Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp708-709

Effects of Silver Nanoparticles Organic Envelope on Pentacene Organic Field-effect Transistors

Keanchuan Lee, Martin Weis*, Xiangyu Chen, Dai Taguchi, Takaaki Manaka, Mitsumasa Iwamoto

Department of Physical Electronics, Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
Phone: +81-3-5734-2191 E-mail: iwamoto@ pe.titech.ac.jp

1. Introduction

Self-assembled monolayers of pure metal nanoparticles (NPs) are envisioned for various novel devices and has opened a new horizon in possible applications. However, organic envelope of NPs which is required for self-assembling must be removed prior further device fabrication. The performance of organic devices which depends on charge transport is one of the most studied phenomena in device physics in last years [1, 2] and variations in device geometries to improve measured current especially in organic field-effect transistors (OFETs) [3] made comparison of device parameters complicated. Hence, for simple quantitative evaluation of the charge transport in the organic material the charge carrier mobility was common used. There are various measurement techniques capable of evaluating carrier mobility such as: measurement of OFET characteristics, the Hall method, time-of-flight (TOF), space-charge limited condition (SCLC) measurement, transient electroluminescence technique, Auston-switch photoconductivity method, or the time-resolved microscope optical second-harmonic generation (TRM-SHG) technique. Except the last technique, each above-mentioned methods needs some specific assumptions or models to evaluate the carrier mobility. For example, the OFET measurement is based on the conductivity evaluation and thus the model of carrier density is required. Any disturbance will affect the estimation of mobility.

On the other hand, nanoparticles (NPs) hold many novel physical and chemical properties owing to the fact that surface atoms have a very high surface area to volume ratio and have possible future applications in electronics, optics, memory devices and so on. The small dimensions of NPs lead to small capacitance, which can be roughly calculated with a model of the concentric spherical capacitor using material parameters. The double-layer capacitance of metallic NPs encapsulated in organic insulator matrix is so small (attofarad) that the single electron charging to and from NPs occurs at room temperature [4]. Despite metal is being a good conductor, metal NPs encapsulated by organic envelope actually act as traps due to their chargingproperties. The charge storage in NPs attracted attention of applied research to develop NP-based nonvolatile memory. and the charge storage was also described by the charge trapping phenomenon [5]. In this study we report an effect of the ozonolysis of the silver NPs (Ag NPs) on the performance of pentacene OFET with Ag NPs monolayer on the organic semiconductor – gate insulator interface. The influence on the organic envelope as well as metal NP core is recorded and the total film resistance is evaluated. The pentacene OFETs used here are used for an illustration of the NP influence on organic device properties. The experimental results are well supported by the Maxwell-Wagner model [6] analysis.

2. Experiment

The Ag NPs encapsulated in oleic acid/oleylamine were synthesized according to the method published in detail elsewhere. NPs were dissolved in chloroform (Sigma-Aldrich) prior the spreading on the water subphase (18.2 MΩ.cm) of the Langmuir trough using a microsyringe (Hamilton, Reno, NV). The monolayer was allowed to equilibrate for 30 min before the compression. This time was found to be sufficient for the solvent evaporation and monolayer formation. Subsequently the Ag NPs monolayer was deposited on the solid substrate by the modified Langmuir-Schäffer (horizontal lifting) technique. The ozonolysis was done by the exposure to the ozone generated in oxygen rich atmosphere aided by UV irradiation (UV/ozone chamber, Nippon Laser & Electronics Lab, Japan) for a specific time. Organic devices used in experiments were top-contact pentacene OFETs. Heavily doped Si wafers with a 500 nm thick thermally prepared silicon dioxide (SiO_2) insulating layer were used as the base substrates. The Ag NPs monolayer was deposited onto Si wafers prior to the deposition of pentacene (100 nm in thickness). During the deposition of pentacene, the pressure was kept at less than 10^{-4} Pa and the deposition rate was fixed at 0.5 Å/sec, monitored by quartz crystal microbalance.

After the deposition of pentacene, gold electrodes (source and drain electrodes) of thickness 100 nm were deposited on the pentacene surface. The designed channel length (L) and width (W) were 30-100 μm and 3 mm, respectively. Prepared devices were characterized by the standard steady-state current-voltage measurement using Keithley 2400 Source Meter. The Ag NPs monolayer conductance measurements were done on the Ag NPs deposited on the glass substrate with gold electrodes fabricated in the same manner as for the OFET device. The conductance measurement results shown here were recorded for 30 μm long channel. All measurements were performed in laboratory ambient atmosphere. For the optical absorbance or electrical conductivity measurements Ag NPs monolayers were deposited on glass substrates (Matsunami S-0313 Neo). Optical spectra were recorded by Jasco V-570 spectrophotometer in the double beam operation inthe spectral region (400 - 800) nm at room temperature.

*Institute of Physics, Slovak Academy of Sciences, Dúbravskácesta 9, 845 11 Bratislava 45, Slovak Republic

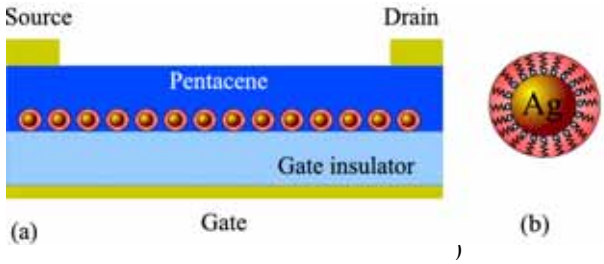

Figure 1 (a) Sketch of the top contact structure of organic field-effect transistor (OFET) with Ag NPs SAM for *I-V* measurements and (b) the stabilized Ag NP structure. The diameter is about 8 nm.

3. Results and discussion

Figure 2 illustrates the transfer and output characteristics of pentacene OFET with Ag NPs monolayer for various UV/ozone exposure times. The pentacene OFET with a pristine Ag NP layer exhibits the trapping of holes. The output characteristics are shown in Fig. 2(a). This is represented by huge threshold voltage shift (to V_{th} =30 V) with respect to the pentacene OFET with bare SiO_2 gate insulator (V_{th}=50 V, measurement not shown here). Obviously, the exposure to the ozone gradually increases the current in the off state of the OFET which results in the transition from the space-charge drain-source current saturation (pristine Ag NPs monolayer without exposure) to the ohmic behaviour as shown in output characteristics (Fig. 2(b)) which delineated by strong increase of the current.

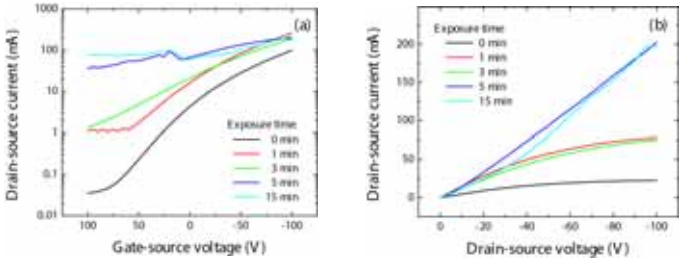

Figure 2 The (a) transfer and (b) output characteristics of pentacene OFET with Ag NPs monolayer for various UV/ozone exposure times.

The summary of the OFET basic properties is depicted in Fig. 3. The increase of current in the off state represents increase of the channel conductivity when exposure time increases. The effective free carrier mobility slightly reduced for a pristine Ag NPs film and almost unchanged after exposure of 1 minute or more. This is easy to understand by the reduction of number of traps (nanocapacitors represented by the Ag NPs with an organic envelope) due to the ozonolysis. Interestingly, there shows a positive threshold voltage shift, ΔV_{th} which indicates the amount of accumulated charge, Q increases with exposure time which is equivalent to 0.24, 0.67, 1.6 and 2.2 mC/cm^2 relative to sample without exposure by applying $Q=C_{ox}.\Delta V_{th}$ where C_{ox} is gate oxide capacitance. Longer ozone exposure reduces number of traps and therefore the threshold voltage returns to the bare SiO_2 gate insulator value. The discrepancy between the behaviour of the effective mobility and the threshold voltage originates in the nonlinear relation between number of traps and the effective mobility.

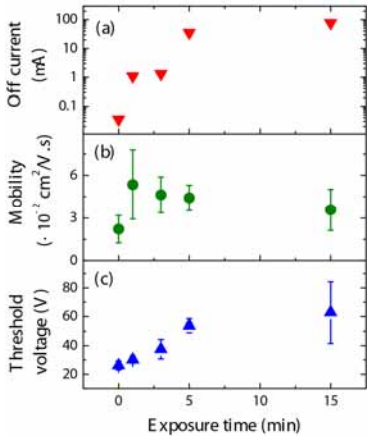

Figure 3: Exposure time dependence of the (a) off-state current, (b) carrier mobility, (c) threshold voltage.

4. Conclusions

We have illustrated the effect of Ag NPs organic envelope removing by the ozonolysis as well as its influence on the OFET behaviour. It was shown that the ozone exposure dissociate insulating organic envelope and enhances the NP monolayer conductivity while incorporation of pristine Ag NP monolayer causes trapping We can conclude that the NP monolayer on the organic semiconductor – gate insulator surface influences charge transport across the OFET and the ozonolysis acts as powerful tool for its modification. Therefore, even though the metal NPs were suggested as a potential way for increase of the effective dielectric constant (high-*k* materials), we illustrated that the conductivity can be influenced too. Thus, the Maxwell relaxation time can be designed in accordance to requirements of application.

Acknowledgements

A part of this work is financially supported by a Grant-in-Aid for scientific research (S) (No. 22226007) from Japanese Society for the Promotion of Science (JSPS) and a Grant-in-Aid for Young Scientists (B) (No. 22760227) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).A part of this work was supported by the Grants-in-Aid for Scientific Research, JSPS (Numbers 20656052 and 19206034).

References

[1] H. E. Katz, Chem. Mater., 16, 4748 (2004)
[2] H. Sirringhaus, Adv. Mater., 17, 2411 (2005)
[3] C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, J. M. Shaw, Science, 283, 822 (1999)
[4] S. Chen, R.S. Ingram, M.J. Hostetler, J.J. Pietron, R.W. Murray, T.G. Schaaff, J.T. Khoury, M.M. Alvarez and R.L. Whetten, Science, 280, 2098 (1998).
[5] M. Weis, J. Lin, T. Manaka, M. Iwamoto, J. Appl. Phys., 104, 114502 (2008).
[6] M. Weis, J. Lin, D. Taguchi, T. Manaka, M. Iwamoto, Jap. J. Appl. Phys., 49, 071603 (2010).