Impurity centers in ZnSe:Na crystals

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The influence of the sodium impurity on photoluminescence (PL) spectra of ZnSe crystals doped in a growth process from a Se+Na melt is investigated. It is shown, that the introduction of the impurity results in emergence of emission bands in the PL spectra due to the recombination of exciton impurity complexes associated with both donors and hydrogen-like acceptors. Apart from that, four bands generated by donor-acceptor pairs recombination and a band produced by electronic transitions from the conduction band to a shallow acceptor are discussed. As a result of the analysis it is concluded, that Na impurity forms in ZnSe lattice Na_{Zn} hydrogen-like acceptors with activation energy of 105±3 meV, Na_i donor centers with activation energy of 18±3 meV, as well as $Na_{Zn}V_{Se}$ and Na_iNa_{Zn} associative donors with activation energy of 35±3 meV and 52±9 meV, respectively.

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1. Introduction

Zinc selenide is a wide bandgap semiconductor with advantageous for optoelectronics optical properties, particularly for light-emitting diodes and lasers working both in visible and infra-red regions of the spectrum. The lack of a suitable and reliable technology for the preparation of stable p-ZnSe materials and ZnSe-based p-n junctions necessary for the development of optoelectronic devices is still a challenge. Efficient doping of ZnSe films with Na acceptor impurity in a growth process from Se+Na melts, and the possibilities of obtaining p-ZnSe material with holes concentration up to $5\cdot10^{18}$ cm^{-3} have been previously demonstrated [1]. However, the dependence of the doping efficiency on the growth temperature, and on the concentration of Na containing compounds in the Se melt, as well as their chemical nature remain still an open question. These issues are related to the optimization of the doping technology and to the understanding of interaction processes between the Na impurity and the native defects resulting in the formation of defect complexes that significantly influence on the doping efficiency.

The available data concerning the energy spectrum of Na-related defects in ZnSe are scarce and inconsistent. The activation energy of Na_{Zn} acceptor centers ($E_a(Na_{Zn})$) estimated from the position of emission bands (2.793÷2.794 eV at 10 K) attributed to exciton impurity complexes (EIC) associated with these centers is in the range of 83 – 92 meV [2], while the value of this activation energy deduced from the position of the emission band associated with free-to bound radiative transitions from the conduction band to the energy level of Na_{Zn} acceptor centers (FA band at 2.712 eV, at 77 K) is about 102 meV [3]. The estimation of $E_a(Na_{Zn})$ from the position of the so-called P band of donor-acceptor pairs (DAP) luminescence (~2.685 eV at 5 K) attributed to transitions between shallow donors and Na_{Zn} acceptors gives a value of 120÷130 meV [2,4]. DAP bands associated with electronic transitions involving a residual Li acceptor impurity (the so-called Q-band at 2.695 eV, at 4 K [2]) as well as those associated with electronic transitions involving Na_{Zn} centers and shallow interstitial Na_i donors (the so-called R band at 2.704 eV, at 4 K [4]) are also characteristic for low temperature photoluminescence (PL) spectra of ZnSe:Na crystals. Unfortunately, there are no data confirming the achievement of p-type conductivity by means of Na doping in a majority of works dealing with the determination of the $E_a(Na_{Zn})$ value and with the identification of centers responsible for various luminescence bands in ZnSe crystals. At the same time, one can deduce from the analysis of the available literature data that the structure of the band-edge PL spectra of high doped p-ZnSe:Na materials grown from Se + Na melt is not investigated in details.