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*Hetero- and low-dimensional structures*

# Structure and electrical resistance of the passivating ZnSe layer on Ge

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**Abstract.** In this article, we have considered the *p-i-n* Ge photodetector with ZnSe passivating layer. Passivation layer needs to be protected photodetector from dust, rain drops and other external influences. However, this passivation layer can cause errors in photodetector image. When creating a passivating ZnSe layer on Ge, which is used in *p-i-n* Ge photodetectors, we found two additional phases GeSe and $GeSe_2$ that do not contradict with their state diagram. The above phases can have an essential effect on performances of the passivating layer. Therefore, to study the electrical resistance of this layer, we prepared model samples of layers containing the GeSe and $GeSe_2$ with the thickness 0.5…1.8 µm and area 1 $cm^2$. To measure the electrical resistance of these layers, we used elastic contacts. The performed measurements have shown that Se layers on Ge have an intermediate resistance between that of ZnSe on Ge and pure Ge, and, therefore, the effect of additional phases practically does not worsen the passivating properties of the ZnSe layer on Ge.

**Keywords:** photodetector, ZnSe layer, GeSe and $GeSe_2$ phases, X-ray phase investigation, electrical resistance, elastic contact.

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## 1. Introduction

In laser ranging and fiber-optic communication, near infrared (NIR) spectral range is usually used, because of this range comprises the so-called "transparency windows" for their operation media (atmosphere, glass, silica, *etc*.) [1]. It is this range that is suitable for wide application of germanium (Ge) photodetectors [2, 3]. In [2], proposed are semiconductor devices, such as the photonics ones, that employ substantially curved-shaped silicon-germanium (SiGe) structures and are fabricated using zero-change CMOS fabrication process technologies. In one example, a closed-loop resonator waveguide-coupled photodetector includes a silicon resonator structure formed in a silicon substrate, interdigitated *n*-doped well-implant regions and *p*-doped well-implant regions forming multiple silicon *p-n* junctions around the silicon resonator structure, and a closed-loop SiGe photocarrier generation region formed in a pocket within the interdigitated *n*- and *p*-doped well implant regions. The closed-loop SiGe region is located so as to substantially overlap with an optical mode of radiation when being present in the silicon resonator structure, and traverses the multiple silicon *p-n* junctions around the silicon resonator structure. Electric fields arising from the respective *p-n* silicon junctions significantly facilitate a flow of the generated photocarriers between electric contact regions of the photodetector. Proposed in [3] is a Ge-on-Si photo-detector constructed without doping or contacting Germanium by metal is described. Despite the simplified fabrication process, the device has responsivity of 1.24 A/W, corresponding to 99.2% quantum efficiency. The dark current is 40 nA at –4 V reverse bias. 3-dB bandwidth is close to 30 GHz.

Various materials are now used for passivation of surfaces in Ge photodetectors. Considered in [4] is the silicon passivation layer on a Ge *p-i-n* photodiode. It was demonstrated that a complementary metal-oxide-semiconductor (CMOS) compatible silicon (Si) surface passivation technique effectively suppress the dark current originating from the mesa sidewall of the $Ge_{0.95}Sn_{0.05}$ on Si ($Ge_{0.95}Sn_{0.05}$/Si) *p-i-n* photodiode. Current-voltage (*I–V*) characteristics show that the sidewall surface passivation technique could reduce the surface leakage current density ($J_{surf}$) of the photodiode by ~100 times. A low dark current density ($J_{dark}$) of 0.073 A/cm$^2$ at the bias voltage –1 V is achieved, which is among the lowest reported values for $Ge_{1-x}Sn_x$/Si *p-i-n* photodiodes. Temperature-dependent *I–V* measurement was performed for the Si-passivated and non-passivated photodiodes, from which the activation energies of dark current are extracted to be 0.304 and 0.142 eV, respectively. In addition, the optical responsivity of the $Ge_{0.95}Sn_{0.05}$/Si *p-i-n* photodiodes to light signals with the wavelengths ranging from 1510 to 1877 nm is reported.

As it is offered in [5], the protective film of photoconverter can be made of zirconium dioxide ($ZrO_2$) or fianite – single crystal of cubic solid solutions based on zirconium dioxide mixed with stabilizing oxides of yttrium ($Y_2O_3$), scandium ($Sc_2O_3$) or lanthanides. This technical solution enables to improve photoelectric parameters, to provide stability, reliability and lifespan to eliminate excess noise in Ge photodiodes of a large area. In its coefficient of thermal expansion, a $SiO_2$ film differs two-fold as compared with that for Ge and creates thermal stress after vacuum depositing and cooling. Besides, there can take place creation of an additional layer from Ge oxide, which worsens dielectric properties of the $SiO_2$ layer.

In multilayer Ge photoconverters [6], the $Si_3N_4$ layer is used as the passivating one. This material possesses a low coefficient of thermal expansion and has many positive properties, namely: mechanical strength, chemical inertness and high dielectric permittivity. But this way has its deficiencies: technological difficulties in manufacturing and necessity to use very expensive equipment. The coefficient of thermal expansion for this material ($3.4\cdot10^{-6}$ K$^{-1}$) approaches to that of germanium ($6.1\cdot10^{-6}$ K$^{-1}$), but differs by the value $3\cdot10^{-6}$ K$^{-1}$, which makes it impossible to deposit protective layers of the necessary thickness close to 1 μm. The layers of this thickness are characterized by increasing the internal stresses, when being used in Ge photoconverters. The internal stresses reduce the operating life and reliability of photoconverters.

As a passivating layer for fast Ge *p-i-n* photodetectors, there used was zinc selenide (ZnSe) [7]. This material has a high transparency in the NIR range, therefore it can be deposited both onto front and side surfaces to protect the *p-i-n* junction. It should enable to provide passivation and improve its performances, including reliability.

Decreasing the surface currents is reached owing to wide forbidden gap inherent to ZnSe 2.7 eV, as compared to that of intrinsic Ge 0.67 eV. One of the advantages for applying ZnSe as the protective and passivating layer for germanium photoconverters is its value of thermal expansion coefficient $6.1\cdot10^{-6}$ K$^{-1}$ that is very close to that of germanium – $7.1\cdot10^{-6}$ K$^{-1}$. It is also important that ZnSe has no oxygen in its composition, therefore it does not oxidize germanium during the technological process of deposition, which provides the absence of an additional layer of germanium oxides.

The optimum values of ZnSe passivating layer thickness lie within the range 0.8…1.5 μm. The detectors with this passivating layer demonstrate high stability of their parameters for more than two years.

To perform X-ray and electrical measurements, we prepared model samples of plates with the area 1 cm$^2$ from germanium and glass covered with ZnSe layers (thermally deposited in vacuum) of various thickness within the range 0.8…1.5 μm. Besides, there prepared were the same plates with Se layers to analyze the created structures and their properties.

The aim of this work was to study the structure and electrical resistance of the layers consisting of ZnSe, GeSe phases as well as $GeSe_2$ on Ge surface.

## 2. Methods of investigations

X-ray phase analysis of the samples was performed using the diffractometer Philips X'Pert PRO-MRD. CuK$_{\alpha1}$ radiation ($\lambda$ = 0.15406 nm) was used in these experiments. The voltage of 45 kV was applied to the tube anode, the current was 40 mA. Diffractograms were taken both in the symmetrical and grazing geometries with various slopes of the sample surface relatively to the direction of X-ray beam. It provided lowering the strong peak from the germanium substrate in orientation (111). The qualitative phase analysis of diffractograms was carried out using the database ICDD.

Studying the electrical resistance of surface layers was performed using the method of elastic contacts [8], which has the following important advantages as compared to the four-probe method:

– large area of the contact zone, which provides a low current density and, respectively, absence of Joule heating;

– low pressure onto the semiconductor surface, which enables to minimize destruction of this surface;

– applying the contacts with the maximum possible area covering the whole sample enables to avoid the influence of geometrical errors.

The theory of electrical contacts is represented in detail in [9]. The elastic contacts are of special interest. Investigations of them started from the work [10]. Composite materials, including those from nanomaterials, are widely researched for applying in electronic facilities as elastic contacting elements [11, 12].

Application of the elastic contacts based on rubber having the anisotropic electrical conductivity is now widely used in liquid-crystal indicators (Liquid Cristal Displays – LCD). We used the contacts manufactured by the firm Fujitsu (Japan).

One of the promising fields of using this method is pulsed voltammetry [13] with its distinctive feature – duration of measuring pulses reaches here 100 ms or higher, while the interval between pulse trains exceeds 1 s. The pulsed methods for measuring the resistance of thin films as well as semiconductor surface layers find their wide application in recent years [14, 15].

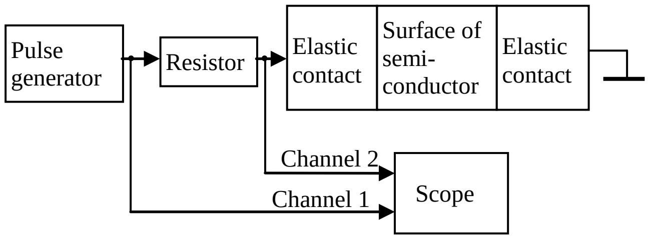


**Fig. 1.** Stand for pulsed measurements of the surface resistance with using the elastic contacts.

Shortening the time for measurements by using short measuring pulses (single or serial with a high off-duty ratio) enables to minimize heating the thin films. The pulse methods allow changing both the amplitude and temporal parameters of pulses: their duration, repetition frequency and off-duty ratio. This enables to optimize the measuring methods for every type of surfaces – various kinds of metals and semiconductors, as well as composites and nanomaterials.

The structural scheme of stand for pulsed measurements of the surface resistance is shown in Fig. 1.

The measurements were performed in the following regime: pulses of the amplitude 4 to 10 V, frequency 160 kHz and off-duty ratio 3 to 8 from the generator enter the voltage divider that consists of the resistor 1…140 kOhm and the studied sample with applied elastic contacts. The signals from generator and the sample (midpoint of the voltage divider) enter the digital oscillograph (channels 1 and 2). The obtained values are used to calculate the surface resistance of the studied sample.

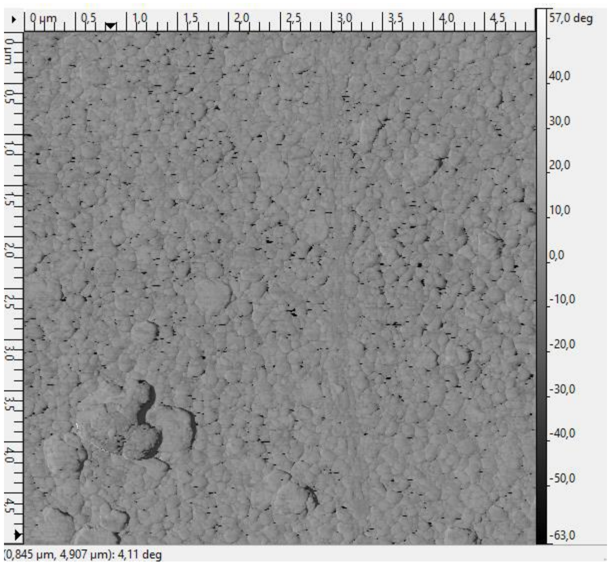


**Fig. 2.** Topology of the ZnSe layer surface after deposition onto germanium.

Before measurements, it was experimentally found that the zone of reliable contact begins from the pressure 20 kPa. After 3-fold increasing it, the resistance value decreases only by one third. Therefore, when measuring the resistance of fragile materials, it is sufficient to use the pressure 20…30 kPa that is two orders less than that used in the four-probe method.

The measurements of electrical resistance we carried out using the pulsed method on the 2101th reading at the scale of digital oscillograph. The instant voltage value at the generator output was kept the same. The pulses were taken from the generator based on the timer NE555, the amplitude of pulses was 4.84±0.04 V. The pressure applied to elastic contacts was 20 kPa.

Topology of the sample surface was studied using the atomic-force microscope.

## 3. Results of measurements and discussion

First of all, the prepared samples of Ge plates with the ZnSe layer were studied using the atomic-force microscope (Fig. 2). It was necessary to determine quality of the ZnSe layer obtained after deposition.

The roughness of the sample was $R_a = 12.7$ nm, $R_z = 25$ nm. These values were typical for all the samples.

The diffractograms of model samples Nos 1 to 4 (Fig. 3) contain the peaks of cubical phase inherent to polycrystalline ZnSe with the lattice parameter $a = 5.6687$ Å [16].

When the diffractograms were taken in the grazing geometry with the angle of X-ray incidence 15°, an additional diffraction peak appears at the angle 25.92° (blue curve in Fig. 4). The appearance of a diffracted beam within the definite narrow interval of angles of incidence onto the sample is usually inherent to textured phases. It is the most probable that this reflection (201) belongs to the hexagonal textured phase GeSe with the following parameters: $a = 8.7$ Å, $c = 8.32$ Å [17].

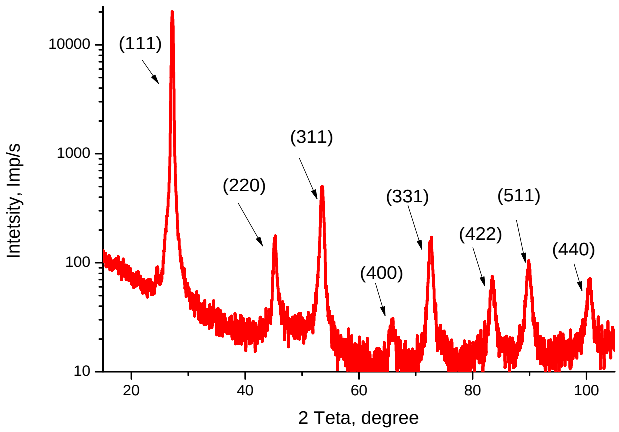


**Fig. 3.** Diffractogram of the sample No 2 (ZnSe layer on Ge, the thickness 0.6 μm).

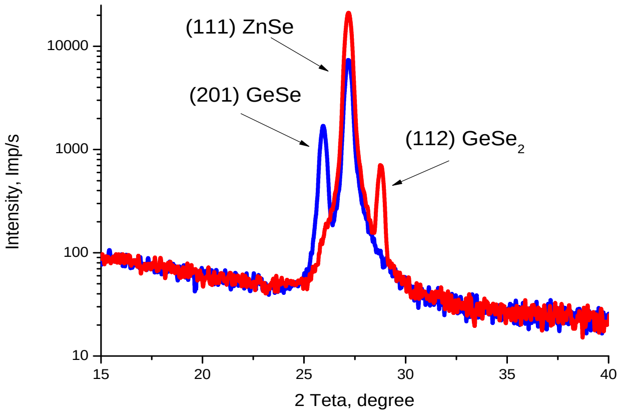


**Fig. 4.** Diffractogram of the sample No 2 (ZnSe layer on Ge). The blue curve corresponds to the angle of X-ray incidence 15°, the red curve – to 10°. (Color online.)

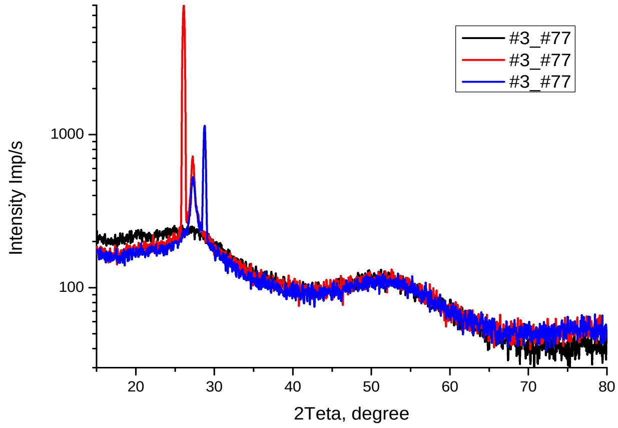


**Fig. 5.** Diffractogram of the sample No 3_77. (Color online.)

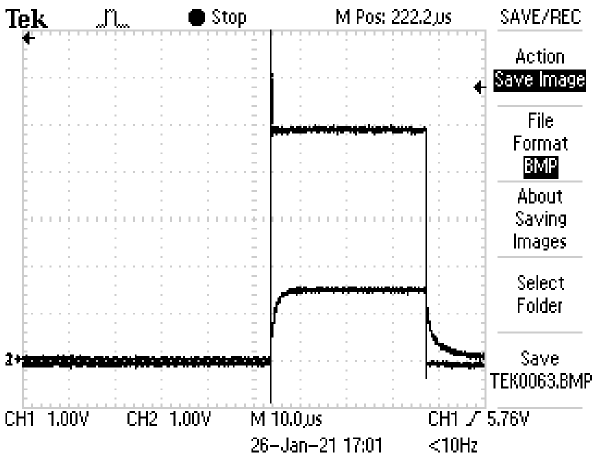


**Fig. 6.** Oscillogram of the sample No 4 (ZnSe layer on Ge, thickness 0.9 μm).

The diffractogram obtained for the angle of incidence 10° contains an additional diffraction peak at 28.76° (red curve in Fig. 4). It is the most probable that it corresponds to the reflection (112) belonging to the tetragonal textured phase of $GeSe_2$ with the parameters: $a$ = 5.7307 Å, $c$ = 9.691 Å [18]. It is worth to note that the axes of GeSe and $GeSe_2$ phases textures practically coincide with the direction of the plane (111) inherent to the Ge substrate and are declined from it by only 5…8 degrees.

When studying the samples with deposited pure Se layers, we observed creation of textured phases GeSe and $GeSe_2$ (Fig. 5). Availability of the increased diffusive background is indicative of the presence of an amorphous phase. It is noteworthy that creation of the Se crystalline phase was not observed. It was logical to assume that the textured phases GeSe and $GeSe_2$ were created at the heteroboundary between pure Ge and amorphous Se layer.

In what follows, we adduce the results of measuring the electrical resistance of some samples. The example of oscillogram for the sample No 4 with the thickness of ZnSe layer 0.9 μm is shown in Fig. 6. The values of specific resistance for the samples Nos 4 and 3_77 are summarized in Table.

The resistance of the samples ZnSe on Ge with the phases GeSe and $GeSe_2$ is higher than that of the samples Se on Ge with the same additional phases. Therefore, one can make the conclusion that the properties of ZnSe layer as the isolating one are more preferable for Ge substrate.

**Table.** Specific resistances of ZnSe and Se layers deposited onto Ge substrates.

| Parameter | ZnSe | | Se |
|---|---|---|---|
| Layer thickness, μm | 0.9 | 1.5 | 1.5 |
| Specific resistance, kOhm/□ | 8.81 ± 0.2 | 13.29 ± 0.2 | 10.1 ± 0.3 |

The same relationship was observed between specific resistances in the samples with ZnSe and Se layers on glass. Therefore, the influence of GeSe and $GeSe_2$ phases on isolating properties of passivating coatings can be considered as insignificant.

## 4. Conclusions

To ascertain the effect of additional phases GeSe and $GeSe_2$ on the passivating properties of ZnSe coating in Ge photodiodes, it has been developed the method based on using the elastic contacts. The studies were carried out on model samples with an area of 1 $cm^2$ and a thickness of ZnSe and Se films of 0.5…1.8 μm containing the indicated phases on Ge substrates, as well as control samples of films of the same thickness on glass. X-ray studies have shown the presence of textured GeSe and $GeSe_2$ phases in samples with both ZnSe and Se films.

The electrical resistance of ZnSe samples on a Ge substrate is higher as compared with the resistance of Se samples on a Ge substrate. Taking into account these results for the electrical resistance in aggregate with the data of small differences in lattice parameters and thermal expansion coefficients of Ge and ZnSe layer (with the thickness 0.8…1.5 μm), which provides the absence of internal stresses, passivation of Ge photodiodes with ZnSe seems to be expedient.

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**Структура та електричний опір пасивуючого шару ZnSe на Ge**

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**Анотація.** У цій статті розглянуто фотоприймач *p-i-n* Ge з пасивуючим шаром ZnSe. Пасивуючий шар фотоприймача повинен бути захищений від пилу, крапель дощу та інших зовнішніх впливів. Однак цей пасивуючий шар може спричинити помилки у зображенні фотоприймача. При створенні пасивуючого шару ZnSe на Ge, який використовується у фотоприймачах *p-i-n* Ge, виявлено дві додаткові фази GeSe та $GeSe_2$, які не суперечать їх діаграмі стану. Вищевказані фази можуть мати істотний вплив на характеристики пасивуючого шару. Тому для вивчення електричного опору цього шару створено модельні зразки шарів, що містять GeSe та $GeSe_2$ товщиною 0,5… 1,8 мкм та площею 1 см$^2$. Для вимірювання електричного опору цих шарів використано пружні контакти. Виконані вимірювання показали, що шари Se на Ge мають проміжний опір між ZnSe на Ge та чистим Ge, і отже, вплив додаткових фаз практично не погіршує пасивуючих властивостей шару ZnSe на Ge.

**Ключові слова:** фотоприймач, шар ZnSe, фази GeSe та $GeSe_2$, рентгенофазове дослідження, електричний опір, пружний контакт.