Studies of photoactive states of isovalently doped ZnSe crystals by the method of scanning photodielectric spectroscopy

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Using methods of photodielectric spectroscopy, studies have been carried out of the energy level structure of the defect complexes in isovalently doped zinc selenide crystals. On variation of light wavelength (λ), small changes in effective values of the real ε' and imaginary ε'' parts of complex dielectric permittivity were measured in the low frequency (1−50 kHz) region using a high sensitivity AC bridge. Different configurations were used of electric and light fields in the crystals. The local energy level spectrum was determined from $\varepsilon'(\lambda)−\varepsilon''(\lambda)$ diagrams presented in the complex plane. Analysis has been carried out of relationship between characteristic features of these diagrams and parameters of photoactive states of different nature. Effects are discussed of the surface potential and band bending upon energetics of the local states.

Методами фотодиэлектрической спектроскопии проведены исследования структуры энергетических уровней дефектных комплексов в изовалентно легированных кристаллах селенида цинка. При варьировании длины волны света (λ) с помощью высокочувствительных мостов переменного тока измерены малые изменения эффективных значений действительной ε' и мнимой ε'' частей комплексной диэлектрической проницаемости образцов в низкочастотной (1−50 кГц) области. Использовались различные конфигурации электрических и световых полей в кристаллах. Спектр локальных энергетических уровней определялся из диаграмм $\varepsilon'(\lambda)−\varepsilon''(\lambda)$, представленных в комплексной плоскости. Выполнен анализ связи характерных особенностей диаграмм с параметрами фотоактивных состояний различной природы. Обсуждается влияние поверхностного потенциала и изгиба зон на энергетику локальных состояний.

The most important feature of the defect structure of binary semiconductor crystals is the presence of a well-developed system of intrinsic defects. Therefore, the dopant atoms introduced into the crystal, interacting with the intrinsic defects, lead to a new state of the whole system of defects [1−3]. Purposeful variation of physical properties of crystals by doping or any other means requires detailed studies of the intrinsic defects. This, in turn, requires the use of new methods of studying the localized states, which should complement the conventional investigation techniques. The present work was aimed at studying photoactive states of

ZnSe(Te), ZnSe(O,Te) and ZnSe(Cd) crystals by methods of scanning photodielectric spectroscopy (SPDS) [4], photoconductivity and photoluminescence.

Isovalently doped zinc selenide crystals were grown in graphite crucibles by Bridgman-Stockbarger method in vertical compression furnaces under argon pressure $5 \cdot 10^6$ Pa [2]. Growth rate was 2 to 5 mm/hour, and the temperature in the crystallization zone was ~1850 K. As initial raw material, we used polycrystalline zinc selenide of 5N offered by ELMA Inc. Concentration of isovalent activator dopants
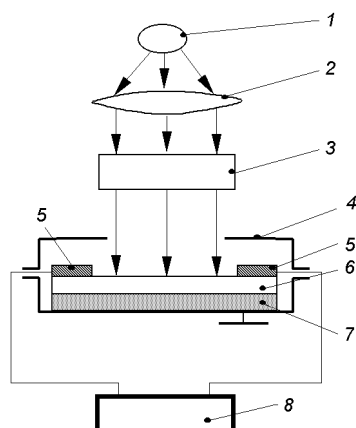
Fig. Block diagram of the device for determination of photoactive centers. 1 — light source, 2 — condenser, 3 — monochromator, 4 — electric screen, 5 — electrodes placed onto the sample in a planar pattern, 6 — sample, 7 — insulator, 8 — high-sensitivity AC bridge.

(Te, O or Cd) was 0.2 to 0.5 mass.%. The main impurity in the grown crystals was carbon (from the growth crucibles), concentration of which was 0.1 to 0.3 mass.%.

Experimental set-up for SPDS measurements is shown in Fig. SPDS studies of photoactive states were carried out using rectangular samples $3\times10\times10$ mm^3 with polished sides. The electrodes were placed onto the sided using two schemes ensuring photoexcitation of the states of predominantly surface or bulk nature. Capacitance C and dielectric losses tgδ for the system "sample-electrodes" were measured at 1 kHz using a precision AC bridge P578. Photoexcitation of samples was carried out by monochromatic light, which caused increases in C and tgδ. These increases were proportional to the increases in effective values of dielectric permittivity $\Delta\varepsilon'_{ef}$ and dielectric losses $\Delta\varepsilon''_{ef}$. Smoothly changing the photoexcitation wavelength λ, we obtained a set of values $\Delta\varepsilon'_{ef}$ and $\Delta\varepsilon''_{ef}$, the number of which is limited by the sample photosensitivity and sensitivity of the AC bridge. This set was presented in the form of a diagram in the complex plane, i.e., parametrically. From the diagram, we determined characteristic values of the wavelength λ_i corresponding to the second derivative maximum in the diagram region. Using λ_i and the band gap value E_g, we calculated the depth of the corresponding energy level with respect to the top of the valence zone:

$$E_i = E_g - hc/\lambda_i,$$

where h is the Planck constant, c — light speed in vacuum. E_i could be determined with accuracy of ±0.005 eV. The spectral distribution of photoconductivity was determined from the similar dependence of tgδ. The measurements were carried out under normal conditions.

Dependences of photoconductivity from λ for ZnSe(Te), ZnSe(O,Te) and ZnSe(Cd) crystals are similar, distinguishing only in the position of the long-wave maximum. This maximum is at $\lambda = 1087$ nm for Te-doped crystals, while with the extra dopant O it is shifted to $\lambda = 1050$ nm. A more short-wave maximum in the photoconductivity spectrum of both crystals is at $\lambda = 499$ nm. As it will be shown below, the same wavelength values as characteristic λ_i were found by SPDS. However, in the latter case the number of λ_i is much higher. This can be due to the fact that SPDS signals are formed not only by the active, but also by the passive component of the current. Alongside with free current carriers, the bound ones also contribute to the signal.

The localized states in the crystals studied, which were found by SPDS, are given in the Table. The most obvious point is the presence of levels with negative depth (with respect to the top of the valence zone E_v. However, this fact cannot be considered as unusual, accounting for the existence of a surface-adjacent electrostatic potential φ_s

Table. Spectrum of energy levels E_i with respect to the top of the valence zone for isovalently doped ZnSe crystals

Crystal	E_i, eV
ZnSe	−0.065; −0.023; 0.003; 0.044; 0.235; 0.710; 1.284; 1.478; 1.531; 1.592
ZnSe(Te)	−0.096; −0.075; −0.061$_a$; −0.032; −0.023; 0.049$_b$; 0.113$_a$ (0.174); 0.211$_b$ (0.162); 0.334; 0.401; 0.707; 1.458; 1.469
ZnSe(O,Te)	−0.140; −0.128; −0.119; −0.114; −0.112; −0.104; −0.085; −0.077; −0.059; −0.037$_a$; −0.019; 0.040$_b$; 0.090$_c$; 0.113$_a$ (0.150); 0.195$_b$ (0.155); 0.247$_c$ (0.157); 0.310; 0.374; 0.603; 1.010; 1.419
ZnSe(Cd)	−0.100; −0.081; −0.049; −0.023; 0.031; 0.043; 0.108; 0.208; 0.499; 0.715; 1.490; 1.553

and the corresponding bending of the energy bands. In the studied ZnSe(Te), ZnSe(O,Te) and ZnSe(Cd) crystals, energy bands are bent downwards. Using the energy spectrum obtained by SPDS, one can calculate φ_s [4]. In this calculation, several (not less than two) energy levels are used, which are repeated with a shift by φ_s. In the Table, these levels bear indexes a, b and c. At the right-hand side, in parentheses, values of φ_s are given for selected pairs of energy levels. We can see that the average value of φ_s for ZnSe(Te) samples is 0.168 eV, while for ZnSe(O,Te) and ZnSe(Cd) samples — 0.152−0.154 eV. Accounting for this, it can be understood that actually the depth of all levels with respect to E_v is positive.

We can suppose that the levels noted in the Table above the 0.049 eV level for ZnSe(Te) and 0.040 eV level for ZnSe(O,Te) and ZnSe(Cd) are of the surface-related nature. This assumption is supported by the results of additional studies of undoped ZnSe crystals, with their surface being primarily a cleavage, and then grinded and polished. According to the data obtained, mechanical treatment of the surface leads to substantial changes in the energy spectrum of the localized states (some levels disappear, and others appear) just at depths lower than 0.10 eV. We do not consider now the question of the depth values of these levels, making it an objective of further studies. However, one can see from the Table an obvious relationship between the number of shallow levels and the presence of oxygen in the crystal.

The levels more deep than 0.1 eV are known from literature. Specifically, levels of (0.1…0.15)eV were observed in crystals annealed in selenium vapor and other similar conditions [5, 6]. Comparing the levels of ZnSe(O,Te) crystals with depth of 0.195 eV, 0.310 eV and more (the level 0.247 eV is excluded from this list) with ZnSe(Te) levels, one can see that these sequences of levels are characterized by a certain relationship, i.e., 1.469 eV > 1.419 eV; 1.458 eV > 1.010 eV, etc. The existence of such shift can be explained by the influence of oxygen, atoms of which, when introduced into point defect complexes, change the corresponding energies, which become lower.

Thus, the presence in ZnSe crystals, alongside with tellurium atoms, of oxygen and cadmium atoms leads to an increase in the surface-adjacent bending of the energy bands and substantially affects the spectrum of the localized states of carriers.

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Дослідження фотоактивних станів ізовалентно легованих кристалів ZnSe методом скануючої фотодіелектричної спектроскопії

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Методами фотодіелектричної спектроскопії проведено дослідження структури енергетичних рівнів дефектних комплексів в ізовалентно легованих кристалах селеніду цинку. При варіюванні довжини хвилі світла (λ) за допомогою високочутливих мостів змінного струму виміряно малі зміни ефективних значень дійсної ε' та уявної ε'' частин комплексної діелектричної проникності зразків у низькочастотному (1−50 кГц) діапазоні. Використовувалися різні конфігурації електричних та світлових полів у кристалах. Спектр локальних енергетичних рівнів визначався із діаграм $\varepsilon'(\lambda)-\varepsilon''(\lambda)$, наведених у комплексній площині. Зроблено аналіз зв'язку характерних особливостей діаграм з параметрами фотоактивних станів різної природи. Обговорюється вплив поверхневого потенціалу та вигину зон на енергетику локальних станів.