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On the Additional Peak in the Photoluminescence Spectrum of Mercuric Iodide

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Introduction Red mercuric iodide (α -HgI₂) is a wide band-gap and high mean atomic number semiconductor, which is used as low noise, room temperature X-ray, and γ -ray nuclear detectors.

While producing these detectors, there appear a lot of trapping and recombination centers in the interfacial region between the contact and HgI, which reduces the sensitivity because of an incomplete charge collection. Photoluminescence gives information about the perfection of the near-surface region equal to the light penetration (≈ 100 nm).

Recently, the authors of /1, 2/ have made an attempt to establish a connection between the performance of the HgI₂ detectors made of the same crystal and their PL spectra. They have discovered that the spectra of the poor-quality detectors contain an emission spectral line at about 542 nm. The line appears after the metallic contact fabrication and shows a fairly consistent trend of increased magnitude with decreased detector performance. After thorough examination of the above PL spectra at different temperatures the authors of /1, 2/ concluded that the additional peak at 542 nm is not a phonon replica of a free exciton emission line and, probably, may be related to the non-stoichiometry of the material. Since the additional peak spontaneously appeared only in some samples when depositing metallic electrodes /1, 2/, an attempt is made in this note to investigate in more detail the effect of non-stoichiometry of HgI₂ on the PL spectra for determining the conditions of appearance of the additional peak.

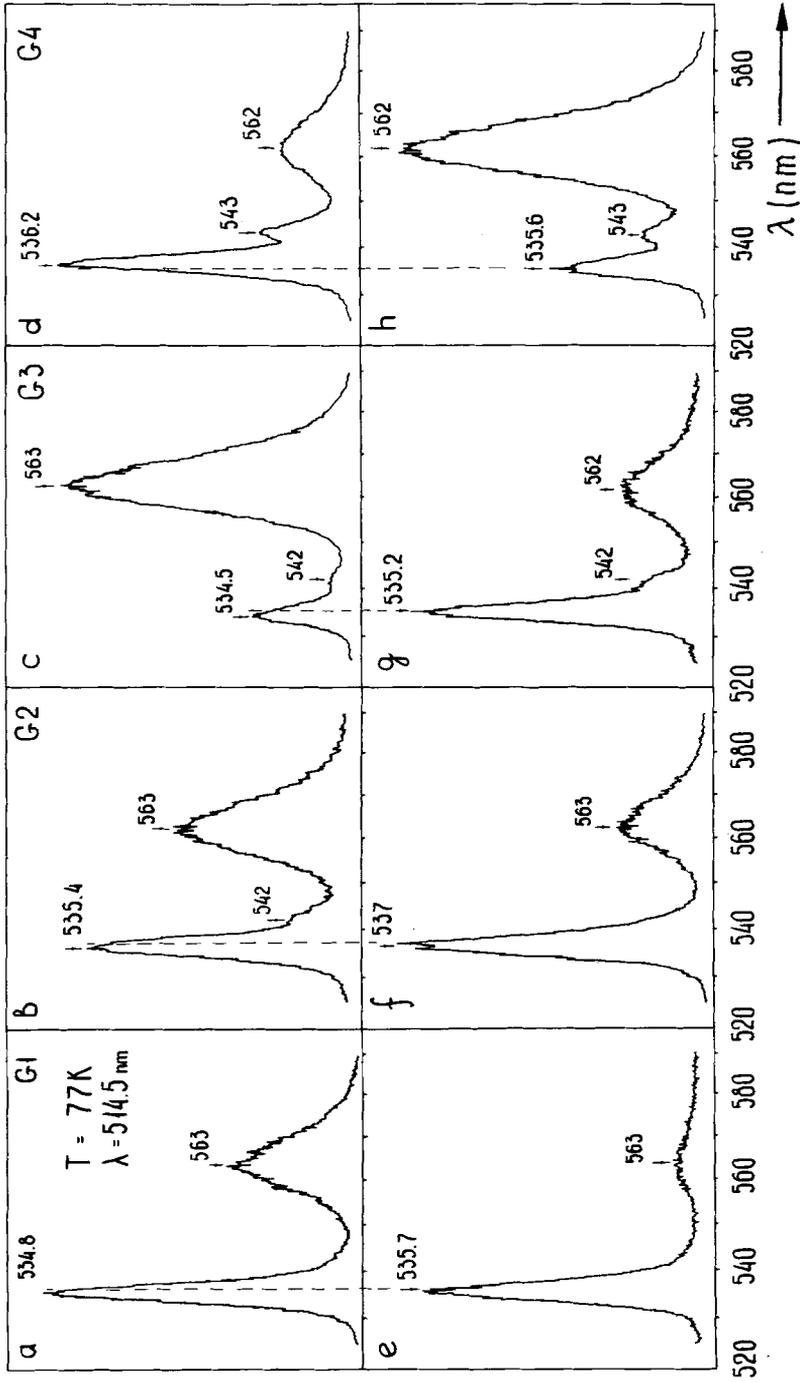
Experimental procedure Photoluminescence was excited by the 514.5 nm green line of an argon ion laser. The samples were immersed in liquid nitrogen. Spectra were recorded using a DFS-52 double monochromator with spectral slit width equal to 0.5 cm⁻¹. The HgI₂ samples were grown by the static sublimation method, then they were melted at 250 °C. After that they were sublimated once again under different conditions: G1 - without additional iodine, G2, G3, and G4 - at iodine vapor pressure equal to 13, 130, and 1300 Pa, respectively. The samples were heated at 100 °C in the air for 5 min for an additional influence on the concentration of stoichiometric defects.

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Results and discussion Fig. 1 shows PL spectra taken before (at the top) and after (at the bottom) heating of samples G1 to G4. In these spectra apart from the known bands at 536 and 563 nm, a new spectral line at about 542 nm was observed in samples G2, G3, and G4 grown with adding excess iodine. This spectral line appears as a well resolved emission peak in crystal G4, and as an obvious shoulder of the band at 536 nm in crystals G2 and G3. This is the same spectral line which was observed /1, 2/ after metallic contact sputtering.

First let us discuss the known PL bands at 536 nm (band 1) and 563 nm (band 2). The main band 1 is determined by emission recombination of the free excitons and its position on the energy scale should depend on the concentration of defects in the sample. The displacement of the emission band maximum with respect to the exciton energy for different quality crystals is due to the emission reabsorption phenomenon /3/. This phenomenon is especially important for direct band-gap semiconductors in question, since their absorption coefficient varies by three to four orders in the free exciton region (on band 1), reaching the maximum value of 10^5 cm^{-1} . As a result, the position on the energy scale and the shape of band 1 are essentially dependent on the depth distribution of excitons in the crystal. For example, in more perfect crystals, the exciton lifetime is longer and, thus, the exciton penetration is deeper. Therefore, the light emitted by the above excitons will be more absorbed inside the crystal, so the maximum of band 1 shifts to the longer wavelength side. Thus, according to Fig. 1e, f, g it follows that the near-surface region of HgI_2 has become more perfect after heating.

Band 2 (at 563 nm) whose nature is still to be discussed, is determined by emission of excitons bound with intrinsic stoichiometric defects. The authors /4/, for example, supposed that this band is due to excitons bound to iodine vacancies, but other authors /5/ referred it to excitons bound to mercury vacancies. According to our spectra, this band seems to be bound to additional iodine, since with the increase of iodine concentration, the intensity of band 2 increases (Fig. 1a, b, c), but after heating it decreases (Fig. 1e, f, g). So, if we take into account the fact that the calculations made in /6/ yield a larger mass of a non-stoichiometric unit cell of HgI_2 than in a stoichiometric material, then we may assume that band 2 is connected with iodine introduced to internodes. This assumption is also confirmed by the spectra of sample G4 in Fig. 1 d,h. So, after the thermal analysis it appeared that the endothermal melting peak of iodine at 113°C was observed only in samples G4. It means that additional iodine in them formed a separate phase embedded in the HgI_2 matrix as clusters. These clusters serve as outflows for free iodine atoms, therefore their concentration in the crystal volume becomes less and, hence, the amplitude of band 2 (Fig. 1d) decreases. On heating sample G4, the reverse process occurs: iodine atoms "evaporate" from clusters, which certainly bring about an increase of concentration of these atoms



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Fig. 1. PL spectra of HgI crystals with increasing concentration of iodine excess: G1 without additional iodine, G2, G3, and G4 at iodine vapor pressure equal to 13, 130, and 1300 Pa, respectively. At the top: before heating, at the bottom: after heating at 100 °C for 5 min

in internodes of the lattice. In this case, band 2 essentially increases (Fig. 1h) and the PL spectrum becomes similar to that of sample G3 (Fig. 1c) which was sublimated at lower pressure (equal to 130 Pa) of iodine vapors. This confirms the above mentioned assumption that band 2 is bound with iodine in internodes.

Let us continue to discuss the additional peak at about 542 nm. It is present in all samples grown with iodine excess. However, the effect of iodine on the additional peak magnitude and on band 2 is different. Thus, in sample G4 with cluster, the low intensity of band 2 indicates that the iodine concentration in internodes is decreased, but the additional peak magnitude is nevertheless high. At the same time, when heating sample G4, band 2 essentially increased (Fig. 1h), the additional peak magnitude did not change. It means that either band 2 and the additional peak are connected with internode iodine atoms of different locations in the crystal lattice, or the additional peak at 542 nm is due to excitons bound to mercury vacancies, which is more probable. This assumption is indirectly confirmed by the results of /5/, where HgI_2 was intensively affected by vapors of different halogens (iodine, bromine, and chlorine). In this case the peak appeared at the same distance from band 1, but in a narrower temperature range from 4.2 to 35 K. The authors of /5/ relate it with internode ions, but in our opinion, the additional peak energy in each case is to change, for the above halogens having essentially different ion radii must differently affect the vicinity of atoms in the crystal lattice. Thereby, this peak is evidently bound to mercury vacancies.

Thus, we can conclude that band 2 in PL spectra is due to excitons bound to iodine atoms in internodes, and the additional peak is due to excitons bound to mercury vacancies. In both cases these defects evidently form more complicated defect-impurity complexes as usual in the case of wide-band gap semiconductors.

In addition, it should be noted that recombination characteristics of the near-surface region do not become worse when the additional PL peak appears (the magnitude and energy position of the main band of the free exciton indicate this fact (Fig. 1d)). Therefore the above complexes serve only as carrier traps in the near-surface region, where accumulation of charges apparently reduces the detector performance, as was observed in /1, 2/.

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