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Radiation-induced changes in dielectric and photoelectric properties of $A^{II}B^{VI}$ crystals

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To determine the kinetics of pre-threshold defect formation, studies have been carried out of dielectric permittivity of isovalently doped zinc selenide and $Cd_{1-x}Zn_xTe$ crystals (x = 0.16). X-ray irradiation of the samples was carried out (W-anode, 100–150 kV), with its dose D varied within the limits of up to 900 R. Dielectric parameters ε' and ε'' were measured by the capacitance technique in the frequency range 1...50 kHz. The photoactive states were studied by the method of scanning photodielectric spectroscopy. Non-trivial changes were noted in parameters ε' and ε'' upon increasing radiation dose. The values and sign of these changes depend upon the dose, as well as on frequency of the AC electric field. It has been shown that, starting from small values of D, transformation occurs of the system of intrinsic structure defects: concentration of initial defects is changed, new defects are formed, as well as their associates. Substantial difference has been noted in behavior of the said parameters for ZnSe and $Cd_{1-x}Zn_xTe$ crystals.

Для определения кинетики допорогового дефектообразования исследовалась диэлектрическая проницаемость изовалентно легированного селенида цинка и кристаллов $Cd_{1-x}Zn_xTe$ (x = 0,16). Облучение образцов производили рентгеновским излучением (W-анод, 100–150 кВ), доза D которого варьировалась в пределах до 900 Р. Диэлектрические параметры ε' и ε'' измерялись емкостной методикой в диапазоне частот 1...50 кГц. Фотоактивные состояния исследовали методом сканирующей фотодиэлектрической спектроскопии. Обнаружены нетривиальные изменения параметров ε' и ε'' по мере возрастания дозы облучения. Величина и знак этих изменений зависят от дозы, а также частоты переменного электрического поля. Показано, что, начиная уже с малых значений D, происходит преобразование системы собственных дефектов структуры: изменяется концентрация исходных дефектов, образуются новые дефекты и их ассоциаты. Наблюдаются существенные отличия в поведении указанных параметров для кристаллов ZnSe и $Cd_{1-x}Zn_xTe$.

Ionizing radiations are known to cause processes of formation, migration and interaction of point defects, in which intrinsic defects of the crystal are also involved. As a result, wide spectrum of crystal properties is changed. In this relationship, studies of irradiated semiconductors touch many problems of physics and technical application of crystals, including modification of their properties by radiation [1]. Such studies are mainly concerned with the radiation type and the absorbed dose, peculiar features of composition and defect structure of the crystal, as well as the electrophysical property under study. The present work was aimed at studying changes in dielectric parameters and energy spectrum of the localized states of isovalently doped ZnSe (ZnSe(IVD)) and $Cd_{1-x}Zn_xTe$ (CZT) crystals that could be caused by effects of X-ray radiation.

Zinc selenide crystals were grown by Bridgman-Stockbarger method in a vertical compression furnace under argon pressure

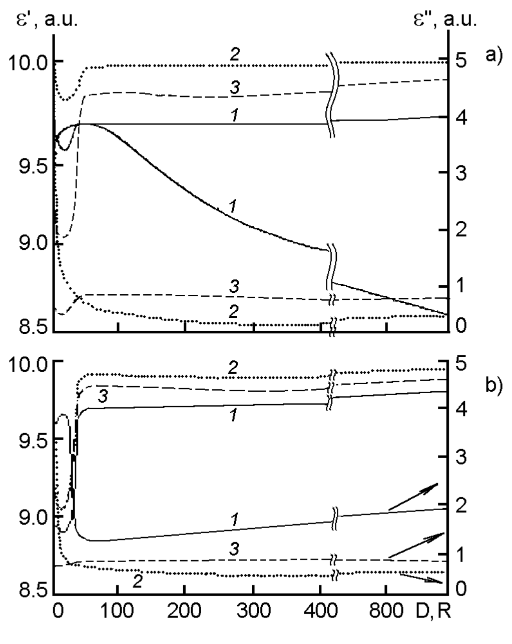

Fig. 1. Dose dependences of ε′ and ε″ for ZnSe(IVD), a — primary (1 h. after X-ray irradiation), b — secondary (24 h. after X-ray irradiation): *1* — 1 kHz, *2* — 5 kHz *3* — 10 kHz

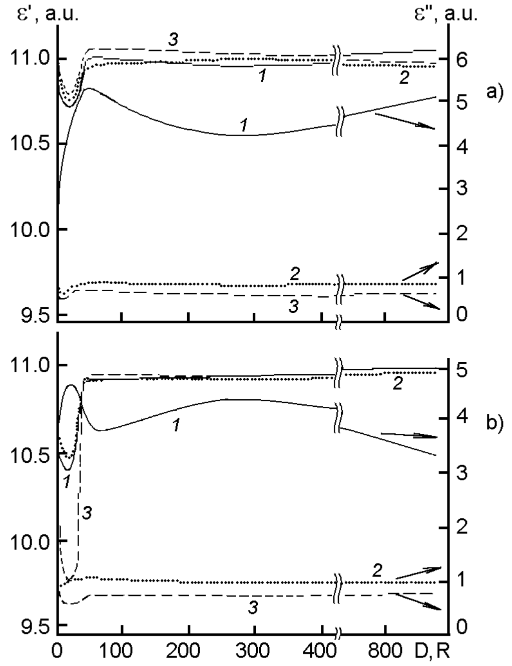

Fig. 2. Dose dependences of ε′ and ε″ for CZT, a — primary, b — secondary: *1* — 1 kHz, *2* — 5 kHz *3* — 10 kHz

of up to $5 \cdot 10^6$ Pa. Graphite crucibles were used. The temperature in the crystallization zone was 1850 K, and the growth rate was 2–5 mm/h. The source materials were ZnSe of 5N offered by ELMA, Inc. The isovalent doping (with tellurium, oxygen or cadmium) was accomplished by adding 0.5–1 mass.% in the charge. Concentration of Zn in CZT crystals was determined by electron probe microanalysis (EPMA) [2]. According to the data obtained, these crystals are solid solutions with Zn concentration $x = 0.12...0.15$. It should be stressed that in the given concentration range optimum combination of high resistivity and transport properties of the charge carriers is observed, which places CZT crystals among the most promising materials for detection of ionizing radiation at room temperatures [3]. Concentrations of admixtures were determined by laser mass-spectrometry (LMS) and did not exceed 10^{-4} mass.% for 75 elements. Irradiation of samples was carried out by X-ray $K_{\alpha 1}$-radiation (W-anode, 150 kV), with exposure dose varying up to 900 R.

Polished ZnSe(IVD) and CZT samples of $10 \times 10 \times 3$ mm^3 size were used. Onto their large faces, electric contacts were applied in the form of eutectics In–Ga. Dielectric permittivity ε′ and dielectric losses ε″ were measured by the capacitance procedure using an R5016 AC bridge. The sample was placed into a specially prepared measurement cell (MC), which ensured high value and stability of electric capacitance between each of its surfaces and the adjacent electrode. Dependences of electric capacitance and dielectric losses of MC upon the absorbed dose had been measured in advance and were accounted for in calculations of ε′ and ε″. The localized states of the carriers were studied by the method of scanning photodielectric spectroscopy [4].

Dose dependences of ε′ and ε″ for ZnSe(IVD) and CZT crystals are shown in Figs. 1 and 2. It can be seen that these dependences for ε′ are similar for all frequencies of the measurement field. A characteristic feature of the presented curves is the presence of regions of rapid changes in the dose range up to 50 R. At higher doses, smooth changes in the values of this parameter are observed: predominant decrease for CZT, but rise for ZnSe(IVD) crystals. For dose dependences of ε″ for the crystals studied, it is essential that their character be determined by the measurement field frequency. One should note the most rapid changes of this parameter that are also observed in the dose range up to 50 R. The largest relative changes were observed at 1 kHz for both types of the crystals studied.

It has been shown that after irradiation dielectric parameters of the crystals studied are changed. These changes characterize the dose dependences (see Figs. 1, 2), each point on which was obtained in 24 h after irradiation of the sample by the corresponding dose. Comparing dose dependences of ε' measured in one hour or 24 h after irradiation, i.e., primary and secondary (after 24 h) ones, we can see that they are similar for crystals of both compounds. At the same time, the secondary dependences show much wider ε' decrease range in the dose range up to 50 R. The secondary dose dependences of ε'' are different in their appearance from the primary ones. This peculiarity of the secondary dependences is more clearly expressed with CZT crystals.

The obtained dependences of dielectric parameters upon the radiation dose allow us to conclude that there are differences in principle for changes of the defect structure of ZnSe(IVD) and CZT crystals in the dose range up to 50 R and above. At low doses, transformation processes of initial defects are predominant, as the probability of such processes is higher than of defect formation processes in the structurally perfect part of the crystal [5]. In fact, at these doses we can speak about "radiation annealing" of the crystal structure defects. At higher doses, the number of primary defects decreases, and the main role is played by formation of radiation defects in the structurally perfect parts. Dependences of dielectric parameters on the absorbed radiation dose becomes uniform.

According our experiments, these assumptions are supported by dependences of ε'' on the coordinate of a light probe, as well as by the energy spectrum of the localized states of carriers (Table 1,2) corresponding to different radiation doses. The data presented in the Tables show that irradiation causes changes in the spectrum of localized states, beginning from the dose of 5 R. It should be stressed that X-ray radiation, having given birth to radiation defects, causes a non-equilibrium state of the system of point defects. Transition of the system to the equilibrium or metastable stable determines continued change of ε' and ε'' after the radiation influence had stopped, which was observed in our experiments. Different behavior of these values at higher doses for different frequencies of the measurement field is probably related with multiplicity of types of the initial structure defects and, as a consequence, the presence of broad distribution of relaxation times. The pre-

Table 1. Trap levels for ZnSe(IVD) crystals after different dozes X-ray irradiation

Groups of trap levels	Doze of X-ray irradiation, *R*				
	0	5	50	300	900
A	–	−0.09...−0.08	−0.10...−0.07	−0.11	−0.10...−0.08
B	−0.07	−0.05...−0.06	−0.05	−0.05...−0.04	−0.05
C	−0.02	−0.02	−0.02	−0.02	−0.02 D
D	0.003	0.003...0.02	0.003	0.003...0.04	0.003...0.003
E	0.05...0.24	0.07...0.49	0.10...0.22	0.09...0.48	0.11...0.50
F	0.61...0.72	0.61...0.72	0.61...0.72	0.61...0.72	0.61...0.72
G	1.29...1.59	1.46...1.58	1.30...1.57	1.47...1.53	1.49...1.53

Table 2. Trap levels for CZT crystals after different dozes X-ray irradiation

Groups of trap levels	Doze of X-ray irradiation, R				
	0	5	50	300	900
A	0.09...0.2	0.08...0.18	0.10...0.16	0.10...0.19	0.12...0.19
B	0.23...0.31	0.27...0.3	0.22	0.23...0.27	0.22...0.26
C	–	–	0.34	0.39	0.41
D	0.51	0.49	0.45	0.46	0.45...0.48
E	0.54	–	–	–	–

dominant change under irradiation of specified defects leads to the largest change in dielectric response at the corresponding frequencies.

Changes in dielectric parameters of ZnSe(IVD) and $Cd_{1-x}Zn_xTe$ crystals under x-ray irradiation are caused by transformation of their defect structure, with the main role played by point defects. Studies of the dielectric response in the low-frequency region in combination with measurement of spectra due to localized states provide us with information on evolution of the defect structure under influence of small doses of radiation. Such information is important both from the point of view of predicting the radiation stability of electron devices and finding out the mechanisms of pre-threshold defect formation in $A^{II}B^{VI}$ crystals.

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Радіаційно-індуковані зміни діелектричних та фотоелектричних властивостей кристалів $A^{II}B^{VI}$

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Для визначення кінетики допорогового дефектоутворення досліджувалася ді-електрична проникність ізовалентно легованого селеніду цинку та кристалів $Cd_{1-x}Zn_xTe$ (x = 0,16). Опромінення зразків проводили рентгенівським випромінbackенням (W-анод, 100–150 кВ), доза D якого змінювалась у межах до 900 Р. Діелектричні параметри ε' та ε'' вимірювалися ємносною методикою у діапазоні частот 1...50 кГц. Фотоактивні стани досдіджували методом скануючої фотодіелектричної спектроскопії. Знайдені нетривіальні змінення параметрів ε' та ε'' при зростанні дози опромінення. Величина і знак цих змінень залежать від дози, а також частоти змінного електричного поля. Показано, що, починаючи з малих значень D, відбувається перебудова системи власних дефектів структури: змінюється концентрація вихідних дефектів, утворюються нові дефекти та їхні асоціати. Спостерігаються суттєві відзнаки у поведінці вказаних параметрів для кристалів ZnSe та $Cd_{1-x}Zn_xTe$.