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Side-surface passivation effect on the electrical properties of metal-CdZnTe-metal structures

Sklyarchuk V.[1], Fochuk P.[1], Zakharuk Z.[1], Grill R.[2], Kutny V.[3], Rybka A.[3], Nakonechny D.[3], Zakharchenko A.[3], Nykoniuk Ye.[4], A. E. Bolotnikov[5], and R. B. James[5*]

1 – Chernivtsi National University, Chernivtsi, Ukraine
2 – Institute of Single Crystals NASU, 60, Lenina Str., Kharkiv, Ukraine
3 – National Science Centre "Kharkov Institute of Physics & Technology Kharkiv, Ukraine
4 – National University of Water Management and Nature Resources Use Rivne, Ukraine
5 – Brookhaven National Laboratory, Upton, NY, USA

A B S T R A C T

One of the ways to improve the charge collection in semiconductor X- and gamma-ray detectors is by increasing the electric-field strength. The limiting factor in this case is the amount of leakage current. It is possible to reduce it by forming a rectified Schottky contact instead of an Ohmic one. That allows the creation of a depletion layer in the semiconductor with an electrical resistance that is much larger than the bulk resistivity. In this case, the electromotive intensity increases 10-100 times. A surface-barrier structure on a semi-insulating Ni-CdZnTe-Ni crystal (n-type) with a resistivity of 10^{10} Ohm-cm at room temperature was formed. The leakage current was measured to be less than 3 nA at 1500 V. Results on the properties of this detector structure will be discussed.

In the last decade significant advances in the growth technology of the wide bandgap semiconductors CdTe and CdZnTe have been achieved. It allowed to create solid-state detectors of ionizing radiation that can operate at room temperature. One of their most important parameters is the energy resolution, which is determined by the quality of charge accumulation that occurs during the gamma-ray absorption. A large number of studies specifically are aimed at improving the charge collection. Of course, one of the ways to improve non-equilibrium charge carrier collection (especially holes) is to increase the electric field. In this case the competing limiting factor is the detector leakage current, which eventually leads to increased noise and, certainly, to deterioration in detector energy resolution.

In order to reduce the leakage current a number of methods can be used: detector annealing with already established contacts, various methods of lateral surface passivation, and detector cooling by thermoelectric elements. It usually concerns the so-called homogeneous detectors, i.e. detectors with ohmic contacts. Often an increase in detector dark current is associated with conduction along the lateral surface, and a decrease of the leakage current is connected with the side surface passivation. Our studies of this detector type show that the challenge to reduce the dark current of the homogeneous detector is complicated by the fact that with increasing of electric field, the leakage current increases linearly at first and then increases superlinearly. Thus, the higher the quality of the semiconductor material, i.e. the smaller is the concentration of free charge carriers, the higher the mobility and lifetime of non-equilibrium charge carriers. In this case the superlinear part of the current-voltage (IV) characteristic begins at the lower electric field. We attribute this phenomenon in the framework of the space-charge-limited current model.

From our point of view, one of the possible solutions to reduce the leakage current is the formation of rectifying contacts (for example, Schottky contacts) instead of an Ohmic contact. In this case, the rectifying contact is formed near the depletion region in which there are practically no free charge carriers. The resistance in this region is substantially higher than the resistance of the homogeneous part of the semiconductor; it allows a significant reduction in the detector leakage current and thus a significant increase in the electric field. All these facts have a positive effect on important key parameters of the detector, such as efficiency and resolution.

Surface current is an important factor which enhances the detector dark current, resulting in a reduction in the apparent semiconductor material resistivity. A dark current increase leads to a deterioration of the detector's energy resolution, because the dark current is the equilibrium current, and acts as a background for current pulses observed during the absorption of ionizing radiation photons. The surface current may appear due to the formation of the inversion layer (depleted by free charge carriers) or the semiconductor layer, enriched by free carriers (Fig. 1c,

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a conductive layer on the surface of the semiconductor (for n-type it is an n^+-layer, while for the p-type it is a p^+-layer). In the case of depleted inversion layer, the appearance of the conductive layer on the semiconductor surface needs an additional explanation.

It is clear that for the production of ionizing radiation detectors one needs crystals with high resistivity, i.e. semi-insulating single crystals with weak n- or p-type conductivity. There are "dangling" bonds on the semiconductor surface, which can create energy levels in the band gap. These levels, or so-called surface energy states, can capture free charge carriers. Charge, which generates at these levels, leads to a curvature of the semiconductor energy zones with potential barrier formation. In Fig. 1a-d the energy diagrams of possible surface state for the n-conductivity type are shown (for p-type semiconductor the conduction situation is similar).

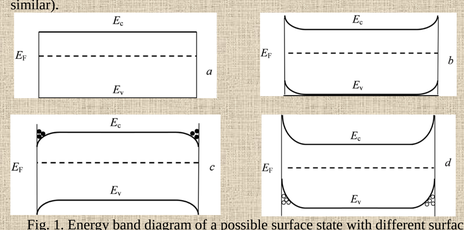

Fig. 1. Energy band diagram of a possible surface state with different surface treatment for a n-type semiconductor: a – flat zone; b - depletion of the subsurface layer without inversion, c - enrichment of the surface layer (accumulation), d – inversion conductivity of the surface layer

In the case of a sufficiently large bending of the energy bands, the Fermi level can approach to the valence band of the semiconductor in the case of the n-conductivity type (Fig. 1d) or to the conduction band in the case of p-type semiconductor. These phenomena lead to the formation of an inversion layer, i.e. layer, which has an opposite conductivity type than the semiconductor bulk. It should be noted that the effect of this layer on the overall crystal conductivity will be noticeable (we mean a decrease in conductivity) only in the case of sufficiently large thickness of the inversion layer. It happens at the potential barrier formation, when its height exceeds the half of the semiconductor band-gap. In other instances the formation of a low potential barrier at the surface, which does not lead to the formation of an inversion layer, might be even helpful (Fig. 1b), i.e. it may reduce the overall surface and dark current. The formation of the enriched

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layer on the semiconductor side surface (Fig. 1c) always leads to a current increase, i.e. in this case it is a harmful factor. In summary, it can be claimed that for dark current reduction, we need such semiconductor surface treatment, which creates either a situation of "flat" zones, i.e. practically an absence of any bending of the bands or, in the ideal case, the zone bending should be small. Then the Fermi level at the surface has energy equal to approximately half of the band-gap width (for an intrinsic semiconductor).

For practical use it is enough to perform such processing of the semiconductor surface when the bending of the bands is minimal, i.e. the height of the potential barrier at the surface should be much smaller than half of the forbidden band width (Fig. 1a, b). An enrichment of the surface (Fig. 1c) is useful in the case of creating an Ohmic contact to the semiconductor. To obtain an Ohmic contact, we seek a surface treatment that ensures the flat zones on the surface (Fig. 1a), i.e. the absence a of potential barrier. In general, these processes are called the surface passivation. But, as we have seen, in the case of surface current minimization and in the case of Ohmic contact formation, the tasks of the passivation are generally different. In addition, for surface passivation one must also solve the problem of creating a protective layer that prevents the possibility of surface contamination, leading to dark current increase.

CZT crystals, containing ~10% zinc, with weak n-type conductivity and resistivity of ~(2-3)*10^{10} ohm*cm at 20 °C were used. For comparison and study of the influence of the side surface passivation processes, Ohmic contacts were formed to a single crystal (6*6*12 mm^3). Important from our point of view is the fact that for reasons of experiment clarity and excluding the effect of possible crystal irregularities at I-V measurements, all technological procedures and I-V measurements were carried out with the same CZT single crystal. In addition the surface with an Ohmic contact was always processed identically, but the side surfaces were treated differently.

Metal for creating an ohmic contact was deposited on the surface 6x6 mm^2. First, after grinding and polishing of the semiconductor surface with a gradual decrease in grain diameter grinding paste, crystals were etched in a bromine-methanol solution and washed with methanol. It is known that the n-conductivity type Ohmic contact of good quality can be obtained by using indium as a metal [5], therefore we used indium to obtain an Ohmic contact. It was applied by thermal evaporation under high vacuum. Side surfaces after Ohmic contact formation were treated in three ways:

1 - in an argon plasma at a voltage of 300-400 V and a current of 40-50 mA;
2 – in a solution #1 (Table 1) at 60 °C (or 80 °C) during 5-15 min;
3 – the samples placed in a drop of the solution #2 ($CdCl_2$ - 0,015, $CS(NH_2)_2$ - 1.5, NH_4OH - 14,3 mol/L) and heated in the oven until the solution evaporated.

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Table 1. The composition of the solution #1

Component	volume, ml	concentration, mol/L
$CdSO_4 \cdot 8H_2O$	0,3	20
$SHCH_2COOH$	0,012	10
H_2O	–	150
NaOH	1	27

In treatments 2 and 3, let us call them passivation 2 and 3, indium ohmic contacts defended chemically by resistant epoxy. The I-V curves for the three types of side surface treatment are shown in Fig. 1.

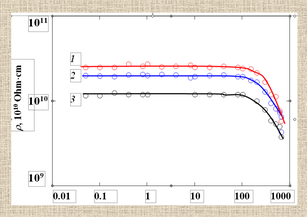

Fig. 2. The dependence of the differential resistance vs the applied voltage for Cd(Zn)Te crystal with indium contacts but with different treatment side surfaces:
1 - side surface was etched in a bromine-methanol solution, and then treated in an argon plasma;
2 – the side surface was treated in solution #1;
3 – the surface was treated in solution #2.

The resistivity of the semiconductor, determined from the linear portion of the I-V curve (for side 1) at 20 °C, was 2.5*10^{10} Ohm*cm. This resistance will serve as a benchmark to which we compare the sample resistivity after passivation processes 2 and 3. This choice was not accidental. Experiments with sample thickness decreasing (from 10 mm to 2 mm) with a good accuracy showed (for the same metallic contact area) the constant semiconductor resistivity for such side surface processing method.

At noticeable currents along the lateral surface the variation in the sample thickness in about 5 times would inevitably lead to a decrease in the crystal resistance. Such processing may not be protected by the side surface operation detector, but may serve as a criterion for evaluating the lateral surface passivation effect on the structure of the dark current. As we noted 2 passivation processes were applied. The effects of passivation on the sample's resistivity is shown in Fig. 2.

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which demonstrates that at the treatment 2 the "specific" resistance is 2*10^{10} Ohm*cm and for the processing 3 - 1.2*10^{10} ohm*cm (both at t=20 °C).

As it is seen from the I-V measurements after passivation the resistivity only decreased, which means that both treatment types resulted (to varying degrees) in the "specific" resistance reducing and, as a consequence, to an increase of dark current. It may indicate that an enriched or inversion semiconductor layer with a lower resistivity than the resistance of the bulk material was formed on the side surface. Thus comparing three different treatments for the sample side surface and the same surface treatment prior to the establishment of the contact (i.e. the end), we can conclude that the different side surface treatment only resulted in an increase in dark current for sample 1.

Of course, it would be interesting to answer the question whether there is an opportunity to decrease the dark current in the sample. We are confident that the minimal dark current of sample 1 is determined (or limited) by its resistivity. This is shown by obtaining the constant resistivity values when changing the sample thickness from 15 mm to 2 mm. In our opinion, further dark current reduction for sample 1 is possible only by changing of the contact formation method. For this purpose, we have decided not to change the lateral surface treatment, but to createcontacts using different methods. Here, we mean different ways to process the end faces and different methods for metal attachment, i.e. we exclude the impact of the lateral surface and want to determine the effect of contact formation method on the dark current value.

The contact area at the end faces of the CZT sample (11*6*6 mm^3) was 6x6 mm^2. It should be noted that for the contact formation studies in all experiments, the same crystal was used. The contacts were obtained by method 1, I-V curves were measured, and then contacts were removed and subsequently created by methods 2 and 3 with the following I-V measurements. We chose the following three different ways to create a contact: 1 - thermal evaporation of indium (sample 1), 2 - chemical precipitation of gold from a solution of gold chloride (sample 2), 3 - thermal spraying of chromium (sample 3). Before contact formation the surface was conventionally etched in a bromine-methanol solution and besides in the method 3, before the chromium sputtering, the surface was additionally treated in an argon plasma at a voltage of 500-600 V and a current of 15-20 mA for 10-15 min. Side surface treatment for all three methods of the contact formation was performed evenly as described above. I-V curves for these structures are shown in Figure 3.

As can be seen from Fig. 3, the obtained I-V curves are quite different. Note that the dark current of the sample 3 does not exceed 3 nA at a voltage of 1500V. For clarity, Fig. 4 shows the dependence of the differential resistance (dV/dI) on the voltage, since the differential resistance is more sensitive to non-linear I-V characteristics. Taking into account the length and the contact area of the sample,

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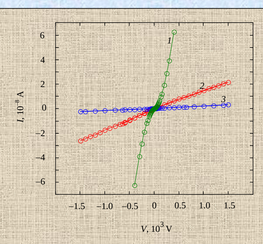

Fig. 3. The current-voltage characteristics of Cd(Zn)Te crystal at 20 °C with different contacts:
1 - indium contacts;
2 - gold contacts;
3 - contacts were formed by vacuum deposition of chromium.

one can calculate the resistivity of the crystal. It should be noted that resistivity refers only to the linear part of I-V curve of the sample 1. For the samples 2 and 3 the hypothetical resistivity was calculated for the comparison with the results of I-V measurements. For the samples 2 and 3 more relevant term is the differential resistance R_{diff}.

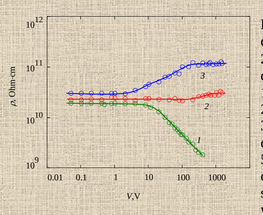

Figure 4. The dependence of the differential resistance on the voltage at 20 °C for Cd(Zn)Te crystal with different contacts:
1 - indium ohmic contacts;
2 - gold contacts;
3 - contacts, obtained by vacuum deposition of chromium. Crystal size 5*6*11 mm^3. Contacts were established on the surfaces of 5*6 mm^2. Lateral surface processing for all contact types was the same.

As we can see from Fig. 4, the differential resistance at the initial part of I-V curve is approximately constant for all samples. Besides it is important that the resistances of samples 2 and 3 are significantly higher than the resistance of the sample 1. It is especially noticeable when the voltage increases. Resistance rise in the samples 2 and 3 with voltage increasing indirectly indicates on the presence of a rectifying barrier, depletion region of which enlarges together with applied voltage. Moreover, resistance of the sample 3 (Cr-CdZnTe-Cr) increases with voltage magnitude increasing on bigger value than for the sample 2 (Au-CdZnTe-Au), which indicates on greater potential barrier height in Cr-CdZnTe-Cr structure than

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in Au-CdZnTe-Au. Since the resistance of the crystal depletion region was bigger than the neutral one, the total resistance of the structure increased with the voltage rise. Since the resistance of the depletion region is close to the resistance of an intrinsic semiconductor, we should expect the change in the temperature dependence of the resistivity. In this case the activation energy of conductivity at lower voltages is expected to be lower than at higher voltages, when the depletion region occupies a significant portion of the crystal. The minimum value of the activation energy of conductivity in our opinion is natural to expect for sample 1 (In-CdZnTe-In) with high-quality ohmic contacts. The temperature dependence of the resistivity for Cr-CdZnTe-Cr structure is shown in Fig. 5, and for sample 1 – in Fig. 6. The temperature dependence of the resistivity for the sample 1 (In-CdZnTe-In) is shown in Fig. 7. As it was expected, the conductivity activation energy for sample 1 (ΔE=0.75 eV) is significantly smaller than for the sample 3 (ΔE=0.85 eV). For the sample 3 it is approximately equal to the half of the CZT forbidden band width at 0 K. It shows that temperature dependence of the depleted layer with almost intrinsic conductivity dominates in the temperature dependence of the Cr-$Cd_{0.9}Zn_{0.1}Te$-Cr structure resistance.

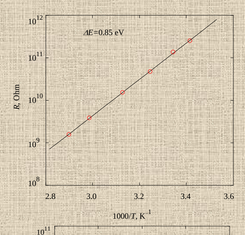

Fig. 6. The temperature dependence of dark Cr-CdZnTe-Cr crystal resistance at 100 V, it corresponds to sub-linear section of I-V curve. Crystal size 5x6x11 mm^3.

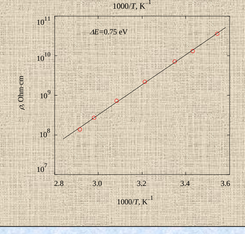

Figure 7. The temperature dependence of the resistivity for the In-CdZnTe-In structure at a voltage within the linear part of the I-V curve (V = 5 V). Crystal size 5*6*11 mm^3.

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carriers, which are available in the semiconductor and should be in thermal equilibrium with the lattice.

Thus, we can say that indium Ohmic contacts practically do not change the basic properties of a semiconductor: the resistivity, the mobility of the main charge carrier, and the lifetime. Rectifying contacts can significantly change the mobility of the majority charge carriers, the material resistivity and lifetime [7]. Therefore, the limiting of operating detector voltage for the crystals of the same thickness occurs at higher voltages than in the case of Ohmic contacts, where the operating voltage is limited by SCLC mechanism. In the case of rectifying contacts the change of some important semiconductor properties, which naturally affects the SCLC mechanism, is observed. The results obtained with respect to homogeneous semiconductor detectors indicate that the maximum operating voltage of the homogeneous detector (i.e. the voltage at which the optimal parameters of the detector are realized or Ohmic region of I-V curve) is limited by SCLC mechanism.

Therefore, if the voltage applied to the detector, exceeds the range of the linear area, current significantly larger than the current in Ohmic part of I-V curve will pass through the detector. On the other hand, it means that at such voltages the equilibrium charge carriers that are injected into the semiconductor from the Ohmic contacts and non-equilibrium charge carriers generated by absorption of ionizing particles will cross the detector without coming to the state of thermodynamic equilibrium with the lattice. These currents will be substantially larger and will produce additional noise, which will lead to a reduction in the detector resolution.

Obviously, the operating voltage restriction leads to a limitation of the electric field, the value of which is important for the efficient collection of non-equilibrium charge carriers. Rectifying contacts, changing semiconductor properties allow much higher voltage being applied to detector, which for the same thickness of the crystal indicates the reaching of substantially high electric field at a lower dark current in the barrier detector, than in the homogeneous detector with Ohmic contacts. Despite the fact that with electric field increasing the reducing of lifetime and charge carrier mobility is possible [4], in general increasing of the electric field has a positive effect on the properties of the detecting detector.

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From our point of view, the set of experiments shows that in the case of samples 2 and 3 we are dealing with rectifying barrier structures and just the presence of the barrier allows us to reduce significantly the dark current in a symmetrical metal-CdZnTe-metal structure, and the role of the lateral surface is minimal. Of course, the current-voltage characteristics of the sample 1 require special attention. The dark current increases (resistivity decreases) with the same side surface processing in samples 2 and 3 at the voltage 20-30 V. We do not link the current increase with the "leakage" associated with a side surface conductivity increase. We associate this process with the current limited by space charge (SCLC). I-V characteristics of the sample in the coordinates of the SCLC are shown in Fig. 8.

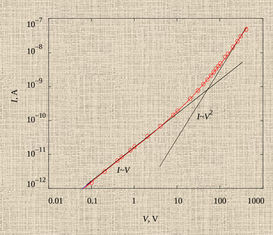

Figure 8. I-V characteristics of the sample 1 in the coordinates of the SCLC at 20 °C.

Fig. 8 shows two characteristic regions: linear (Ohmic, where I~V) and quadratic (where I~V^2 and corresponds to currents limited by space charge). Voltage V_o, which is determined by the intersection of the lines I~V and I~V^2, is called the Ohmic voltage to quadratic transition region of I-V curve. In our studies the V_o value well followed the dependence V_o~d^2, which is typical for SCLC [6]. At the same time, we restrict the analysis of SCLC mechanism, because it is not the main purpose of this work, and it will be investigated in our next work. An important conclusion to be drawn from the analysis of I-V characteristics of the sample 1 is as following: SCLC limits the operating voltage in detector with high-quality Ohmic contacts, i.e. with such contacts, which inject the main free charge carriers from the metal into the semiconductor in such a way that the average energy of charge carriers introduced into the semiconductor does not differ from the average energy of the free charge carriers of the crystal, i.e. that thermal balance remains in the semiconductor. In other words, the free charge carriers should not be hot when entered into semiconductor, but should differ a little in the energies of charge

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Conclusions

Our results allow us to suggest that the dark current of a homogeneous detector with Ohmic contacts is limited by semiconductor detector resistivity and the operating voltage – by currents, limited by space charge. Detector with rectifying barrier has significantly lower dark current at the same voltage and contact geometry, and it has larger voltage with the same treatment of the detector sides.

Our research showed that the main factor reducing detector dark current is a formation of a rectifying barrier during creating contacts to the detector, and the role of the lateral surface passivation in this case is minimal. Passivation plays the main and major role in Ohmic contact formation for homogeneous (resistive) detectors, where the electric field uniformity is important inside of the detector volume or for determining the resistivity of the semiconductor detector material and for other studies, where the electric field uniformity is important.

A C K N O L E D G E M E N T

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*** E-mail: fochukp@gmail.com**

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