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Electrophysical properties of metal-semiconductor-metal structures based on isovalently doped zinc selenide crystals

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Electric capacitance C and dielectric losses tgδ have been determined for metal-semiconductor-metal structures based on isovalently doped ZnSe crystals. It has been shown that annealing of the grown crystals in zinc atmosphere causes the increase of C by 2–3 orders of magnitude. This parameter, as well as tgδ becomes dependent upon the bias voltage U, with regions of negative and of positive slope observed on the $C(U)$ plots. It has been shown that dependences $C(U)$ and tgδ(U) are determined by changes with voltage in the two oppositely switched Schottky barriers.

Исследованы электроемкость C и тангенс угла диэлектрических потерь tgδ структур металл-полупроводник-металл на основе изовалентно легированных кристаллов ZnSe. Установлено, что отжиг кристаллов в атмосфере цинка обусловливает увеличение C на 2–3 порядка. Параметры C и tgδ становятся зависящими от смещающего напряжения U, причем в зависимости $C(U)$ наблюдаются участки как с отрицательным, так и с положительным наклоном. Показано, что зависимости $C(U)$ и tgδ(U) определяются изменением с напряжением двух, включенных навстречу друг другу, барьеров Шоттки.

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Isovalent dopants introduced into zinc selenide crystals are known to form associates with the intrinsic structure defects. This causes substantial changes in the spectrum of charge carrier localized states and, as a consequence, improvement of the luminescent properties [1]. Closely related to point structure defects are also dielectric properties of the crystals, e.g., dielectric losses [2] or dielectric relaxation [3]. Therefore it could be expected that introduction of isovalent dopants would allow control of electrophysical and, in particular, of dielectric parameters of the said crystals, conditioning their application in various techni-

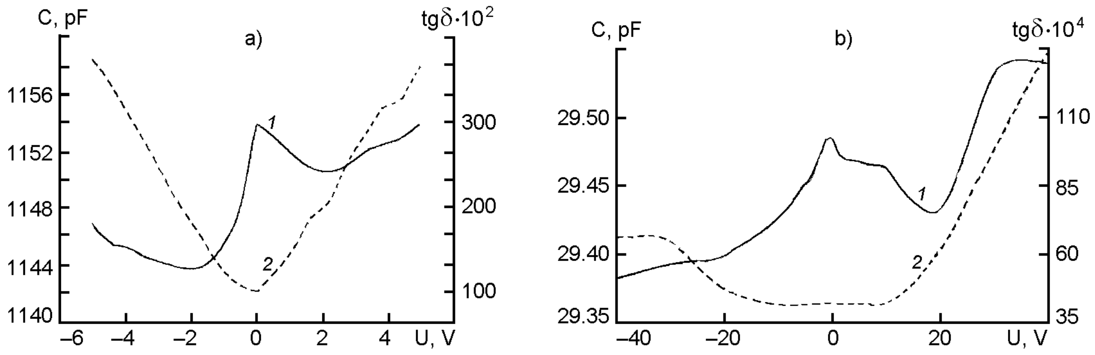

Fig. 1. Typical dependences of electric capacitance (*1*) and dielectric losses (*2*) of MSM structures on the basis of crystals ZnSe (a) and ZnSe(Te) (b) upon the bias voltage.

cal devices. However, effects of isovalent dopants upon the dielectric response, as far as we are informed, has not yet been studied. Carrying out such studies was the principal purpose of the present work.

We have studied ZnSe, ZnSe(Te) and ZnSe(O,Te), grown from the melt under high argon pressure using two different technologies. This enabled us to obtain scintillators of two types. Scintillators of the first type (I) were prepared from ZnSe(Te) crystals, as well as ZnSe crystals grown using the standard technology. They are characterized by high light output (up to 140 % with respect to CsJ(Tl)), luminescence spectra with maximums at 630–640 nm, and decay times reaching ~100 ms. The preparation technology of ZnSe-based scintillators of the second type (II) is related to crystal growth under additional doping with oxygen. Such scintillators have lower light output and smaller decay times. The maximum of the luminescence spectrum is shifted towards shorter wavelengths (λ_{max} = 600–610 nm). After growth, some of the samples were annealed in zinc atmosphere in vacuum-sealed quartz ampoules at 1290 K during 24–48 hours.

The concentration of tellurium was determined by scanning electron microscopy with X-ray microanalysis using an ISM-820 electron microscope with a Zink AN10185S microanalysis system (EMPA-electron-probe microanalysis). The determination accuracy was 0.3÷0.5 mass %. Electrophysical measurements were carried out on 5×5×3 mm^3 large samples. Onto the large sides, electric contacts were applied in the form of In–Ga eutectics, thus forming a metal-semiconductor-metal (MSM) structure. Measurements of the capacitance *C* and dielectric losses tgδ of the structure were carried out in the low-frequency range using a R589 AC bridge, and in the high-frequency range — a BM 560 Q-meter.

With any dopant composition, in the low-frequency range electric capacitance of MSM-structures based on non-annealed ZnSe crystals did not exceed several pF, which is in agreement with the known values of the dielectric constant for undoped crystals [4]. Dielectric losses are also rather low (tgδ~10^{-2}). Both parameters are weakly dependent upon temperature and the electric field frequency. An essential feature of the dielectric response of structures based on annealed ZnSe(Te) and ZnSe(O,Te) crystals is unexpectedly high value of their capacitance, which reached 2 nF in several samples. With that, average values of *C* for ZnSe(O,Te) — based structures were much larger than those observed for ZnSe(Te) crystals. However, the average tgδ values of the said structures are related by an inverse relationship.

To clear up the nature of high polarizability of MSM-structures, we have measured their volt-capacitance characteristics (VCC). Dependence of *C* and tgδ upon the applied voltage *U* would indicate a substantial role of electrode-adjacent potential barriers in the process of electric polarization of the structure. In fact, electric capacitance and dielectric losses of the structures on the basis of annealed ZnSe(Te) and ZnSe(O,Te) samples depend upon the value and polarity of the applied bias voltage. A typical appearance of such plots for the opposite polarities of the bias voltage is shown in Fig. 1. Characteristic features of the shown *C*(*U*) dependence is the presence of regions with positive or negative slope at low and relatively high voltages, respectively, as well as different dependences for opposite directions of the applied field. However, the tgδ(*U*) dependence is not substantially changed when polarity of the bias voltage field is reversed. One should note that asymmetry of the $C(U)$ plots is reproduced upon removal and subsequent new application of the electric contacts upon the samples; this asymmetry is characteristic for all structures on the basis of annealed crystals. It is important to note that the capacitance and dielectric losses of MSM-structures based on annealed ZnSe crystals are also dependent upon the bias voltage (Fig. 1,b). However, in this case the observed changes in these parameters are by nearly two orders of magnitude lower than in the case of the above-described structures.

The surface of zinc selenide crystals is known to be covered by a thin oxide film. Therefore, when the sample is placed between the two electrodes, the resulting structure can be called "metal-dielectric-semiconductor-dielectric-metal" (MDSDM). In such structures, VCC minimum has been reported at $U = 0$ [5], which does not agree with our experiments. Hence, the effects of the oxide films upon the above measurement results may be neglected, and we can treat ZnSe(O) and ZnSe(O,Te) crystals with electrodes as structures "metal-semiconductor-metal" (MSM). In other words, the structures studied are, in fact, two Schottky diodes switched in mutually opposite directions.

The AC bridge R589 used in our measurements involved the parallel substitution scheme of the object (Fig. 2,a). The directly measured values are electric capacitance and tgδ of the object

$$\mathrm{tg}\delta = \frac{1}{\omega RC}, \tag{1}$$

($\omega = 2\pi f$). Neglecting crystal volume effects upon VCC of the MSM structure, its equivalent electric diagram can be presented as two series-connected R-C-chains (Fig. 2, b). Each of the chains corresponds to a Schottky barrier at the metal-semiconductor boundary. The capacitances of the depleted boundary layers are C_1 and C_2, respectively. It should be noted that when the bias voltage applied to the structure is increased, one of the capacitances will be increasing, while the other will decrease. Assuming that R_1 and R_2 are equal, the equivalent capacitance of the structure, defined by connection in series of C_1 and C_2

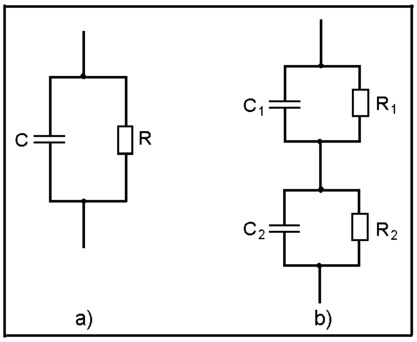

Fig. 2. Equivalent electric substitution diagrams of the measurement object (a) and MSM-structure (b).

$$C = \frac{C_1 C_2}{C_1 + C_2} \tag{2}$$

would also decrease. Such behavior of $C(U)$ was actually observed in the region of weak bias voltage fields (see Fig. 1). However, upon further rise of U, the capacitance of the MSM structure increases. This can be explained by the effects of resistivity of the depleted layers, which, decreasing with rising U, shunts the lowest capacitance of the MSM structure.

To check up the above assumption, mathematical modeling of the $C(U)$ function was carried out for a MSM-structure. It was assumed that the resistance of each of the depleted layers is a function of voltage determined by the expression:

$$R = R_0 \exp(bU), \tag{3}$$

where b is a constant.

As U is an algebraic value, the voltage fall on each of the barriers (U_1 and U_2, respectively) was calculated by iterations carried out for each value of the applied voltage U. U_1 and U_2 that had been thus determined were used in calculations of the depleted layer capacitance [6]

$$C_i = \sqrt{\frac{e\varepsilon\varepsilon_0 N_d}{2\left(V_b - V_i - \frac{kT}{e}\right)}}, \tag{4}$$

where e is the electron charge, ε_0 — dielectric constant, ε — dielectric permittivity of the crystal, N_d — concentration of the donor dopant, V_b — bending of zones in the depleted layer region, k is the Boltzmann constant, and T is the absolute temperature.

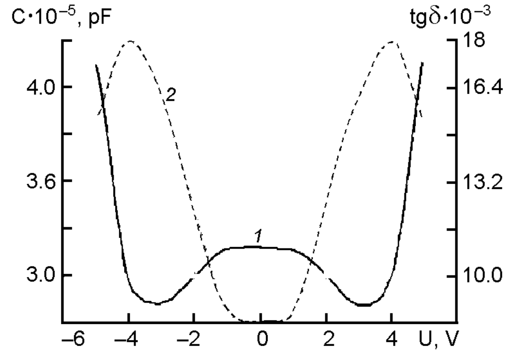

Fig. 3. Electric capacitance (*1*) and dielectric losses (*2*) as function of the bias voltage, obtained as a result of modeling.

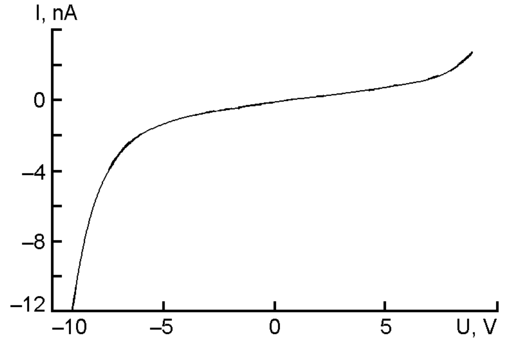

Fig. 4. A typical voltage-current characteristic of MSM structures on the basis of ZnSe(Te,O) crystals.

The equivalent capacitance of a MSM structure is described by expression

$$C = \omega^2\left(\frac{C_1}{\frac{1}{R_1^2} + \omega^2 C_1^2} + \frac{C_2}{\frac{1}{R_2^2} + \omega^2 C_2^2}\right)^{-1}. \tag{5}$$

The expression for the equivalent resistance of a MSM-structure has the form:

$$R = \frac{R_1^{-1}}{R_1^{-2} + \omega^2 C_1^2} + \frac{R_2^{-1}}{R_2^{-2} + \omega^2 C_2^2}. \tag{6}$$

The modeled functions $C(U)$ and tgδ(U) are shown in Fig. 3. Apart from the lowest voltage region for $C(U)$ and the highest voltage region for tgδ(U), these functions are qualitatively similar to those observed experimentally (cf. Fig. 1 and Fig. 3). Among possible reasons for the rise of tgδ in the highest voltage region are ionization losses, which were not accounted for in the modeling. The question of discrepancies between experimental and calculated $C(U)$ dependences at the lowest voltages requires further studies, including studies of the dielectric response of the crystal.

In our opinion, a subject of a separate study can be the asymmetry of $C(U)$ and tgδ(U) (see Fig. 1). As shown by additional studies, the asymmetry of these curves is accompanied by the dependence of the voltage-current characteristics upon polarity of the applied voltage (Fig. 4). In principle, these asymmetries can be explained assuming the presence of gradients of some physical parameters directed normally to the surface. However, this assumption does not agree with the results on Zn distribution profile stu dies in the annealed zinc selenide crystals, as well with the fact that the asymmetry of characteristics is observed at any orientation of the sample surface with respect to the ingot surface.

Concluding, it can be noted that MSM-structures based on annealed ZnSe(Te) and ZnSe(Te,O) crystals have non-linear volt-ampere characteristics related to the formation of Schottky transitions. Control of the capacitance of such structures by means of external voltage allows substantial broadening of the functional possibilities of non-polarizing detectors of ionizing radiation that are being developed on the basis of broad-band semiconductors [7].

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Електрофізичні властивості структур метал-напівпровідник-метал на основі ізовалентно легованих кристалів селеніду цинку

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Досліджено електроємність C и тангенс кута діелектричних втрат tgδ структур метал-напівпровідник-метал на основі ізовалентно легованих кристалів ZnSe. Встановлено, що відпал кристалів у середовищі цинку обумовлює збільшення C на 2–3 порядки. Параметри C і tgδ стають залежними від зміщуючої напруги U, причому в залежності $C(U)$ спостерігаються області як з негативним, так і з позитивним нахилом. Показано, що $C(U)$ і tgδ(U) визначаються залежністю від напруги двох бар'єрів Шотткі, що ввімкнено назустріч один одному.