4. Source-gate I-V characteristics of the field effect transistors fabricated using different organic semiconductors ($U_{\text{source-drain}} = 0$ V)

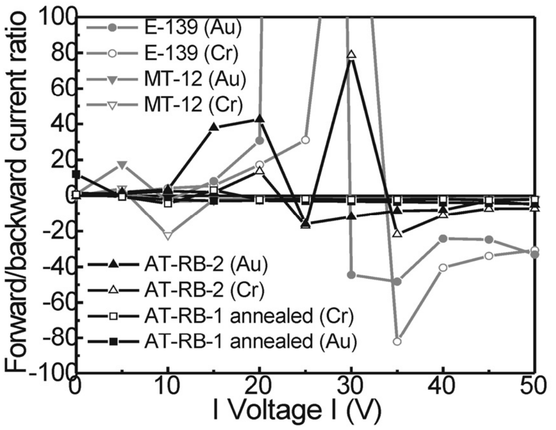

Fig. 5. Forward/backward current ratio for the source-gate I-V characteristics of the field effect transistors fabricated using different organic semiconductors ($U_{\text{source-drain}} = 0$ V)

Typical I-V characteristics of the organic field effect transistors are presented in Figs. 6 – 9. It should be mentioned, that increase of the both negative gate voltage and negative gate and drain potential resulted in increased source-drain current for all fabricated field effect transistors. It is typical for p-type semiconductors. [8]. It can be mentioned, that in the case of the field-effect transistors fabricated using vacuum annealed AT-RB-1 semiconductor layers as well as AT-RB-2 semiconductor layers and Cr as a source and drain electrode metal in the ~1/2 of the all samples investigated effect of the source-drain current amplification (induction of the channel) by gate voltage wasn't observed. No saturation of the source-drain current was observed in 0 V – (–50 V) voltages range for all the samples. Except one field effect transistor fabricated using AT-RB-2 organic semiconductor layer (Fig. 7), dependence of the source-drain current on gate voltage at $U_{\text{source-drain}} = 0$ V was observed. Values of the currents mentioned above (Figs. 6 – 9) are close to the currents measured between the source and gate electrodes (Fig. 4). It means, that leakage currents flowing through the gate dielectric layer are large enough to make influence on the I-V characteristics of the organic field-effect transistor.

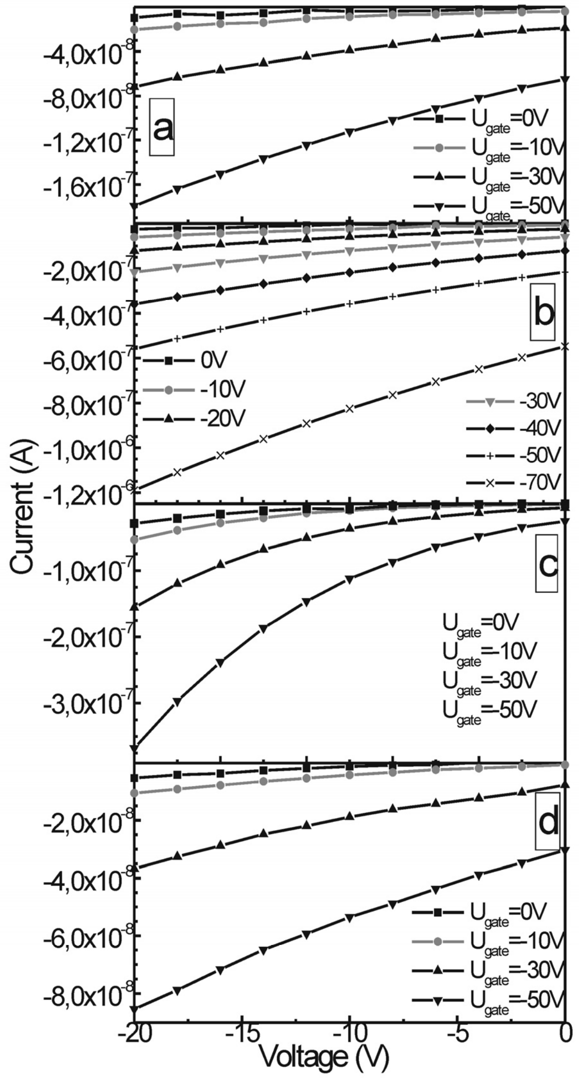

Fig. 6. I-V characteristics of the organic field effect transistors fabricated using semiconductor AT-RB-1 (a, c – source and drain electrode metal Au; b, d – source and drain electrode metal Cr). Semiconductor layer of samples c, d was vacuum annealed at 40 °C temperature before deposition of the source and drain electrodes

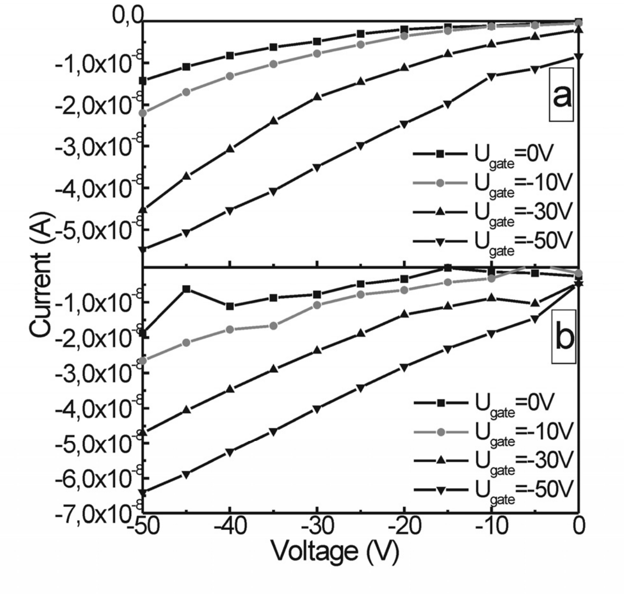

Fig. 7. I-V characteristics of the organic field effect transistors fabricated using semiconductor AT-RB-2 (a – source and drain electrode metal Au, b – electrode metal Cr)

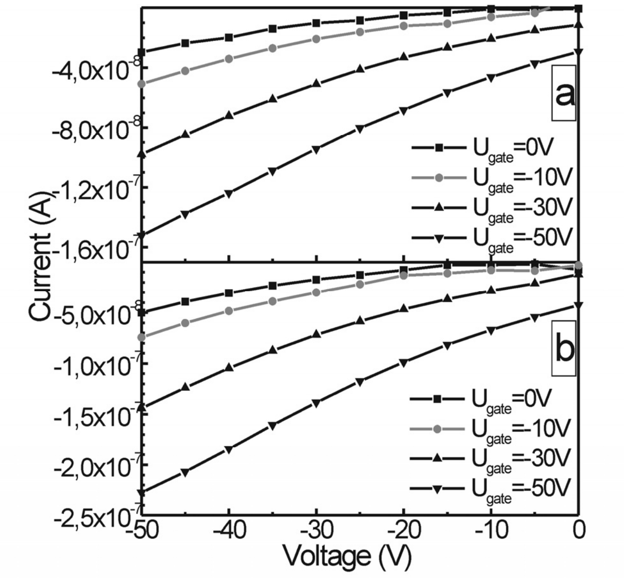

Fig. 8. I-V characteristics of the organic FETs fabricated using semiconductor E-139 (a – source and drain electrode metal Au; b – source and drain electrode metal Cr)

The dependence of the source-drain current on gate voltage (when $U_{\text{source-drain}} = \text{const.}$) is presented in Figs. 10 – 13. In many cases quasi-linear dependence of the source-drain current on gate voltage can be observed. Especially in the case of E-139 semiconductor based field effect transistors (Fig. 12) and for part of the MT-12 organic semiconductor based field effect transistors (Fig. 13). In the case of the AT-RB-2 based FET's quasi-linearity is less pronounced (Fig. 11).

Typical dependences of the organic field effect transistor on/off ratio on gate voltage (when $U_{\text{source-drain}} = \text{const.}$) are presented in Figs. 14, 15. In all cases the ratio decreased with increase of the drain voltage. In most cases on/off ratio was less than 5 when drain voltage was –50 V. It should be mentioned, that for field effect transistors fabricated using the same organic semiconductor different on/off ratio's can be observed. Numerical elimination of the gate leakage current from the I-V characteristic (by subtraction of source-drain current at $U_{\text{source-drain}} = 0$ V) of AT-RB-1 based organic field effect transistor with Cr as a source and drain electrode metal resulted in substantial decrease of the on/off ratio – up to 3 times.

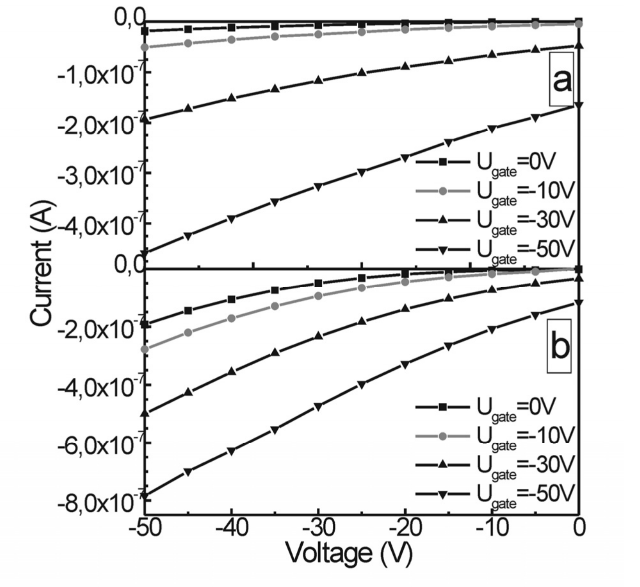

Fig. 9. I-V characteristics of the organic field effect transistors fabricated using semiconductor MT-12 (a – source and drain electrode metal Au, b – source and drain electrode metal Cr)

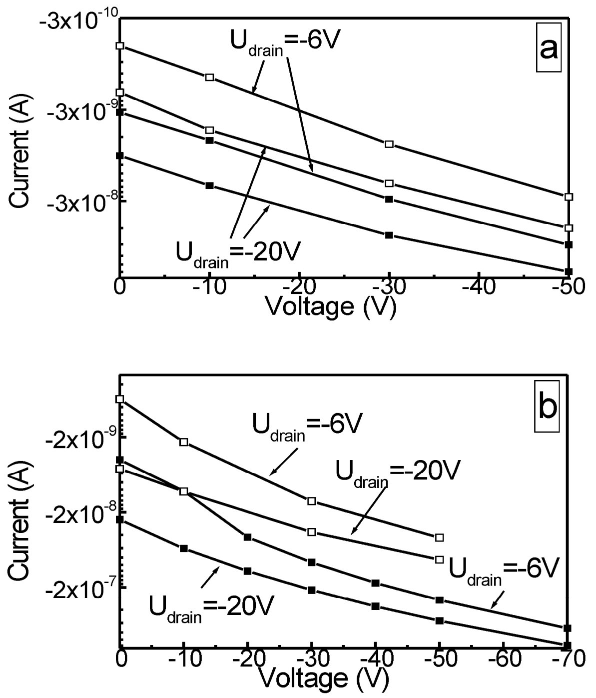

Fig. 10. Typical source-drain current Vs gate voltage characteristics of the field effect transistors fabricated using AT-RB-1 organic semiconductor (a – source and drain electrode metal Au, b - source and drain electrode metal Cr). Open squares refer to the semiconductor layer vacuum annealed at 40 °C temperature before deposition of the source and drain electrodes

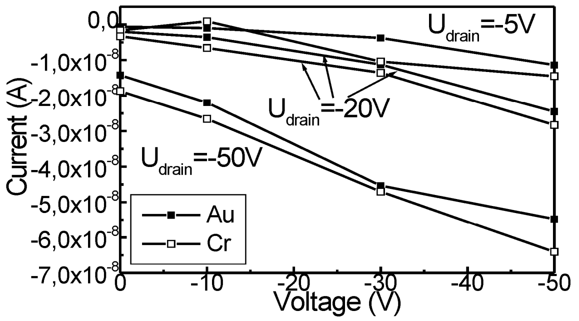

Fig. 11. Typical source-drain current Vs gate voltage characteristics of the field effect transistors fabricated using AT-RB-2 organic semiconductor (Au – source and drain electrode metal Au, Cr – electrode metal Cr)

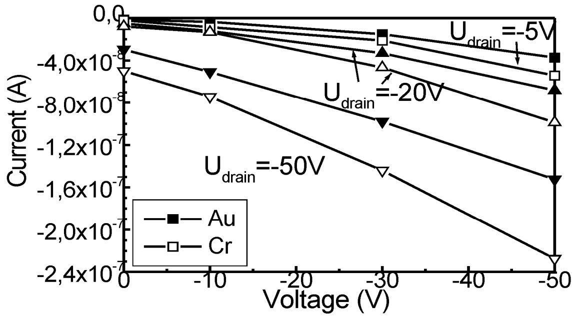

Fig. 12. Typical source-drain current Vs gate voltage characteristics of the field effect transistors fabricated using E-139 organic semiconductor (Au – source and drain electrode metal Au, Cr – electrode metal Cr)

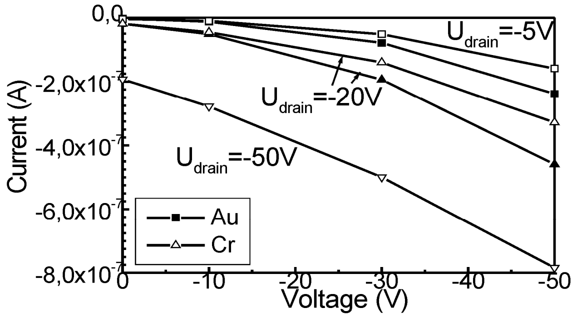

Fig. 13. Typical source-drain current Vs gate voltage characteristics of the field effect transistors fabricated using MT-12 organic semiconductor (Au – source and drain electrode metal Au, Cr – electrode metal Cr)

Largest on/off ratios (>100) were observed in the case of the field effect transistors fabricated using AT-RB-1 and MT-12 organic semiconductor channel layers (Figs. 14, 15). On/off ratios of E-139 semiconductor based field effect transistors were lower (Fig. 15). The smallest on/off ratio was observed in the case of AT-RB-2 organic semiconductor based field effect transistors. It should be mentioned, that no correlation between the I-V characteristics of the fabricated organic field effect transistors from one hand and hole drift mobilities of the solid solutions as well as glass transition temperatures from the other hand has been observed.

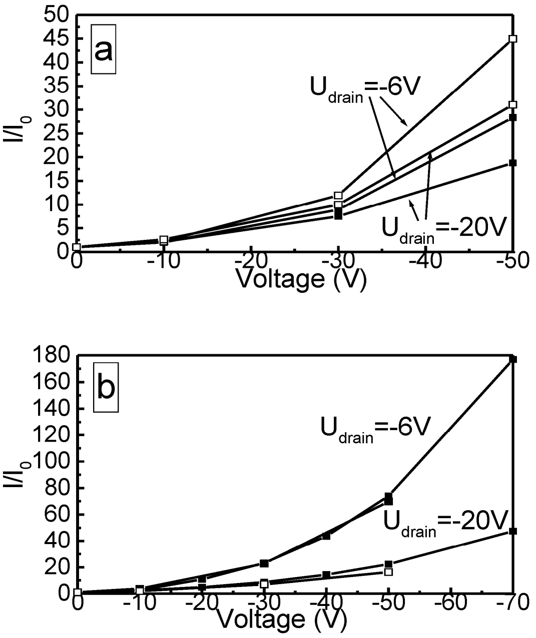

Fig. 14. On/off current ratio Vs gate voltage of the field effect transistors fabricated using AT-RB-1 organic semiconductor (a – source and drain electrode metal Au; b – source and drain electrode metal Cr). Open squares refer to the semiconductor layer vacuum annealed at 40 °C temperature before deposition of the source and drain electrodes

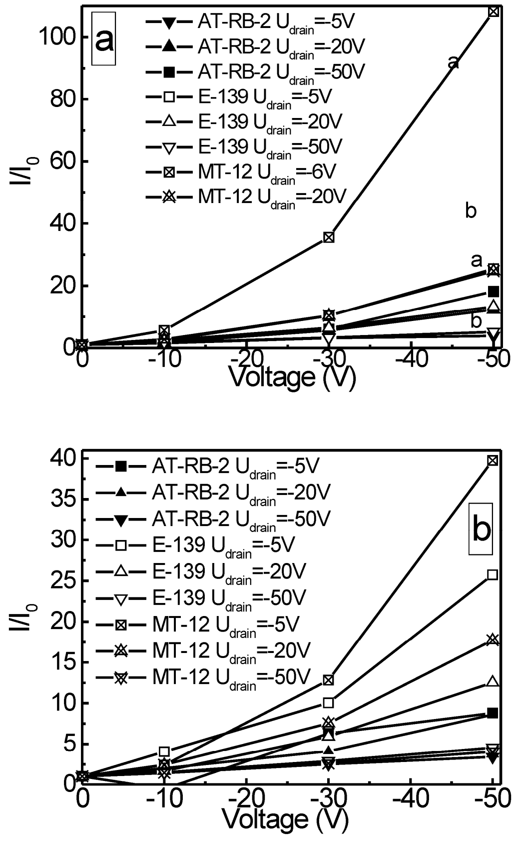

Fig. 15. Typical on/off current ratio Vs gate voltage of the field effect transistors fabricated using AT-RB-2, E-139 and MT-12 organic semiconductor layers (a – source and drain electrode metal Au; b – source and drain electrode metal Cr)

CONCLUSIONS

In conclusion p-type channel organic field effect transistors were fabricated using four novel organic semiconductor compounds. For all samples investigated on/off current ratio decreased with increase of the drain voltage. The highest on/off ratio was observed in the case of the organic field effect transistors fabricated using AT-RB-1 and MT-12 organic semiconductors (up to 180). The lowest on/off ratios were observed for organic transistors fabricated using AT-RB-2 semiconductor. No correlation between the I-V characteristics of the fabricated organic field effect transistors from the one hand and hole drift mobilities of the solid solutions as well as glass transition temperatures from the other hand has been observed. There were observed no dependence of the I-V characteristics and on/off ratio of the fabricated field effect transistors on type of the electrode metallization used.

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