



Wide band-gap II–VI compounds—can efficient doping be achieved?

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Direct band-gap II–VI semiconductors have a potential for a variety of light-emitting devices spanning the entire range of the visible spectrum, should the persevering difficulties in achieving efficient doping be solved. In this paper a number of possible doping-limiting mechanisms and various approaches to avoid or overcome them are summarized and analyzed, including author's personal contributions to these efforts. The main mechanisms limiting efficient doping in equilibrium conditions have been identified as: compensation by native defects and/or pairs, lattice relaxation around doping atom resulting in formation of compensating deep localized levels, amphoteric behavior of some prospective dopants, and insufficient solubility of the others. The greatly extended theoretical and practical work in understanding relevant mechanisms during the last several years confirmed the seriousness of the doping problems, but at the same time showed the way toward their solution(s). New approaches include: low temperature crystal growth (particularly with MBE and other low-temperature growth/doping techniques), doping by ion implantation, co-doping with more than one dopants, etc. The most promising way to solve the doping problems in II–VI compounds are non-equilibrium processes, where excellent results have been obtained, opening the ways for much wider applications of these materials in the near future. © 1998 Elsevier Science Ltd. All rights reserved

1. Introduction

The II–VI semiconductors, possessing direct band-gaps from infrared to ultraviolet, could be the basis for a variety of efficient light-emitting devices spanning the entire range of the visible spectrum. The recent successes in obtaining first blue-green lasers^{1,2} have intensified interest in wide band-gap materials and have greatly stimulated new experimental and theoretical investigations. However, persevering difficulties in achieving efficient doping of wide band-gap II–VI compounds both *p*- and/or *n*-type still remain the main obstacle in applications, and also a continuous unsolved puzzle about this whole class of materials. Only CdTe can be easily doped to a reasonably high concentrations of both types, while ZnSe, CdSe and CdS can be easily doped only on *n*-side, and ZnTe (and some newly synthesized IIa–VI compounds) only on *p*-side.

In this paper a number of possible doping-limiting mechanisms in II–VIs are critically reviewed and analyzed, particularly: self-compensation by native point defects or native defect-dopant pairs, chemical solubility limit of dopants, lack of appropriate shallow acceptors/donors, deactivation of dopants due to lattice relaxation and limit imposed by formation of second phase (new compound). Furthermore, various approaches aimed to surpass these limits and to obtain high doping concentrations are analyzed. Among equilibrium approaches the co-doping on both II and IV site, co-doping with donors and acceptors (unwanted dopant being much more mobile) and “indirect doping” method

were analyzed. The conclusion is that non-equilibrium processes like ion implantation and particularly low-temperature crystal growth (MBE, VPE), offer the best practical hope to transcend doping limits and to obtain material suitable for various application.

2. Mechanisms limiting efficient doping in II–VI compounds

2.1. Spontaneous formation of native point defects. Although there is ample and long standing evidence of compensation of dopants by spontaneous formation of some native defects having opposite charge to the doping atoms, there has been no consensus yet on how important this mechanism really is. Furthermore, the complete theoretical calculation which would give quantitative valuation of this effect is still lacking. A wide band-gap, generally, gives a strong incentive for the introduction of compensating defects since formation of compensating defects would lower the total energy of the crystal by an amount close to the band-gap energy for a singly ionized species, or twice as much for a double ionized one. If the energy gained by compensation is higher than the energy which is needed to create a compensating defect, the process of spontaneous formation of native compensating defects will proceed in parallel with the dopant incorporation, and any concentration of added dopants will be compensated by an equal concentration of oppositely charged native defects. The first thermodynamic calculations and principles of this mechanism were

given by Mandel,³ and that mechanism was the most widely accepted and intensively studied for decades.³⁻⁷

2.1.1. The role of native vacancies and interstitials. The importance of vacancies is illustrated in Fig. 1, where the relative sizes of atoms (and hence the relative sizes of respective vacancies) for II-VI compounds are shown, together with experimentally observed tendency towards *n*- or *p*-type conductivity. Although relative size is only just one of the factors, it is indicative that in each case larger metal atom (vacancy) corresponds to an inclination towards *n*-doping and spells difficulties for *p*-type doping, while compounds having larger halcogenide atoms (vacancies) show just the opposite tendency. Only CdTe which has almost equally sized atoms can be doped both types.

Mandel³ calculated the effect of spontaneous self-compensation by comparing band-gaps and defect formation energies, evaluated from the available cohesive energies of several compounds. His calculation predicted even for optimally selected experimental parameters, the complete spontaneous compensation of dopants with oppositely charged native vacancies for KCl (as a representative of I-VII compounds), a considerable compensation of *n*-ZnTe, lower compensation for *n*-CdTe and practically no compensation for *n*-GaAs. Our contribution was the first (and up to now the only) calculation of the minimal degree of self-compensation by ionized native vacancies for practically all III-V and II-VI compounds (22 cases).⁸ The vacancy formation energies and enthalpies were calculated using Phillips-Van Vechten's two-band theory,^{9,10} and the chemical potentials were calculated from the dissociation pressures of the compounds

and partial pressures of the constituents. There thermodynamical calculations showed a considerable tendency towards self-compensation of acceptors in most II-VI compounds, (CdS, CdSe, ZnSe, CdSe) and GaN, and donors in ZnTe, and no compensation in other cases (Fig. 2). Results of vacancy self-compensation calculations, although obtained with an approximate theory of vacancy formation, exactly follow the trends observed experimentally for all these compounds but in most cases the calculated vacancy self-compensation is insufficient to explain the extent of observed doping problems.

Even much stronger compensation by native vacancies was predicted¹¹⁻¹³ when parameters deduced from high temperature Hall-effect data were used in similar thermodynamical calculations.

Quite different conclusions were obtained with total energy (*ab initio*) calculations. These calculations for stoichiometric ZnSe predict that the concentrations of all relevant point defects in all achievable charge states are not high enough to be responsible for doping problems.¹⁴ It was argued that this conclusion is valid also for other wide band-gap semiconductors,¹⁵ in spite of the fact that large native defect concentrations are predicted for off-stoichiometry crystals.¹⁵

Experimental results can help to resolve at least some of the dilemmas. It seems that interstitials (which in thermodynamical calculations are equivalent to vacancies, and in *ab initio* calculations¹⁵ are a favored compensating species) can be excluded, at least for *p*-ZnSe: even in heavily doped ZnSe, with [N] above 10²⁰/cm³, native interstitials are not present, as shown by ion beam scattering.¹⁶ However, there is ample experimental evidence

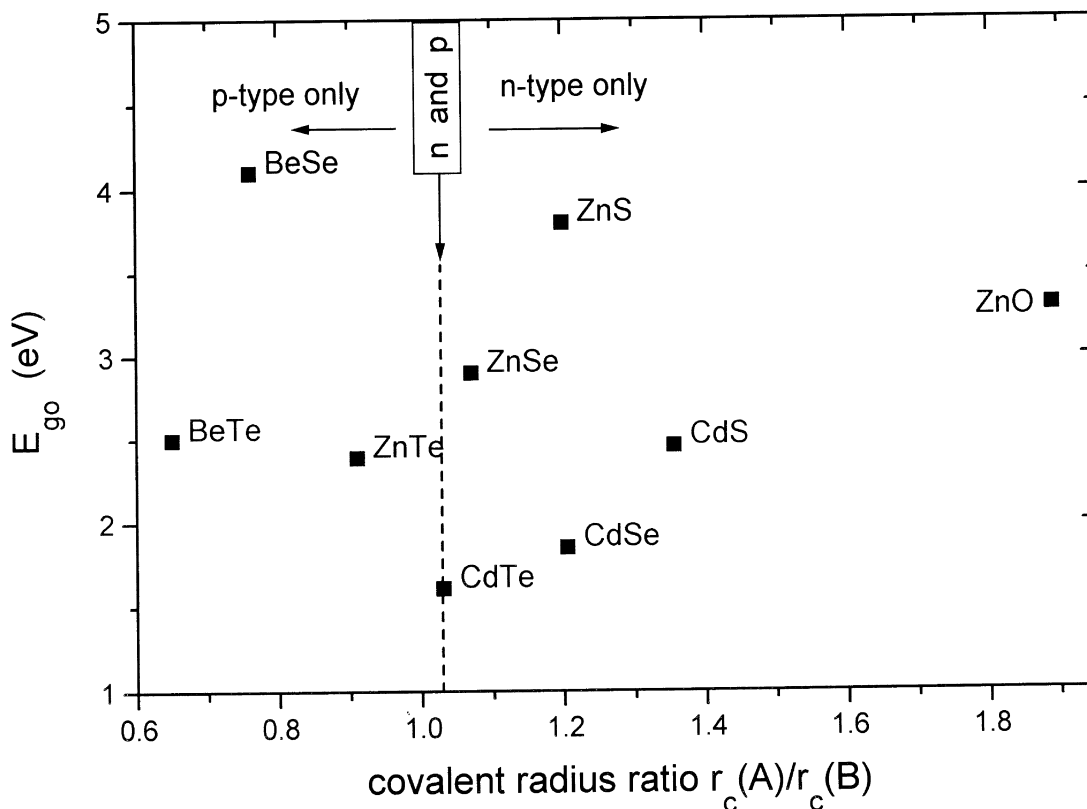


Figure 1. Experimentally observed trends toward *n*- or *p*-type conductivity for II-VI compounds. The role of relative size of atoms (and respective vacancies) in each compound, as well as of the energy band-gaps (E_{go}) are discussed in the text.

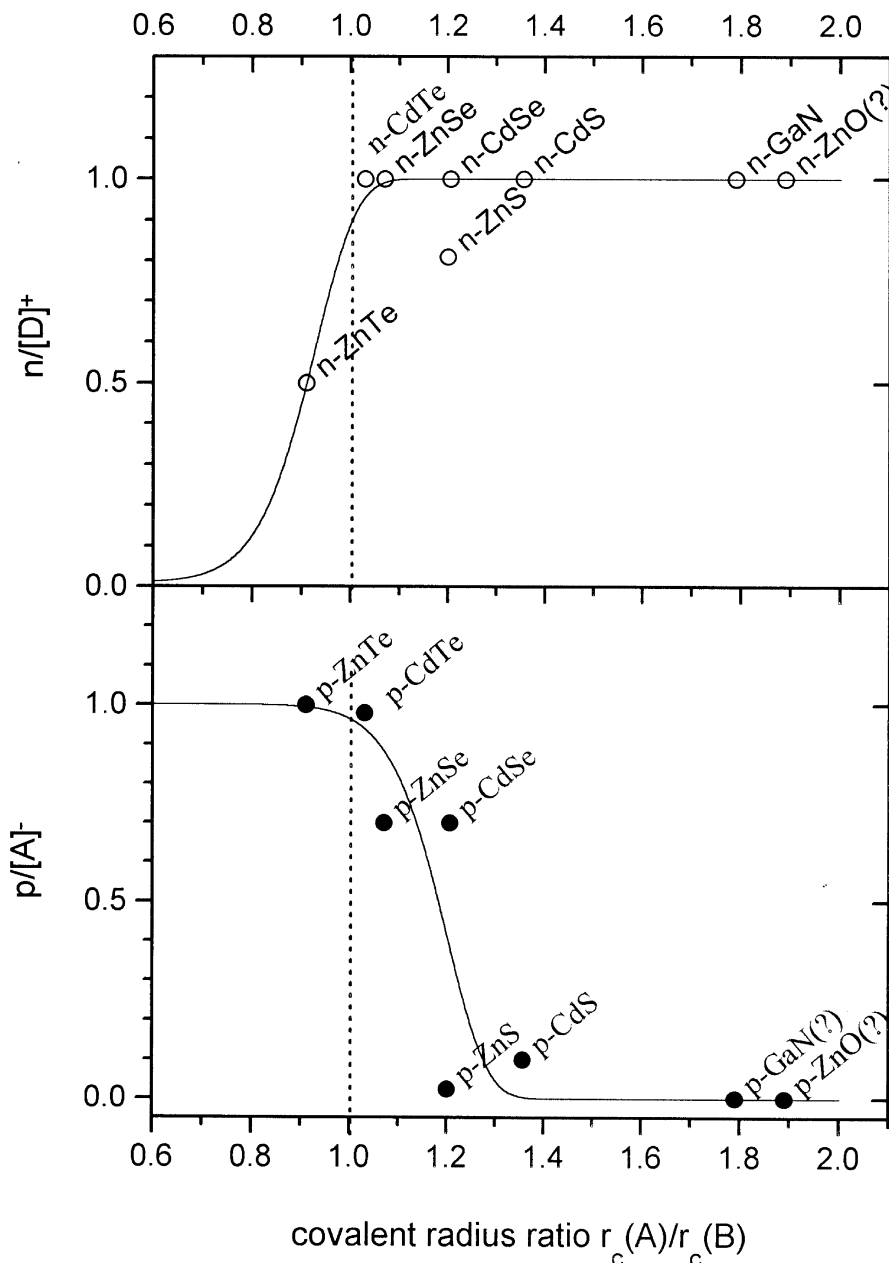


Figure 2. Maximal efficiency of doping with donors, $n/[D]^+$, and acceptors, $p/[A]^-$, limited by self-compensation with native vacancy, calculated for conditions of thermodynamical equilibrium. Results are presented in dependence of relative atom (vacancy) size of each compound. (?) denotes that some input data were incomplete, and hence were estimated.

that large concentrations of vacancies exist in highly doped material. This has been concluded either from direct observation of vacancies via positron annihilation (PA) studies,^{17,18} or indirectly, from the interpretation of results from a number of other experimental methods.¹⁹

Although the question of the importance of vacancies is far from being settled yet, the emphasis of compensation studies is now somewhat shifted from isolated vacancies toward defect pairs which include vacancies, and other more complex defects.

2.1.2. Complexes including native point defects. Many experimental results indicate that high concentrations of compensating

complexes which include vacancies do exist in highly doped II-VI compounds. For example, in N doped ZnSe some new deep donors, probably responsible for the electrical compensation of acceptors N_{Se} , emerge for higher doping, especially when $[N]$ exceeds $10^{18}/\text{cm}^3$. New donor-acceptor (DAP) line appears in Photoluminescence (PL) spectra, 44-45 meV below the conduction band; LO phonon line in Raman spectra shifts with the increase of $[N]$ indicating the presence of native defects, and lattice parameter of ZnSe changes with $[N]$ faster than would be expected from the contribution from shorter Zn-N bonds alone.¹⁹ Furthermore, optically detected magnetic resonance (ODMR)¹³ and spin-flip Raman scattering detected deep donor

(with $g = 1.38$) in the similarly N doped ZnSe crystals.¹⁹ All these observations are consistent with the existence of a compensating complex defect involving V_{Se} . Recent total energy calculations²⁰ give strong support to this model. The difference to previous similar *ab initio* calculations^{14,15} is that the strong lattice relaxation of V_{Se} , which occurs when V_{Se} becomes doubly positively charged, is taken into account. Lattice relaxation effectively reduces the formation energy of the native vacancy, allowing its formation in large concentrations. When the V_{Se}^{2+} pairs with a singly ionized dopant acceptor (i.e. N^-), the charged vacancy not only neutralizes this acceptor but this pair ($V_{Se}^{2+} - N^-$)⁺ (now singly ionized) remains a donor, which compensates another single acceptor. This leads to a prediction of complete compensation and saturation of free carrier concentration at $[N] > 10^{18} - 10^{19}/\text{cm}^3$.²⁰ Very recent thermodynamic calculation,²¹ which also assumed the same pair as a dominant charged defect in the neutrality equation came to the same conclusion. It seems that this mechanism, based on the pairing of dopant and oppositely double-charged native vacancy might be responsible for compensation in a number of cases,²¹ including N doping of ZnTe (where saturation at higher level, close to $10^{19}/\text{cm}^3$, has been observed, probably due to the lower incorporation energy of N into ZnTe (0.27 eV) than in ZnSe (0.38 eV).²² Arguments are given that dopant-vacancy pair formation limits the doping also in acceptor-doped CdTe and donor-doped ZnSe, CdTe, CdS and CdSe,²¹ although there is a new evidence that (at least) in CdS this mechanism can be avoided.²³ Especially strong and convincing experimental proof was given for In-doped CdTe, where the $(In_{Cd} - V_{Cd})$ acceptor pairs formation compensates the remaining In_{Cd} donors²⁴⁻²⁶ even for processing under Cd pressure (which was proven to be optimal). The free carrier concentration, n , remained saturated at $\sim (1-2) \times 10^{18}/\text{cm}^3$ despite the fact that $[In]$ exceeded $10^{19}/\text{cm}^3$. Generally, it seems that this mechanism limits p -type doping for less electronegative group V acceptors already at low concentrations. Furthermore, it probably also limits n -side doping in many II-VI compounds (ZnSe, CdSe and CdTe) but only at pretty high dopant concentrations. We have found that in In doped CdS^{23,27,28} the concentration of thermally created V_{Cd} is proportional to $[In]$ up to $[In] \sim 10^{20}/\text{cm}^3$, but in this compound these vacancies can be completely avoided (or even subsequently annihilated) by choosing annealing conditions for which the chemical potential of Cd is very high.

2.2. Bond breaking due to large lattice relaxation. Incorporation of most dopants into lattice induces some relaxation of surrounding atoms, which can reduce the total energy of the crystal. As a result of such relaxation a bond in the vicinity of the foreign atom can break, leading to the formation of a charged, compensating defect center.²⁹⁻³⁶ In many cases it seems that such a defect center has a lower formation energy than a compensating native point defect, therefore becoming a dominant mechanism for doping neutralization. This mechanism can be effective for both donors and acceptors, and is analogous to the DX center observed in a GaAs and Ga-Al-As system.³⁷ The idea was proposed to explain why As and P dopants in ZnSe do not behave as substitutional shallow acceptors, as expected. Total energy calculation^{30,31} showed that these dopants possess two distinct stable configurations in ZnSe, a “normal” substitutional position in which the As (or P) atom captures an electron and has 4 equidistant bonds, and a “relaxed” configuration (AX center), where As (or P) atom has three shortened bonds with three neighboring Zn atoms, and a broken bond with the fourth Zn, as

a result of the considerably increased distance in its direction. It was shown that the relaxed configuration, which produces deep levels (hole traps) instead of a shallow acceptor level, is energetically more favorable preventing efficient p -type doping. The same type of calculations showed that small and more electronegative dopants like N and Li (and also isoelectronic O) do not produce large relaxation, which in the same time explained relative successes in obtaining p -type doping with these dopants and also stimulated their further study. The doping efficiency of number of donors might be limited (although usually only at quite high doping level) by the same mechanism. The possibility of large impurity displacement in the lattice leading to a deep state and a donor de-activation was first suggested for Cl in CdTe.²⁹ More recent calculations³⁴ predicted lattice relaxation and formation of DX centers with deep levels for In, Ga, Al and Cl in CdTe, when these dopants are introduced in large concentrations into CdTe to form ternary alloys.³⁴ (The shallow-deep transition can also be achieved even if isoelectronic Zn, Mn, and Mg are added in high enough concentrations).^{25,34} The predicted doping limits for CdTe were $1.8 \times 10^{18}/\text{cm}^3$ for In and $6 \times 10^{18}/\text{cm}^3$ for Cl, in good agreement with experimental data.²⁵ The formation of DX center is also expected for B in ZnSe³⁶ but not for In and Tl.³⁶ For Ga and Al in ZnSe the DX center has a higher energy than a shallow donor configuration^{32,36} but it is observable at lower temperatures as a metastable defect.³⁸ The strong tendency toward relaxation and formation of DX center was also found for donors in ZnTe (and MgTe)^{32,36} which was used to explain the inability for n -type doping in these compounds. The possibility of lattice reconstruction is also supported by findings from some other methods (existence of persistent current, some PL and far IR signals etc.). More recent calculations also suggest that relaxation around dopant atom, which produces deep compensating levels might be even more complex and result in breaking of two host bonds (DBB) and the creation of VI-VI dimer bond.³⁵

2.3. Amphoteric incorporation of dopants. Some dopants/impurities tend to incorporate at different places in the crystal, which may result in mutual electrical compensation. The best documented case is Lithium in ZnSe.^{1,15,39-42} Li was the first dopant to yield reproducible p -doping of ZnSe.^{1,41} Being an atom from the I row, Li was considered to be an excellent candidate for p -type doping in ZnSe: energy of formation (incorporation) of Li_{Zn} relatively low (0.4 eV³⁹, 0.51 eV⁴³) and in substitutional configuration it produces negligible distortion⁴³ and relaxation.^{15,30,42} However, a fraction of Li atoms goes into tetrahedral interstitial sites, Li_i , where they act as donors.^{39,44} This might be one of the reasons why the maximal hole concentration ever achieved with Li:ZnSe was relatively low ($p \approx 10^{17}/\text{cm}^3$). The same problem was encountered with Na in ZnSe,^{15,39} Li in CdTe⁴⁵ etc. The amphoteric behavior is expected also for column IV dopants (which can be important since Si is a constituent of quartz vessels and can be an unwanted compensating impurity acquired during thermal processing) for transition metals (Cu, Ag, Fe) which is particularly inconvenient since these species are fast diffusers and contaminants that are especially hard to avoid. Although antisite defects are in II-VIs energetically less favorable than in III-Vs, in some specific cases this type of amphoteric incorporation was reported to play a role (P_{Zn}^{3+} compensating P_{Se}^- in ZnSe,³³ Se_{Zn}^{2+} compensating acceptors¹⁵). Interstitial N was also proposed⁴⁶ as a species which limits p -doping activity of N_{Se} in N:ZnSe, but this is probably not the right compensation

mechanism for N, since ion scattering in ZnSe proved no presence of N interstitials even in samples doped with [N] above $10^{20}/\text{cm}^3$.¹⁶

2.4. Chemical solubility and some specific mechanisms. All the doping limiting mechanisms previously proposed tacitly assumed that (a) the solubility of the dopants is not the problem; and (b) that these donors/acceptors are shallow enough that they are readily ionized at room temperature. There are, however, serious arguments that these requirements might not always be easy to meet. Namely, wide band-gap materials also pose a fundamental problem in achieving a high equilibrium solubility, due to the high energy of incorporation for most dopants. Some early thermodynamical estimates predicted the true equilibrium dopant solubility to be as low as 10^{16} – $10^{18}/\text{cm}^3$ in II-VI materials.⁴⁷ The problems were analyzed in a number of experimental and theoretical papers.^{15,21,39,47–49} Finally theoretical minimum total energy calculation was performed for Li, Na and N in ZnSe^{15,42} and ZnTe.⁵⁰ Calculations yielded solubility limits for ZnSe grown/doped at 250°C, to be $4 \times 10^{15}/\text{cm}^3$, $6 \times 10^{18}/\text{cm}^3$ and $2 \times 10^{19}/\text{cm}^3$ for Na, Li and N, respectively, and much higher solubilities (for Li 10– 10^3 times higher) in ZnTe. Successes of these calculation were predictions that the solubility of these acceptors is considerably higher in ZnTe than in ZnSe, and that N has a higher solubility than Li and much larger than Na, which are all consistent with available experimental data. These results explained why ZnTe is much easier *p*-dopable than ZnSe, clarified the lack of success of Na doping of ZnSe⁵¹ and gave an alternative explanation of doping limit of Li as acceptor dopant. The solubility of Li, Na and N in ZnSe was calculated to be limited by the formation of a new phase, Li₂Se, Na₂Se and N₃Se₄, respectively.¹⁵ Theory has not yet been applied to other dopants and other compounds to see whether and where solubility problems have to be expected. We have found recently²³ that the solubility in In implanted CdS was limited by the formation of a second phase, CdIn₂S₄, which appears at very high In concentrations (above $10^{19}/\text{cm}^3$).

For some dopants an additional problem is that they form relatively deep levels in the band-gap⁵² with the consequence of an incomplete ionization at RT.

An interesting approach is that of a phenomenological model, developed first for III-V compounds⁵³ and only recently applied to II-VI compounds as well.^{49,54} This model uses the energetic position of the compound band edges with respect to an absolute reference level (vacuum), and determines a Fermi stabilization level at which the creation of a new defect does not cause further change of the free energy of the crystal. Although this treatment does not bring nor specifies any information about the nature of the compensating defect(s), it can predict viability of *n*- and *p*-type dopability and can offer valuable suggestions how to avoid/alleviate doping problems. When fully developed this approach seems very promising for that important practical purpose.

The magnitude of the problem in discerning the relative and absolute importance of a particular doping limiting mechanism is best illustrated with the (most studied) example of N dopant in ZnSe.^{55,56} The various suggested mechanisms included: solubility limit of N; compensation by native V_{Se}; compensation by V_{Se}-N_{Se} pair; by N_i; by V_{Se}-N_i pair; by V_{Zn}-N_{Se} antisite; by formation of N₂ molecule either in interstitial or in Se place; and relaxation-related bond breaking. Needless to say, all authors gave good arguments for their assignments. Quite generally, it seems that

the difficulties arise primarily due to a very similar energy of the formation of most of the mentioned defects or complexes.

3. Some specific approaches for higher and more efficient doping

This survey of mechanisms limiting efficient doping leads us to two conclusions: first, there are serious problems for most of dopants in various II-VI semiconductors in obtaining high dopability, that severely reduces the choice of convenient dopant/semiconductor combinations—at least in equilibrium conditions. Secondly, the enormous amount of theoretical and experimental work, done especially in the last several years, brought us to a much better understanding of the problems and opens avenue to their solution.

All of the above approaches assume that the semiconductor is in equilibrium with the external (vapor) phase. Hence most of the efforts to circumvent doping limits are aimed toward procedures which include either non-equilibrium doping or processing.

3.1. Low-temperature methods of crystal growth. The best results in obtaining good *n*- and *p*-type dopability were obtained up to now with molecular beam epitaxy (MBE).⁵⁷ This method, extensively used in manufacturing of III-V epitaxial devices (including 3–5 million lasers/month for compact discs), proved also very useful for low-T growth of II-VI compounds. The first II-VI blue laser was produced with MBE.¹ Although even in MBE growth the surface mobilities of all species should be in principle sufficient to enable the surface of growing semiconductor to relax toward its equilibrium state, in practice the lower the growth temperature the better is a likelihood to avoid thermodynamical restraints and to surpass the limitations they pose. The other possible advantage of low temperature growth is the benefit of lower concentration of compensating defects. For *p*-type ZnSe, the best doping is obtained up to now with N dopant ($p = 1.2 \times 10^{18}/\text{cm}^3$) with a reasonably low compensation, i.e. high doping efficiency, $p/[N] = 0.6$, with ZnSe layer being grown at only 220°C.⁵⁵ N was incorporated in concentrations even above $10^{20}/\text{cm}^3$,^{3,16} but then with substantially lower doping efficiency (*p* again in $10^{18}/\text{cm}^3$ range). Li yielded *p* doping up to $2 \times 10^{17}/\text{cm}^3$,^{3,44} while other *p*-dopants yielded substantially lower *p*. MBE also produced the highest doping of ZnSe on *n*-side, with Cl as a dopant: above $10^{19}/\text{cm}^3$, and even above $10^{20}/\text{cm}^3$ with selective doping.⁵⁸ ZnTe was doped with MBE up to $10^{20}/\text{cm}^3$ on *p*-side,⁵⁹ again with N. In CdTe, In doping resulted in a maximum electron concentration of $2 \times 10^{18}/\text{cm}^3$,²⁶ and Iodine doping of $5 \times 10^{18}/\text{cm}^3$,¹⁸ while doping on *p*-side resulted up to now in $p = 2 \times 10^{17}/\text{cm}^3$ for N doping and an order of magnitude lower for As doping.⁶⁰ Much less work is done on other binary II-VI compounds. Taking also into account the convenience of MBE for growing ternary and quaternary II-VI compounds,^{48,49,61} heterojunctions and multilayers which can be optimized to have close matching of lattice constant, MBE seems to be the most prospective method for the production of commercial blue/green II-VI lasers once the doping limitations and other problems (like thermal stability at least around RT, good contacts, etc.) are finally fully understood and put under full control. A blue laser diode was also obtained recently with a somewhat less expensive growth method like metalorganic chemical vapor deposition (MOCVD), with growth in the 330–480°C range, again by N doping of ZnSe, but the maximum obtained *p* was only $1.4 \times 10^{16}/\text{cm}^3$.² Metalorganic vapor phase epitaxy (MOVPE) also

succeeded in obtaining p close to $10^{18}/\text{cm}^3$ in N doped ZnSe layers grown at 430–570°C.^{62,63}

3.2. Ion implantation. Ion implantation allows dopant introduction at as low a temperature as desired. First type conversions were obtained with implantation: n - to p -conversion of ZnSe with Li, N or P implants, n - to p -CdS with P and Bi, p - to n -ZnTe with F and Cl, and conversion to both types in CdTe.⁶⁴ However, this method has two serious drawbacks: first, thermal processing up to some moderate temperature is still needed (at least 400°C but usually higher) in order to anneal implantation-induced damage, and secondly, implantation creates a lot of lattice defects which can react with implanted atoms or between themselves forming relatively stable compensating defects. Recent study on Zn implanted ZnSe showed that some point defects are mobile already at RT and that they migrate rapidly under ion implantation.⁶⁵ Cl doped ZnSe showed high level of compensation of Cl_{Se} donors, presumably with $\text{Cl}_{\text{Se}}-\text{V}_{\text{Zn}}$ pairs, which are acceptors, as concluded from results of RBS, PIXE, Raman and electrical measurements. Hence a better understanding of implantation induced disorder is needed in order to fully unleash the potentials of this method. A positive example is a very high concentrations of holes, up to $p = 5 \times 10^{19}/\text{cm}^3$ (the maximum value achieved up to now by any method), obtained in CdTe by implantation of P and pulsed electron beam annealing.⁶⁶ In a recent study of In

implanted CdS^{23,27,28} we have obtained $\sim 100\%$ implanted In atoms in substitutional Cd place, In_{Cd} , for a very wide In dose range ($10^{16}/\text{cm}^3$ – $10^{19}/\text{cm}^3$) after appropriate annealing under Cd pressure. On the contrary, annealing under S pressure resulted in completely compensated material and the compensating acceptor was identified as $\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}}$ pair,²⁷ (Fig. 3). Analogous pairs were observed with PAC in other In doped II–VI compounds.⁶⁷ Annealing of n -CdS under S pressure showed that the dynamics of the electrical compensation follows the increase of the fraction of $(\text{In}-\text{V}_{\text{Cd}})$ compensating acceptors at the expense of the fraction of In_{Cd} donors in undisturbed surroundings,^{23,28} (Fig. 4). These results proved that, contrary to CdTe²⁶ and most other II–VI compounds, In can be incorporated in CdS up to very high concentrations into undisturbed In_{Cd} place by implantation and proper annealing procedure, without formation of compensating pairs predicted for thermodynamical equilibrium conditions.²¹ The doping limit of In implanted in CdS is the formation of the CdIn_2S_4 compound, as assumed from the analysis of PL spectra⁶⁸ and recently proven with PAC measurements.²³

3.3. Effect of co-doping. Effects of co-doping with more than one species in order to obtain higher free carrier concentration were not yet systematically investigated but there are a number of indications that co-doping could result in higher doping concentrations. Even simple co-doping with two different acceptors

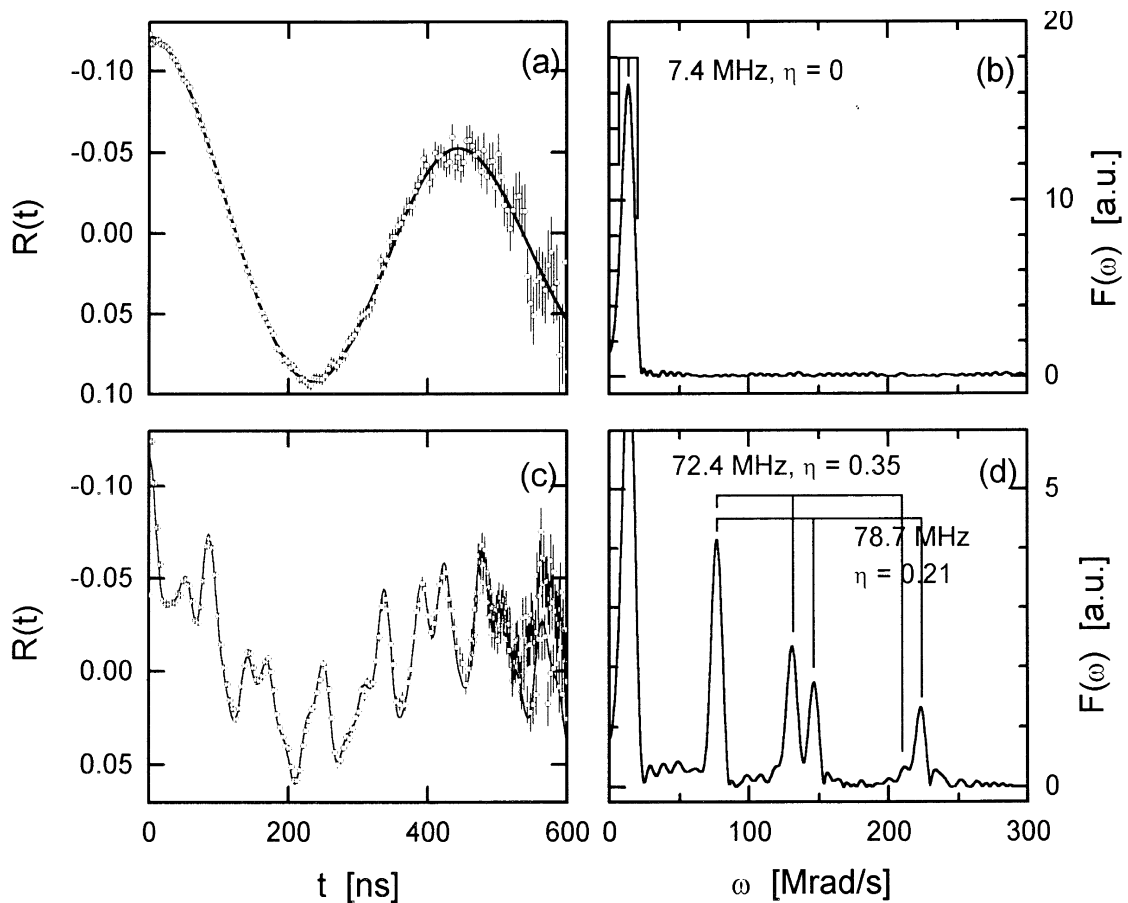


Figure 3. PAC time spectra $R(t)$ (left) and their Fourier transformations (right). Spectrum (a), obtained after annealing of In implanted CdS under Cd pressure, describes situation in which all probe ^{111}In atoms are placed in substitutional Cd places, In_{Cd} , in undisturbed surroundings. Spectrum (b), obtained after annealing of implanted CdS under S pressure, shows the existence of comparable fractions of In_{Cd} and $\text{In}_{\text{Cd}}-\text{V}_{\text{Cd}}$ pairs.

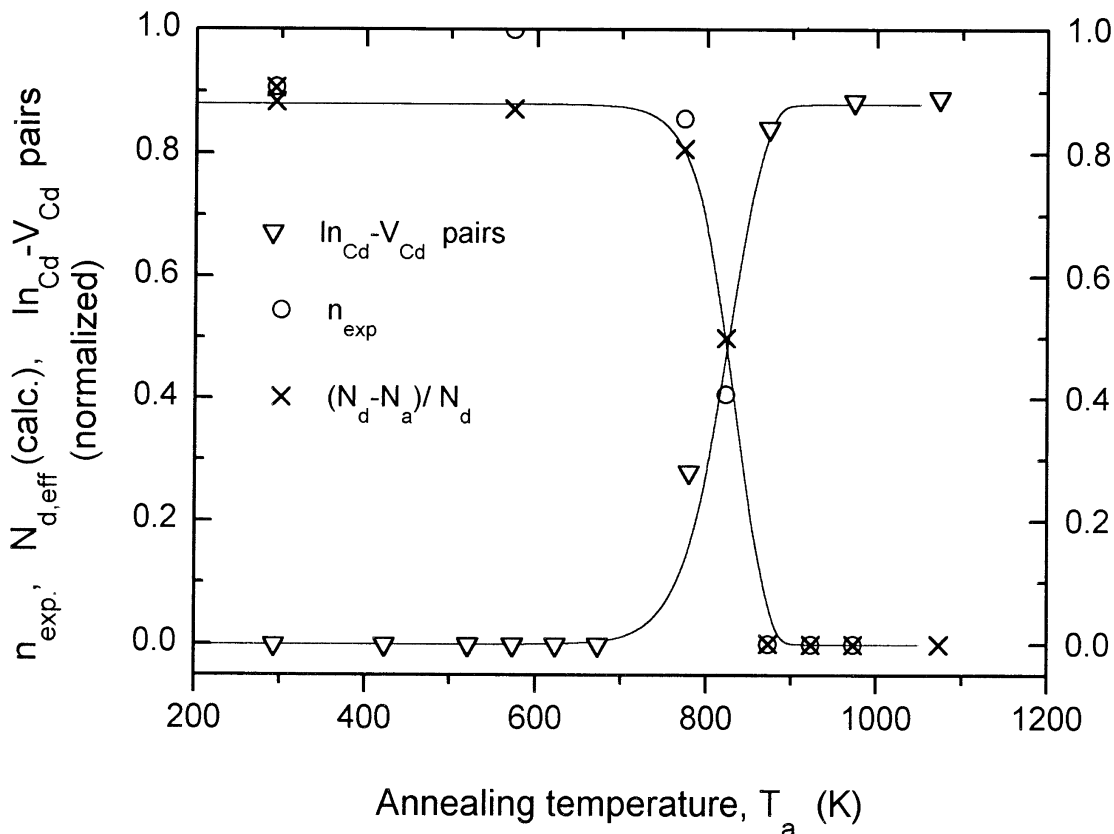


Figure 4. Dynamics of the decrease of free electron concentration (and calculated uncompensated donor concentration) as well as the increase of In_{Cd}-V_{Cd} pairs, as a function of annealing temperature for *n*-CdS annealed under *S* pressure.

(Li_{Zn} and N_{Se}), in opposite sublattices resulted in increased *p*-doping of ZnSe when low-T diffusion with Li₃N is performed (430–470°C).⁶² At higher diffusion temperatures the *p* concentration drops down, since—probably due to compensation requirements—Li starts to occupy also the compensating donor-like interstitial site, Li_i as well.^{39,45} However, there are more subtle possibilities.

First successful *n*-type doping of ZnSe was obtained by the use of excess Zn during growth, doping or annealing.⁶⁹ It has been shown that the desired donor dopants, in fact, were successfully incorporated in ZnSe thanks to the (accidental) “co-doping” with acceptor impurities (like Cu), which—being much more mobile—were subsequently removed by getting into excess Zinc.^{47,69} The presence of oppositely charged atoms/defects increases the solubility of the desired dopant. The co-doping of ZnSe with acceptor N and Te (which is isoelectronic with Se but electrically acts as a deep donor), considerably increases N incorporation.⁷⁰ Even the presence of oppositely charged native defects, as in donor doped CdS, markedly increases the solubility of In.⁷¹ The only intentional attempt I am aware of, to use this effect was with the amphoteric species Li in ZnSe:⁷² The author tried to tip the balance of donor-acceptor (Li_{Zn}-Li_i) toward more (desired) acceptors by removing the more mobile Li_i. Quenching from moderate temperature indeed lowered resistivity and hence compensation, by several orders of magnitude. However, at higher T (which are needed here to benefit from the drastic increase of total dopant equilibrium solubility with temperature) Li_{Zn} also started to migrate, resulting in loss of these acceptors. This result

suggests that the use of more stable acceptor dopants (like N in ZnSe) together with a mobile co-dopant (like Li, which would, due to compensation, tend to be interstitial at higher T) might be beneficial: it should increase the thermal stability of acceptor species (N_{Se}) and hopefully lead to the increase of *p* after removal of the compensating and more mobile Li_i.

Another option is co-doping with oppositely charged dopants, one of them being temporary dopant. This method of “indirect doping”^{73,74} proposes the doping of the desired dopant together with oppositely charged radioactive atoms. Example is donor ¹¹¹In, which after decaying to ¹¹¹Cd (life time 2.8 days) becomes just an ordinary host atom in Cd compounds. However, while being a ¹¹¹In donor it ensures the increased incorporation of the desired co-doped acceptor and reduces the formation of other compensating (native) defects during the critical time of necessary thermal treatment.

There are also additional arguments that co-doping might be helpful in transgressing doping limits: one of the reasons for lattice relaxation and compensation is the difference in size between dopant and the replaced host atom, especially at higher doping concentrations. Co-doping with two atoms of different sizes (say N and As at VI site), one larger and the other smaller than the host atom, might counterbalance the size mismatch and be beneficial (in comparison with single-species doping) in reducing total strain in the lattice. Besides that effect, co-doping with two types of acceptors (donors) at different lattice sites (one example is the already mentioned co-doping with Li and N) would reduce the drive for the departure from stoichiometry,

which by itself introduces native defects in large concentrations.^{15,21}

None of these interesting possibilities of co-doping was as yet adequately explored neither theoretically nor experimentally.

4. Conclusion

Revived interest for II-VI compounds in this decade has inspired numerous theoretical and experimental studies of these materials leading to identification of doping problems which were drastically reducing the applicability of these materials in the past. These problems are in particular: compensation by spontaneously generated native defects having opposite charge to dopants, compensation caused by strong relaxation of the lattice around doping atoms resulting in breakage of bonds with host atoms and formation of compensating deep levels, problems of inadequate solubility, resulting in low concentration of many dopants, and finally, the insufficiently shallow level of some dopants, which makes them non-ionized at RT. Despite the confirmation that the doping question is indeed a very serious one, and revelation that almost every potentially "good" dopant has one or several serious drawbacks, the greatly extended theoretical and practical understanding of the mechanisms which cause doping problems opened the way toward its solution(s). A number of possibilities to reduce or circumvent doping problems, (doping during low temperature crystal growth, doping by ion implantation, co-doping with more than one dopants, etc) have been discussed and analyzed and some new ideas are proposed. The author's contribution to the investigation of doping problems and their solution (calculations of the degree of self-compensation by native vacancies, amphoteric behavior of Li as a dopant in CdTe, method of indirect doping for avoiding self-compensation, study of Cd-vacancy compensation in ¹¹¹In implanted CdS) were also included.

The most promising way to solve the doping problems in II-VI compounds appears to be non-equilibrium processes, by which excellent results have been obtained, opening the way to much wider applications of these materials.

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