

Fabrication and preliminary characterization of infrared photodetectors based on graphene

R. Mroczyński^{*a}, N. Kwietniewski^a, J. Piotrowski^a, J. Judek^b, M. Zdrojek^b, P. Szczepański^a

^aInstitute of Microelectronics and Optoelectronics, Warsaw University of Technology,
Koszykowa 75, 00-662 Warsaw, Poland

^bFaculty of Physics, Warsaw University of Technology, Koszykowa 75, 00-662 Warsaw, Poland

ABSTRACT

In this work, we report the technology of infrared photodetectors based on graphene layers (GLs). In the course of this work the new set of photolithography masks was especially designed to fabricate test structures. The new masks-set contains a matrix of different types of photodetector structures with varied active area dimensions, as well as additional module for characterization of electro-physical parameters of graphene and graphene-based devices. After careful optimization of consecutive technological steps, test structures were fabricated. First results of electrical characterization of obtained graphene-based photodetectors demonstrated that the developed technology was successful, however, further detailed optical characterization towards sensing parameters and potential applications in infrared detectors is necessary.

Keywords: graphene, infrared photodetectors, structural and electrical characterization

1. INTRODUCTION

It is commonly observable that nowadays „state-of-the-art” infrared photodetectors are based on narrow-band-gap semiconductors, i.e., HgCdTe or InSb^{1,2}. However, after discovery of graphene in 2004 – a monolayer to few layers of sp² bonded carbon in a honeycomb lattice – the extensive studies of its potential application have been performed³. This is due to the fact that graphene is characterized by very high intrinsic carrier mobility (in theory even 200 000 cm²/Vs) with a good mechanical and thermodynamic stability^{4,5}. Graphene seems also to be a good candidate for potential application in a variety of optoelectronic and photonic devices. The graphene-based photodetectors, due to its unique band structure, can exhibit relatively ultra-wide range of operational wavelengths, with high operating speed⁶.

In this work we report the technology of infrared (IR) photodetectors based on graphene monolayers (GLs). In the course of this work the new set of photolithography masks was especially designed to fabricate test structures. After optimization of consecutive technological steps, test structures were fabricated. The obtained photodetectors based on graphene were preliminary characterized by means of electrical (current-voltage characteristics – I-V), and optical methods. Presented characteristics of particular structures demonstrated repeatable character and clearly visible optical response to the induced radiation.

2. EXPERIMENTAL

In the course of this work 2 in. boron-doped (1-10Ωcm) silicon (Si) substrates with the crystalline orientation <100> have been used. Semiconductor substrates before processing steps were cleaned by means of Radio Corporation of America (RCA) procedure. Then, the silicon substrates were thermally oxidized in order to form 30nm SiO₂ gate dielectric film. The processing steps for the fabrication of photodetector structures demands five-level photolithography with the implementation of, simultaneously, classical positive photolithography and lift-off process, especially in the case of conductive materials deposition. The conductive materials used as the photodetector Source/Drain (S/D) regions, i.e., titanium (Ti), palladium (Pd), aluminum (Al), and gold (Au), were deposited by means of thermal and e-gun vacuum evaporation (Balzers reactor). In the course of this work, graphene monolayers were grown on copper foil by means of Chemical Vapor Deposition (CVD) process, and then, transferred onto silicon substrates by means of electrochemical delamination procedure described elsewhere^{7,8}. Depending on the particular step of fabrication process, standard positive and negative photolithography in UV light (i.e., ~400nm) have been adopted, with the use of maP-1215, and maN-1420 photoresist (made by Microresist Technology), respectively. The full procedure of photodetector test structures is

described below in paragraph 3.2. The electrical measurements of fabricated detectors were performed with the Keithley 4200 semiconductor characterization system equipped with SUSS PM-8 probe station allowing characterization also at elevated temperatures. For the optical characterization of the obtained conductive and dielectric layers spectroscopic ellipsometer Horiba Jobin-Yvon – UVISEL, allowing measurements in the wide range of wavelength (190 – 850nm) was used.

3. RESULTS & DISCUSSION

3.1 Design of photolithography masks-set

For the purpose of the fabrication of infrared photodetectors based on GLs, there was a need for the concept of new photolithography masks-set compatible with the equipment available at the technological laboratory (clean-room) located at Institute of Microelectronics and Optoelectronics of Warsaw University of Technology (IMiO WUT). On the basis of literature and our experience from previous works we have decided to choose three different types of photodetector structures, namely: the p-i-n diode structure, and photo-transistors with single-, or double gate structure. Schematic cross-sections of mentioned above structures were depicted in Fig. 1. The working principles of these structures are based on the separation of charge carriers due to the induced infrared radiation. An asymmetric conductive materials scheme for S/D regions was adopted to break the symmetry of internal electric-field profile in conventional graphene field-effect structure, and thus, the electron-hole pairs generation.

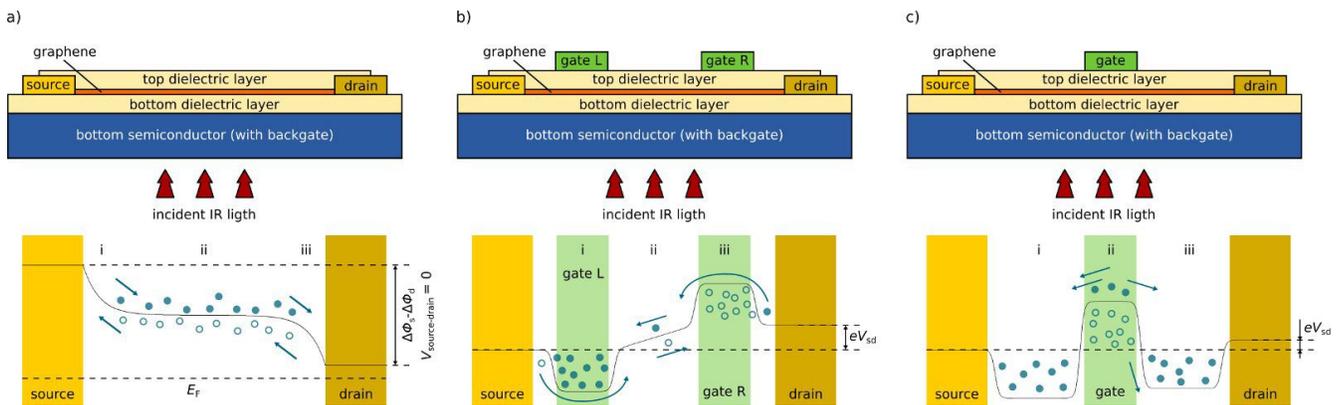


Figure 1. Schematic cross-sections and idea of photodetector based on graphene monolayer with asymmetric S/D regions; the p-i-n diode structure (a), phototransistor with double- (b), and single-gate (c); following notations have been used: $\Delta\Phi_S - \Delta\Phi_D$ – the difference between work function values of particular conductive material, $V_{source-drain}$ – source to drain voltage value, E_F – Fermi level energy, eV_{sd} – the potential corresponding to external polarization.

Moreover, we have selected different types of test structures for the additional characterization of electro-physical properties of graphene, as well as graphene-based structures, i.e., TLM, CTLM lines, and Van der Pauw structures for the contact resistance and mobility investigations. The top-view of designed masks-set for test structures fabrication, as well as particular module of the masks-set with elementary photodetector scheme are presented in Fig. 2.

The designed masks-set covers five photolithography levels, and the matrix of photodetector structures with different active area dimensions. In addition, the design was divided into two different shape of conductive paths, namely ‘fingers’ and ‘meanders’, which may results in difference in photoresponse of final detector structures. The critical dimension (CD) of designed photolithography masks is 2 μm . The fabrication procedure requires standard optical lithography in the UV (i.e., the wavelength $\sim 400\text{nm}$). The design is very universal, since the same masks-set can be used for the fabrication of test structures on different semiconductor substrates. As a consequence, the optimization of the photodetectors technology can be done on typical substrates (e.g., silicon), while the fabrication of final structures can be performed on more expensive and more suitable semiconductors for detector applications, e.g., gallium arsenide (GaAs). Such a concept allows also for more effective use of financial resources in the course of experimental studies.

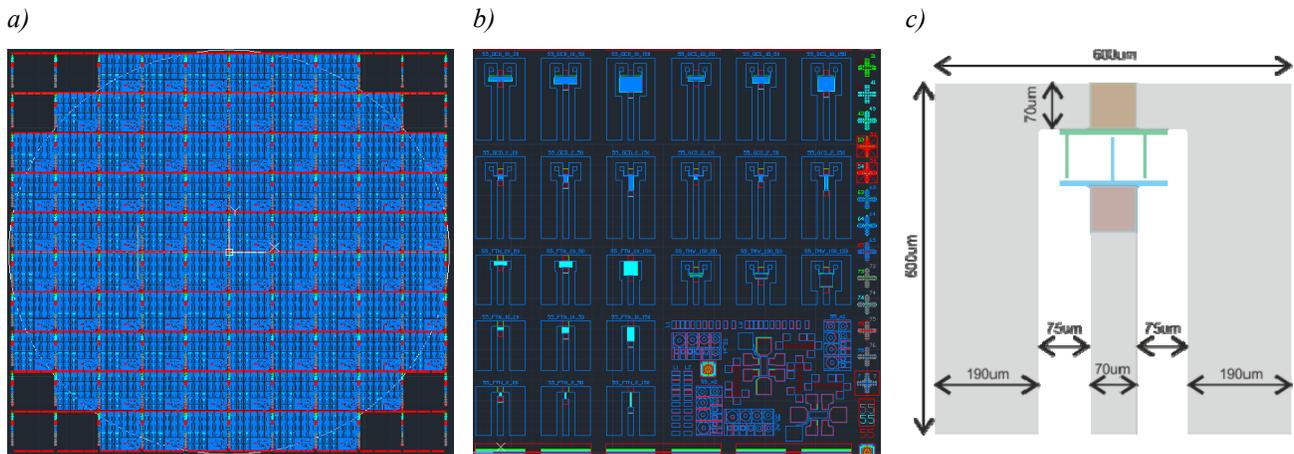


Figure 2. Top-view of designed topography of photodetectors test structures (a); particular module with detectors matrix, as well as additional test structures for graphene characterization (b) with elementary photodetector schematic (c).

3.2 Technology of test structures fabrication

For the purposes of technological experiments performed in the course of this work 2-in. boron-doped (1-10 Ωcm) silicon (Si) substrates with the crystalline orientation $\langle 100 \rangle$ have been used. After semiconductor substrates cleaning by means of Radio Corporation of America (RCA) method there was performed a thermal oxidation in pure oxygen in order to fabricate 30nm of silicon dioxide (SiO_2) film as the gate dielectric. The first step was the graphene transfer from the Cu foil. For this purpose the electro-chemical delamination method was modified. Such a method results in a significant increase of the process kinetics and a higher graphene purity compared to the typically used chemical methods. Moreover, there was developed a method for GLs cleaning after the PMMA etching. There were performed experiments with the elevated temperature annealing of graphene monolayers in controllable atmosphere (i.e., in argon). Raman spectroscopy has proved the very high quality of transferred graphene monolayers.

The next step was the etching of graphene for the photodetector’s active area formation. This process demands a classical photolithography step with positive-tone photoresist. The active area formation was done by means of Reactive Ion Etching (RIE) process in oxygen (O_2) based plasma. The critical issue in this step was the selective removal of photoresist after the RIE process. The comparison of surface state before and after the active graphene area formation was depicted in Fig. 3.

The next processing steps were the most critical from the point of view of photodetector quality since there was performed the deposition of conductive materials directly onto GLs, and thus, the keeping of the high quality of active areas was of the most importance. Both S/D regions have been fabricated by means of lift-off process. In the latter method, in contrary to standard photolithography procedure, the photoresist is spinned-off and developed before the technological layer formation. After the layer is deposited, unnecessary areas of photoresist are removed in a solution selective to remaining technological layers on the substrate, i.e., the most commonly in an acetone batch at elevated temperature.

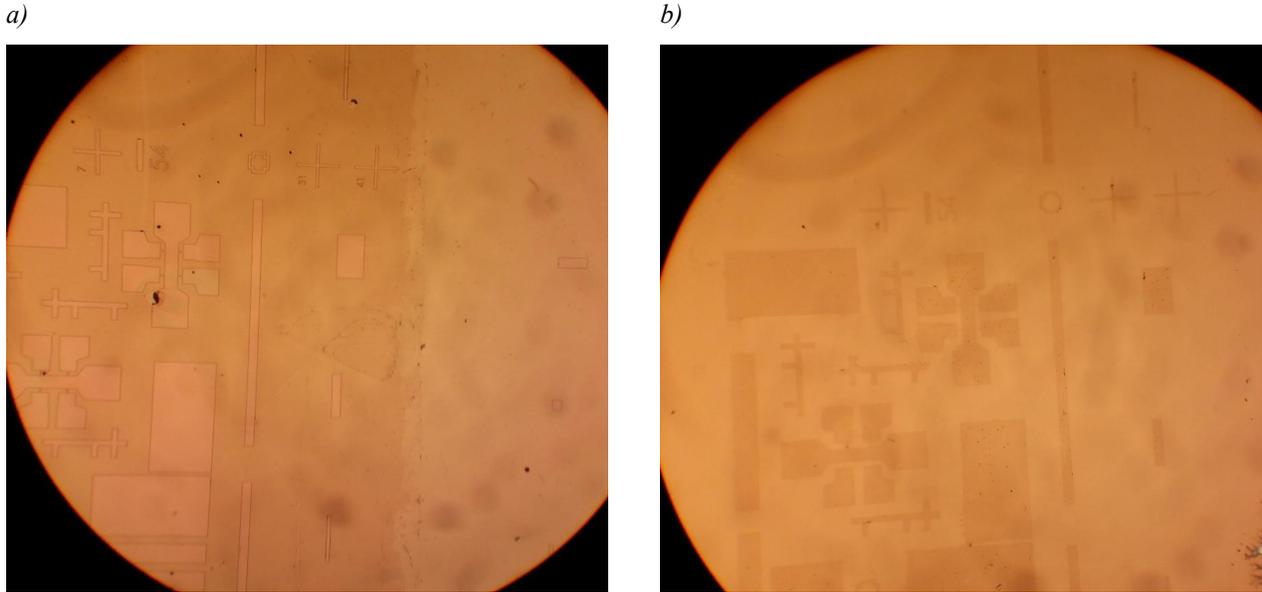


Figure 3. Graphene patterning before (a), and after (b) RIE process followed by photoresist removal; dark areas visible in the picture (b) represent graphene monolayers.

After photoresist is developed the conductive layer can be deposited. In the course of this study both conductive films were deposited by means of e-gun thermal evaporation. It has allowed a freedom in the choice of type of metallization used for both detector contact areas. We have investigated several pairs of materials with significantly different work function values, however, the final test structures are characterized by S/D regions formed with the use of Ti/Au, and Pd/Au contacts. Such a pair of conductive materials seems to be the most attractive from the point of view of field effect intensity in graphene active area of particular infrared photodetector. This is due to the fact that such a pair of material can be characterized by significantly different work function values, i.e., 4.3eV versus 5.3eV for titanium, and palladium, respectively. Moreover, the technology of these materials is easily accessible with the research infrastructure located in IMiO PW technological laboratory. In Fig. 4 there were depicted consecutive steps of conductive pads formation.

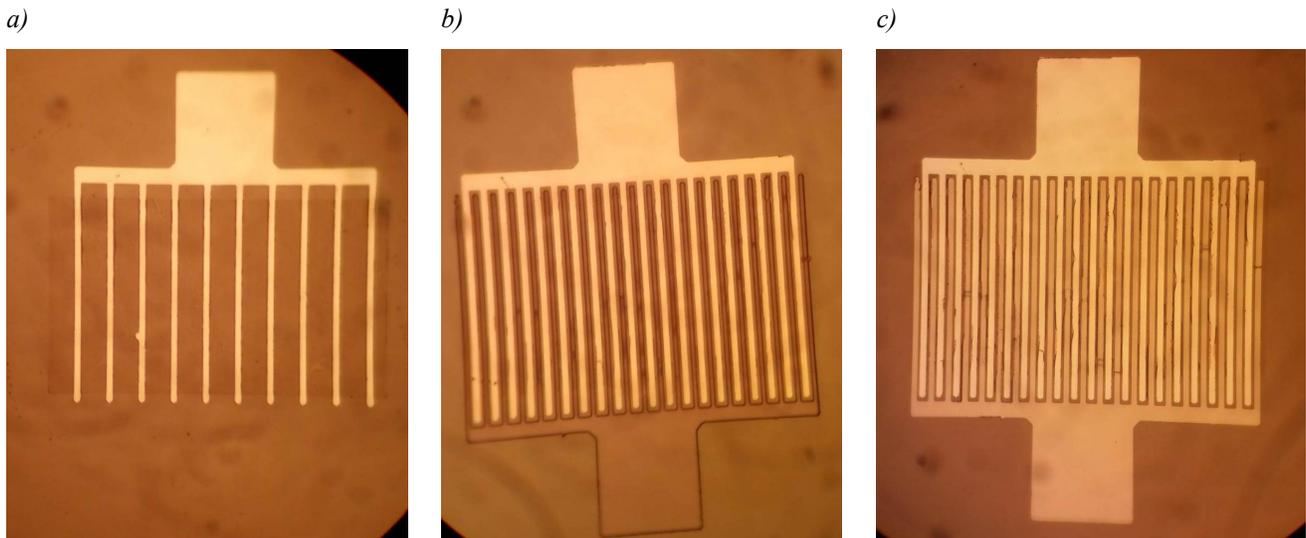


Figure 4. Consecutive steps of conductive pads formation by the lift-off process to photodetector active area; metal 1 deposition (Ti/Au) and lift-off (a), negative-tone photoresist development (b), and metal 2 (Pd/Au) deposition and lift-off (c).

In the next step the photodetector structures were passivated by means of thin dielectric material deposition (i.e., ~50nm). In this step we have investigated two types of dielectric films, i.e., aluminum oxide (AlO_x) and silicon nitride (SiN_x) fabricated by means of reactive magnetron sputtering process and Plasma-Enhanced Chemical Vapor Deposition (PECVD), respectively^{9,10}. Unfortunately, due to the oxygen radicals presence in the reactive chamber there was not possible to fabricate neither aluminum oxide, nor any other oxide materials by means of sputtering process directly on GLs. Although in the PlasmaLab System 400, which has been used as a tool for the sputtering process, the plasma region is separated of the table with samples under processing, there was observable the damage and partial etching of graphene. As a result, for the passivation of fabricated devices the PECVD SiN_x layer was used, which deposition occurs due to the reaction of silane (SiH_4) with ammonia (NH_3). Such a deposition hasn't deteriorated the graphene quality.

The passivation of devices was followed by via etching through the passivation layer. For the purpose of via formation, standard wet etching procedure of dielectric passivation layers were used. The last step was the fabrication of co-planar waveguides (CPWs) for high-frequency characterization. For this purpose the aluminum layer deposited by means of thermal evaporation was used, which after the positive photolithography process was etched in batch H_3PO_4 -based solution.

As a consequence, the full processing steps towards infrared photodetectors fabrication are following:

- Semiconductor wafers cleaning by RCA procedure
- SiO_2 gate oxide fabrication by means of thermal dry oxidation
- Graphene transfer
- Photolithography and RIE in O_2 -based plasma
- Metal 1 evaporation and lift-off
- Metal 2 evaporation and lift-off
- Passivation
- Via formation
- Deposition and patterning of CPW lines

3.3 Preliminary characterization of fabricated photodetector structures

First results of electrical characterization of obtained test structures demonstrated that the developed technology was successful, as the electrical characteristics of fabricated structures show typical behavior compared to other works found in the literature¹¹. In the Fig. 1a there is presented the exemplary current-voltage characteristics of fabricated photodetector structures with dimensions of active graphene area $50\mu\text{m} \times 150\mu\text{m}$, while in the Fig. 1b there are presented the I-V characteristics of CTLM structures with varied dimensions in order to evaluate the contact resistance to GLs. Presented results demonstrated that photodetectors were fabricated successfully, since obtained I-V characteristics are in accordance to assumptions. Moreover, the position of Dirac point is very close to 0V value. However, the contact resistance to graphene seems to be much larger (i.e., ~50k Ω) which suggests the presence of imperfections of contact areas to GLs. It has to be underlined that in the course of photodetectors fabrication we have not performed any post-metallization annealing process, which could improve the contact properties to GLs.

At this stage of photodetectors characterization we have performed investigations of photoelectrical response only to visible light. The source of radiation was from the top-side of detector structure, directly on the graphene active area. We have also taken into consideration the first batch of non-passivated test structures.

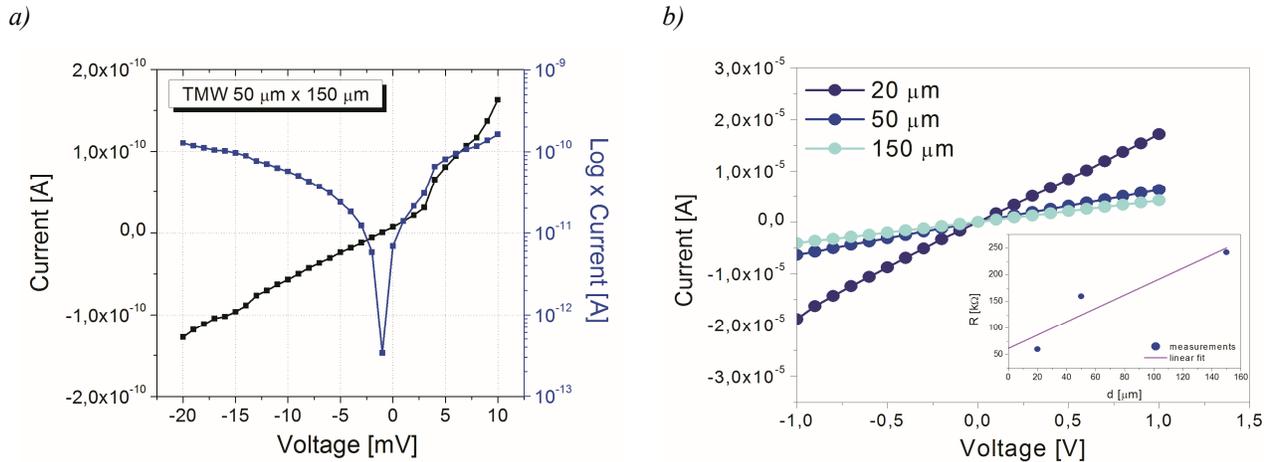


Figure 5. Exemplary I-V characteristics of particular detector (a) and electrical characteristics of photodetectors with varied active area lengths (b); the inset show contact resistance value to GLs measuring by means of CTLM structures.

In Fig. 6 there are presented I-V characteristics of photodetector structure with active area dimensions 150μm x 150μm. It is clearly visible that due to the light absorption there was obtained a varied current-voltage characteristics depending on the light intensity. The fastest photodetector structures investigated at this stage of characterization were characterized by time constant lower than 40ps. However, in order to characterize the full potential of fabricated detector structures, further optical characterization towards sensing parameters and potential high-speed applications is necessary. We plan also to perform electro-optical characterization of passivated structures, as well as provide an additional thermal annealing process of conductive layers into the fabrication procedure of photodetector structures for the decrease the contact resistance.

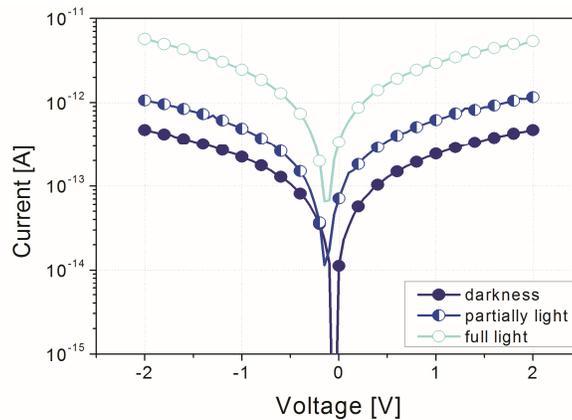


Figure 6. Exemplary photoelectric response of particular test structure.

4. CONCLUSIONS

In this work we report the technology and preliminary results of characterization of infrared photodetectors based on graphene layers. We have designed the new set of photolithography masks in order to fabricate test structures. The consecutive steps towards the fabrication of detector matrix have been designed, performed and optimized. We have investigated different materials for conductive pads, as well as gate dielectric, and passivation layers. The most suitable pair of conductive materials for S/D regions seems to be Ti/Au and Pd/Au films. Preliminary results demonstrated that detectors have been successfully fabricated according to original assumptions. The electrical characteristics have shown that the contact resistance to graphene monolayers is relatively large which could limit the photoelectric response. Moreover, the I-V characteristics of particular structures demonstrated repeatable character, and clearly visible optical response to visible light. However, further advanced and quantitatively optical characterization in terms of infrared

radiation, and high frequency capabilities is needed. Furthermore, the last step of characterization procedures is the photoelectrical measurements of passivated (by means of PECVD silicon nitride layers – SiN_x) photodetector structures.

ACKNOWLEDGMENTS

This work was supported by The National Centre for Research and Development through the project “Photograph – Ultra-fast Photodetector based on Graphene” (GRAF-TECH/NCBR/13/20/2013)

REFERENCES

- [1] Rogalski A., in “Intersubband Infrared Photodetectors”, edited by V. Ryzhii, World Scientific, Singapore, p. 1 (2003).
- [2] Choi K.K., “The Physics of Quantum Well Infrared Photodetectors”, World Scientific, Singapore (1997).
- [3] Xia F. et al., “Photocurrent imaging and efficient photon detection in a graphene transistor”, *Nano Lett.* 9, 1039–1044 (2009).
- [4] Bolotin K.I., Sikes K.J., Jiang Z., Funderberg G., Hone J., Kim P., and Stormer H.L., *Solid State Commun.* 146, 351 (2008).
- [5] Booth T.J., Blake P., Nair R.R., Jiang D., Hill E.W., Bangert U., Bleloch A., Gass M., Novoselov K.S., Katsnelson M. I., and Geim A. K., *Nano Letters* 8, 2442 (2008).
- [6] Mueller T., Xia F., and Avouris P., “Graphene photodetectors for high-speed optical communications”, *Nature Photonics Letters* 4, 297, May (2010).
- [7] Ciuk T., Pasternak I., Krajewska A., Sobieski J., Caban P., Szmids J., and Strupinski W., “Properties of Chemical Vapor Deposition Graphene Transferred by High-Speed Electrochemical Delamination”, *J. Phys. Chem. C*, 117 (40), pp 20833–20837 (2013).
- [8] Wang Y., Zheng Y., Xu X., Dubuisson E., Bao Q., Lu J., and Loh K.P., “Electrochemical Delamination of CVD-Grown Graphene Film: Toward the Recyclable Use of Copper Catalyst”, *ACS Nano* 5 (12), pp 9927–9933 (2011).
- [9] Mroczynski R., Jasiński J., Gottlob H., and Schmidt M., “Double gate dielectric stacks with Gd₂O₃ layer for application in NVSM devices”, *Microelectronic Engineering* 115, pp. 61-65 (2014).
- [10] Krysiński A., Śmietana M., Mroczynski R., Kwietniewski N., Bock J.W., Mikulic P., “Silicon nitride (SiN_x) plasma deposition on optical fiber sensors: coating symmetry perspective”, *Proc. of SPIE* 8902 89021P-1 (2013).
- [11] Damon B. Farmer, Hsin-Ying Chiu, Yu-Ming Lin, Keith A. Jenkins, Fengnian Xia, and Phaedon Avouris, “Utilization of a Buffered Dielectric to Achieve High Field-Effect Carrier Mobility in Graphene Transistors”, *Nano Letters* 9, 12, 4474-4478 (2009).