Form 1

2017 Report Form for Collaboration with Research Center for Biomedical Engineering

Year/month/date	
Number	2015

20 /March/2018

date:

To Chairman, Board of Directors, Research Center for Biomedical Engineering

Applicant

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Report Form for Collaboration Research

Research Theme	Development of Cd(Zn)Te-based X/gamma-ray detectors with high resolution for security and diagnostics instruments
Research Area	1. Biomaterials 2. Bioengineering 3. Functional molecules (4.) Chemistry/Electrical Engineering/Mechanical Engineering/Materials Science
Research Period	From: 01/07/2017 To: 31/03/2018

Applicant Organization			
Name	Department	Title	Role
Volodymyr Gnatyuk	Department of Physics of Defects and Nonequilibrium Processes in Complex Semiconductors, V.E. Lashkaryov Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine	Ph.D., Associate Professor, Senior Scientist	Leader
Sergiy Levytskyi	Department of Detector Physics and Nonequilibrium Processes in Complex Semiconductors, V.E. Lashkaryov Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine, Kyiv, Ukraine	Ph.D., Research Scientist	Participant
Kateryna Zelenska	Faculty of Physics, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine	Ph.D., Engineer	Participant

Collaboration Partners in the Research Center	Toru AOKI, Ph.D., Professor Research Institute of Electronics, Shizuoka University, Japan

Research Results (Including Purpose, Results, Figures, etc.)

1. Introduction

The purpose of the project is the elaboration of methods and technologies of fabrication of uncooled Cd(Zn)Te)-based X/γ-ray detectors with high energy resolution for instruments designed for detection of ionization sources, identification of radioactive contaminations, monitoring of environment and nuclear power plants, formation of images in medicine, customs, industry, cosmic astronomy and other application fields.

The main our ideas in the development of Cd(Zn)Te) semiconductor-based X/γ-ray detectors, which allow us to obtain nuclear radiation sensors with high energy resolution and low leakage current are the application of the advanced methods of surface processing of semiconductor crystals, laser-induced doping:

- Cd(Zn)Te detectors will be developed as M-p-n structured diodes with a built-in shallow and abrupt *p-n* junction formed by laser-induced solid phase doping;
- Cd(Zn)Te detectors will be developed as Schottky diodes using special treatment of the crystal surfaces before electrode deposition to form a high barrier Schottky contact and Ohmic contact.

2. Semiconductor samples for investigation

For fabrication of diode-based X/γ-ray detectors, commercial CdTe single-crystal wafers produced by Acrorad Co., Ltd. by THM we used. Semi-insulating Cl-compensated CdTe semiconductor showed weak *p*-type conduction with the room temperature resistivity ρ = (2-4) × 10^9 Ω·cm that was close to the intrinsic value. Parallelepiped-like (111) oriented CdTe single-crystal samples with the thickness of 0.5 mm and 0.75 mm, and area of 5×5 mm^2 and 10×10 mm^2 were used.

3. Development of CdTe-based diodes with a laser induced p-n junction

Laser-induced solid-phase doping of the CdTe surface region was employed to create a shallow and abrupt built-in *p-n* junction. Three techniques of In doping of a thin CdTe surface layer and formation of In/CdTe/Au diodes with a *p-n* junction under irradiation of CdTe crystals have been developed: (i) liquid-phase doping using a thin (20 ns) In dopant film; (ii) solid-phase doping using a thick (300-600 nm) In dopant film; (iii) space-confined doping by irradiation of the CdTe sample pre-coated with a thick In film from the CdTe side, i.e. directly affecting the CdTe-In interface with YAG:Nd laser pulses (1064 nm) through the CdTe.

Before doping and metal deposition, the CdTe crystals were subjected to the preliminary surface processing for cleaning and removing of a disordered surface layer. Evaporation of an In dopant (electrode) film and then an Au electrode was carried out using the masks for contact deposition in the vacuum system for thermal annealing and electrode deposition. The surface area of the CdTe(111)B face pre-coated with a In dopant film was entirely and uniformly irradiated with single nanosecond laser pulses in different conditions at room temperature.

Fig. 1 shows the procedure (ii) of laser irradiation of the In/CdTe structure thick (400 nm) In dopant film by a nanosecond pulse in water. For the simulation of laser-induced thermal processes, the following three-region structure was considered: environment (water layer with the depth of 3-5 mm) / metal dopant film (In film with the thickness of 400 nm) / semiconductor substrate (CdTe crystal with the thickness of 0.5 mm) (Fig. 1). The corresponding data characterizing thermal and optical properties CdTe and In were taken from the literature. The result of the calculation of the temperature distributions in the structure of water (3-5 mm)/In (400 nm)/CdTe (0.5 mm) under laser radiation is shown in Fig. 2. As seen, the temperature increases with increasing laser pulse energy density, while the shape of the temperature distributions does not change.

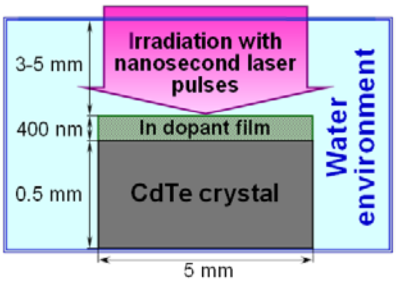
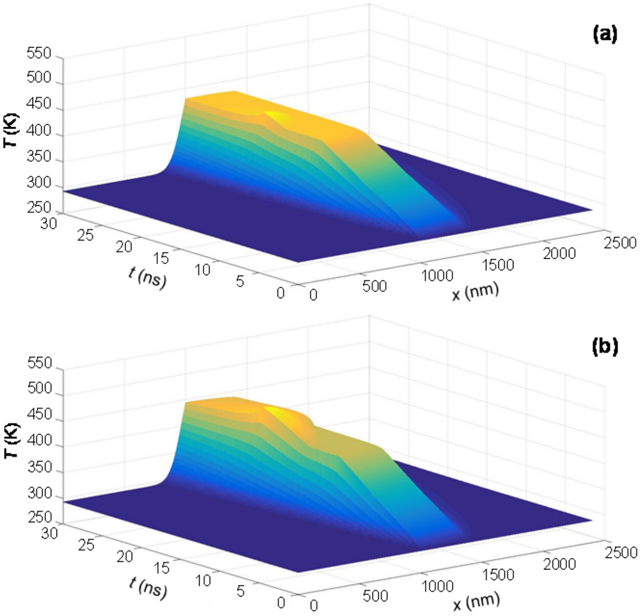


Fig. 1. Schematic illustration of irradiation of the In film - CdTe crystal structure with a single nanosecond laser pulse in water environment.



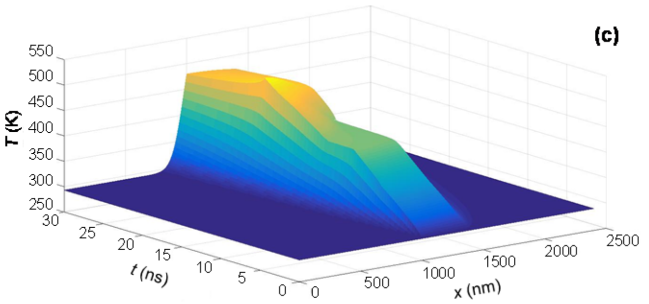


Fig..2. Temperature distribution in the structure of water environment/In film/CdTe crystal under irradiation from the In film side with laser pulse energy density E (J/m^2): 1100 (a), 1300 (b), 1500 (c).

The time (a) and coordinate (b) distribution profiles, depending on the laser energy density, are shown in Fig.3 1.3. According to the calculation results, the temperature increases linearly (not counting the region where the indium melts) that is associated with high laser pulse energy density. The influence of the cooling water layer and cooling due to “evaporation” of In atoms from the dopant film surface is small and it does not have a noticeable effect during the irradiation of this structure by a short laser pulse. In order to finally verify this, the heating flux of transmitted laser radiation into the In film (~10^{12} W/m^2) and fluxes of the cooling indium surface are compared (Fig. 4). As seen, the cooling flows from surfaces film are several orders of magnitude lower than the heating flow of the structure of water (3-5 mm)/In (400 nm)/CdTe (0.5 mm) under pulse laser radiation.

The whole In film (400 nm) was melted at laser pulse energy densities above 1300 J/m^2. The melting time at E = 1500 J/m^2 was about 13 nanoseconds, but the temperature at the boundary of the In film and CdTe substrate did not reach the semiconductor melting threshold (Fig. 1.3(b)). There was no melting of a CdTe layer near the In/CdTe interface (Fig. 5). Thus, mixing of these substances (In and CdTe) in liquid (melted) state could not occur.

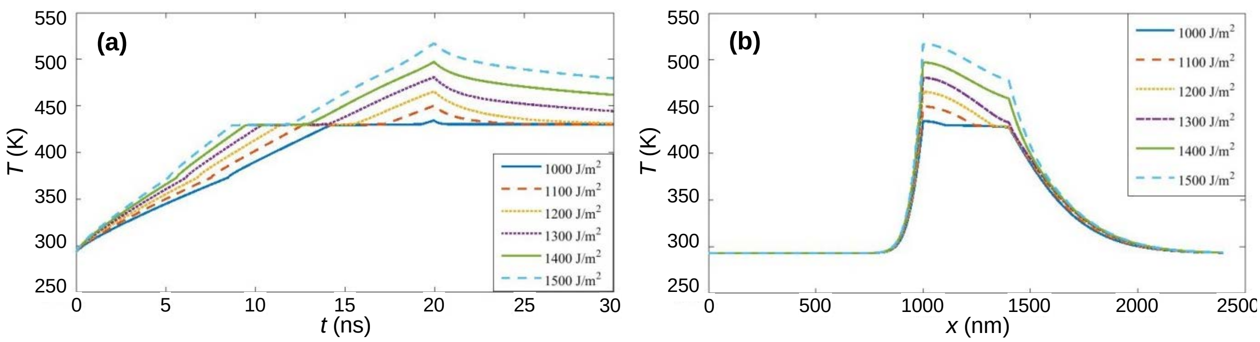


Fig.3. Temperature distribution in the structure of water environment/In film/CdTe crystal under irradiation from the In film side in dependence on laser pulse energy density vs time for the maximum temperature layer (a) and vs coordinate in 20 ns after irradiation starts (b).

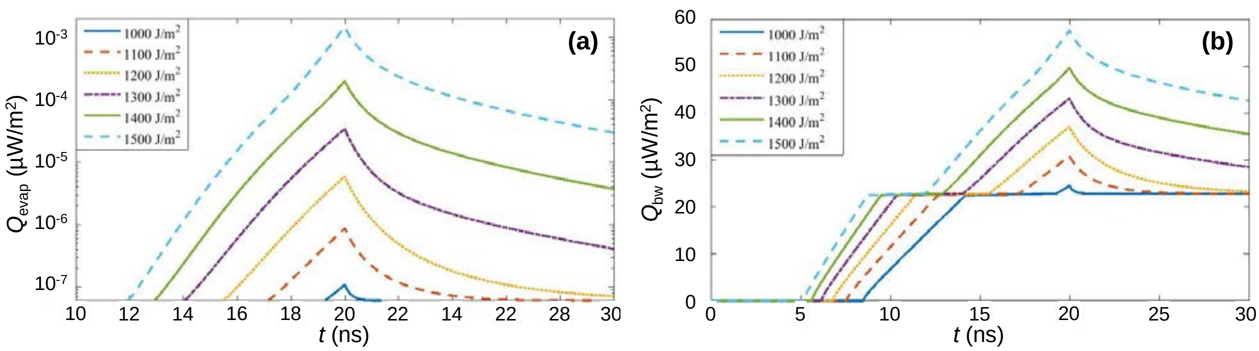


Fig.4. Cooling flows from the In film surface in the structure of water environment/In film/CdTe crystal due to In evaporation (a) and boiling of water near the In film surface (b) in dependence on laser energy density.

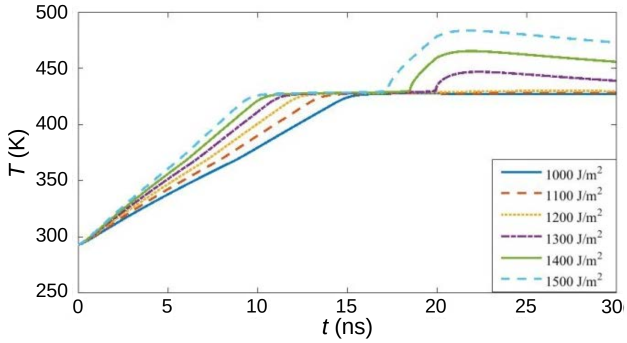


Fig. 5. Temperature distribution at the boundary of the In film/CdTe crystal in the structure of water environment/ In film/CdTe crystal under irradiation from the In film side with different laser pulse energy densities.

Thus, the computational simulation of thermal processes and calculations of the time-dependent temperature distributions in the structure of water environment (3-5 mm)/In film (400 nm)/CdTe crystal (0.5 mm) under irradiation from the In film side in water with KrF excimer laser pulses (λ = 248 nm, τ = 20 ns) (Figure 1.1) has demonstrated that the In film was completely melted at laser pulse energy density E = 1300-1500 J/m^2, however the temperature at the In film/CdTe crystal boundary was still much lower the melting point of CdTe. Cooling due to "evaporation" of In atoms and boiling of the surrounding water layer did not significantly affected the laser heating process. As shown, the cooling flows were several orders of magnitude lower than the heating flux of laser radiation. The results can be used for optimization of the laser-induced doping of CdTe and formation of In/CdTe/Au diodes with a *p-n* junction for X/γ-ray detectors.

The fabricated In/CdTe/Au diodes, created, by laser-induced doping, demonstrated high rectification *I-V* characteristics (Fig. 6(c)). The spectroscopic performance of the fabricated M-*p-n* structured In/CdTe/Au detectors was tested for radiation detection of a ^{137}Cs radioisotope. Good results were obtained with detectors formed on the base of CdTe crystals with sizes of 5×5×0.75 mm^3 by laser-induced doping according to the procedure (ii), in particular the best energy resolution (FWHM) was less than 1%@662keV (Fig. 7).

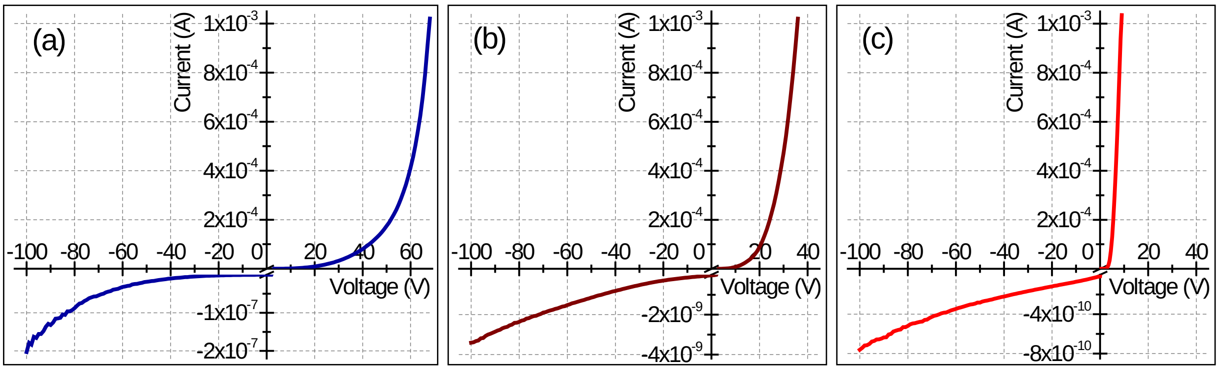


Fig. 6. *I-V* characteristics of the In/CdTe/Au structures before (a) and after (b, c) irradiation from the In film coated side (procedure (ii)) by nanosecond laser pulses energy densities: E (J/m^2): 1000 J/m (b) and 1200 J/m (c).

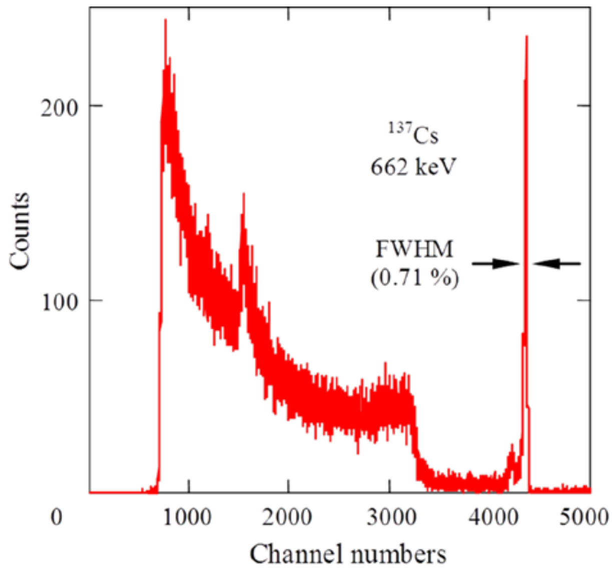


Fig. 7. Room temperature spectrum of a ^{137}Cs radioisotope taken by the In/CdTe/Au detector with a *p-n* junction at applied bias voltage of 700 V.

4. Development of CdTe-based diodes with a Schottky barrier

The Schottky diode detectors were prepared using CdTe crystals with sizes of 10×10×0.75 mm^3 by formation of a rectifying Schottky contact on the CdTe(111)B-face (Te-terminated) by thermal deposition of a Ni film in vacuum. An Ohmic contact was created on the opposite CdTe(111)A-face (Cd-terminated) by chemical deposition of an Au film. Before Ni and Au electrode deposition, both the CdTe crystal surfaces were treated with an Ar ion plasma in different regimes (voltage, current and time), respectively. The fabricated Schottky diode type detectors were tested by for radiation of ^{241}Am and ^{137}Cs radioisotopes. The spectroscopic performance of ten Ni/CdTe/Au detectors with a Schottky barrier is shown in Fig. 8.

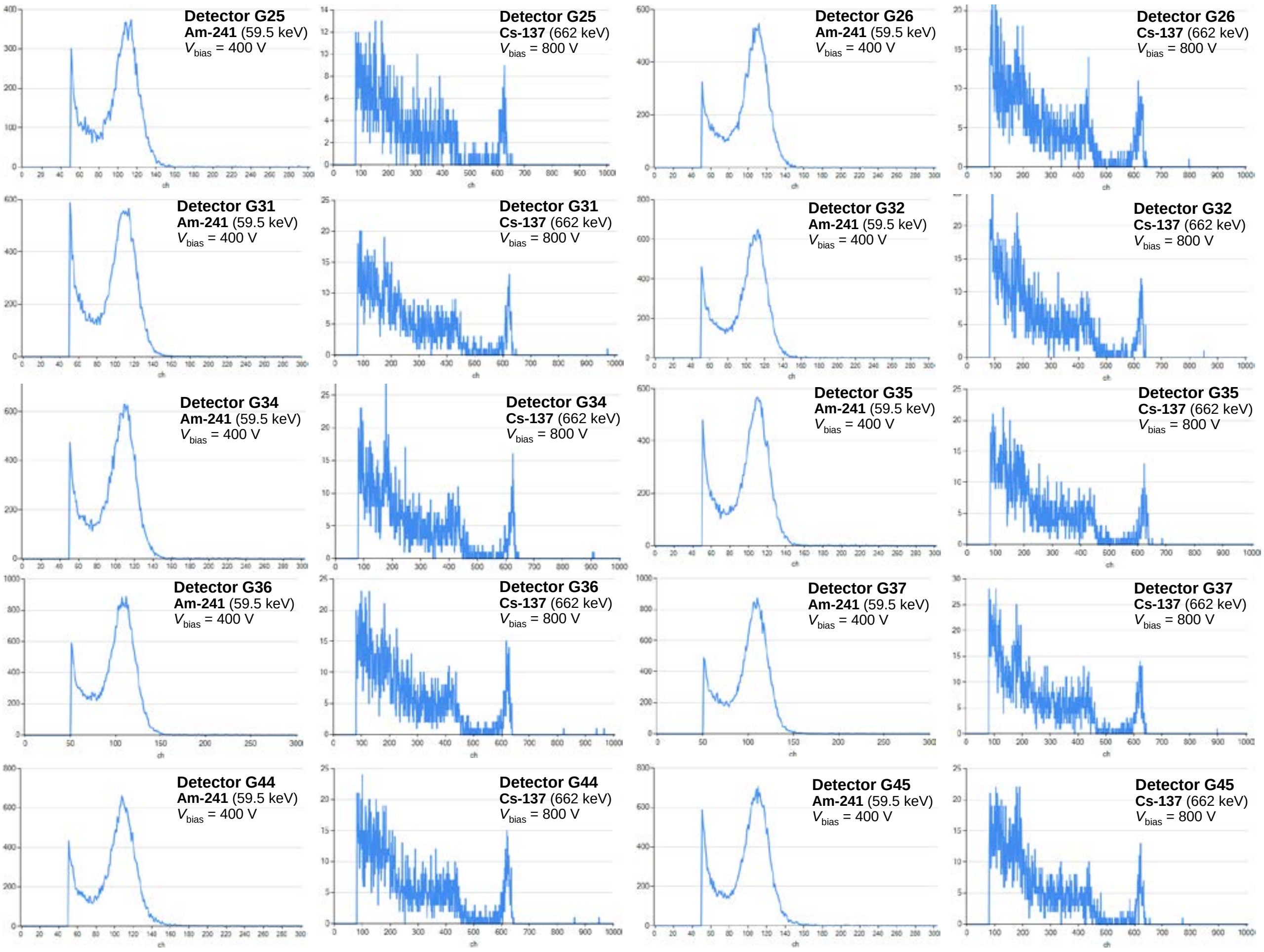


Fig. 8. Room temperature energy spectra of ^{241}Am and ^{137}Cs radioisotopes taken by ten Ni/CdTe/Au Schottky diode detectors.

5. Conclusion

M-*p*-*n* structured diodes and Schottky diodes have been fabricated using semi-insulating *p*-like CdTe wafers and two principal technologies, which have been developed: (I) laser-induced doping of a thin CdTe region and formation of a *p*-*n* junction, and (II) creation of both rectifying (Schottky) and Ohmic contacts using preliminary treatment of the CdTe surface by an argon ion bombardment. The In/CdTe/Au diodes with a *p*-*n* junction and Ni/CdTe/Au diodes with a Schottky barrier showed good detection efficiency as X/γ-ray detectors and demonstrated high energy resolution. The highest energy resolution, achieved in the best samples, was FWHM = 0.7-1.5%@662keV.

List of Publications Related to the Collaboration Research

1. V.A. Gnatyuk, V.L. Dubov, D.V. Fomin, A.Yu. Seteikin, T. Aoki, **Temperature fields in the In/CdTe structure under laser-induced doping in liquid**, *Recent Advances in Technology Research and Education. Inter-Academia 2017. Advances in Intelligent Systems and Computing*, Vol. **660** (**Sep. 2018**) 87-95.
2. O.L. Maslyanchuk, M.M. Solovan, V.V. Kulchynsky, V.A. Gnatyuk, T. Aoki, **Space-charge limited transport in CdTe-based X- and γ-ray detectors**, *2016 IEEE Nuclear Science Symposium, Medical Imaging Conference and Room-Temperature Semiconductor Detector Workshop (NSS/MIC/RTSD), Conference Record*, (Oct. 2017) 2 pages.
3. O.L. Maslyanchuk, M.M. Solovan, V.V. Kulchynsky, V.V. Brus, P.D. Maryanchuk, I.M. Fodchuk, V.A. Gnatyuk, T. Aoki, C. Potiriadis, Y. Kaissas, **Possibilities of CdTe-based X/γ-ray detectors with MoO_x contacts**, *2016 IEEE Nuclear Science Symposium, Medical Imaging Conference and Room-Temperature Semiconductor Detector Workshop (NSS/MIC/RTSD), Conference Record*, (Oct. 2017) 3 pages.
4. V.M. Sklyarchuk, V.A. Gnatyuk, W. Pecharapa, **Low leakage current Ni/CdZnTe/In diodes for X/γ-ray detectors**, *Nuclear Instruments and Methods in Physics Research A*, Vol. **879** (Jan. 2018) 101-105.
5. O.L. Maslyanchuk, M.M. Solovan, E.V. Maistruk, V.V. Brus, P.D. Maryanchuk, V.A. Gnatyuk, T. Aoki, **Prospects of In/CdTe X- and γ-ray detectors with MoO Ohmic contacts**, *Proceedings of SPIE*, Vol. **10612** (Jan. 2018) 10612V-1-6.
6. O. Maslyanchuk, M. Solovan, V. Brus, P. Maryanchuk, E. Maistruk, I. Fodchuk, V. Gnatyuk, T. Aoki, C. Lambropoulos, C. Potiriadis, **Comparative study of X- and γ-ray detectors with MoO_x, TiO_x and TiN Schottky contacts**, *2017 Nuclear Science Symposium, Medical Imaging Conference and Room-Temperature Semiconductor Detector Workshop (NSS/MIC/RTSD), Conference Record*, (2018) 5 pages, *in press*.
7. V.M. Sklyarchuk, V.A. Gnatyuk, T. Aoki, **Determination of the depletion region thickness in X/γ-ray detectors with a Schottky contact**, *2017 Nuclear Science Symposium, Medical Imaging Conference and Room-Temperature Semiconductor Detector Workshop (NSS/MIC/RTSD), Conference Record*, (2018) 2 pages, *in press*.
8. V.A. Gnatyuk, K.S. Zelenska, V.M. Sklyarchuk, T. Aoki, **Enhanced X/γ-ray detection efficiency in CdTe-based Schottky diode detectors operated in a stacked mode**, *2017 Nuclear Science Symposium, Medical Imaging Conference and Room-Temperature Semiconductor Detector Workshop (NSS/MIC/RTSD), Conference Record*, (2018) 2 pages, *in press*.

List of Presentations (Conference, Meeting, etc.)

1. V. Gnatyuk, K. Zelenska, T. Aoki, **Doping and metallization of the CdTe crystal surface by laser irradiation of the metal substrate through the semiconductor**, *The conference on Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XIX (Conference 10392), Part of 2017 SPIE Optics + Photonics: Optical Engineering + Applications, Technical Program*, 2017, Abstract No 10392-46, 161. (6-10 August 2017, San Diego, CA, USA).
2. O. Maslyanchuk, M. Solovan, E. Maistruk, V. Brus, V. Gnatyuk, T. Aoki, **Prospects of In/CdTe X- and γ-ray detectors with MoO Ohmic contacts**, *The 13th International Conference on Correlation Optics "Correlation Optics'17", Programme*, 2017, Abstract No M25, 1 page. (11-15 September 2017, Chernivtsi, Ukraine).
3. V.A. Gnatyuk, **Laser modification of electronic properties of semiconductors: formation of photosensitive structures**, *The 16th International Conference on Global Research and Education, Inter-Academia 2017 (iA-2017), Book of Abstracts*, 2017, Abstract No IL.04, 6. (25-28 September 2017, Iasi, Romania). (Invited report).
4. K. Zelenska, V. Sklyarchuk, V. Gnatyuk, T. Aoki, **Spectroscopic studies of Ni/CdTe/Au Schottky diode X- and γ -ray detectors**, *The 16th International Conference on Global Research and Education, Inter-Academia 2017 (iA-2017), Book of Abstracts*, 2017, Abstract No O.06, 16. (25-28 September 2017, Iasi, Romania).
5. V.A. Gnatyuk, V.L. Dubov, D.V. Fomin, A.Yu. Seteikin, T. Aoki, **Temperature fields in the In/CdTe structure under laser-induced doping in liquid**, *The 16th International Conference on Global Research and Education, Inter-Academia 2017 (iA-2017), Book of Abstracts*, 2017, Abstract No O.12, 22. (25-28 September 2017, Iasi, Romania).
6. O. Maslyanchuk, M. Solovan, V. Brus, I. Fodchuk, P. Maryanchuk, V. Gnatyuk, T. Aoki, C. Lambropoulos, C. Potiriadis, **Comparative study of X- and γ-ray detectors with MoO_x, TiO_x and TiN schottky contacts**, *The 24th International Workshop on Room-Temperature Semiconductor Detectors (RTSD 2017), 2017 IEEE Nuclear Science Symposium & Medical Imaging Conference (2017 NSS/MIC), Conference Program & Abstracts*, 2017, Abstract #2524. (21-28 October 2017, Atlanta, USA).
7. O. Maslyanchuk, M. Solovan, V. Brus, I. Fodchuk, P. Maryanchuk, V. Gnatyuk, T. Aoki, **Graphene/semi-insulating CdTe X-ray and γ-ray radiation detectors**, *The 24th International Workshop on Room-Temperature Semiconductor Detectors (RTSD 2017), 2017 IEEE Nuclear Science Symposium & Medical Imaging Conference (2017 NSS/MIC), Conference Program & Abstracts*, 2017, Abstract #2546.

(21-28 October 2017, Atlanta, USA).

8. V.M. Sklyarchuk, V.A. Gnatyuk, T. Aoki, **Determination of the depletion region thickness in X/γ-ray detectors with a Schottky contact**, *The 24th International Workshop on Room-Temperature Semiconductor Detectors (RTSD 2017), 2017 IEEE Nuclear Science Symposium & Medical Imaging Conference (2017 NSS/MIC), Conference Program & Abstracts*, 2017, Abstract #2991. (21-28 October 2017, Atlanta, USA).
9. J. Nishizawa, V.A. Gnatyuk, K. Zelenska, A. Koike, T. Aoki, **Doping of CdTe by indium or aluminum with Nd:YAG laser**, *The 24th International Workshop on Room-Temperature Semiconductor Detectors (RTSD 2017), 2017 IEEE Nuclear Science Symposium & Medical Imaging Conference (2017 NSS/MIC), Conference Program & Abstracts*, 2017, Abstract #3897. (21-28 October 2017, Atlanta, USA).
10. V.A. Gnatyuk, K.S. Zelenska, V.M. Sklyarchuk, T. Aoki, **Enhanced X/γ-ray detection efficiency in CdTe-based Schottky diode detectors operated in a stacked mode**, *The 24th International Workshop on Room-Temperature Semiconductor Detectors (RTSD 2017), 2017 IEEE Nuclear Science Symposium & Medical Imaging Conference (2017 NSS/MIC), Conference Program & Abstracts*, 2017, Abstract #4164. (21-28 October 2017, Atlanta, USA).
11. V.A. Gnatyuk, **Laser-stimulated modification of surface state and photoelectrical properties of crystals and films of CdTe-based solid solutions**, *The First Materials Research Society of Thailand International Conference (1st MRS Thailand International Conference), Abstract Book*, 2017, 15_2. (31 October – 3 November 2017, Chiang Mai, Thailand). (Keynote report).

List of Awards

Owing to the obtained results, the leader of the research team Dr. Volodymyr A. Gnatyuk was awarded by three financial grants to visit and carry out the synchrotron measurements at Synchrotron Light Research Institute in Thailand in July and November (Project No 2885 and No 2888) 2017, respectively:

1. Characterization of CdTe-based structures with a surface nanolayer doped with an In or Al impurity using nanosecond laser irradiation.
2. Characterization of Cd(Zn)Te crystals subjected to different surface processing (chemical etching, thermal heating, nanosecond laser irradiation.
3. Characterization of CdTe and Cd(Zn)Te crystal surfaces and interfaces after laser deposition of a metal contact film.

Research plan for the next year (from April 1, 2018 to March 31, 2019), if the collaboration research is continued. Prior consent from the collaboration partner in the Research Center is necessary.

Different techniques of laser processing of semi-insulating *p*-like CdTe crystals and CdTe-metal interfaces will be developed to create X/γ- ray radiation diode type detectors:

(i) laser transfer of a thin In film, pre-deposited on the glass substrate by laser ablation of an In target irradiated through the glass, on the CdTe surface;
(ii) laser deposition of In on the CdTe surface by irradiation of an In target through the CdTe crystal;
(iii) activation of the CdTe-In interface by laser irradiation of CdTe crystals, pre-coated with an In dopant (electrode) film, (a) from the metal side or (b) through the semiconductor.

Applying infrared nanosecond laser pulses it will be possible to introduce and electrically activate In dopant atoms with high concentration in the thin surface region of CdTe crystals and thus, to form an In(Al)-doped layer. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) with synchrotron radiation as an excitation light, photoconductivity, *I-V* characteristics and radioisotope spectrum measurements will be applied to study laser-induced doping and test the obtained In(Al)/CdTe/Au diodes with a *p-n* junction.