The technology of low defect density, "epiready" substrates on the basis of $ZnSe_{1-x} S_x$, $x \leqslant 0.15$, crystals

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The comparison of results presented at the last three conferences [1−3] on the physics and applications of widegap AII − BVI semiconductors with those for GaN based compounds showed that there is no chance for remarkable improvement of parameters of AII − BVI green-blue lasers until currently used GaAs substrates are replaced by good quality ZnSe based crystals. Because of the thermal expansion differences between GaAs substrates and II -- VI epilayers cooling down the structures to the room temperature provokes a tensile strain and defects migration, which contribute to a laser degradation. Actually, the best results presently achieved in room temperature continuous mode operating lasers reach 102h of work in Sony laboratories, 2.5h in Philips Labs and similarly at the Brown University. These lasers are made on heteroepitaxial ZnMgSeS, $ZnSe_{1-x}S_x$ and $ZnCd_{1-x}Se_x$ structures deposited on GaAs substrates [1−4].

International experts presented at the above mentioned conferences the same opinion: a further progress may be expected provided that substrate of ZnSe (or even better $ZnSe_{1-x}S_x$) of suitable dimensions (at least 1 inch), low defect density [EPD (etch pit density) $<< 10^4/cm^2$], free of twins and structurally uniform could be used. For $x = 0.06$ the best matchieng with GaAs lattice constant is achieved.

The separate problem is obtaining similar quality substrates of $ZnMg_{1-x}Se_x$ or $ZnMn_{1-x}Se_x$ for $x \leqslant 0{,}15$ which have energy gap larger than that of ZnSe (similarly as in the case of $ZnSe_{1-x}S_x$), but they are closer to or even strictly matched to the lattice of presently used lasing layer of $Cd_{1-x}Zn_xSe$ (see Fig. 1).

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Pretty good quality ZnSe substrates, which are not commercially available, are only manufactured in Eagle-Pitcher Industries in the USA and in Prof. Hartman's group at Humboldt University, Berlin.

The other semiconductors from mentioned above have not been grown yet as substrate quality crystals.

In the frames of a presently conducted research project, which is partially supported by the State Committee for Scientific Research, we have elaborated a method of growth of low defect density crystals with EPD $\leqslant 5 \times 10^4$ cm^{-2} of ZnSe and $ZnSe_{1-x}S_x$, $x \leqslant 0.15$.

The crystals are grown by the physical vapour transport method (PVT). An ingot of $ZnSe_{1-x}S_x$ and monocrystalline plates of this material are shown in Fig. 2 and Fig. 3. In our opinion it is worth emphasizing that technological conditions influence photoluminescence (PL) spectra. These are strongly dependent on the quantity of Zn vacancies and a number of acceptors, associated with them, which create compensating centres. By means of the controlled PVT we can grow crystals, which PL spectra consist of only one line attributed to the recombination of a donor bound exciton, i.e., in which there exists only one recombination channel which gives very strong stimulated emission. This is a clear indication that the quality of crystals is high and which type of material should be used for lasing layer. Moreover, it should be noticed, that such crystals present no absorption in the part of the spectrum beyond the absorption edge. For this reason they could serve, after fabricating p−n junction, as a material for solar light blind detectors of the blue light.

An interesting question which is being discussed, is the origin of the spectrum presented in Fig. 4. From the technology viewpoint it is not difficult

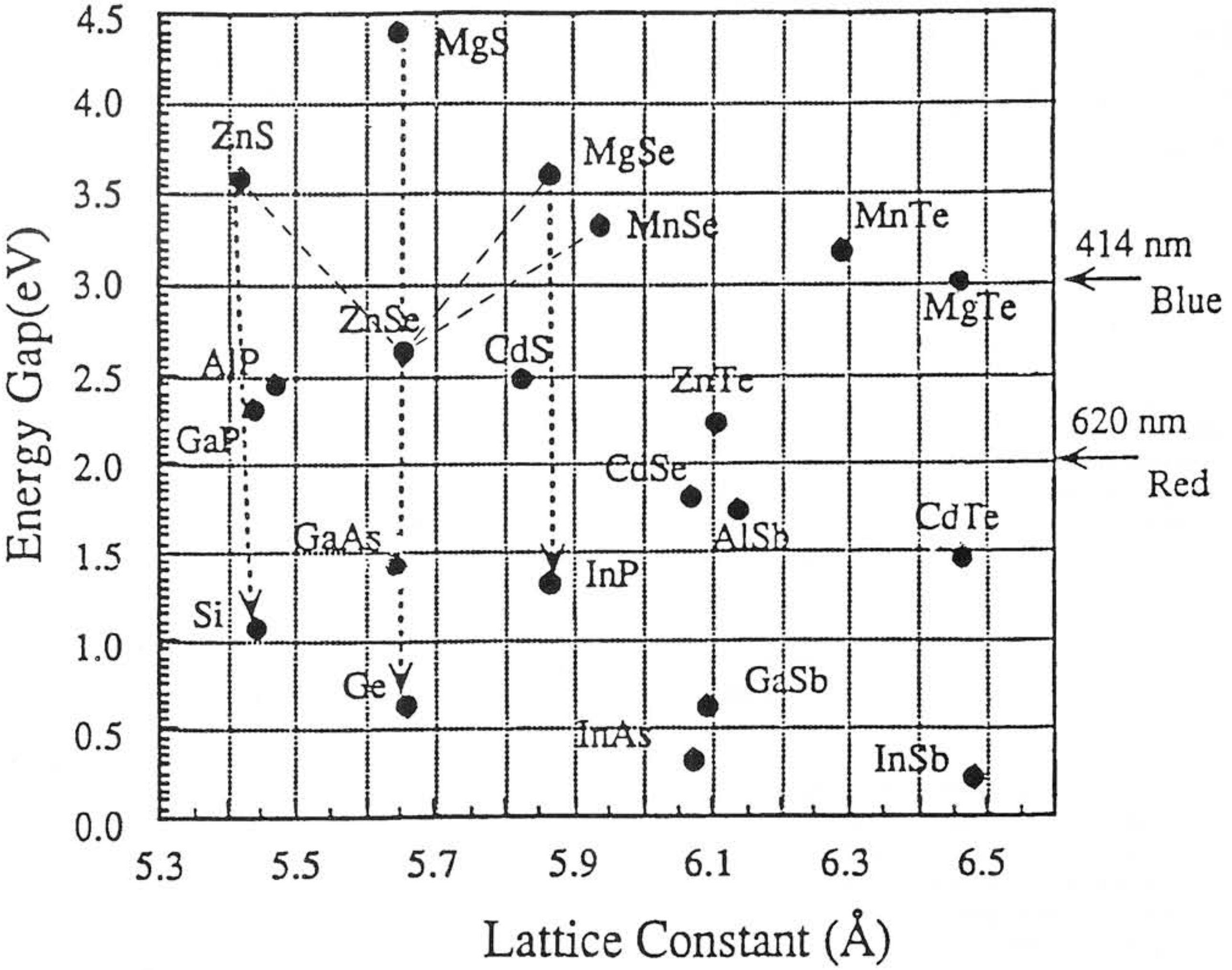

Fig. 1. Energy gaps vs lattice constants for groups of II–VI and III–V semiconductors.

to grow a crystal of $ZnSe_{1-x}S_x$, $0.10 \leqslant x \leqslant 0.20$, presenting a PL spectrum with one dominating line located at a little smaller energy than that of a free exciton (FE). The former interpretation attributes this line to the FE recombination. Presently more authors ascribe this feature to the recombination of an exciton localized on chemical disorder potential fluctuations. The chemical disorder always takes place in ternary and quaternary compounds, but additionally if there exist band offsets between matrix constituents, especially between valence bands, they lead to chemical disorder potential fluctuations. Passing from ZnSe to ZnS we can expect significant band offsets of valence bands. It is an advantageous situation in respect to the localization of a hole in an exciton. The mechanism of such localization is supposed to be very effective and expected energy of this localization in $ZnSe_{1-x}S_x$, $x = 0.1$, would be equal to a few meV. From private information we have learned that Prof. S. Nakamura from Nichia Chemical Industries Ltd. attributes the emission of light from GaN based diodes to excitons localized on chemical disorder stimulated potential fluctuations. These ideas create an entirely new perspective and may appear fundamental in elaborating and designing lasers emitting blue and violet light.

Now we start to realize a new research project, which is based on unique diversity of potential joined in our laboratory. By that I mean the possibility of obtaining ultra pure elements like: Zn, Se, S, Mg, Mn, growing high quality ZnSe based crystals, homoepitaxial layers and p-n junctions and characterization of the above mentioned products.

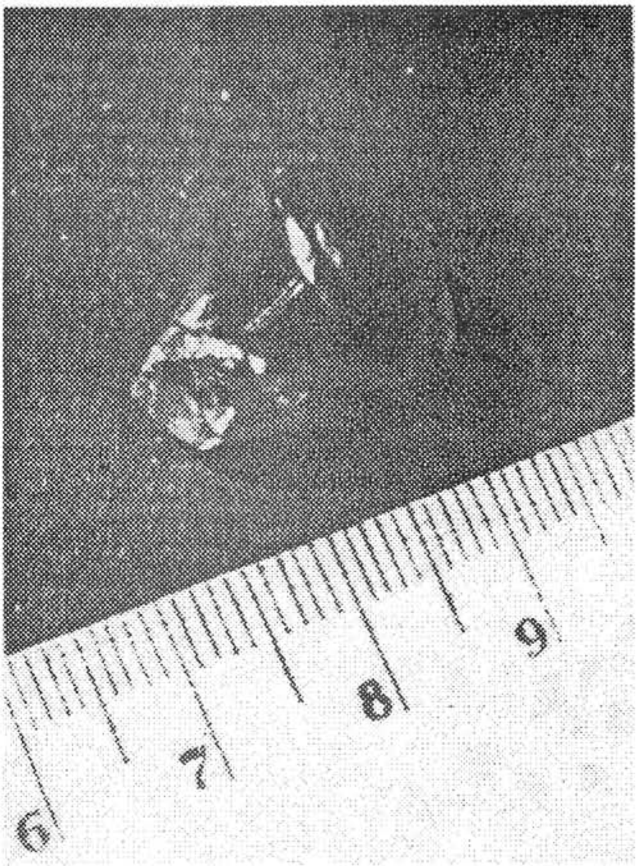

Fig. 2. An ingot of monocrystalline $ZnSe_{1-x}Se_x$, $x = 0.12$, grown by the physical vapor transport (PVT) technique.

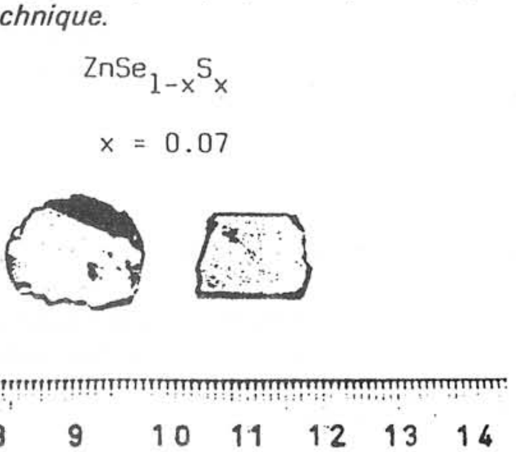

Fig. 3. Twin free, (110) oriented crystalline plates of $ZnSe_{1-x}Se_x$, $x = 0.07$.

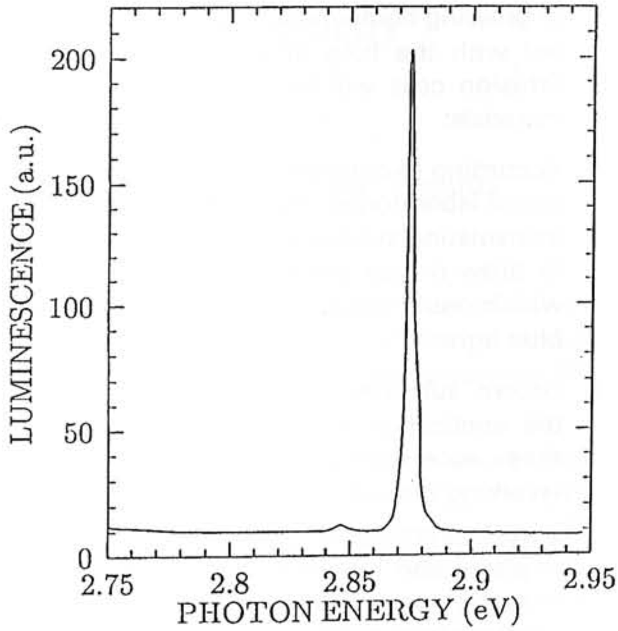

Fig. 4. Photoluminescence spectrum of $ZnSe_{1-x}Se_x$, $x = 0.10$, with one dominating line.

The detailed plan of forthcoming tasks is as follows:

1. In the frame of elaborated PVT technique for ZnSe and $ZnSe_{1-x}S_x$ we will focus on an acceleration of the growth process from 3 mm /day to 6 mm/day through a modification of a very specific temperature profile in the furnace, a selection of a proper inert gas atmosphere in a growth ampoule and finding a suitable excess of one of the components. At the same time we shall try to enlarge diameters of ingots from 25 mm to 35 mm and lengths to 50 mm.
2. PVT technique will be used to grow $Mg_{1-x}Zn_xSe$ and $Mn_{1-x}Zn_xSe$ crystals. Crystals with Mn are expected to be magnetic field tunable and thus very attractive for practical applications.
3. Methods of surface treatment such as mechanical and chemical polishing and ion etching have to be worked out for twin free, (001) or (111) oriented crystalline plates.
4. The quality of the substrates surfaces will be improved by growing homoepitaxial layers on them. These will be done in a special chamber and pumping set in which vacuum of 10^{-8} Torr is available. The apparatus will be equipped with a substrate holder, effusion cells and ion etching equipment of our own construction. A crystallizing surface will be controlled by means of a recently described method [5], with the use of He-Ne and Ar lasers. The thickness

of growing homoepitaxial layers will be evaluated with the help of a piezoquartz element. Effusion cells will be filled up with our own materials.

5. According to opinions of experts from different world laboratories, the most important are semiinsulating substrates. We shall try, however, to grow n-type substrates and p-n junctions, which could serve as detectors or sources of blue light.

6. Grown substrates will be characterized with the application of different methods, mainly those accessible in our laboratory and in co-working groups.
   - real structure of grown crystals, substrate plates and homoepitaxial layers will be investigated by X-ray methods in X-ray laboratory in our institute;
   - composition of crystals and layers will be done by X-ray fluorescence method;
   - trace elements of impurities in our product will be searched in Jeol Mass Spectrometer in the Institute of Vacuum Technology, Warsaw;
   - the quality of crystals will be additionally evaluated by optical methods: investigations of Cd-He laser stimulated photoluminescence, reflectivity in free-exciton region and absorption for light energies 0.3 eV $\leqslant \hbar\omega < E_g$;
   - stimulated emission under the excitation by high power lasers Nd:YAG and the YAG stimulated dye laser will be studied;
   - electrical parameters will be estimated for annealed and doped samples;
   - substrate – homoepitaxial layer interface will be investigated in an electron microscope.

Moreover, our crystals will be accessible for a wide community of physicists for common studying of more specific problems.

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