The transconductance of a nano-clustered subsurface layer in Si⁺-implanted PMMA^{*}

G. B. HADJICHRISTOV^{*}, V. K. GUEORGUIEV, TZ. E. IVANOV, Y. G. MARINOV, V. G. IVANOV^a, E. FAULQUES^b

Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria

^a Sofia University, Faculty of Physics, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria

^b Institut des Matériaux Jean Rouxel, UMR6502 CNRS, Nantes Atlantic Universities, 2 rue de la Houssiniere,

44 322 Nantes, France

The transconductance of a nano-clustered organic subsurface layer of a thickness of about 100 nm, formed in polymethylmethacrylate (PMMA) by implantation with silicon ions at an energy of 50 keV, is examined as a function of the Si^+ fluence in the range $10^{15} - 10^{17}$ cm⁻². Depending on the implantation regime, the ion-modified region of the Si^+ -implanted PMMA exhibits a transconductance and a field effect that can be used for electronic applications.

(Received November 5, 2008; accepted December 15, 2008)

Keywords: Ion implanted polymers, Organic field-effect devices, Polymethylmethacrylate (PMMA)

1. Introduction

Nanoscale structures, based on the localized chemical modification of organic polymers by the ion implantation technique, can significantly change their electrical properties. In these materials, the ion irradiation or ion implantation at an appropriate ion energy and fluence leads to the formation of a carbonaceous layer, exhibiting an enhanced electrical response [1–3] which is of interest for electronic applications [1,4,5]. It has been also observed a transconductance of the structures created in the ion-implanted polymers [1,6].

Upon the irradiation of the highly insulating polymer poly-(methyl methacrylate) (PMMA) with ions, even with energies of a few keV, one observes the formation of a subsurface layer and a large enhancement of the electrical conductivity [7]. As found in our previous study [8], a carbon-based nanostructure is formed upon implantation of PMMA with a silicon ion beam with an energy of 50 keV. For some electrical applications of ion-implanted PMMA, e.g. for all-organic field-effect elements,the transconductive properties of this material are also of interest. We have probed the transconductance of Si⁺-implanted PMMA in the fluence range 10¹⁵ to 10¹⁷ ions/cm².

2. Experimental

SA series of samples of size 1 cm \times 1 cm were cut from 5-mm-thick PMMA (commercially available, Röhm) and were implanted with silicon ions at an energy of 50 keV and fluences ranging from 10¹⁵ to 10¹⁷ cm⁻² [8]. The transconductance of the Si⁺-implanted PMMA structures was examined at room temperature using a computercontrolled Keithley 617 Programmable Electrometer. Narrow, 1 cm-long, electric contacts from silver paste were deposited on two opposite edges of the implanted surface of the PMMA samples, as schematically shown in Fig. 1.



^{*} Paper presented at the International School on Condensed Matter Physics, Varna, Bulgaria, September 2008

Fig. 1. Schematic cross-section of the spatial structure of Si⁺-implanted PMMA with source (S), drain (D) and gate (G) electrodes: (1) porous low-conductive ion-modified layer; (2) conductive ion-implanted layer; (3) pristine PMMA.

Since the width of the contacts was 1 mm, they completely covered the two layers formed by the ion implantation: the low-conductivity porous layer (1) and the buried conductive ion-implanted layer (2). Due to the spatial distribution (depth profile) of the ion-implanted material, there was no sharp boundary between the two layers. A third (gate) electrode (copper, 3 mm width, 1 cm length) was placed on the implanted PMMA surface between the two side-contacts (the drain and the source). In this arrangement, the in-plane dimensions of the conducting channel were $W \times L = 10 \text{ mm} \times 3 \text{ mm}$, i.e. the width-to-length ratio for the channel situated within the conductive layer (2) was $W/L \approx 3$.

3. Results and discussion

Our previous study on the same Si⁺-implanted PMMA samples [8] revealed the formation of an in-depth carbonaceous layer. The main type of bonding in the ion-implanted layer is sp^2 , with carbon atoms organized in rings in nanometer-sized domains (1 - 3 nm). As is known, the ion implantation of hydro-carbon polymers leads to the formation of conjugated double C=C bonds and C-clusters, which define the electronic and thereby the electrical properties of the material [1,2,9].

The implantation of silicon ions at an energy of 50 keV into PMMA ($C_5H_8O_2$, density 1.19 g/cm³) was simulated by Monte Carlo calculations [10]. The electrically active layer in ion-implanted polymers is usually related to the mean range of ions, about 100 nm in our case. To a good approximation, this value can be accepted as the thickness of the Si⁺-modified subsurface region in the host polymer PMMA.



Fig. 2. Output characteristics $I_d(V_d)$ of Si^+ -implanted PMMA (fluence $3.2 \times 10^{15} Si^+/cm^2$) with the electrode configuration shown in Fig. 1.

The properties of the nano-scaled subsurface layer created by ion implantation make feasible a field effect in the formed structure, with the electrode configuration shown in Fig. 1. The field effect found in the Si⁺-implanted PMMA structure can be seen in the corresponding output characteristics (the drain current I_d versus drain voltage V_d for several values of the gate voltage V_g (Fig. 2). These characteristics are similar to those of an n-channel field-effect transistor (FET) [11] in the electron accumulation mode with an applied positive gate voltage. The lack of saturation in the $I_d(V_d)$ plots can be ascribed to both the high carrier density due to the electrons induced by the gate voltage V_g and the contribution of the electrons associated with the intrinsic bulk current.

The increase in I_d with increasing V_g (Fig. 2) is indicative of field effect enhancement. Both the spatial characteristics and electrical properties of the sandwich structure of the type dielectric/semiconductor/insulator, created in the host polymer, are responsible for the field effect and transconductive properties of the Si⁺-implanted layer (2) (Fig. 1) formed in PMMA. Thus, the structure of Si⁺-implanted PMMA with an appropriate electrode configuration enables the control of the channel current by the potential difference and resistance, upon applying an external electric field (gate voltage).

The transfer characteristics $I_d(V_g)$ of the sample implanted at a fluence of $3.2 \times 10^{15} \text{ Si}^+/\text{cm}^2$ is shown in Fig. 3. In contrast to the transfer characteristics typical for conventional organic FETs with a good performance [12], as well as for good-performance organic field-effect memory devices, no clearly defined threshold for V_g takes place for the Si⁺-implanted PMMA material.



Fig. 3. Transfer characteristics $I_d(V_g)$ of the same Si^+ implanted PMMA structure as in Fig. 2.

From the transfer characteristics $I_d(V_g)$, one can obtain the transconductance of the channel, calculated from the slope $(\partial I_d / \partial V_g)$ [11,12] at a constant drain voltage, e.g. $V_d = 20$ V. Relevant to the examined series of Si⁺-implanted PMMA samples, the corresponding dependence on the ion fluence is shown in Fig. 4. This dependence is closely related to that of the direct-current conductivity, measured for the same samples as a function of the ion fluence [13].



Fig. 4. The channel transconductance in Si⁺-implanted PMMA samples, versus the ion fluence.

As is known, the electrical conductivity of ionimplanted polymers originates in the π -electrons in the conjugated double C=C bonds and is controlled by an electron hopping mechanism between the conducting Cclusters [1,2,9]. Such a mechanism has been established for PMMA subjected to low-energy ion implantation [7]. Since both the density of the delocalized π -electrons and the size of the C-clusters increase with the implantation fluence [1–3], the conductivity of Si⁺-implanted PMMA also increases, in accordance with the common trend known for ion-implanted hydrocarbon polymers [1,3,5]. A number of factors, including Si-related effects, on the conductivity of Si⁺-implanted PMMA, play a role in the saturation and the decrease observed for the transconductance at higher fluence levels (Fig. 4). In view of the implantation conditions, an effect of silicon on the transconductance of Si⁺-implanted PMMA is not excluded at fluences above 10^{16} si^+/cm^2 [14], although the Si concentration in the electrically-active subsurface layer is small (< 1 at. %).

The possibility to form, by an ion-beam implantation technique, a thin semiconductive buried layer with a controlled degree of modification should allow one to choose implantation conditions that produce a subsurface layer with properties tuned to match the field effect in the formed structure. We conducted such experiments in Si⁺-implanted PMMA samples. We found a well-pronounced FET-like operation with an enhancement mode, in the classical sense, only for the sample implanted to a fluence of $3.2 \times 10^{15} \text{ Si}^+/\text{cm}^2$. Obviously, the implantation conditions (ion energy and fluence) are very important for

the formation of a field-effect structure in Si^+ -implanted PMMA. The implantation regime defines the nanostructure and electronic properties of the formed organic material, the depth profile of the layer (2) (i.e. the thickness of both nano-sized layers (1) and (2), Fig. 1), plus the dielectric and conductive properties of the material in these layers, as well as the organic unimplanted/implanted interface between them. Thus, ion implantation produces an electrically active subsurface layer, with characteristics suitable for operation in a FET-like regime, only if occurs for an appropriate matching of all necessary factors.

4. Conclusions

A field-effect transconductance depending on the ionimplantation conditions was observed in PMMA implanted with silicon ions at an energy of 50 keV. Such an implantation-induced transconductance could be applied in highly integrated plastic electronics, e.g. for transistor-like active elements. Generally, the channel current and the functionality of such elements could be enhanced by device architecture optimization. Since the key features of PMMA subjected to ion implantation are the bio-compatibility and bio-sensitivity, electronic devices made from Si⁺-implanted PMMA may be attractive for electrical bio-sensing and bio-medical systems.

Acknowledgements

We acknowledge financial support by the Swiss National Science Foundation (Project No. IB7420-110981/1 "Southern NanoEngineering Network", SONNET). This work was partially supported by the PAI-RILA 2/5 French-Bulgarian bilateral project, the National Science Fund of Bulgaria (contract IRNI 21/2007) and Sofia University (contract UFNI 075/2008).

References

- D. V. Sviridov, V. B. Odzhaev, I. P. Kozlov, in Electrical and Optical Polymer Systems – Fundamentals, Methods and Applications, eds. D. L. Wise, G. E. Wnek, D. J. Trantolo, T. M. Cooper, J. D. Gresser, Marcel Dekker, New York (1998), p. 387.
- [2] D. Fink, Fundamentals of Ion Irradiated Polymers, Springer-Verlag, Berlin (2004).
- [3] P. Mazzoldi, G. W. Arnold, Ion beam modification of insulators, Elsevier, Amsterdam (1987).
- [4] D. Fink, Transport Processes in Ion-Irradiated Polymers, Springer-Verlag, Berlin (2004).
- [5] R. E. Giedd, M. G. Moss, J. Kaufmann, Y. Q. Wang, in Electrical and Optical Polymer Systems – Fundamentals, Methods and Applications, eds. D. L. Wise, G. E. Wnek, D. J. Trantolo, T. M. Cooper, J. D. Gresser, Marcel Dekker, New York (1998), p. 1011.

- [6] V. N. Popok, I. A. Karpovich, V. B. Odzhaev, D. V. Sviridov, Nucl. Instrum. Meth. B 148, 1106 (1999).
- [7] Y. Koval, M. V. Fistul, P. Müller, J. Vac. Sci. Technol. A 23, 1375 (2005).
- [8] G. B. Hadjichristov, V. Ivanov, E. Faulques, Appl. Surf. Sci. 254, 4820 (2008).
- [9] S. Bhattacharyya, S.V. Subramanyam, in Electrical and Optical Polymer Systems – Fundamentals, Methods and Applications, eds. D. L. Wise, G. E. Wnek, D. J. Trantolo, T. M. Cooper, J. D. Gresser, Marcel Dekker, New York (1998), p. 201.
- [10] J. F. Ziegler, J. P. Biersack, U. Littmark, The Stopping and Range of Ions in Solids, Pergamon, New York (1985).

- [11] S. M. Sze, Physics of Semiconductor Devices, Wiley, New York (1981).
- [12] C. D. Dimitrakopoulos, D. J. Mascaro, IBM J. Res. Dev. 45, 11 (2001).
- [13] G. B. Hadjichristov, V. K. Gueorguiev, Tz. E. Ivanov, Y. G. Marinov, V. G. Ivanov, E. Faulques, Org. Electron., DOI:10.1016/j. orgel.2008.08.003 (2008).
- [14] A. Moliton, C. Moreau, J. P. Moliton, Nucl. Instrum. Meth. B 80/81, 1028 (1993).

^{*}Corresponding author: georgibh@issp.bas.bg