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Changes in donor and acceptor states in Au-doped ZnSe samples induced by ageing at room temperature

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Abstract

Photoluminescence (PL) spectra of n-ZnSe single crystals doped with Au are investigated at temperatures between 4.4 and 300 K immediately after doping and after storage for four years at room temperature in darkness in air. The formation of donor-type Au_i interstitial defects stimulated by time is found in ZnSe for the first time. Changes in the structure of the edge and long-wavelength PL spectra with the course of time are observed. The long-wavelength band attributed to $(Au_{Zn}-D_{III,VII})$ acceptors is not found in the PL spectra of the stored samples. At the same time, a green PL band with maximum at 527 nm (2.35 eV) appears. This band is ascribed to $(V_{Zn}-Au_i)$ acceptors formed as a result of displacement of the Au_{Zn} atoms into interstitial sites due to deformation forces. When the Au concentration in the Zn + Au melt exceeds 1 at.%, an Au_i -donor impurity band is formed and the intensities of all the PL bands are reduced.

1. Introduction

Utilization of high-quality ZnSe single crystals as conductive homoepitaxial substrates for the fabrication of blue and green laser diodes, mixed colour and white LEDs [1, 2], ultraviolet photodetectors [3] and doped ZnSe for nanotechnology (in particular, Ag-doped ZnSe nanowires [4]) has renewed the interest in investigation of the fundamental properties of doped ZnSe. While acceptors can be generated in ZnSe by doping with group-I elements, the possibility of getting p-type conductivity, which is of great interest for applications, is limited by strong self-compensation. The amphoteric character of the group-I elements in II–VI semiconductors has been confirmed by means of perturbed $\gamma\gamma$ angular correlation

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experiments [5]. We have observed the amphoteric character of Ag in ZnSe stimulated by ageing [6] and also that of Au immediately after doping [7]. In the present paper, we discuss the time dependence of the formation of Au_i donor states in bulk ZnSe.

It is well established that doping of ZnSe with transition metal impurities such as copper, silver and gold results in the formation of deep simple and complex acceptor centres [8–13]. Substitution of copper [8] or silver and gold [10] for zinc leads to the formation of simple acceptors, Cu_{Zn} , Ag_{Zn} , Au_{Zn} , as well as acceptor-type complexes with co-activators [13] or native defects [14], which play an important role in electrical and luminescent properties of ZnSe. As the atomic number of the group-IB dopant element is increased, the probability of the formation of interstitial donors such as Cu_i , Ag_i , and Au_i increases because of the growing difference between the ionic radii of Zn (0.74 Å) and the dopant elements Cu (0.96 Å), Ag (1.26 Å) and Au (1.37 Å). When Ag and Au atoms substitute for Zn, strains are induced in the zinc sublattice since the size of Ag and Au exceeds that of the zinc vacancy (V_{Zn}). Since the interatomic Zn–Zn distance, 4.01 Å, is much larger than the ionic radius of the Ag and Au atoms, these dopants form mainly interstitial defects.

As shown recently [6], Ag_{Zn} acceptor states are unstable in ZnSe. During prolonged room-temperature storage of Ag-doped n-ZnSe, the lattice tends to return to its normal equilibrium state by displacing the Ag ions into interstitial sites. As a result, donor-type Ag_i interstitial defects are formed in the samples and this process is enhanced when the Ag concentration is increased. The formation of donor-type interstitial defects by ageing, as observed for the first time in Ag-doped ZnSe [6], may also take place in Au-doped ZnSe, since the ionic radius of Au exceeds that of Ag.

In the present paper, we investigate the photoluminescence (PL) spectra of n-ZnSe single crystals doped with various concentrations of Au. The influence of the composition of the Zn + x at.% Au melt on the structure of the PL spectra and the mechanisms of radiative recombination, observed immediately after doping the samples and after storing for four years at room temperature, is discussed.

2. Experimental methods

Melt-grown high-resistive ($\rho \approx 10^8 \Omega \text{ cm}$) n-ZnSe single crystals were doped with Au during long-term (100 h) high-temperature (950 °C) treatment in a melt of metallic Zn double purified by vacuum sublimation and Au of 99.9999% purity. The doping level was varied by changing the Au content in the melt from 0.01 to 10 at.%. The samples were annealed in quartz ampoules evacuated down to $p = 10^{-4}$ Torr and rapidly cooled after annealing to room temperature. The surfaces of the samples were etched in 7% Br–CH₃(OH) solution and then boiled in 40% NaOH.

The PL spectra were excited by a nitrogen laser and registered at temperatures between 4.4 and 300 K using an Oriel Instruments monochromator MS257TM with reciprocal dispersion of 3.2 nm/mm.

3. Experimental results and discussion

3.1. Time stimulation of the formation of Au_i donor states in Au-doped ZnSe

The PL spectra of the Au-doped ZnSe samples measured at 86 K immediately after doping and after storage for four years are shown in figure 1. The numbers attached to the curves indicate the Au content, x , in the Zn + x at.% Au melt. The I_2 -line with maximum at 2.781 eV (445.5 nm) in the PL spectrum of the sample annealed in pure Zn ($x = 0$) is attributed to

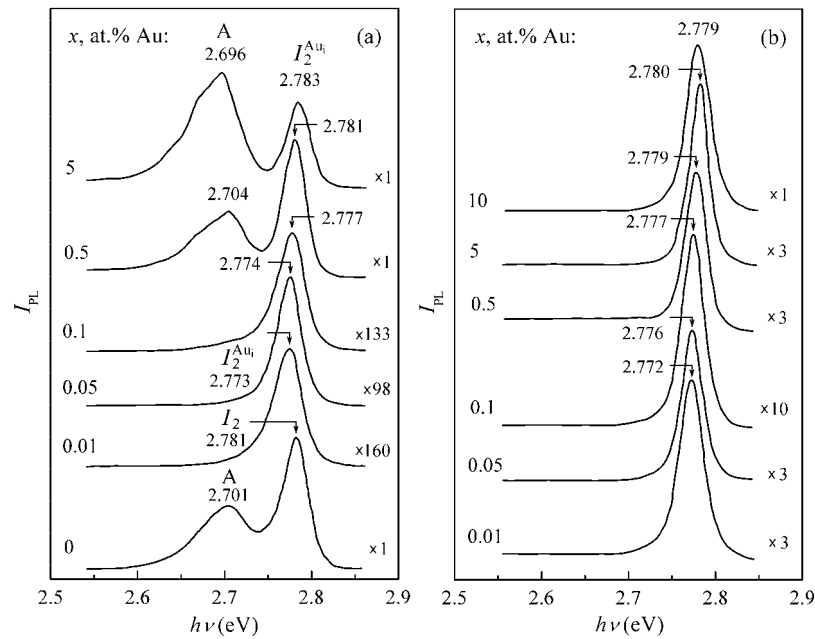


Figure 1. Edge PL spectra of n-ZnSe crystals annealed in Zn + x at.% Au melt, measured at 86 K (a) immediately after doping with Au and (b) after storage for four years under normal room conditions. To obtain the real spectrum intensity, the intensity values should be multiplied by the numbers on the right-hand side of the curves.

annihilation of excitons bound to V_{Se} native defects ($E_D \approx 10$ meV) [15], the number of which increases during annealing [16]. The A-band localized at 2.701 eV (458.7 nm) is attributed to radiative transitions of free electrons to complex acceptors $(V_{Zn}-D)^-$, where both the V_{Se} and the impurity-based defects (Al_{Zn} , Ga_{Zn} , In_{Zn}) are donors.

In the PL spectrum of the lightly doped sample with $x = 0.01$, the $I_2^{Au_i}$ -line is observed at 2.773 eV (446.8 nm) (figure 1(a)). The long-term storage of the sample has no influence on the spectral position and the shape of this line (2.772 eV) (figure 1(b)). We suppose that the lightly doped samples contain mostly donor-type Au_i interstitial defects binding the excitons responsible for the $I_2^{Au_i}$ -line [17]. This line attributed to Au_i donor-bound excitons (DBEs) is the only feature in the edge PL spectrum of the lightly doped samples with $x = 0.01$ –0.1.

As shown in figure 1, the edge PL spectrum of the samples with $x \geq 0.5$ changes with the course of time. In the spectra observed immediately after doping (figure 1(a)), the A-band with maximum at 2.704 eV and some low-energy broadening appears. With increasing Au concentration, the intensity of this band increases relative to the intensity of the $I_2^{Au_i}$ -line. In our opinion, this redistribution of the PL band intensities is due to the increased formation of Au_{Zn} defects and related $(Au_{Zn}-Au_i)$ acceptors, which are responsible for the A-band in the case of the Au-doped samples. The predominant formation of Au_{Zn} and $(Au_{Zn}-Au_i)$ acceptors in the samples annealed in Zn + Au melts with $x \geq 0.5$ has also been established by means of Hall measurements [17]. The formation of $(Au_{Zn}-Au_i)$ defects reduces the probability of forming the simple Au_i donors and, consequently, the number of Au_i donors and the intensity of the $I_2^{Au_i}$ -line are decreased. After prolonged storage of the samples at normal room temperature, the A-band is not observed even at the maximum Au concentration (figure 1(b)). This behaviour supports the model proposed in [6] for the group-IB transition metal dopants.

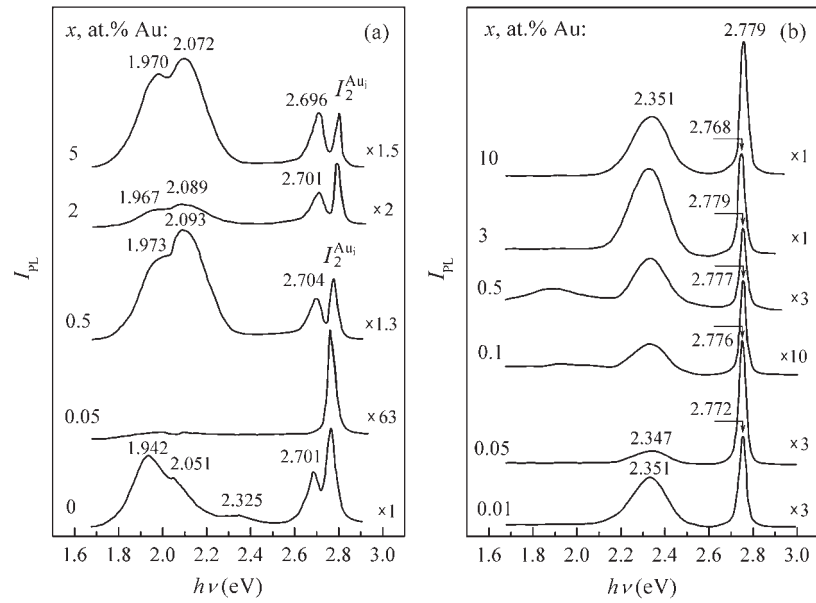


Figure 2. PL spectra of n-ZnSe crystals annealed in Zn + x at.% Au melt, measured at 86 K (a) immediately after doping with Au and (b) after storage for four years under normal room conditions. To obtain the real spectrum intensity, the intensity values should be multiplied by the numbers on the right-hand side of the curves.

As the ionic radius of Au greatly exceeds that of Zn (see section 1), the formation of Au_{Zn} acceptors ($x \geq 0.5$) leads to a strong deformation of the ZnSe lattice. During the room-temperature storage of the samples, the lattice tends to return to its normal equilibrium state by displacing the Au ions into interstitial sites. When the donor-type Au_i defects are formed, the concentration of the acceptor-type Au_{Zn} defects decreases and a great number of Zn vacancies (V_{Zn}) appears. As a result, the number of the $(\text{Au}_{\text{Zn}}-\text{Au}_i)$ acceptors decreases and the A-band disappears from the edge PL spectra (figure 1, curves for $x \geq 0.5$).

As shown in figure 2, the long-wavelength PL spectra also exhibit changes induced by the sample storage. For concentrations with $x \geq 0.5$, a wide PL band with maximum at 2.072–2.093 eV (592–598 nm) and another component around 1.973 eV (628 nm) can be observed immediately after the sample doping. This complex band consists of four single components attributed to radiative transitions of free electrons from the conduction band to the Au_{Zn} and $(\text{Au}_{\text{Zn}}-\text{D}_{\text{III,VII}})$ acceptors [13]. The decrease of the excitonic line intensity and the increase of the long-wavelength emission with increasing Au concentration (figure 2(a), curves for $x = 2$ and 5) can be explained by predominant formation of these Au-based acceptors in the samples. The room-temperature storage of the samples reduces the concentration of simple Au_{Zn} and Au_{Zn} -based defects. As a result, the long-wavelength PL band with the maximum at 2.072–2.093 eV (figure 2(a)) practically disappears (figure 2(b)). Displacement of the Au atoms into interstitial sites increases the concentrations of the native (V_{Zn}) and impurity-related (Au_i) defects. New $(\text{V}_{\text{Zn}}-\text{Au}_i)$ defects responsible for the green PL band at (2.351 ± 0.004) eV ((527 ± 1) nm) are formed. As the Au content in the melt increases from $x = 0.05$ to 10, the intensity of this band is at first doubled and then decreases, while its half-width ≈ 200 meV is not influenced. Thus, the formation of the Au_i donors during ageing of the samples manifests itself in a redistribution of the intensities of the edge and long-wavelength PL bands.

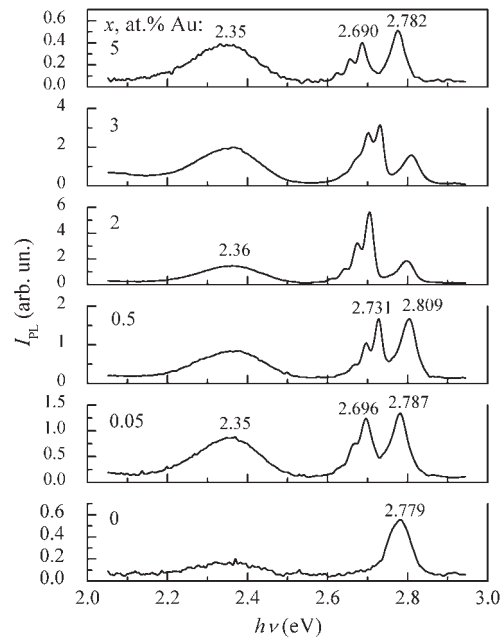


Figure 3. The PL spectra of n-ZnSe crystals annealed in Zn + x at.% Au melt and measured at 4.4 K after storage for four years under normal room conditions.

3.2. Evolution of PL spectra with temperature and Au concentration

Low-temperature (4.4 K) PL spectra of ZnSe samples doped with different concentrations of Au and stored for four years at normal room conditions are shown in figure 3. These spectra consist of the edge DBE-band, the A-band with two equidistant LO-phonon replicas ((31 ± 2) meV) on the low-energy side and a wide green PL band. Figure 4 shows the intensity and the peak position of these bands as a function of the Au concentration in the melt. The DBE-band intensity increases when the Au concentration is increased to $x = 0.5$ (figure 4(a)) because the Au ions are preferentially introduced into the interstitial sites, forming the Au_i donors. A limited number of these defects participate in the formation of $(Au_{Zn}-Au_i)$ and $(V_{Zn}-Au_i)$ acceptors, which are responsible for the A-band (figure 4(b)) and the green PL band (figure 4(c)), respectively. With further increase of the Au content, the A-band and the green PL band intensities rapidly increase. After prolonged storage of the samples, a certain concentration of the Au_{Zn} defects is still preserved in the samples with $x > 0.5$, and they become a part of the $(Au_{Zn}-Au_i)$ complex acceptors. This is a likely reason for the increase of the A-band intensity with increasing Au content up to $x = 2$ (figure 4(b)). Simultaneously, the $(V_{Zn}-Au_i)$ complex acceptors are formed because of the increasing concentrations of the V_{Zn} and Au_i defects. As a result, the intensity of the green PL band rises with increasing Au concentration up to $x = 3$ (figure 4(c)). With further increase of the Au concentration, the intensities of all the PL bands rapidly decrease due to the formation of the Au_i donor impurity band in the band gap of ZnSe. Delocalization of the Au_i donor states, which takes place at the formation of the impurity band, results in a decrease of local Au_i centres and, consequently, the $(Au_{Zn}-Au_i)$ and $(V_{Zn}-Au_i)$ centres. The formation of an Ag-related impurity band in ZnSe single crystals after prolonged storage at room temperature has been established by means of Hall measurements [6].

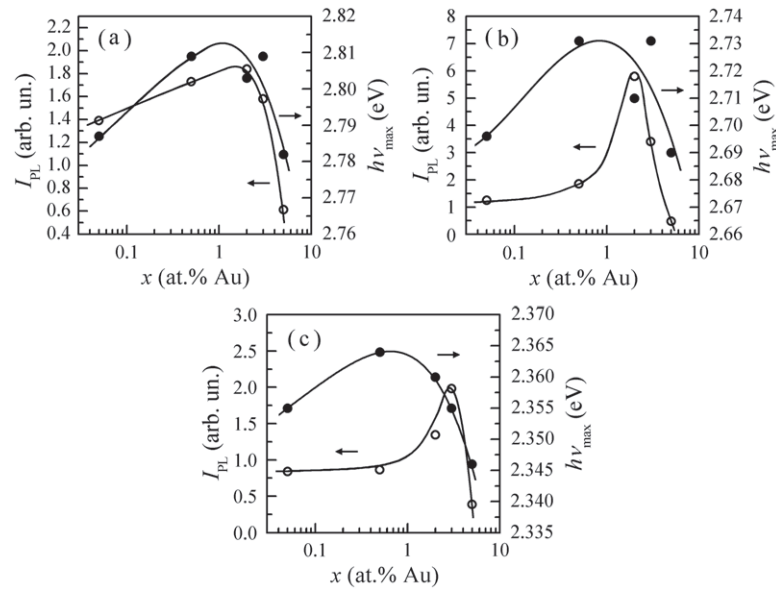


Figure 4. The intensity and peak position of (a) the edge DBE-band, (b) the A-band and (c) the green PL band versus Au concentration in the Zn + x at.% Au melt, measured at 4.4 K after storage for four years under normal room conditions.

The large half-width (~ 45 – 50 meV at 4.4 K) of the edge DBE-band is caused by the fact that the edge luminescence results from both Au_i -DBE and V_{Se} -DBE defect centres [15]. As the ionization energy of the V_{Se} donor, $E_D(V_{Se}) \approx 10$ meV [15], is less than the ionization energy of the Au_i donor, $E_D(Au_i) \approx 22$ meV [17], the $I_2^{V_{Se}}$ -DBE line is located at higher energies than the $I_2^{Au_i}$ -DBE line. When the Au content increases to 1 at.%, the redistribution between the contributions of the Au_i -DBEs and V_{Se} -DBEs shifts the maximum of the edge PL towards higher energies (figure 4(a)). The contribution of the Au_i -DBEs decreases due to the formation of the Au_i -based complex acceptors ($V_{Zn}-Au_i$) and $(Au_{Zn}-Au_i)$. At higher Au concentrations, the donor impurity band is formed, which gradually overlaps the local energy levels of shallow V_{Se} centres, and the contribution of the Au_i -DBEs becomes predominant again. As a result, the PL peak shifts towards lower energies. The formation and development of the donor impurity band enhances the shift of all the PL peaks towards lower energies (figure 4) as the radiative transitions take place from the impurity band.

The evolution of the edge and green PL bands with temperature is shown in figures 5 and 6 for the sample annealed in the Zn + 0.5 at.% Au melt. All the other Au-doped samples exhibit similar quenching of PL with increasing temperature. A characteristic feature of these spectra is a rapid quenching of the intensity of the A-band and the phonon replicas (figure 5). At temperatures above 80 K, the A-band is not observed in the PL spectra of the Au-doped samples. As stated above, normal room-temperature storage of the samples reduces the concentration of the $(Au_{Zn}-Au_i)$ acceptors, which are responsible for the A-band, due to decreasing concentration of the Au_{Zn} centres. At the same time, the concentration of Au_i , V_{Zn} and $(V_{Zn}-Au_i)$ defects increases significantly, which makes the DBE and green luminescence less sensitive to thermal quenching.

An Arrhenius plot of the temperature dependence of the DBE-band intensity is shown in figure 7. Quenching of the edge PL becomes significant above 40 K. As can be concluded from

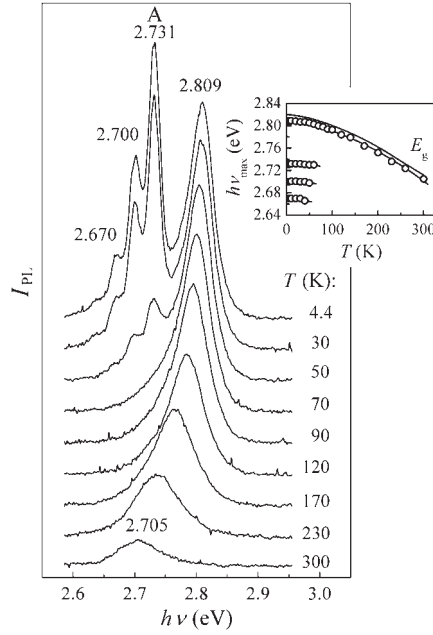


Figure 5. Edge PL spectra of the ZnSe sample annealed in Zn + 0.5 at.% Au melt, measured at different temperatures after storage for four years under normal room conditions. Inset: the position of the PL bands versus temperature; the line represents the calculated temperature dependence for the band gap energy.

the inset, the thermal activation energy, found from the slopes of the temperature dependences of PL at high temperatures, is the smallest for the undoped ZnSe sample (17 meV) due to thermal dissociation of the ‘shallow’ V_{Se} -DBEs. For the sample with $x = 0.5$, the thermal activation energy is 30 meV due to thermal dissociation of the ‘deeper’ Au_i -DBEs. In the sample with $x = 5$, there is a well-formed Au_i -donor impurity band. The electrons are excited to the conduction band from the lowest states of the donor band and the PL intensity decreases with the activation energy of 27 meV.

Figure 8 shows the temperature dependence of the DBE-band position for Au-doped ZnSe crystals. The calculated temperature dependence of the band gap, $E_g(T)$, is shown for comparison. For the samples with $x = 0.5$ and 3 at.% Au, the experimental values of $h\nu_{max}(T)$ are located between the $E_g(T)$ and the free exciton emission energy calculated from equation [18],

$$E_x(T) = E_x(4.2 \text{ K}) - 8.59 \times 10^{-4} \frac{T^2}{405 + T}, \quad (1)$$

where $E_x(4.2 \text{ K}) = 2.8021$ [19]. This is related to the beginning of the formation of the Au_i -impurity band (for $x = 0.5$) and its development (for $x = 3$) and, as a consequence, to the change from the excitonic mechanism of the luminescence to radiative recombination of the impurity band electrons with the valence band holes. A drastic shift of the edge PL peak to lower energies observed at all temperatures for the sample annealed in the melt with 5 at.% Au indicates the enhanced formation of Au_i -donor states. As a great number of the compensating defects (V_{Zn}) appear in this process, the impurity band electrons are localized in deep tails of the states below the band bottom. Recombination of these electrons with the valence band holes explains the localization of the PL band below the free exciton emission energy (figure 8).

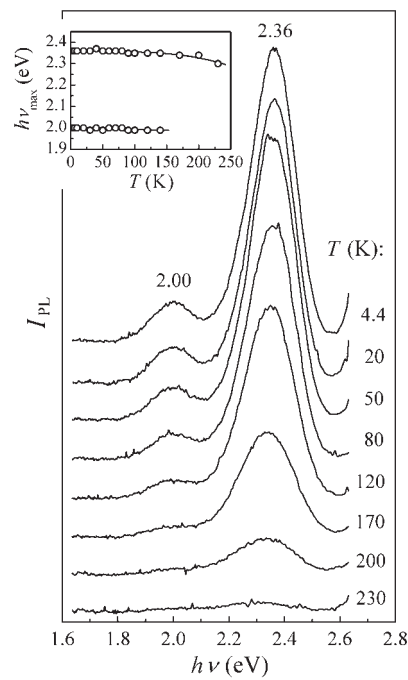


Figure 6. Long-wavelength PL spectra of the ZnSe sample annealed in Zn + 0.5 at.% Au melt, measured at different temperatures after storage for four years under normal room conditions. Inset: the position of the PL bands versus temperature.

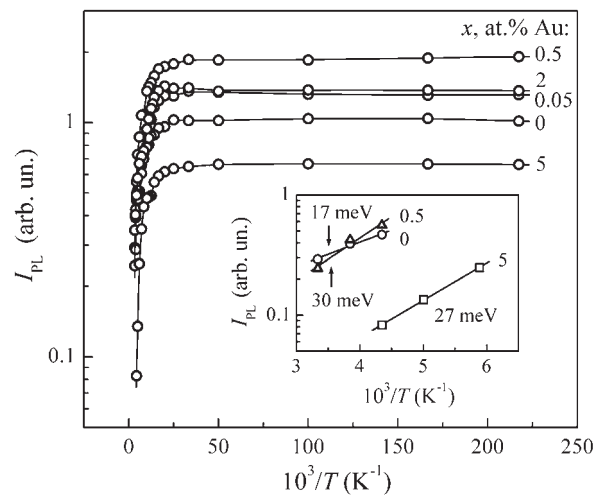


Figure 7. Arrhenius plot for the edge DBE-band intensity of n-ZnSe crystals annealed in Zn+x at.% Au melt and stored for four years under normal room conditions. Inset: the high-temperature range of the dependence of I_{PL} on inverse temperature.

As the compensation of the donor impurity increases with increasing Au content ($x > 3$), the intensities of all the PL bands decrease (figure 4).

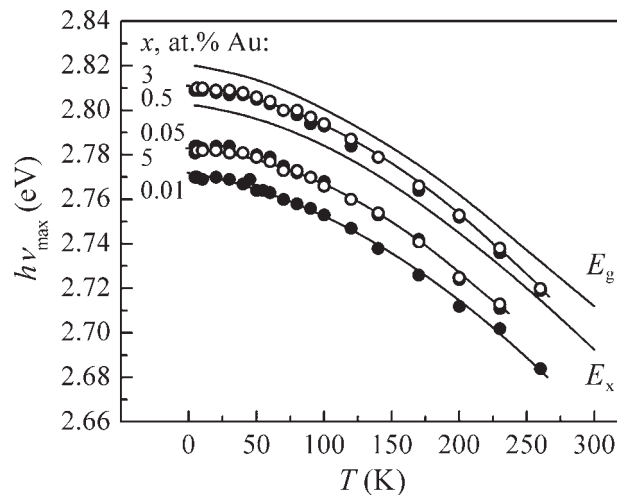


Figure 8. Temperature dependence of the edge DBE-band position for n-ZnSe crystals annealed in Zn + x at.% Au melt and stored for four years under normal room conditions. The single lines represent the calculated temperature dependences of the band gap, E_g , and the free exciton energy, E_x .

4. Conclusion

Comparative analysis of the PL spectra of the Au-doped ZnSe single crystals, measured immediately after doping and after four-years' storage of the samples at normal room conditions in darkness, shows significant redistribution of the edge and long-wavelength PL bands during the storage. It is concluded that displacement of the Au ions from lattice sites into interstitial sites by the lattice deformation forces decreases the concentrations of the simple Au_{Zn} and complex $(Au_{Zn}-Au_i)$ acceptors and increases the concentrations of the Au_i donors and the V_{Zn} acceptors. As a result, complex $(V_{Zn}-Au_i)$ centres are formed and a new PL band of green emission with maximum at 2.351 eV (527 nm) is observed in the PL spectra of the samples subjected to prolonged storage. At the same time, the A-band associated with the $(Au_{Zn}-Au_i)$ centres and the long-wavelength PL band attributed to $(Au_{Zn}-D_{III,VI})$ centres disappear from the PL spectra measured at 86 K due to a drastic decrease of the Au_{Zn} defects. The changes in the PL parameters such as the peak position and the intensity after ageing of the Au-doped samples indicate the development of an Au_i -donor impurity band in the energy band gap of the samples with Au contents above 1 at.%. Thus, just as was shown for the Ag-doped ZnSe samples [6], the formation of Au_i donor states with time is found in the Au-doped ZnSe single crystals, too.

From our results for doping of bulk ZnSe with Ag and Au, we conclude that the properties of these materials are modified due to large lattice relaxation during ageing. This fact should be taken into account in optoelectronic applications of doped ZnSe and related compounds.

Acknowledgments

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