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POSITRON ANNIHILATION CHARACTERISTICS IN $Zn_{1-x}Mg_xSe$ MIXED CRYSTALS

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Positron annihilation characteristics as a function of composition and annealing in zinc vapour were measured and compared with photoluminescence spectra for $Zn_{1-x}Mg_xSe$ mixed crystals with $0 \leq x \leq 0.6$. The positron annihilation data show that there is a substantial number of divacancies present in the system under study. The concentration of such defects is reduced at least by the factor of two upon annealing in zinc vapour.

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Positron annihilation technique is often used as a technique to study vacancies in semiconductors [1, 2]. This work presents results of investigations of positron annihilation and photoluminescence in $Zn_{1-x}Mg_xSe$ mixed crystals as a function of composition. These crystals were grown by the high pressure Bridgman method [3–5]. The original ZnSe was of 6N purity while the purity of magnesium itself was only 99.8%. The sample structures were sphalerite for $x < 0.19$ and wurtzite-type for larger magnesium content [4, 5]. The Mg concentrations in the investigated $Zn_{1-x}Mg_xSe$ crystals were: $x = 0.0$, 0.047, 0.25, 0.47 and 0.56. All these crystals were not annealed in zinc vapour. A separate pairs of samples were prepared with $x = 0.27$ and $x = 0.52$. The half of these samples was annealed in zinc vapour at the temperature 1230 K while the another half was not annealed. The as-grown crystals exhibit a very high electric resisitivity indicating the presence of cation vacancies or their complexes which act as deep compensating acceptors. It has been found that annealing of $Zn_{1-x}Mg_xSe$ samples with relatively low magnesium content ($x < 0.25$) in zinc atmosphere at temperatures from 1070–1250 K during the period of 2 days transforms the material into n-type with the free electron concentration of the order from 10^{17} cm^{-3} to 10^{14} cm^{-3} at room temperature.

The measurements of the average lifetime as a function of temperature (in the range from 77 K up to room temperature) show that a rather little admixture of magnesium makes a quite appreciable average lifetime increase. The temperature evolution of τ_{bulk} seems to be non-monotonous. The average lifetime as a function of temperature obtained for pairs of samples with $x = 0.27$ and $x = 0.52$, as-grown and annealed in Zn vapour, are presented in Fig. 1. For the sample with $x = 0.047$ a clear separation of the spectra into two components can be made, but the short (τ_1) and long (τ_2) lifetimes as well as the relative intensities of these two components cannot be determined with a high precision. Only average lifetime may be determined quite accurately. Therefore in most of the final data handling we were usually fixing the long-lifetime to 325 ps, as the most reliable one, and carrying out the fits with τ_1 and I_2 as free parameters. The results obtained in this way reveal that the τ_1 decreases steadily and amount of the long-lifetime component increases with an increase in temperature, which

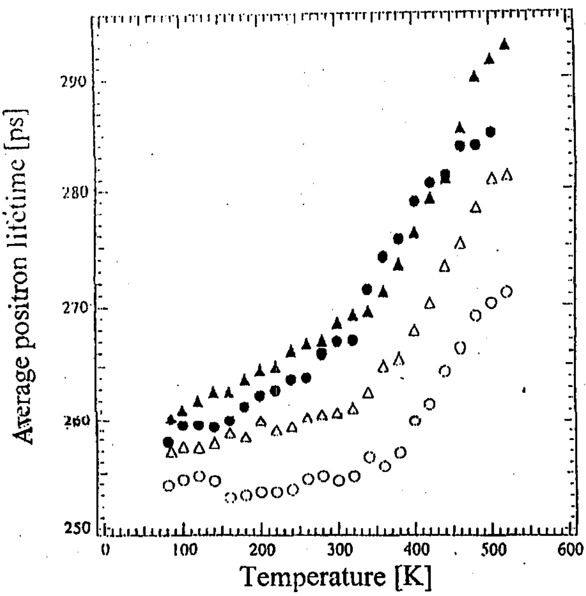

Fig. 1. The temperature dependence of the average positron lifetime for $Zn_{0.73}Mg_{0.27}Se$ — circles and $Zn_{0.48}Mg_{0.52}Se$ — triangles. Full circles and triangles correspond to as-grown samples while open symbols — to those annealed in zinc vapour.

shows that the one-type vacancy model may be applicable here. Decomposition of the spectra for $x = 0.27$ and $x = 0.52$ samples, as-grown and annealed in Zn vapour, quite clearly show that the effect of annealing is much more pronounced for the sample containing a smaller concentration of magnesium. The average lifetime increases with temperature and saturates slightly probably above 500 K. The saturation values for the $x = 0.27$ sample are about 285 ps for as-grown crystal and 271 ps for the annealed one. These times are increased by roughly 10 ps when x changes to 0.52. We also note that the short lifetime in the $x = 0.27$ sample decreases with temperature much more rapidly for the annealed sample. Taking the smallest value of τ_1 as the one characterising the material, and accepting 250 ps as the bulk lifetime, one can estimate that the annealing is causing the vanishing of at least half of the defects (vacancies).

Photoluminescence spectra were measured from 40 K up to room temperature. Typical photoluminescence spectrum (Fig. 2) consists of a narrow emission line connected with recombination of free exciton, while the wider band is associated with recombination of shallow donor–acceptor pairs and two other relatively wide bands "green" and "red" due to recombination going through deep levels. The relative intensity of deep levels luminescence compared to free exciton emission decreases with increasing magnesium content. It was also established that for $x < 0.5$ the ratio of intensities of "green" to "red" luminescence bands increases with increasing Mg content and decreases substantially after annealing of $Zn_{1-x}Mg_xSe$ samples in zinc vapour. Comparing results of measurements of electrical properties and luminescence spectra one can suppose that the "green" band is due to the cation vacancies or complexes of such vacancies.

The calculations of the positron lifetime for certain types of possible defects in $Zn_{1-x}Mg_xSe$, carried out using the superimposed atom model of Puska and Nieminen [6], showed that the lifetime increases slightly with increasing magnesium content. The measured bulk lifetime at the lowest temperatures is around 250 ps almost independently of magnesium concentration. This value is close to the calculated values (250.5 ps for $x = 0.0$ and 264.3 ps for $x = 0.5$). The experimental long-lifetime component, about 330 ps, is also the same for all samples. In accordance with the calculations the long-lifetime component should be close either to 270 ps in the case of single vacancies or to 350 ps in the case of divacancies. Our experimental value is close to 330 ps, which indicates that a divacancy leading to an inward lattice relation is the most probable candidate for the defect observed. It is impossible to say whether the divacancy is of the $V_{Zn}V_{Se}$ or $V_{Mg}V_{Se}$ type. Both kinds of defects exhibit almost the same lifetimes and bonding energies (varying from about 0.32 eV at $x = 0.0$ to 0.36 eV at $x = 0.5$).

In the case of single vacancies, zinc and magnesium vacancies are exhibiting almost the same lifetimes while the selenium vacancy leads usually to a longer lifetime of about 280 ps. The bonding energy is apparently the highest one for selenium vacancy and the smallest for zinc vacancies. If these vacancies were used as a starting point for interpretation of our results, we would have to assume that a very large outward lattice relaxation would have to accompany the creation of such defect. It seems thus unlikely that the τ_2 observed in our experiment may be due to a single vacancy.

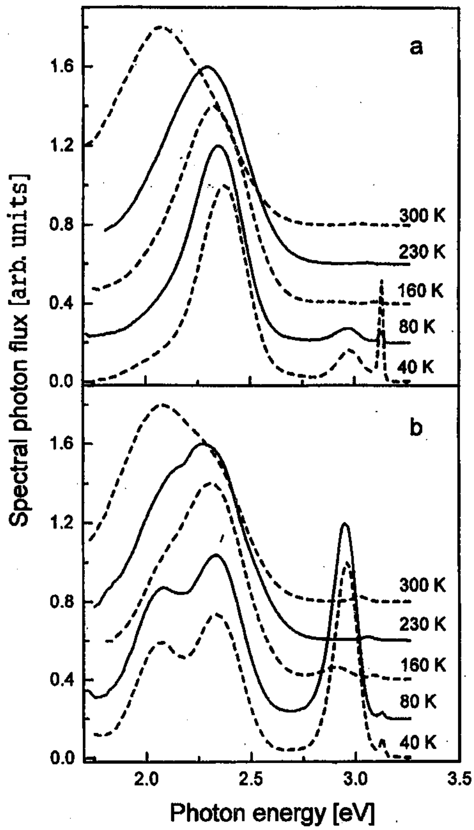

Fig. 2. Photoluminescence spectra of $Zn_{0.73}Mg_{0.27}Se$ crystals; (a) as-grown, (b) annealed in zinc vapour.

Concluding, we have presented results of measurements of the positron lifetimes in $Zn_{1-x}Mg_xSe$ for $0 \leq x \leq 0.6$. The analysis based on the calculations of lifetimes for various types of vacancies indicate that there is a substantial number of divacancies. The concentration of such defects is reduced at least by the factor of two upon annealing in zinc vapour. Comparing the positron annihilation results with the results of photoluminescence studies, we observe that the sample annealing in zinc vapour leads to a decrease in both the relative intensity of the long-lifetime component in the positron annihilation spectra and the relative intensity of the "green" band with respect to the "red" one. An increase in magnesium component in the crystal results not only in a relative increase in the defect concentration but also in lowered susceptibility to the annealing in zinc vapour. A fuller account of the experimental and theoretical studies of divacancies in $Zn_{1-x}Mg_xSe$ system will be published elsewhere.

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