Electrical properties of PMMA ion-implanted with low-energy Si⁺ beam

G B Hadjichristov¹, V K Gueorguiev¹, Tz E Ivanov¹, Y G Marinov¹, V G Ivanov² and E Faulques³

¹ Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria
² Sofia University, Faculty of Physics, 5 James Bourchier Blvd., 1164 Sofia, Bulgaria
³ Institut des Matériaux Jean Rouxel, UMR6502 CNRS, Nantes Atlantic Universities, 2 rue de la Houssiniere, 44 322 Nantes, France

Abstract. The electrical properties of polymethylmethacrylate (PMMA) after implantation with silicon ions accelerated to an energy of 50 keV are studied under DC electric bias field. The electrical response of the formed material is examined as a function of Si⁺ fluence in the range 10¹⁴ – 10¹⁷ cm⁻². The carbonaceous subsurface region of the Si⁺-implanted PMMA displays a significant DC conductivity and a sizable field effect that can be used for electronic applications.

1. Introduction

In the last years there has been a growing interest concerning the ion-implanted polymers and their application in electronics, biotechnology and medicine [1–3]. Especially, the controllable modification of the electrical conductivity and electrical properties of the ion-implanted polymers are of great importance for their electronic applications.

As known, the ion implantation of hydro-carbon polymers leads to a formation of conjugated double C=C bonds organized in a nanoclustered carbonaceous conductive material [1–3]. The electrical conductivity of the ion-implanted polymers originates in the π-electrons in the conjugated double C=C bonds and is controlled by the electron hopping mechanism between the conducting C-clusters [1–3].

Poly-(methyl methacrylate) (PMMA) is known to be highly sensitive to accelerated ions [4, 5] and is thereby used in ion-beam lithography and in UV photolithography. For example, masking media (UV-opaque PMMA films) have been produced by implantation of PMMA with 150 – 200 keV silicon ions [6]. Also, very low energy (250 – 1250 eV) Ar⁺ irradiation has shown an enhancement of the electrical conductivity of PMMA [7].

Here we report results on the electrical properties of PMMA ion-implanted with a 50 keV silicon ion beam at a fluence in the range from 10¹⁴ to 10¹⁷ ions/cm². The electrical response of this material, as well as of the corresponding filed-effect structure, is studied under a direct current (DC) electric bias field and is related to the structure formed in the polymer PMMA upon Si⁺ implantation.

4 To whom any correspondence should be addressed. E-mail: georgibhi@issp.bas.bg
According to data from [4, 8], a significant contribution of nuclear interactions and of collision damage at the end of the ion range and direct displacement of polymer atoms can be expected under these implantation conditions.

2. Experimental
Six identical PMMA samples of 1×1 cm²-size with a thickness of 5 mm were implanted with Si⁺ ions at an energy of 50 keV and for various fluences ranging from \(3.2\times10^{14}\) cm\(^{-2}\) to \(10^{17}\) cm\(^{-2}\). The experimental details have been described elsewhere [9]. The thickness of the ion-implanted subsurface region was roughly estimated using Monte Carlo calculations [8]. Usually related to the mean range of ions in polymers, a value of ~100 nm can be considered as the thickness of the electrically active layer in Si⁺-implanted PMMA. This value was used for the conductivity calculations.

Narrow, 1 cm-long electric contacts from silver paste were deposited at two opposite edges of the implanted surface of the PMMA samples, as schematically shown in figure 1. The electrical properties of Si⁺-implanted PMMA were studied at room temperature. Direct current (DC) measurements were conducted by Keithley 617 Programmable Electrometer controlled by computer using IEEE-488 data interface.

In order to probe the field-effect transistor, (FET)-like properties of the Si⁺-implanted PMMA structure, a third (gate) electrode (copper, 3 mm width, 1 cm length) was placed on the implanted PMMA surface between both side-contacts (the drain and the source) (figure 1).

3. Results and discussion
Si⁺-implanted PMMA studied herein possesses electro-transport properties characteristic of the ion-implanted hydro-carbon polymers [1–3]. Electron hopping mechanism of conductivity has been established for PMMA subjected to low-energy ion implantation [7]. The linear current-voltage plots (figure 2) for resistive Si⁺-implanted PMMA samples (no gate electrode) reveal ohmic conductance and are consistent with the hopping model [10].

![Figure 1](image1.png)

**Figure 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.

![Figure 2](image2.png)

**Figure 2.** (a) DC current-voltage characteristics of Si⁺-implanted PMMA structure shown in figure 1 (without gate); (b) the same, but in a logarithmic scale. The labels from 1 to 6 refer to the fluences as: \(3.2\times10^{14}\), \(1\times10^{15}\), \(3.2\times10^{15}\), \(1\times10^{16}\), \(3.2\times10^{16}\) and \(1\times10^{17}\) [Si⁺/cm²].
The DC conductivity, $\sigma$, of the samples as a function of the Si$^+$ fluence is presented in figure 3. The ion-induced improvement of $\sigma$ is consistent with room-temperature data reported for other C-H containing polymers implanted with ions at similar ion energy and fluence levels [11,12]. A two-decade increase in fluence results in a six-decade increase of $\sigma$ and at $3.2 \times 10^{16}$ Si$^+$/cm$^2$ $\sigma$ attains values almost eleven orders of magnitude higher than that of unimplanted PMMA ($\sigma$$_{PMMA}$ $\sim 10^{-15}$ S/cm, typical for the good electrical insulators). Nevertheless, the DC conductivity of Si$^+$-implanted PMMA studied herein is still smaller than that (up to $10^2$ S/cm) measured in amorphous carbon [13]. Also, the implantation effect is less compared to the conductivity enhancement in polymers irradiated with MeV accelerated ions [14,15].

As evidenced in our previous study [9], a nanoclustered hydrogenated amorphous carbon structure is formed in Si$^+$-implanted PMMA samples studied herein. The size of the $\pi$-bonded C-clusters of fused sixfold rings is closely related to the energy band gap which controls the electrical conductivity of this material – the band gap varies roughly inversely with the cluster size [16]. The altering of the spatial distribution (depth profile) of the layer created within PMMA by Si$^+$ ion implantation beneath the polymer surface plays also a significant role. Most likely, with increasing ion fluence the depth profile of the implantation-modified layer is moved toward the surface. Thus, by Si$^+$-implantation one can adjust the spatial characteristics and electrical properties of the ion-modified subsurface region in the polymer PMMA, similarly to the well known tailoring of the refractive index of ion-modified PMMA [17].

![Figure 3](image3.png)

**Figure 3.** The DC conductivity of Si$^+$-implanted PMMA samples versus the ion fluence.

![Figure 4](image4.png)

**Figure 4.** Output characteristics of Si$^+$-implanted PMMA structure (fluence $3.2 \times 10^{15}$ Si$^+$/cm$^2$).

The possibility to form by 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 a field effect in the formed structure. In addition to the significant enhancement of the DC conductivity with the implantation fluence, we have found a sizable field effect in Si$^+$-implanted PMMA structure. Figure 4 represents the output characteristics (the drain current, $I_d$, versus the drain voltage, $V_d$, for several values of the gate voltage, $V_g$) of Si$^+$-implanted PMMA sample with the electrode configuration shown in figure 1. The results imply a typical N-channel enhancement transistor behaviour and an electron accumulation mode achieved with a positive $V_g$. The lack of saturation in the $I_d(V_d)$ plot can be ascribed to the electrons associated with the intrinsic bulk current through the gate and takes also place by negative biasing (figure 4).

Generally, $I_d$ could be enhanced by the optimization of the device architecture. However, the most important is that both the spatial characteristics and the electrical properties of the sandwich structure of the type dielectric/semiconductor/insulator created within the polymer allow the field-effect transistor (FET)-like operation. Thus, the Si$^+$-implanted PMMA structure with an appropriate electrode configuration enables the control of the channel current by a potential difference and a resistance upon applying an external electric field (gate voltage). Since the implantation conditions (ion energy and fluence) determine the spatial structure, as well as the nano-scale structure, and thereby the electronic
and electrical properties of the formed material, they are very important for the formation of a field-effect structure and define the operation in a FET-like regime upon appropriate conditions.

4. Conclusions

A significant enhancement of the conductivity with the implantation fluence, as well as a field effect depending on the ion-implantation conditions, were observed in Si⁺-implanted PMMA. The implantation fluence provides the tunability of the implantation-induced electrical conductivity of the formed organic material. These properties show that the Si⁺-implanted PMMA appears to be a promising material for highly integrated organic electronic applications, e.g. transistor-like active elements. The bio-compatibility and bio-sensitivity of PMMA subjected to ion implantation make such devices very attractive for electrical bio-sensing and bio-medical systems.

Acknowledgements

This work was supported by the Swiss National Science Foundation (Project No. IB7420-110981/1 "Southern NanoEngineering Network", SONNET), National Science Fund of Bulgaria (contract IRNI 21/2007) and Sofia University (contract UFNI 075/2008).

References

[1] Fink D 2004 Fundamentals of Ion Irradiated Polymers (Berlin: Springer Verlag)
[2] Fink D 2004 Transport Processes in Ion-Irradiated Polymers (Berlin: Springer Verlag)
[3] Sviridov D V, Odzhaev V B and Kozlov I P 1998 Electrical and Optical Polymer Systems – Fundamentals, Methods and Applications, ed D L Wise, G E Wnek, D J Trantolo, T M Cooper and J D Gresser (New York: Marcel Dekker) chapter 11 pp 387–422
[4] Biersack J P and Kallweit R 1990 Nucl. Instrum. Meth. B 46 309
[5] Venkatesan T, Calcagno L, Elman B S and Foti G 1987 Ion Beam Modification of Insulators, ed P. Mazzoldi and G.W. Arnold (Amsterdam: Elsevier) pp 301–79
[6] Kenty J L, Puzio L C and Schauerte F J 1983 J. Vacuum Sci. Techn. B: Microelectron. Nanometer Structures 1 1211
[7] Koval Y, Fistul M V and Müller P 2005 J. Vac. Sci. Technol. A 23 1375
[8] Ziegler J F, Biersack J P and Litmark U 1985 The Stopping and Range of Ions in Solids (New York: Pergamon Press)
[9] Hadjichristov G B, Ivanov V and Faulques E 2008 Appl. Surf. Sci. 254 4820
[10] Hesto P 1986 Instabilities in Silicon Devices vol 1, ed G. Barbottin and A. Vapaille (Amsterdam: North Holland) chapter 5 p 263
[11] Bedell C J, Sofield C J, Bridwell L B and Brown I M 1990 J. Appl. Phys. 67 1736
[12] Wang Y Q, Giedd R E, Moss M G and Kaufmann J 1997 Nucl. Instrum. Meth. B 127–128 710
[13] Hauser J J 1975 Solid State Commun. 17 1577
[14] Venkatesan T, Forrest S R, Kaplan M L, Murray C A, Schmidt P H and Wilkens B J 1983 J. Appl. Phys. 54 3150
[15] Kaplan M L, Forrest S R, Schmidt P H and Venkatesan T 1984 J. Appl. Phys. 55 732
[16] Robertson J and O’Reilly E P 1987 Phys. Rev. B 35 2946
[17] Biersack J P and Kallweit R 1990 Nucl. Instrum. Meth. B 46 309