Doping of zincselenidetelluride

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Doping of zinc-selenide-telluride

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We investigate the doping behavior of ZnSe/ZnTe short period superlattices. *p*-type doping is achieved with a dc nitrogen plasma source, *n*-type doping with chlorine from a ZnCl₂ Knudsen source. Even a small Te content has a strong positive effect on *p* doping: Doping levels in the upper 10¹⁹ cm⁻³ range are achieved, and ohmic contacts can be obtained even for low carrier concentrations. The data are in excellent agreement with a theory based on the amphoteric native defect model. The opposite is valid for *n* doping: At Te concentrations above 20% electron concentrations are below 10¹⁶ cm⁻³. As a possible way to get both good *n*- and *p*-type doping at the same lattice constant we propose the use of the quaternary compound Zn_(1-y)Mg_(y)Se_(1-x)Te_(x).

The recent breakthrough in blue semiconductor laser technology was driven by the introduction of activated nitrogen as a *p* dopant for ZnSe.¹⁻⁴ However, the performance of blue laser devices suffers from the fact that the obtainable hole concentrations in ZnSe are still too low (in the upper 10⁷ range), and the contact resistance between *p*-ZnSe and metals is very high. On the other hand, the hole concentrations reported for ZnTe doped with activated nitrogen using rf plasma are much higher (near to 10¹⁹), and ohmic contacts to this material can be easily obtained.⁵ It would be an obvious advantage if these properties could be exploited in blue laser structures. One recent attempt to do this was the use of a ZnTe contact layer which is connected to the ZnSe by a graded ZnSe_(1-x)Te_(x) region.⁶ In fact this allowed the formation of ohmic contacts to *p*-ZnSe. However, the large lattice mismatch (8%) between ZnSe and ZnTe induces the introduction of a very dense dislocation network that again severely limits device performance.

An alternative way would be the use of ZnSe_(1-x)Te_(x) mixed crystals or ZnSe/ZnTe short period superlattices (SLs) instead of the currently used ZnS_(1-x)Se_(x). Since the obtainable *p*-doping levels in ZnTe are much higher than in ZnSe, one would expect that the admixture of Te has a positive effect on *p* doping and contacting. Besides the difference in dopability, a second distinct difference between ZnSe and ZnTe is the fact that in an absolute energy scale the ZnTe valence band edge lies 1 eV higher with respect to the ZnSe valence band edge. A similar correspondence between doping behavior and band edge positions is observed in III-V's, and the so-called amphoteric native defect model gives a quantitative correlation between these two properties.⁷ It has been suggested recently that this model can also be applied to wide gap II-VI materials,⁸ and especially the doping of ZnSeTe and ZnMgSe was discussed by Chadi.⁹ An estimate of the effect of Te alloying can therefore be gained by determining the influence of Te on the position of the valence

band edge. We calculated this effect by simulating the mixed crystals with ZnSe/ZnTe short period SLs. The average Te content of the SLs was varied between 10% and 90%, while the period of each SL was adapted in a way that the effective superlattice energy gap calculated with a Kronig-Penney type model corresponds to the known energy gap of the alloy with the same average Te content.¹⁰ Because of this adjustment we assume that the alloy will behave accordingly. The parameters used in the calculation were effective electron and hole masses of 0.16/0.75 *m_e* for ZnSe, and 0.13/0.6 *m_e* for ZnTe. The valence band offset between ZnSe and ZnTe was assumed to be 970 meV.¹¹ The advantage of this procedure is that the Kronig-Penney calculation gives the energy positions of the SL minibands with respect to the ZnSe and ZnTe conduction and valence bands. Figure 1 shows the resulting change of the valence and conduction band edge as a function of the Te content (symbols). The solid lines are polynomial fits through the calculated points.

It can be seen that the shift of the valence band edge is more pronounced at low Te contents. Therefore we expect an effect on *p* doping already at moderate Te content.

In order to clarify this point experimentally, we grew a series of doped short period ZnSe/ZnTe SLs (periods between 1.5 and 2.5 nm) with varying average Te content. SLs instead of mixed crystals were chosen since the molecular beam epitaxy (MBE) growth of ZnSe_(1-x)Te_(x) mixed crystals with controlled composition is difficult because of a competition reaction between Se and Te on the surface of the growing film.¹² In one sample, 15% Mg were added to check the influence of Mg on *p* doping. The samples were grown in a vertical MBE reactor equipped with Cd, Zn, Mg, and Te effusion cells, a Se-cracker cell, a ZnCl₂ source for Cl doping, and a dc plasma source for nitrogen doping. The dc plasma source was mounted with a sample-source distance of 5 cm. It was operated at a power of 15 W.

Details of the *p* doping of ZnTe with this source are reported elsewhere.¹³ The achieved hole concentrations in ZnTe depend only weakly on stoichiometry, with the highest values (10²⁰ cm⁻³) obtained for slightly Te stabilized conditions, as determined by the disappearance of half-order

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FIG. 1. Calculated position to the conduction and valence band edge of $\text{ZnSe}_{(1-x)}\text{Te}_x$ as a function of the tellurium content (symbols). The solid lines are polynomial fits to the calculated values. As a reference, the positions of the ZnSe and ZnTe conduction and valence bands are indicated as broken lines. The line labeled E_{SI} represents a reference energy level.

RHEED (reflection high energy electron diffraction) streaks in the (001) azimuth, indicating the transition between a $c(2 \times 2)$ reconstruction typical for metal stabilization to a (2×1) reconstruction typical for an anion stabilized surface. Since such slightly anion stabilized conditions are reported to be also optimal for p doping of ZnSe,³ for the ZnSe part of the SLs the Se flux was adjusted accordingly. The substrate temperature for all samples was 280 °C.

Additionally, we investigated the doping of such SLs with Cl. The ZnCl_2 source was used under conditions optimized to obtain high doping levels in ZnSe (1.5×10^{19} for a source temperature of 140 °C). Each SL had a thickness of 0.5 μm and was grown on a 0.5-m-thick ZnSe buffer on (100) oriented GaAs. The average Te content of the SLs was determined by fitting the x-ray diffraction spectrum of each SL using dynamical diffraction theory. Carrier concentrations and mobilities were measured by Hall effect in Van der Pauw geometry at room temperature.

The measured Hall mobilities for holes are rather low ($\sim 10 \text{ cm}^2/\text{Vs}$). This value gets higher (up to $40 \text{ cm}^2/\text{Vs}$) if the doped zone is separated from the heterointerface by an undoped spacer which reduces the dislocation density.¹⁴ However, in contrast to the mobility, the measured carrier concentrations turned out to be independent of the spacer layer thickness, showing that a large dislocation density leads to low mobilities, but that dislocations are not acting as compensating centers which reduce carrier concentrations.

Figure 2 shows the achieved p - and n -doping levels as a function of the average Te content (symbols). Although a wide stoichiometry range was investigated for pure ZnSe samples, the obtained hole concentrations in ZnSe were below the detection limit of our Hall apparatus ($\sim 10^{16} \text{ cm}^{-3}$). This could be due to two reasons: First, the plasma power possible with our dc source is an order of magnitude lower than the power used for rf plasma doping (15 W compared to 150 W,¹⁵ so that lower doping levels could be expected. Second, the activated nitrogen species in a dc and a rf plasma need not necessarily be the same. This would also explain

the fact that our ZnTe doping levels are an order of magnitude higher than the ones reported for rf plasma doping, although doping is not very sensitive to stoichiometry in either case.^{5,13}

The solid line in Fig. 2 is a fit based on the previously mentioned amphoteric native defect model.⁷ This model predicts that N_A/N_C is proportional to $\exp[2(E_F - E_{SI})/kT]$, where N_A is the concentration of impurity atoms on substitutional sites, N_C the concentration of impurities on compensating sites, E_F the Fermi level, and E_{SI} a reference energy level that is constant with respect to the vacuum level for all materials as long as the compensation mechanism is the same. For strong compensation N_A/N_C is close to one, i.e., E_F will approach E_{SI} . The standard relationship between the hole concentration and the Fermi energy allows us then to calculate the maximum obtainable hole concentration at the growth temperature (550 K) from the relative position of E_{SI} with respect to the valence band edge. We used E_{SI} as a parameter to fit the experimental values. Although the carrier concentrations were determined at 300 instead of 550 K, this is justified, since illumination of the samples had no effect on the measured doping levels, showing that nearly all acceptors are activated at room temperature. The best fit was achieved for $E_{SI} = 0.58 \text{ eV}$ above the ZnSe valence band edge. This value is also plotted in Fig. 1, showing that E_F at 550 K lies high in the forbidden gap for Se-rich alloys, while it lies deep in the valence band for Te-rich alloys. As soon as the position of E_{SI} is deep enough in the band that the resulting carrier concentration approaches the solubility limit of the impurity, E_F will be higher than E_{SI} , with the consequence that N_A/N_C will be large. This means that compensation is negligible and the carrier concentration should be determined only by the solubility. In fact we observe a saturation of the hole concentration at a Te content of 40%, where E_F lies 100 meV below the valence band edge, corresponding to a hole concentration of 10^{20} cm^{-3} . Consequently we interpret this value as the solubility limit of nitrogen in $\text{ZnSe}_{(1-x)}\text{Te}_x$. A number of further conclusions can be drawn from Fig. 2.

FIG. 2. Obtained p - and n -doping levels as a function of the average Te content of ZnSe/ZnTe short period SLs (symbols). The lines represent the results of calculations for p -type (solid) and n -type material (dotted), which depend on the indicated reference energy level E_{SI} .

(i) In the case of nitrogen doping, even low Te contents lead to a significant improvement of the doping behavior. The good correspondence between the data and the fit shows that the position of the valence band edge with respect to a reference energy level is in fact a key parameter for p doping. If a similar description is valid for ZnSe doped with rf plasma, the model would predict a steep rise in hole concentrations for even lower Te contents.

(ii) Te alloying is especially beneficial for contacting: Even at the lowest measured hole concentration of 2×10^{16} (which is near to the detection limit of our Hall apparatus) we obtained good ohmic contacts by evaporating 100 nm Au and soldering with In. This is a significant improvement compared to ZnSe, where ohmic contacts cannot even be obtained for the highest possible doping levels. The implication is that the Te content of ZnSeTe contact layers to ZnSe lasers could be fabricated with a much lower Te content than previously used.⁶

(iii) For chlorine doping, the addition of Te has a strong negative effect on the obtained carrier concentrations, and above a Te concentration of 20% we obtain no measurable electron concentration at all. This is in contrast to the predictions of Chadi (Chadi), who assumes a downward bowing of the conduction band of ZnSeTe mixed crystals, which would result in a higher carrier concentration in the mixed crystal than for ZnSe. The fact that this is not observed is a hint that our calculation of the valence and conduction band variation is more realistic.

The dotted lines in Fig. 2 represent attempts to fit the n -type data with the model used for p -type material for two different values of E_{SI} . As seen from Fig. 1, the energy shift of the conduction band edge in the composition range below 20% is much smaller than the corresponding shift of the valence band edge, with the consequence that the slope of the calculated carrier concentration is much smaller for electrons than for holes, and cannot be fitted to the data. Therefore another mechanism, e.g., the formation of deep complexes involving Cl and Te, must be responsible for the abrupt drop in the carrier concentration. Electron paramagnetic resonance studies are currently on the way to clarify this point.

(iv) There exists no composition range where p - and n -doping levels are both high enough for reasonable device applications. The difference in composition between n -type and p -type material with 10^{18} carriers per cubic centimeter is about 10%, corresponding to a lattice mismatch of about 0.8% between n -type and p -type material. A way out of this dilemma is the use of the quaternary system

$\text{Zn}_{(1-y)}\text{Mg}_{(y)}\text{Se}_{(1-x)}\text{Te}_{(x)}$ as proposed by Chadi.⁹ In this system, compounds with different Te content can be realized at the same lattice constant. In addition, Mg has the beneficial effect to compensate for the decrease of the energy gap introduced by the Te, so that the resulting energy gap of the quaternary is in the blue region of the spectrum. Preliminary attempts to realize p -type $\text{Zn}_{0.85}\text{Mg}_{0.15}\text{Se}_{0.75}\text{Te}_{0.25}$ showed that the hole concentrations are not affected by a Mg concentration of 15%, and the luminescence shifts from yellow to blue-green. Since Chadi predicts good n dopability of this system for low Te contents,⁹ we feel that our doping results are encouraging and make detailed studies of the quaternary system attractive.

In conclusion we showed that the addition of Te to ZnSe has a strong positive effect on the hole concentration, even at low Te content. Probably the most important effect is that ohmic contacts can easily be formed on p -ZnSe $_{(1-x)}$ Te $_{(x)}$. This behavior can be quantitatively understood in terms of the amphoteric native defect model. The opposite holds for n doping: At compositions with good p dopability, the obtained n doping levels are below 10^{16} . As a way to get structures with both good p - and n -doping behavior we propose the use of the quaternary system $\text{Zn}_{(1-y)}\text{Mg}_{(y)}\text{Se}_{(1-x)}\text{Te}_{(x)}$.

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