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DEEP LEVELS IN PbSe

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Deep defect levels in the gap of monocrystalline PbSe were observed. Their position relative to the band edges is strongly temperature dependent. Optical data agree well with the assumption of a localized defect potential. By implantation of Pb and Se ions and subsequent annealing of the lattice damage the number of states in the gap was varied, indicating that the observed deep levels are created by intrinsic point defects.

I. Introduction

In the last years some effort has been spent on the studies of defect levels in undoped lead chalcogenides. For PbS [1], PbSnTe [2] and PbTe [3] the observation of deep levels in the gap and of defect states degenerate with the conduction band [4] has been reported.

In this paper we report on the first observation of deep levels in undoped PbSe epitaxial films. The concentration and energetic position of these levels were measured by Hall-effect, impurity-photoconductivity and magneto-optic experiments. Implantation of Pb and Se ions and subsequent annealing of the lattice damage changed the concentration of the observed deep levels. This may serve as an indication for the fact that intrinsic point defects, probably Se vacancies, create these localized states in the gap of PbSe.

II. Experimental Results

All samples used were monocrystalline epitaxial layers of PbSe grown by hot-wall epitaxy [5] on the (111) surface of BaF_2 substrates. Pb and Se used was of 6-9 purity and no dopants were added intentionally. Both p- and n-type layers with carrier concentrations in the range of 10^{23} m^{-3} were produced.

In Fig.(1) the hole concentration of some representative samples is plotted versus temperature. The carrier concentration was calculated from the measured Hall coefficient by assuming a constant scattering factor equal to one. However the scattering factor will change in the investigated temperature region [6] by less than 10%, but this variation cannot account for the observed change in hole concentration. The mobility followed a $T^{-5/2}$ law and the intrinsic concentration n_i was at least one order of magnitude smaller than the observed carrier concentration. Therefore effects of sample inhomogenity and of intrinsic conduction can be ruled out.

We propose that the observed variation of the hole concentration (circles in Fig.(1)) results from freeze out of free carriers into bound states in the gap. The constant hole concentration at low temperatures is attributed to crystal defects, which do not create bound states in the gap (similar to Pb vacancies in PbTe [7]). The curves in Fig.(1) show the results of a model calculation of the hole concentration. The best fit was obtained with defect levels in the gap separated by $E_D = 130 + 0.32T$ meV from the conduction-band edge. The position of the levels in the gap is shown as solid line in Fig.(3). The density of deep levels N_D, which is a fitting parameter in the calculation, is indicated for each curve in Fig.(1). We assumed that each defect can bind two carriers. Only in this case the level position obtained from Hall data and optical data agreed well.

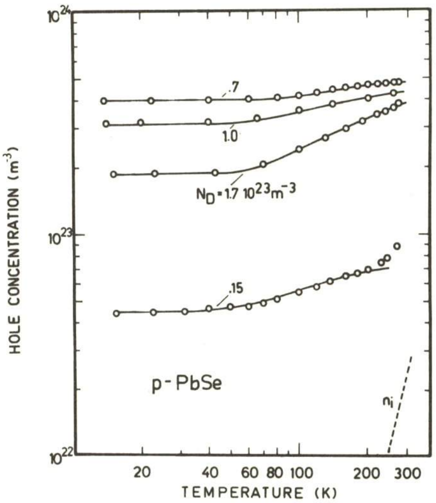

Fig.1 Carrier concentration vs. temperature for different p-type PbSe samples: The full curves were calculated assuming deep levels in the gap of PbSe $E_D = 130 + 0.32T$ meV below the conduction band edge. The defect concentration N_D in units of $10^{23}\ m^{-3}$ is indicated for each curve.

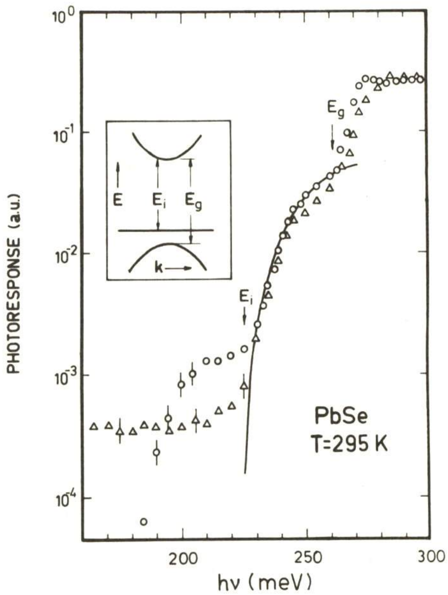

Fig.2 Spectral photoresponse of (▲) n- and (o) p-type PbSe: The full curve was calculated assuming transitions between deep levels and conduction band states. A δ -function like defect potential was assumed.

Photoresponse versus light energy for p- and n-type samples was measured at several sample temperatures. Experimental results for 295K are shown in Fig.(2). In the impurity photoconductivity region ($h\nu < E_g$) the photoresponse of the p-type sample had two pronounced shoulders, whereas for the n-type sample only one shoulder and no cut off in the investigated spectral range was observed. Lucovsky [8] calculated the optical cross section for impurities with a δ -function like impurity potential. The full curve in Fig.(2) was obtained using Lucovsky's model. We assumed that this part of the photoresponse curve is due to transitions of electrons from localized bound-state levels near the valence band to the conduction band. The position of these levels obtained from photoresponse is indicated by circles in Fig.(3). The agreement of optical and Hall data was excellent.

A detailed discussion of the photoresponse for $h\nu < E_i$, which probably is caused by transitions to levels in the upper half of the gap, will be given elsewhere.

The influence of a high magnetic field B (up to 8T) on the impurity photoresponse of n-type PbSe ($n = 6.10^{22} m^{-3}$) was studied. Experiments were carried out in Faraday configuration with B parallel <111>. The quantum energy $h\nu$ of the light used was 151 meV. For sample temperatures of 38K, 41K and 45K we observed a peak photoresponse at 6.5T, 5.8T and 4.5T respectively. For these temperatures E_g is larger than $h\nu$ even without magnetic field. Therefore it is suggested that resonant transitions of electrons from occupied deep levels to the lowest conduction band Landau level 0^- were observed. The position of the levels obtained in this way is indicated by dots in Fig.(3).

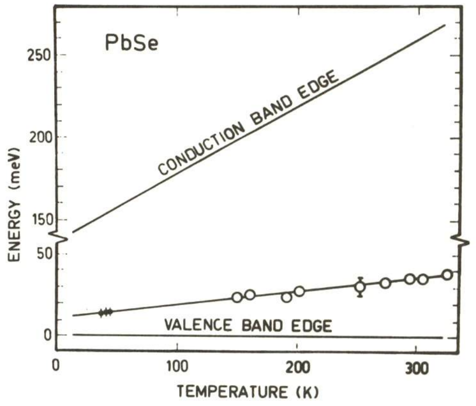

Fig.3 Deep level position in the gap of PbSe vs. lattice temperature: The full line was obtained from best fit of Hall-data (full curve in Fig.(1)). The circles show results from spectral photoresponse experiments. The dots were obtained from resonant transitions between deep levels and the lowest conduction band Landau level.

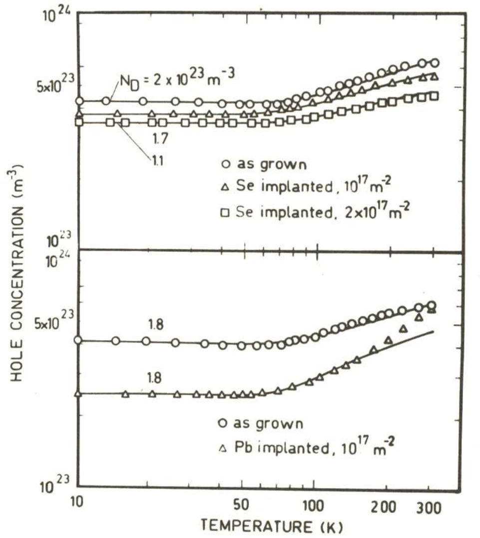

Fig.4 Temperature dependence of the hole concentration for Se-implanted (upper part) and Pb-implanted (lower part) PbSe: The points are experimental values, the curves were calculated. The impurity concentration N_D used in the calculation is indicated in the figure.

To get some information about the nature of the defects we have implanted thin samples (~1µm) with Pb and Se. The implantation was carried out with energies of 300 keV in the <111>-channel direction. After annealing of the damage at 280°C the range of implanted ions is then more or less equal to the sample thickness. The results of Hall-effect measurements on implanted samples are shown in Fig.(4), where the hole concentration is plotted as a function of the temperature. Experimental data are shown by dots, the lines are calculated. By implantation of Se the impurity concentration N_D decreases (upper part of Fig.(4)), whereas it remains fairly constant by implantation of Pb (lower part of Fig.(4)). The deviation of the experimental values from the calculated line at $T > 200K$ for the Pb-implanted sample is due to two-band conduction as indicated by a decrease of the mobility; higher Pb doses result in n-type conduction.

Since the carrier concentration in the lead chalcogenides is in general governed by simple point defects (vacancies and interstitials) and the variation of the defect concentration by implantation is of the same magnitude as the carrier concentration in the as-grown samples, it seems evident that the observed deep levels originate from such intrinsic defects. Bearing in mind that an excess of Pb leads to n-type conduction and a deficiency of Pb to p-type conduction [6], we conclude that the observed defect levels are due to Se vacancies.

III. Conclusions

By investigation of Hall-effect, photoresponse and magneto-optic properties of epitaxial PbSe layers the existence of levels in the band gap has been shown for the first time. Despite the fact that these levels are close to the valence band edge, they show significant properties of deep levels: i) The energetic distance of these levels relative to the conduction and valence band edge exhibits a pronounced temperature variation, ii) the optical data support the assumption of a strongly localized defect potential.

The concentration of defects correlated with the observed deep levels was changed by implantation of Pb and Se ions. This fact favours the assumption that deep levels in PbSe are created by intrinsic point defects, most probably by Se vacancies.

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