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Laser ablation and photostimulated passivation of $Cd_{1-x}Zn_xTe$ crystals

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Proposed is a new technology of passivation of $Cd_{1-x}Zn_xTe$ crystals which comprises preliminary treatment of their surface by laser ablation aimed at removal of the disturbed surface-adjacent layer arising due to mechanical treatment (cutting, grinding, polishing) of the samples. Degradation of the spectrometric characteristics of the detectors after chemical etching is compared with their degradation caused by the proposed passivation method.

Предложен новый технологичный способ пассивации кристаллов $Cd_{1-x}Zn_xTe$, включающий предварительную обработку поверхности кристаллов с помощью лазерной абляции с целью удаления нарушенного приповерхностного слоя, возникающего после этапов механической обработки (порезка, шлифовка, полировка) образцов. Изучена деградация спектрометрических характеристик детекторов после обработки химическим травлением в сравнении с деградацией после обработки предложенным методом пассивации.

1. Introduction

Nowadays $Cd_{1-x}Zn_xTe$ ($0 \le x \le 0.1$) semiconductor solid solution is considered to be one of the most promising materials for the making of X- and γ-ray detectors and spectrometers [1–5]. The manufacturing process of detectors includes the step of mechanical treatment (cutting, grinding, polishing) of semiconductor crystals gives rise to the formation of disturbed surface-adjacent layer which is usually removed by chemical etching [6–8].

A large number of aqueous solutions of chemical etchants [7–10] and many-stage (containing 2–5 steps) processes of chemical treatment of $Cd_{1-x}Zn_xTe$ [9, 10] surface are described in the literature. The next stage of the making of $Cd_{1-x}Zn_xTe$ detectors is passivation of their surface which allows to reduce leakage currents and to prevent degradation of the spectrometric characteristics of the detectors.

There exist chemical and physical methods of passivation, as well as their combinations. Most widely used are the chemical methods resulting in the formation of protective sulfide or oxide films on CdZnTe surface. The physical passivation methods comprise ion beam and plasma sputtering of passivating protective film by means of vacuum setups using electric arc, oxidation in low- and high-energy oxygen atoms fluxes, etc. [11–13]. The chemical methods imply contact of the samples with water which is a potential source of contamination of the crystal surface and a factor reducing the surface electrical resistance.

Though "dry" physical passivation methods reduce surface leakage currents more

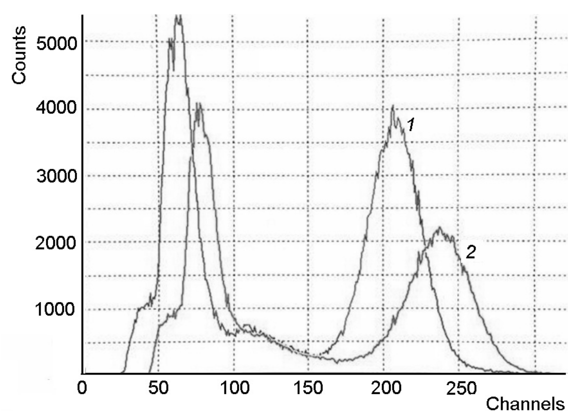

Fig. 1. Energy spectra of $Cd_{1-x}Zn_xTe$ detector with chemically etched surfaces obtained immediately after etching (*1*) and 90 days later (*2*).

effectively than "wet" chemical methods, they are laborious and require complex equipment [14].

However, it should be noted that both physical and chemical passivation methods cannot provide complete removal of the so-called crystallization water which penetrates the surface-adjacent layer of the samples in the process of mechanical treatment [15]. This is evident from nonlinearity of the I–V characteristics of $Cd_{1-x}Zn_xTe$ detectors [16–18]. The influence of the chemical methods of surface passivation manifests itself in subsequent degradation of the spectrometric characteristics of the detectors [16–19].

Fig. 1 points to degradation of the spectrometric characteristics of $Cd_{1-x}Zn_xTe$ detector with contacts formed on chemically etched surface, since in 90 days the FWHM of the energy spectrum of ^{241}Am essentially increased.

In view of the above-said, development of new effective methods for passivation of the surface of $Cd_{1-x}Zn_xTe$ detectors is a topical problem.

Earlier we have proposed dry methods of photostimulated passivation (PhSP) and photo-electrostimulated passivation (PhESP) of $Cd_{1-x}Zn_xTe$ [7, 8] which provide an effective reduction of leakage currents due to the obtaining of a high-resistance oxide layer on the sample surface. In the present work we propose a new method of dry passivation. In this method the disturbed surface layer is removed by laser ablation (LA) with subsequent passivation of the surface using PhSP or PhESP.

2. Experimental

The disturbed layer was removed from the side surface of the samples in the process of their irradiation by successive laser radiation pulses. Fig. *2* presents the scheme of the setup for laser ablation of the disturbed layer from the side surface of crystalline $Cd_{1-x}Zn_xTe$ samples and subsequent obtaining of a high-resistance protective layer on this surface by the method of PhSP. YAG:Nd-laser radiation at the fundamental frequency (with λ =1064 nm) was converted into the radiation at the second harmonic frequency with λ = 532 nm.

Ablation of $Cd_{1-x}Zn_xTe$ surface was realized using 10 ns laser radiation pulses with

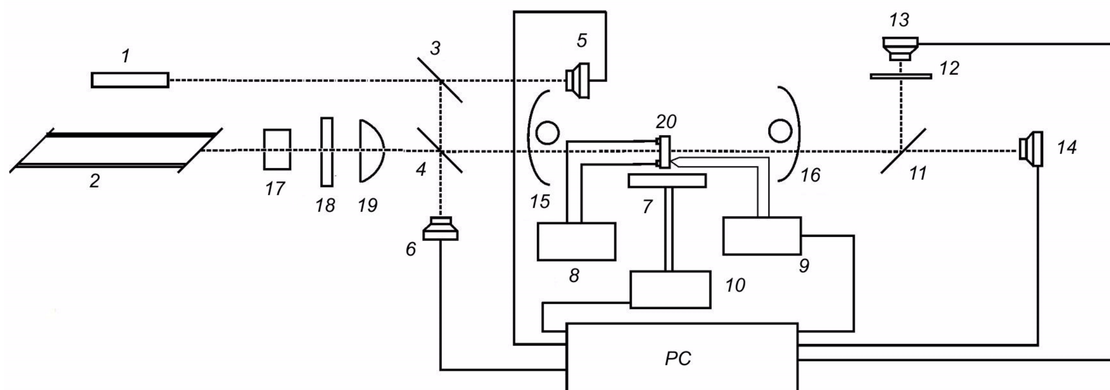

Fig. 2. Scheme of the experimental setup for the obtaining of oxide coatings on the surface of semiconductor substrates by the method of PhSP (PhESP) and laser ablation: *1*– He-Ne laser; 2- YAG:Nd laser; *3,4,11* – translucent plates; *5,13* – diode photoreceivers; *6,14* – calorimetric power meters; *7* – rotating crystal holder; 8 – power supply for PhESP; *9* – thermocouple and unit for treatment of its signals; *10*–electrical engine; *12* – light filter; *15,16* – mercury lamps; *17* – KDP-based converter of the second harmonic of YAG:Nd laser (λ=532 nm); *18* – light filter; *19* – focusing lens, *20* – crystalline sample.

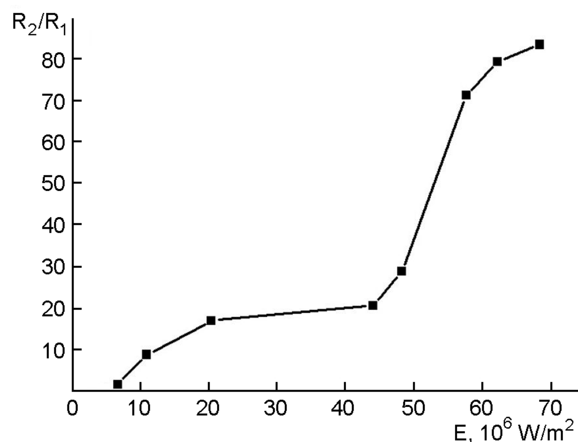

Fig. 3. Dependence of the ratio of the crystal resistances after the treatment (R_2) by LA+PhSP to the initial resistance (R_1).

an average power density of 10...70 MWt/cm^2. The irradiation dose was 0.25...3.0 J/cm^2.

The duration of the laser ablation process (0.5...5.0 min) was determined experimentally depending on the dimensions of the samples, the velocity of their rotation in the crystal holder and the period of laser pulses repetition. The power density providing effective removal of the disturbed layer and the laser irradiation dose were determined experimentally, too.

At laser irradiation doses lower than 0.25 J/cm^2 the disturbed layer was not removed completely. The use of the doses higher than 3.0 J/cm^2 did not lead to a noticeable improvement of the spectrometric and electrical characteristics of the detectors.

In the course of our investigations we established the dependence of the ratio of the crystal resistances after the treatment to the initial resistance on the intensity of incident laser radiation (Fig. 3).

The obtained results (Fig. 3) may be explained as follows. The rise of the resistance ratio on the initial segment of the curve (up to 10 MWt/cm^2) is caused by photostimulated passivation of the crystal (without laser irradiation). The said intensity is the lowest one used in the present investigation. The second segment where the resistance ratio smoothly increases corresponds to near-threshold intensity of laser radiation. Insignificant rise of the dependence in this region may be connected with burning out of different organic impurities caused by the growth of laser radiation intensity and removal of water vapors from the surface and thin surface-adjacent layer of the sample. As a consequence, the efficiency of photostimulated passivation increases.

Fig. 4 presents the microphotographs of the surface of crystalline $Cd_{1-x}Zn_xTe$ sample obtained using an electron microscope JSM-820 before (a) and after (b) laser ablation. The power density of laser ablation was equal to 57 MWt/cm^2 (λ = 532 nm, the pulse duration was 10 ns). As is seen, laser ablation leads to clearing of the treated sample surface.

Fig. 5 illustrates the behavior of the electrical resistance of crystalline $Cd_{1-x}Zn_xTe$ samples under the influence of different methods of passivation of their surface: the proposed method (LA + PhSP, curve *1*), chemical etching + PhESP (curve *2*) and chemical etching + PhSP (curve *3*), depending on the intensity of UV irradiation.

As seen from the presented graphs, the proposed method (LA + PhSP, curve *1*) makes it possible to essentially increase the surface

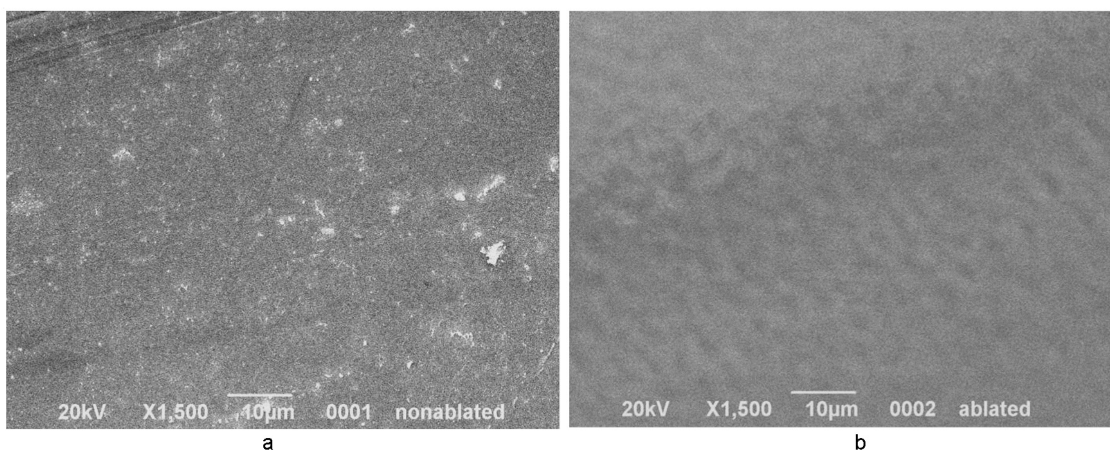

Fig. 4. Electron microphotographs of the surface of $Cd_{1-x}Zn_xTe$ crystals before (a) and after (b) laser ablation.

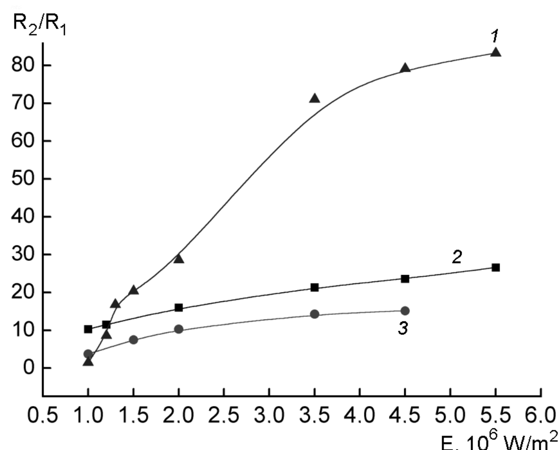

Fig. 5. Behavior of the electrical resistance of $Cd_{1-x}Zn_xTe$ detectors depending on the intensity of UV-radiation at different passivation methods: *1* — LA+PhSP, *2* — chemical etching + PhESP, *3* — chemical etching + PhSP.

electrical resistance of $Cd_{1-x}Zn_xTe$ detectors and to diminish leakage currents on their side surfaces. Such an effect is achieved due to the formation of a thick oxide TeO_2 layer followed by a sharp (practically down to zero) diminution of the concentration of free Te in the surface-adjacent layer of the samples. This is confirmed by the results of the study of the sample surface composition by the method of X-ray photoelectron spectroscopy (Fig. 6).

The data presented in Fig. 6 were obtained by the method of X-ray photoelectron spectroscopy on a spectrometer XPS-800 Kratos (10^{-8} Torr vacuum, MgK_α — radiation, $h\gamma = 1253.6$ eV, 15 kV $\times$ 20 mA X-ray tube power). The kinetic energy of electrons was analyzed by a semispherical electrostatic analyzer. The resolution of the spectrometer was 1eV, the accuracy of bonding energy determination equaled 0.3 eV. Layer-by-layer etching was realized

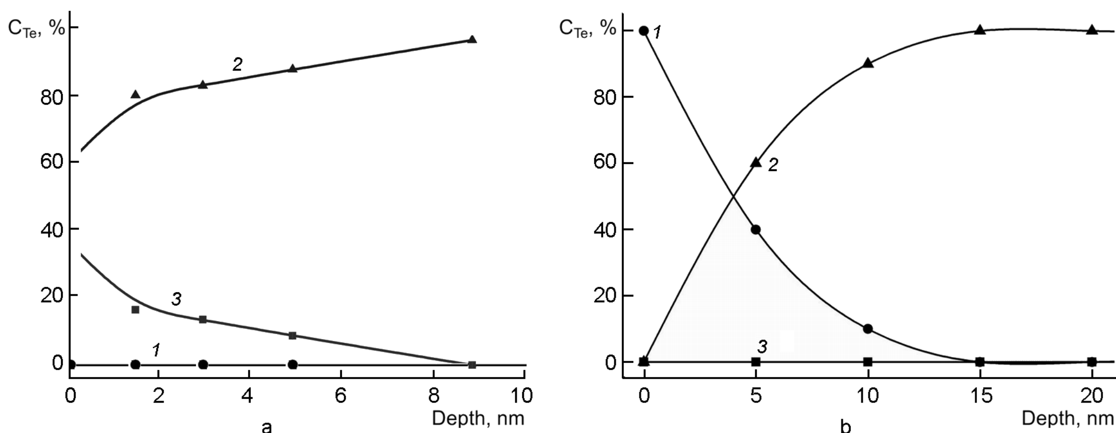

Fig. 6. Profiles of Te distribution between the formed compounds TeO_2, CdTe and free Te after the treatment of the sample by the methods of LA (a) and LA + PhSP (b): *1* – TeO, *2* – CdTe, *3* – free Te.

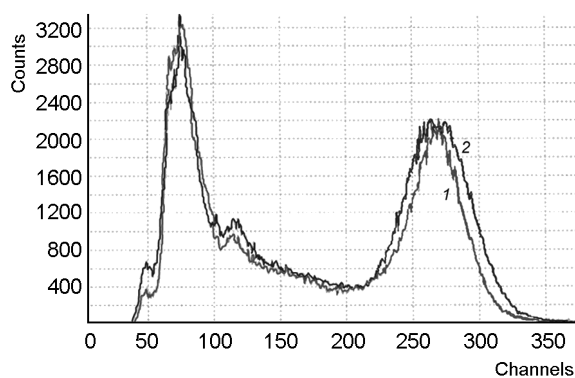

Fig. 7. Degradation of the energy spectra of $Cd_{1-x}Zn_xTe$ detector after the treatment by the method of LA+PhSP.

using an electron gun (Ar^+, E = 2 keV), the etching rate being ~ 0.6 nm/min.

The sample surface composition was established from the ratio of the areas of the lines C1s, O1s, Mg2p, Zn3p, Se3d (skeleton shells) and ZnLMM (Auger line) taking into account the coefficients of element sensitivity. The thickness of the analyzed layer was ~ 5 nm.

Fig. 7 presents the energy spectra of ^{241}Am isotope for $Cd_{1-x}Zn_xTe$ detector measured immediately after the treatment by the method of laser ablation and photostimulated passivation (curve *1*) and 90 days later (curve *2*).

This figure testifies to minimization of degradation of the spectrometric characteristics for $Cd_{1-x}Zn_xTe$ detectors treated by the method of LA+PhSP in comparison with such a degradation after chemical etching (Fig. 1).

3. Conclusions

The proposed passivation method (LA+PSP) provides the obtaining of thick homogeneous high-resistance oxide films, that essentially diminishes leakage currents on the side surface of $Cd_{1-x}Zn_xTe$ detectors. The method is reproducible and allows to exclude the use of highly toxic chemical components for the making of spectrometric detectors based on $Cd_{1-x}Zn_xTe$. Such a method of passivation allows to minimize degradation of the spectrometric characteristics of the detectors.

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Лазерна абляція та фотостимульована пасивація кристалів $Cd_{1-x}Zn_xTe$

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Запропоновано новий технологічний спосіб пасивації кристалів $Cd_{1-x}Zn_xTe$, що включає попередню обробку поверхні кристалів за допомогою лазерної абляції з метою видалення порушеного при поверхневого шару, який виникає після етапів механічної обробки (порізка, поліровка, шліфовка) зразків. Вивчено деградацію спектрометричних характеристик детекторів після обробки запропонованим методом пасивації.