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Composition and Surface Optical Properties of GaSe:Eu Crystals before and after Heat Treatment

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Abstract: This work studies the technological preparation conditions, morphology, structural characteristics and elemental composition, and optical and photoluminescent properties of GaSe single crystals and Eu-doped β–Ga_2O_3 nanoformations on ε–GaSe:Eu single crystal substrate, obtained by heat treatment at 750–900 °C, with a duration from 30 min to 12 h, in water vapor-enriched atmosphere, of GaSe plates doped with 0.02–3.00 at. % Eu. The defects on the (0001) surface of GaSe:Eu plates serve as nucleation centers of β–Ga_2O_3:Eu crystallites. For 0.02 at. % Eu doping, the fundamental absorption edge of GaSe:Eu crystals at room temperature is formed by $n = 1$ direct excitons, while at 3.00 at. % doping, Eu completely shields the electron–hole bonds. The band gap of nanostructured β–Ga_2O_3:Eu layer, determined from diffuse reflectance spectra, depends on the dopant concentration and ranges from 4.64 eV to 4.87 eV, for 3.00 and 0.05 at. % doping, respectively. At 0.02 at. % doping level, the PL spectrum of ε–GaSe:Eu single crystals consists of the $n = 1$ exciton band, together with the impurity band with a maximum intensity at 800 nm. Fabry–Perrot cavities with a width of 9.3 µm are formed in these single crystals, which determine the interference structure of the impurity PL band. At 1.00–3.00 at. % Eu concentrations, the PL spectra of GaSe:Eu single crystals and β–Ga_2O_3:Eu nanowire/nanolamellae layers are determined by electronic transitions of Eu^{2+} and Eu^{3+} ions.

Keywords: chalcogenides; gallium(III) trioxide; native oxide; Eu doping; single crystals; layers; optical properties; photoluminescence

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1. Introduction

Gallium monoselenide (GaSe) is one of the outstanding representatives of group III–VI lamellar, quasi-two-dimensional (2D) materials, with a direct band gap of 2.00 eV and pronounced anisotropy of mechanical, electrical and optical properties [1–3].

Its single crystals exhibit a typical layered structure, each layer being composed of elementary stratified Se–Ga–Ga–Se (Chalcogen–Metal–Metal–Chalcogen) packages, with predominantly covalent bonding inside a package and weak polarizational bonds, of the van der Waals type, between the packages [4–6]. Depending on the mutual arrangement of elementary planar packages along the C6 axis, several polytypes are distinguished: ε, β and δ, displaying hexagonal lattice, and γ, with rhombohedral crystal lattice. In crystals obtained by the Bridgman–Stockbarger technique, ε polytype is reported to be predominant [1,4]. The weak bonds between planar packages facilitate obtaining 2D ultrathin lamellae, which exhibit special optoelectronic properties [7,8]. Based on GaSe nanolayers, a broadband photodetector with a photoresponse of 4.5 A/W at ~120 °C was fabricated [8].

As demonstrated in works [9–12], doping with isovalent elements (Al, In, Er and Tm) of ε–GaSe crystals leads to significant deformation of their hexagonal crystal lattice and also influences their optical and luminescence properties. Aluminum, in small amounts ($c \approx$ 0.01–0.05 at. %), is able to liquidate the vacancies in the gallium sublattice, thus contributing to the increase of the absorption coefficient in the center of n = 1 exciton band; whilst, at higher concentrations ($c \geq 0.2$ at. %), the defects induced by dopant shield the exciton bonds, which is manifested by the decrease in the intensity of the exciton absorption band. Indium as a dopant engenders structural defects in ε–GaSe which, together with the shielding of electron–hole bonds, lead to the formation of donor–acceptor pairs and of the impurity PL band [10]. Also, the rare earth elements (Er and Tm) are able to occupy gallium vacancies [11,12]. By doping GaSe with Tm^{3+}, luminescence centers are formed in the near-IR region, while Er, in low concentrations, can form localized states within the GaSe bandgap, responsible for its red PL.

The surface of GaSe plates, kept for a long time in a normal atmosphere, is covered with a nanosized gallium oxide layer [13], while as a result of the heat treatment in an atmosphere enriched with oxygen and water vapor, a layer of β–Ga_2O_3 nanoformations is formed on the surface of GaSe plates [14–16]. Under the presence of water vapor and ultraviolet (UV) radiation, the formation of Ga_2O_3 and SeO_2 oxides on thin GaSe plates' surface is stimulated [16,17]. Since the valence bonds are practically closed at the (0001) surface of GaSe plates, the formation process of β–Ga_2O_3 oxide is initiated on the edge or in high surface defect density regions of GaSe plates.

In [18], Eu-doped β–Ga_2O_3 nanowires were obtained by consecutive heat treatments, at temperatures of 1500 °C and 1350 °C, of nanowires obtained from the vapor phase. As a characteristic feature, the cathodoluminescence spectrum of β–Ga_2O_3:Eu^{3+} nanowires contains the Eu^{3+} emission band with a maximum intensity at 610 nm. In the works [19,20], Chen and co-authors obtained, appealing to the PLD technique and using a mixture of β–Ga_2O_3 and Eu as evaporation material, β–Ga_2O_3:Eu thin films exhibiting intense red and violet luminescence, determined by radiative transitions of Eu^{3+} and Eu^{2+} ions, respectively.

The β–Ga_2O_3 is an n–type semiconductor with an ultra-wide energy band gap (4.80–4.90 eV) and moderate concentration of majority charge carriers [21,22]. Since undoped GaSe is a p–type semiconductor, through heat treatment in a water vapor-rich atmosphere (AVH_2O), nanoscale n/p β–Ga_2O_3/GaSe heterostructures can be obtained.

This paper studies the surface photoluminescence (PL) of the GaSe plates doped with Eu, and the composition and optical properties of the β–Ga_2O_3:Eu^{3+} layer formed on the surface of GaSe:Eu plates following the heat treatment in an AVH_2O at temperatures below the melting point.

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