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Highly Conductive ZnSe Layers by Plasma-Assisted Epitaxy

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Highly conductive ZnSe layers with resistivity $10^{-3}\Omega$cm (electron density: 2.8x 10^{19}cm^{-3}, Hall mobility: 140cm^2/Vs) have been epitaxially grown on (100)GaAs by plasma-assisted epitaxy at 318°C in mixed plasma of hydrogen and HCl. The excess doping above 10^{19}cm^{-3}, however, reduces the conductivity by inducing complex defects. The effective collection of photo-excited carriers are observed in n-ZnSe/p-GaAs heterojunction diodes.

§1. Introduction

ZnSe has recently been extensively investigated in view of its application to opto-electronic devices, in addition to III-V compound semiconductors already in practical use. It has been widely recognized, however, that the growth of II-VI compound semiconductors of controlled electronic properties is much more difficult than IV and III-V materials because the self-compensation effect by native defects or residual impurities, which are easily incorporated particularly at high growth temperatures, prevents adequate control of their electronic properties. Thus non-thermal equilibrium growth at lower temperatures by MBE and MOCVD has recently been attracting wide attention. The first purpose of this paper is to describe the growth of high-quality ZnSe layers at relatively low temperatures (300°C-400°C) by plasma-assisted epitaxy (PAE) in hydrogen plasma.

It is also essential to develop a technology to grow highly conductive ZnSe layers which can be grown epitaxially on such lattice-matched substrates as GaAs and Ge or on which active layers can be successively and epitaxially grown, preferably at low temperatures, in order to bring this material into practical application, particularly for such devices as LED, dc EL and solar cells which should use efficient carrier injection or extraction. Successful reduction of resistivity down to $10^{-3}\Omega$cm by chlorine doping in PAE will then be described.

§2. Plasma-assisted epitaxy of ZnSe

An experimental PAE apparatus and typical deposition conditions are shown in Fig.1. and Table I, respectively. The details of growth procedure has been described elsewhere.[1)]

Fig.2 shows the photoluminescence spectrum

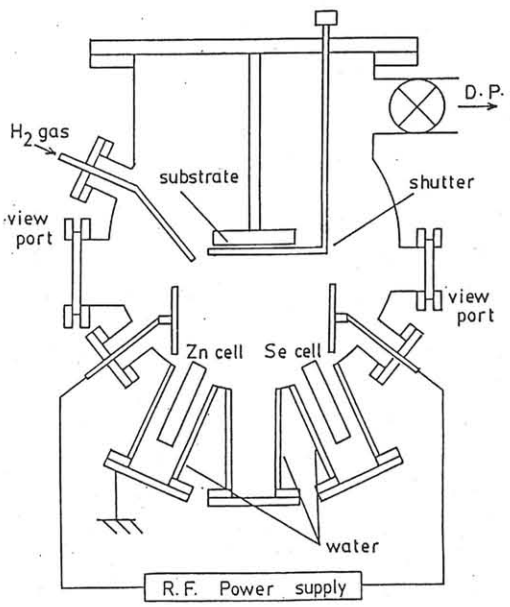

Fig.1 An Experimental PAE apparatus for ZnSe.

Table I Typical deposition conditions for PAE ZnSe growth.

Total Pressure	0.1 Torr
HCl Content	0~5 %
R.F. Power	20 W
Zn Temp.	470 °C
Se Temp.	295 °C
Sub.Temp.	318 °C
Growth Rate	~1.0μm/h

of a nominally undoped ZnSe layer observed at 4K by 500W Xe lamp excitation with a filter UVD-36A for cutting off the light of wavelength longer than 400nm. The main peaks consist of a donor-acceptor pair (DA) emission and its phonon replica in addition to so called I_2 (exciton emission bound to a neutral donor), and only very weak luminescence due to deep levels is observed.

The resistivity of undoped layers were around $10^4\Omega$cm.

§3. Growth of highly conductive layers

One of the advantages of PAE is the ability of efficient heavy doping[2] and HCl gas was mixed into hydrogen gas plasma in order to dope ZnSe with Cl. Fig.3 shows the electron density, Hall mobility and conductivity of Cl-doped ZnSe layers epitaxially grown on (100) semi-insulating GaAs at 318°C, measured by van der Pauw method, as a function of the fractional content of Cl in hydrogen gas. The lowest resistivity of 1.6×10^{-3} Ωcm with electron density 2.8×10^{19}cm^{-3} and Hall mobility 140cm^2/Vs, was obtained by mixing about 2.2% HCl. It is to be noted that excessive doping of Cl reduces the conductivity, probably by introducing Cl-related complex defects, as described below.

Fig.4 shows the temperature dependence of electron density and Hall mobility, and indicates that this ZnSe layer is doped up to degenerate level but has considerably high electron mobility.

The effect of Cl-doping on photoluminescence spectra is shown in Figs.5 and 6. The donor level responsible for the present DA emission is considered to be Cl and, as expected, the peak of this emission shifts to shorter wavelength and

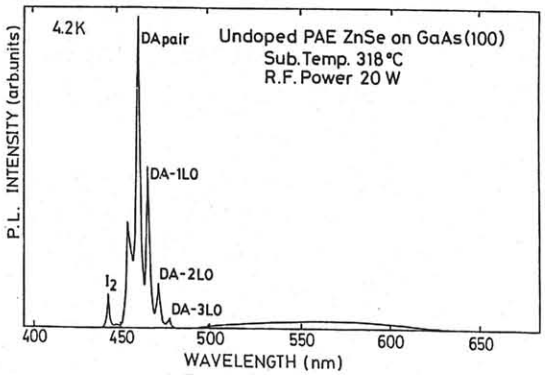

Fig.2 Photoluminescence spectrum of an undoped PAE ZnSe layer grown on (100)GaAs.

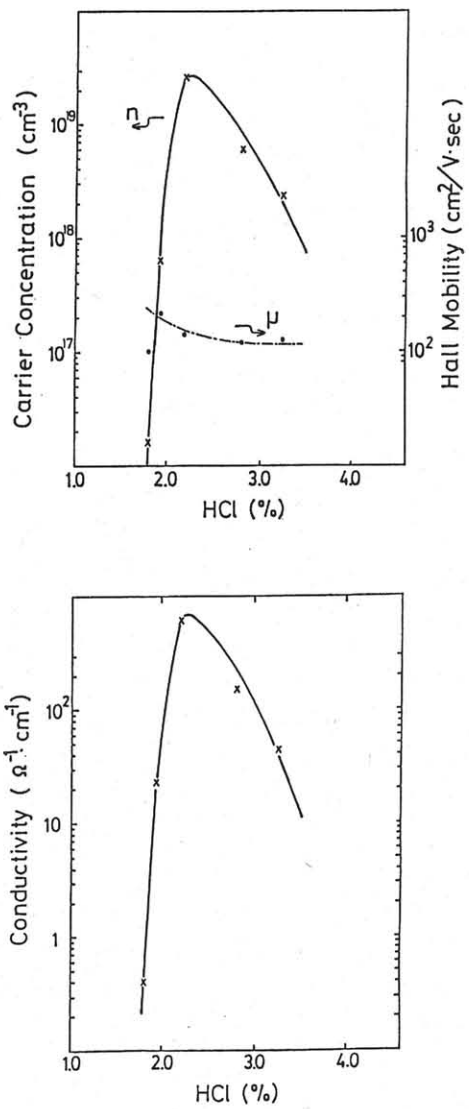

Fig.3 Electron density, Hall mobility and conductivity of Cl-doped PAE ZnSe layers as a function of HCl content in hydrogen.

the spectrum becomes broader as the doping concentration of Cl is increased. Another emission peak between I_2 and the DA emission is considered to be due to the electron transition from conduction band to acceptor level, as also supported by the reduction of this emission intensity relative to the DA emission as the Cl-doping is increased. Then the energetic depth of Cl donor level is estimated to be 26meV in close agreement with Dean et al.[3)]

As shown in Fig.6, the intensity of DA emission is drastically decreased above doping level where the electron density ceases to increase, as shown in Fig.3. On the contrary, the intensity of self-activated (SA) emission due to SA centres which are considered to be zinc vacancies associated with Cl,[4)] tends to increase. It is then considered that the Cl-doping above $10^{19}cm^{-3}$ induces complex defects including SA

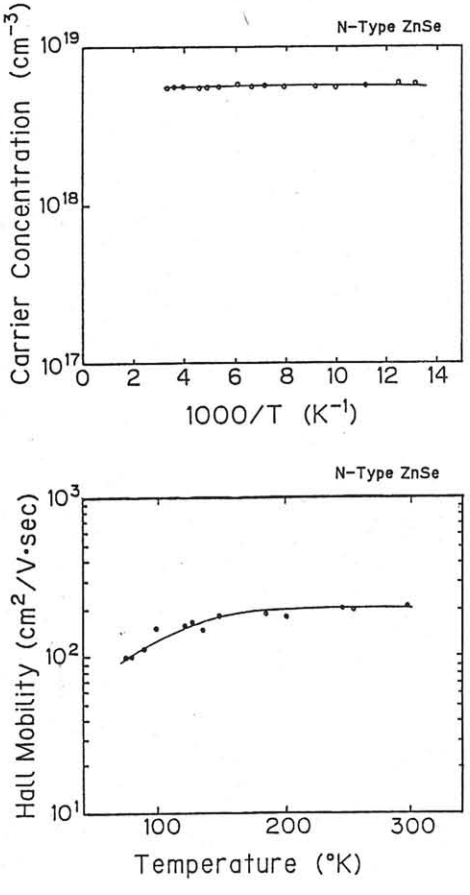

Fig.4 Temperature dependence of electron density and Hall mobility in a heavily Cl-doped PAE ZnSe layer grown on (100) semi-insulating GaAs at 318°C.

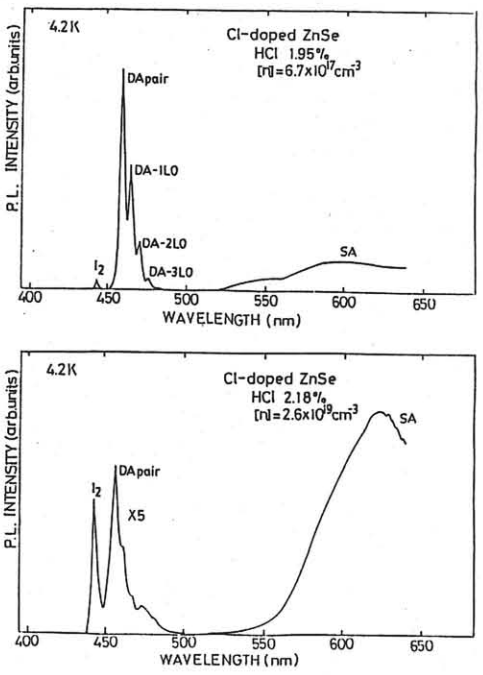

Fig.5 Photoluminescence spectra of Cl-dped PAE ZnSe layers.

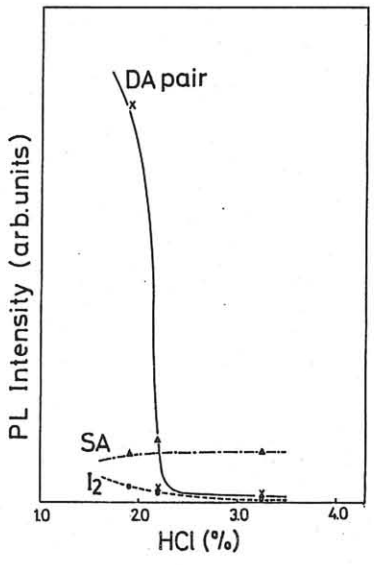

Fig.6 The variation of each emission band of photoluminescence in Cl-doped PAE ZnSe layers as the HCl content in hydrogen gas is increased.

centres.[5]

§4. ZnSe/GaAs heterojunction diodes

The highly-conductive n-type ZnSe layers described above were then employed to fabricate n-ZnSe/p-GaAs heterojunction diodes. In order to observe how effective this conductive ZnSe is in collecting carriers which are photo-excited apart from the electrode, a He-Ne laser beam was scanned about 1.5mm above the electrode (see the insert of Fig.7) without applied voltage. The result shown in Fig.7 indicates that almost all the photo-excited carriers are collected, with rather enhanced response at the periphery of the ZnSe layer, probably due to geometrical effect.

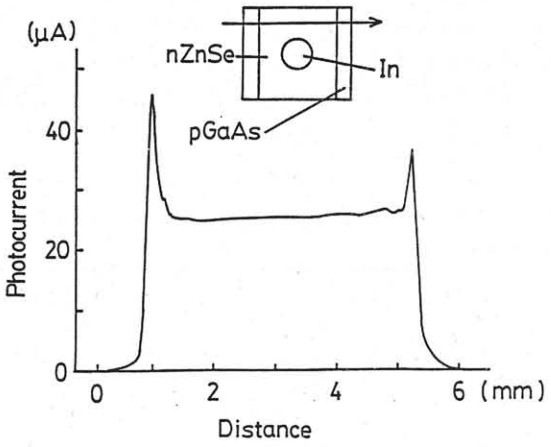

Fig.7 Spatial distribution of collection efficiency of photo-carriers excited apart from the electrode on a n-ZnSe/p-GaAs heterojunction diode.

§5. Conclusions

Highly conductive n-type ZnSe layers with resistivity down to $10^{-3}\Omega$cm can be grown epitaxially on (100)GaAs by plasma-assisted epitaxy in mixed plasma of hydrogen and HCl. Excessive Cl-doping above 10^{19}cm^{-3} by mixing more than 2.5% HCl into hydrogen plasma, however, reduces the conductivity by inducing complex defects. This highly-conductive ZnSe layers will be useful for application to homojunction or heterojunction optoelectronic devices which require efficient carrier injection or extraction.

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