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Radiative-recombination transitions in sulphur-doped GaSb

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ABSTRACT

Photoluminescence (PL) of sulphur-doped gallium antimonide prepared by a liquid-phase-electro-epitaxy growth method was investigated. Pumping-intensity-dependent and temperature-dependent PL measurements were carried out, properties of individual spectral bands were studied, and their physical origin was specified in detail. Sulphur caused compensation in GaSb, which is usually p-type if it is undoped due to the high concentration of its characteristic native acceptor (NA). As a result of compensation, recombination occurred under the condition of a fluctuating potential and spectral properties characteristic for such a material state were observed. Three bands formed the low-temperature PL spectra. Band A_U, connected with the NA, exhibited extremely low peak energy for some samples (down to 765 meV). Together with the presence of a "moving" PL, with a moving rate of approximately 10 meV per decade of the pumping intensity, it is a direct consequence of perturbed energy bands. Band S, peaking at about 732 meV, is a characteristic one for sulphur-doped GaSb and is most probably connected with a sulphur-donor-to-valence-band transition. The thermal decay of the band agrees with this supposition. Intensity-dependent and temperature-dependent PL of band A_I (maximum at 705–710 meV) both indicate that the band is connected with the ionised NA. PL intensity of the peak is relatively high, because compensation enhances the concentration of such centres.

1. Introduction

Reports on the successful growth of sulphur-doped GaSb crystals by epitaxial [1–6] as well as by Czochralski methods [7,8] were published by several research teams. Doping GaSb with sulphur is a technological task stimulating researchers for several reasons. Like doping with tellurium or selenium it could provide n-type GaSb, whereas GaSb produced by standard growth techniques is usually p-type [9]. Doping with sulphur poses also some technological problems [1,2,4,8]. It is necessary to find a doping source with suitable physical properties as well as to tackle the effect of a strong sulphur volatility during the crystal growth. Another interesting subjects of the research are deep levels with DX-like properties [3,7] and the phenomenon of the persistent photoconductivity [7], both observed in GaSb:S crystals.

Photoluminescence (PL) characterisation of GaSb:S was referred in a few articles [1,5,6]. The most distinctive feature of the spectra was a band around 732–735 meV. The other two bands at around 770 and 705 meV were also observed at 6 K [5,6] and the first one was intuitively assigned to the radiative transitions related to the characteristic GaSb native acceptor (NA). To interpret such PL spectra correctly and unambiguously, one needs to understand in detail the recombination processes that lead to the spectra studied. This work presents the results of PL characterisation of sulphur-doped GaSb prepared by a liquid-phase-electro-epitaxy (LPEE) method. The aim was to study some characteristic properties of the spectra and find their connection with the electronic state of the crystals (presence of the strong compensation, perturbation of the energy bands). For this purpose, a series of measurements was performed at varied values of the pumping-beam intensity and the sample temperature. From the intensity-dependent measurement, the conclusion on compensation-caused perturbation of the energy bands and the localization of recombining electrons and holes in the spatially separated potential wells can be drawn. The temperature-dependent measurement helps to assess the activation energy and the type of a recombination centre. At the end, a closer picture of the overall recombination scheme can be proposed.

2. Experiment

We studied a set of samples prepared by an LPEE method [4,5]. The apparatus design and physical principles of the growth were described in Ref. [4]. Ref. [5] gives a detailed description of the growth procedure and the results of a basic electrical and optical characterisation of the samples. Antimony sulphide Sb_2S_3 of

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purity level 5N served as the sulphur-doping source. Its amount in the melt varied from 0 to 124 mg in different growth runs [4,5] and formed only a small portion of the melt, less than 1% at the highest doping level. Crystal without intentional doping, KNF1, served as a reference one for the whole set of doped samples. The growth temperature was held close to 550 °C for all samples [4,5]. At this temperature, a melt composition with a strong excess of gallium corresponds to the solid–liquid equilibrium. The doping process resulted in a substantial lowering of the hole concentration in the crystals and a growth temperature of 535 °C even led to the overcompensation to n-type in one sample (see Refs. [4,5] and tables reported therein).

For PL measurements, the samples were placed in an optical cryostat with a temperature control. An argon-ion laser (the 488 nm line) was used for the sample pumping at a pumping power density of approximately $1\,W\,cm^{-2}$. To carry out the measurements at the varied pump intensity, a circular neutral density filter was used to damp the laser beam. PL radiation was filtered by a quarter-meter monochromator and the light from the monochromator output was detected by a liquid-nitrogen-cooled PbS photodetector. The detector signal was amplified and recorded using a standard lock-in technique.

3. Results and discussion

Fig. 1 shows PL spectra of the studied samples. In the inset of the figure, the spectrum of undoped sample KNF1 (hole concentration of $7.8 \times 10^{16}\,cm^{-3}$ at room temperature) is depicted [5] in

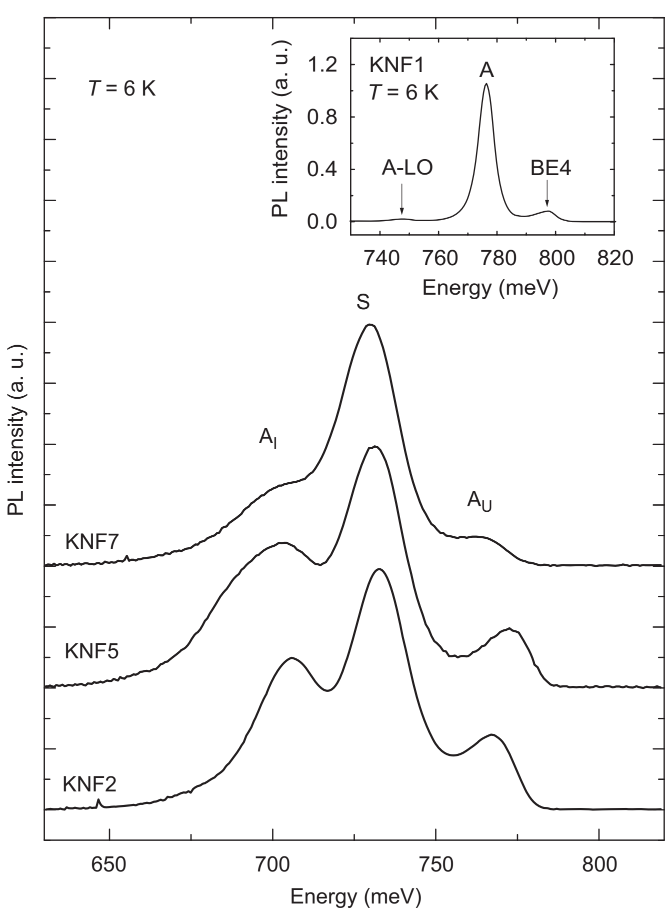

Fig. 1. PL spectra of the sulphur-doped GaSb samples at 6 K. The assignment of the spectra to the samples is indicated on the left-hand side of the PL lines. In the inset a picture of a PL spectrum of reference sample KNF1 is shown.

order to demonstrate the impact of the doping on the PL spectral shape. One can clearly see the difference between PL spectra of the doped samples and the undoped one. The spectrum of sample KNF1 is a typical one for undoped GaSb prepared by a standard growth technique [9]. The most significant feature of such spectra is the dominant peak A with a maximum at around 777 meV usually accompanied with peak BE4 at around 796 meV as well as weak band A-LO at approximately 748 meV. It is generally accepted that the peaks represent an electron-to-acceptor transition, recombination of an acceptor-bound exciton, and an LO-phonon replica of peak A [9,10]. GaSb NA $V_{Ga}Ga_{Sb}$ is assumed to be the recombination centre involved in the transitions [10].

The spectra of the sulphur-doped samples (KNF2, KNF5, and KNF7 with room-temperature hole concentrations of 6.6×10^{16} cm^{-3}, $3.4 \times 10^{15}\,cm^{-3}$, and $4.5 \times 10^{16}\,cm^{-3}$, respectively [4,5]) exhibited common characteristic features. Similar spectral lines were observed also in MOCVD-grown GaSb:S [6], with only a small difference in the shapes and the relative intensities of the individual peaks. The use of different substrates for the growth (undoped p-type or tellurium-doped n-type, see Ref. [4] and the table reported therein) had no effect on the sample spectral shape. Therefore we conclude that all the specific features of the spectra, which make a difference with the reference-sample spectrum, are the consequence of the doping procedure. The spectra consist of three bands, designated S, A_U, and A_I in the figures throughout this article. The bands are markedly broadened; hence energy levels are much more "smeared" compared to the reference sample. Peaks S and A_I were completely absent in undoped reference sample KNF1. Band A_U is positioned at a lower energy than band A in standard undoped GaSb samples; however, this energy difference is not very large. It implies a supposition that band A_U results from the same transitions as band A does, but the transition is modified by some way. In the following paragraphs we discuss properties of bands S, A_U, and A_I. Pumping-intensity-dependent and temperature-dependent PL spectra are studied and related to the electronic state, especially the status of compensation of the crystals. On this basis, some details of the radiative-recombination scheme can be deduced.

Band S peaking around 732 meV has been a characteristic and dominant one for all GaSb:S crystals investigated by PL so far [1,4,5]. It is reasonable to assign it to a sulphur-related centre. In Ref. [1] such a conclusion was made for the band peaking at 735 meV at 70 K and supported by DLTS measurements, which indicated a deep donor with the activation energy of about 75 meV. If peak S in Fig. 1 is related to a donor-to-valence-band transition, then the activation energy equals to about 80 meV, taking the value 812 meV for the GaSb band-gap at 6 K [9]. Another possible explanation of the peak origin is a donor–acceptor transition. The NA, with an energy level positioned 34.5 meV over the top of the valence band [9], is the most probable candidate for the acceptor centre in such a transition. Then the resulting donor-activation energy equals approximately 45 meV. The value is very close to the one obtained from temperature-dependent Hall measurements in Ref. [7]. One cannot also exclude the possibility of a conduction-band-to-acceptor transition with a sulphur-related centre as an acceptor. It is generally accepted that in tellurium-doped GaSb, a $V_{Ga}Ga_{Sb}Te_{Sb}$ complex is formed, which is responsible for a low-temperature electron-acceptor PL band at about 730 meV [11]. Sulphur belongs to the same group VI of the periodic table of elements as tellurium, so an analogical centre could be also formed with the sulphur atoms. The evidence of such a centre has not yet been referred in the literature, so we will not include this alternative into the recombination scheme introduced in this work.