Band structure engineering and doping of wide gap II–VI superlattices

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It is shown that the free hole concentration for nitrogen doped ZnSe/ZnTe short period superlattices with a given average Te content of 15% can be increased from 10^{16} to 10^{19} cm^{-3} by just increasing the SL period from 2.5 to 4.5 nm. This behavior can be understood in terms of a model that assumes a pinning of the Fermi level at an energetic position that is fixed with respect to the vacuum level. The model can be applied to other II–VI superlattices, and alternative cladding layers for blue laser diodes are proposed that should exhibit significantly higher *p*-doping levels than the currently used ZnMgSSe claddings. © *1995 American Institute of Physics.*

Although the operation of deep blue II–VI laser diodes with a Zn Se quantum well embedded in ZnMgSSe has been demonstrated at low temperatures,[1] state of the art room-temperature devices emit blue-green rather than blue light. This is a consquence of the fact that the *p*-dopability of ZnMgSSe decreases drastically with increasing energy gap, and becomes too low for practical applications for energy gaps above 3 eV.[2] Room-temperature operation requires both good electrical and optical confinement, a condition that can be fulfilled only if the energy gap difference between the cladding layer and the active zone is sufficiently large, i.e., on the order of 500 meV. Consequently, the energy gap of the quantum well cannot be significantly larger than 2.5 eV, corresponding to CdZnSe with a Cd content of about 20%.

Besides the fact that operation at lower wavelengths is desirable, the use of a ZnSe quantum well instead of CdZnSe would have a number of further potential advantages, like narrower luminescence due to the lack of alloy broadening,[3] better resistivity against the multiplication of dislocations during operation,[4] and higher gain.[5] It is therefore of major importance to understand the reason for the decrease of the free hole concentration in ZnMgSSe, in order to find solutions that allow a higher doping of the cladding layer.

Recently, we presented a doping model of wide gap II–VI compounds that is able to describe the dopability of ZnMgSSe and other II–VI compounds quantitatively. The model is based on the assumption that the Fermi level gets pinned at localized centers with energetic positions nearly independent of the host lattice, but fixed with respect to the vacuum level.[6–8] Such centers, associated with vacancies, have been identified in III–V materials, and it was shown that they affect the dopability of these compounds.[9,10] Such a behavior can be qualitatively understood if one considers that the dangling bonds associated with vacancies do not ''know'' which atom is missing at the vacancy[11] (e.g., for a Zn-dangling bond in ZnSSe, a S and Se vacancy are identical). As soon as the Fermi level during growth rises above the energy of such a center, it becomes energetically favorable for the crystal to form the localized center that traps the electron, rather than an electrically active shallow impurity. As a consequence, the Fermi level cannot rise above the energy of the localized center and gets effectively pinned.

The maximum obtainable free electron or hole concentration is then determined by the energetic position of the conduction or valence band edge relative to the constant Fermi level. This dependence is illustrated in Fig. 1, where the highest experimentally obtained carrier concentrations of many II–VI compounds doped with different dopants are plotted as a function of their conduction or valence band edge position. The data are taken from Refs. 2, 6, 7, and 12–14, the position of the bands is determined based on Refs. 15–17. The positions at which the Fermi level is pinned can be determined from these data. The values are 130 meV above the ZnSe conduction band edge for *n*-doping, 120 meV above the ZnSe valence band edge for *p*-doping with rf nitrogen plasma, and 580 meV above the ZnSe valence band edge for *p*-doping with dc nitrogen plasma.[6–8]

It is evident from Fig. 1 that the key factor for the improvement of *p*-doping levels is to raise the position of the valence band edge. One attractive possibility to do that is to use superlattices (SLs) instead of mixed crystals, since in that case the positions of the first conduction and valence minibands, that determine the superlattice energy gap, can be

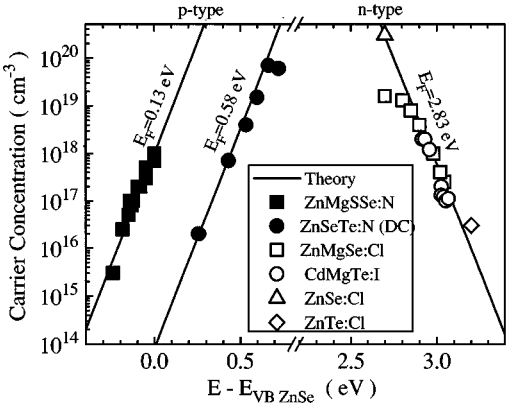

FIG. 1. Experimentally obtained doping levels of various II–VI compounds as a function of the energetic position of their conduction and valence band edges. The arbitrary energy zero point is the ZnSe valence band edge.

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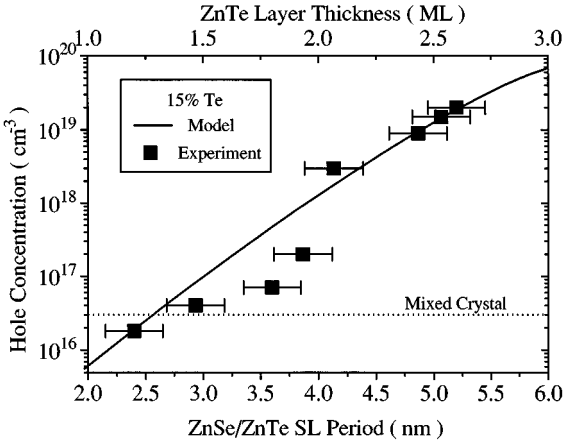

FIG. 2. Free hole concentration of ZnSe/ZnTe SLs with an average Te content of 15% as a function of the SL period. The solid line is the result of a model calculation, the dashed line indicates the doping level obtained for a ZnSeTe mixed crystal with 15% Te.

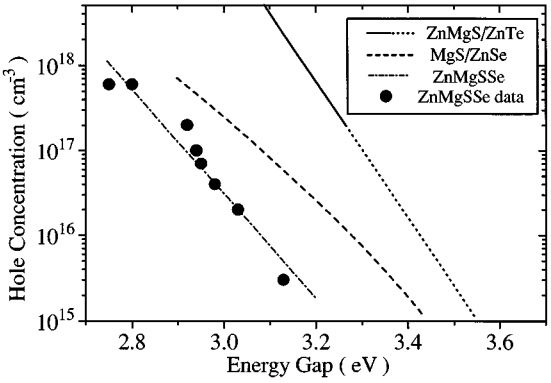

FIG. 3. Calculated free hole concentration for $(MgS)_n/(ZnSe)_n$ and $(Zn_{0.5}Mg_{0.5}S)_{3n}/(ZnTe)_n$ SLs. For comparison, calculated and experimental values for ZnMgSSe mixed crystals are also shown.

shifted up and down by simply changing the SL period. As a model system to test this assumption we used ZnSe/ZnTe SL's, where large effects can be expected due to the large valence band offset. The SLs were doped with a dc nitrogen plasma. The average Te content of all SLs was kept constant at 15%, a value that allows a *p*-doping level of $\sim 3 \times 10^{16}$ cm^{-3} for ZnSeTe mixed crystals doped with dc plasma.[6] Details of the SL growth and doping procedure have been reported elsewhere.[6] Since gold forms Ohmic contacts on these superlattices, the free hole concentrations could easily be determined by Hall measurements in Van der Pauw geometry.

In Fig. 2 the obtained free hole concentrations are plotted versus the SL period. An increase of the period from 2.4 to 5 nm leads to a dramatic increase of the hole concentration from 2×10^{16} to 3×10^{19} cm^{-3}. The solid line is the calculated carrier concentration according to our model for miniband positions that are determined from a Kronig–Penney calculation of ideally abrupt superlattices with heavy hole masses of 0.78 for ZnSe and 0.6 for ZnTe. This simple model in fact reproduces the large increase in carrier concentration, although good coincidence with the data is obtained only for large periods. This is not too surprising if one considers that at an average Te content of 15% the thickness of an individual ZnTe layer is extremely small for all SLs under consideration. To illustrate this, the ZnTe layer thickness in monolayers (MLs) is given on the upper *x*-axis of Fig. 2. It is clear that for ZnTe layer thicknesses below two monolayers the assumption of ideally abrupt quantum wells is not realistic.

This is also evident from an x-ray analysis that we performed for a 3 ML/3 ML SL grown under identical conditions. For such a symmetrical SL the relative intensity of the SL satellite peaks is strongly influenced by interdiffusion. For this SL, a $+1$ and a -1 order satellite peak could be detected in a diffraction scan around a symmetric (004) reflex, but their intensity relative to the zero-order peak is significantly lower than expected for an ideal SL. We modeled the diffraction of this SL using the dynamic scattering theory and an interdiffusion profile that assumes an exponential decrease of the Te concentration in ZnSe and vice versa. The Te and Se composition of the interface is assumed to be 0.5. Taking into account the strain of the layers, excellent agreement between data and calculation is achieved for an interdiffusion length (the value at which the Te concentration in ZnSe reaches $0.5/e$) of 0.35 nm or approximately 1 ML.

This illustrates that indeed only ZnTe quantum wells of more than two MLs can be reasonably treated as ideal. SLs with a lower ZnTe layer thickness are heavily interdiffused, with the consequence that their doping behavior becomes more mixed-crystallike and the dopability approaches the mixed crystal value given as a dotted line in Fig. 2.

Taking these facts into account, the Fermi level pinning model is able to give a good description of the dopability of the ZnSe/ZnTe SLs. Since the same model is able to describe the dopability of many II–VI mixed crystals, it is reasonable to assume that it can also be used to predict the behavior of other II–VI SLs. Of highest technological interest are SLs with an average in-plane lattice constant matched to GaAs, since they could be implemented pseudomorphically into existing laser structures. Therefore, we calculated the miniband structure and the corresponding doping levels for two examples of such SLs, namely $(MgS)_n/(ZnSe)_n$ and $(Zn_{0.5}Mg_{0.5}S)_{3n}/ZnTe_n$, two combinations that are reasonably well lattice matched to GaAs. The former has the advantage that it uses the same components as the quaternary ZnMgSSe, the latter contains ZnTe with its very high valence band edge, which in turn leads to a high heavy hole SL miniband. Since no data exist for the effective masses in MgS and $Zn_{0.5}Mg_{0.5}S$, the ZNS heavy hole mass value of 1.2 has been used for these two components in the Kronig–Penney calculation. A larger value would lead to doping concentrations slightly lower than the values given here. In contrast to the dc nitrogen plasma doped ZnSe/ZnTe SLs treated above, these calculations were performed for the technologically more important case of doping with radio frequency nitrogen plasma.

The results of the calculation are plotted in Fig. 3, together with the calculation and the data[2] for ZnMgSSe mixed crystals. The dotted part of the curve for $(Zn_{0.5}Mg_{0.5}S)_{3n}/(ZnTe)_n$ represents the region where the

ZnTe thickness is lower than 2 ML, and the calculation is expected to be inaccurate due to interdiffusion.

For MgS/ZnSe an increase of the hole concentration by a factor of five compared to ZnMgSSe is expected. For cladding layers with an energy gap of 2.95 eV as they are currently used in blue-green lasers, this would represent an increase of the hole concentration to 5×10^{17} cm^{-3} which could help improve device performance.

The predicted behavior of the $Zn_{0.5}Mg_{0.5}S$/ZnTe SLs is still more promising. Even combinations with an energy gap up to 3.2 eV are predicted to exhibit hole concentrations above 10^{17} cm^{-3}. For such a cladding material, the use of a ZnSe quantum well with all the benefits outlined above would no longer be unrealistic. Since the cladding is separated from the active zone by a relatively thick guiding layer, we expect that the use of Te in this cladding would not influence the luminescence properties. Nevertheless, it must be considered that the improvement in vertical transport, which is decisive for a laser device, will be somewhat smaller than the predicted increase in dopability, since the carriers will have to tunnel through the barriers introduced by the superlattice structure. In addition to that, the conduction band edge of such a cladding layer would already be so high that the *n*-dopability is expected to be very poor. As a consequency, for a deep-blue room-temperature laser we propose to use an asymmetric device design with a ZnMgSSe cladding on the *n*-side and a $ZN_{0.5}Mg_{0.5}S$/ZnTe cladding on the *p*-side.

In conclusion, we showed that the free hole concentration in ZnSe/ZnTe superlattices doped with dc nitrogen plasma can be drastically increased by slightly increasing the superlattice period. This behavior can be understood in terms of a model that assumes a pinning of the Fermi level at an energetic position that is constant with respect to the vacuum level. The model can be applied to other II–VI superlattices that are lattice matched to GaAs. Based on these calculations we propose the use of MgS/ZnSe or $Zn_{0.5}Mg_{0.5}S$/ZnTe superlattices as new cladding layers for blue laser diodes.

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