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DOPING LIMITS IN II-VI COMPOUNDS – CHALLENGES, PROBLEMS AND SOLUTIONS

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Abstract

Wide-band-gap II-VI semiconductors have a potential for a variety of applications especially in the areas of light-emitting and light-detecting devices, photovoltaic conversion (solar cells), X-ray and γ–ray detection, *etc.* In all applications, a good bipolar electrical conduction, i.e. efficient doping from both *n*- and *p*-side is essential, but due to the reasons which are not yet fully understood, it is still difficult to achieve. In this paper, a number of possible doping-limiting mechanisms in II-VI's are critically analyzed, in particular: self-compensation by spontaneous formation of native defects, amphoteric behavior of several potential dopants, lattice relaxation around some doping atoms, insufficient solubility of the others, and 'softness' of the lattice of the IIB-VI compounds. In the third part of the paper, various approaches to overcome doping difficulties have been analyzed, in particular growth and doping under non-equilibrium conditions (low-temperature growth/doping techniques, particularly MBE, MOVPE, MOCVD), doping by ion implantation, co-doping with more than one dopant, non-equilibrium doping using ultra-fast techniques, *etc.*, as well as the reinforcement of crystal lattice by alloying with some IIA-VI compounds. The results of these efforts are overviewed, including the status of maximum *p*- and *n*-doping so far achieved in each of II-VI compounds. It is concluded that a much greater range of applications of the II-VI's, in accordance with their extraordinary properties and potential in many fields, can be expected in the foreseeable future.

1. INTRODUCTION

1.1. Organization of the paper

The introduction reviews the extensive but still untapped potential of II-VI compounds for many applications and underlines the importance of overcoming doping problems in order to unleash this potential (Section 1.2.). The scope of the paper and terms and notations frequently used are defined(1.3.). A short overview of a few important methods for the identification of defects responsible for doping problems is also included (1.4.). Second part of the paper considers possible doping-limiting mechanisms in II-VI's. Critical evaluation and analysis is given for: self-compensation by native point defects, especially vacancies (2.1.1.), native interstitials (2.1.2.), antisites

(2.1.3.), dopant-vacancy pairs (2.1.4.). Furthermore, de-activation of dopants due to: lattice relaxation (2.2.), amphoteric incorporation (2.3), formation of second phase (solubility limits) (2.4.), or lack of appropriate shallow acceptors/donors (2.5) have been also analyzed. A useful phenomenological model for prediction of doping limits is described in Section 2.6. Additionally, the role of the 'softness' of the lattice has been examined. This accounts for some of the above mechanisms in IIB-VI compounds that are more difficult to prevent or avoid (2.7). Finally, critical evaluation of all these factors, including their relative importance in particular dopant/compound combination, is presented (2.8.). Special emphasis is given to the dopant/compound combinations that are most prospective for applications, and about which -not accidentally- there is also the most abundant wealth of reported results. In the closing section of the Chapter 2 (Section 2.9), the relative size of constituent atoms of the IIB-VI compounds and alloys is identified as an important factor and, possibly, as a common origin of various doping-limiting mechanisms. Third part of the paper is devoted to various approaches aimed to surpass or avoid the mechanisms elaborated in the Chapter 2, in order to obtain free carrier concentrations at levels needed in applications. Growth and doping or processing under non-equilibrium condition are recognized as optimal strategies. These approaches include: low-temperature techniques for crystal growth/doping, such as MBE, MOVPE, MOCVD, *etc.* (Section 3.1), ion implantation (3.2), and ultra-fast processing (3.3). Reinforcement of the lattice by alloying with Be-VI compounds is recognized as a particularly important advancement (Section 3.4.). Furthermore, several non-conventional approaches are proposed, particularly, co-doping with two dopants of different sizes or even different charges, and 'indirect doping', which uses radioactive atoms in order to trick self-compensation (3.5.). Present status of the dopability of each of II-VI compounds, both from the *n*- and *p*-side, has been overviewed in Chapter 4. Long and painstaking efforts to understand the causes of doping problems and recent successes and fast progress in acquiring control over the dopability, thus opening way to much wider applications of the II-VI compounds, are summarized in the concluding part (Chapter 5.).

1.2 Motivation

In today's applications of semiconductors, an overwhelming majority of all devices are made of silicon, whereas a full commercial use of the II-VI compounds is just at its beginnings, and far beyond their true potentials. The main reason is a considerably better understanding of basic properties of silicon, which provides much better control over technological processes. Consequently, even in the applications in which the physical properties of silicon are clearly inferior, the market share of other, superior materials is still relatively small. The best example is photovoltaic conversion: CdTe has band gap at room temperature (RT) of 1.5 eV, which perfectly matches the maximum of the solar energy spectrum. It also has a direct band-gap. As a consequence, already a very thin layer can absorb most of solar radiation. Both properties are very favorable for high efficiency solar cells. However, presently, silicon still holds practically the whole solar-cell market, 80% of which belongs to crystalline Si, c-Si, and 20% to amorphous Si, a-Si. The c-Si has not only a non-optimal gap width (E_g=1.12 eV) but also an indirect band gap, thus the thickness of a few hundred microns is generally needed for solar cells. This situation may soon change, since, recently 16%-efficient CdTe solar cells have been produced[1] confirming CdTe, with its theoretical limit of about 30%, as one of most promising materials for micron-thin solar cells. Such development has a potential to cut the solar electricity price to less than 1 ECU/W_p (Watt at peak solar intensity). On the other hand, the market of solar cells is expected to explode in the near future. For example, in the MUSICFM[2] study funded by the European Commission, the annual production volume of solar cells is expected to increase from 100 MW_p in the year 1996 to 220 MW_p in 2000, and to 680 MW_p in the year 2005. Crystalline-silicon market share is expected to drop to 60% in the year 2000 and in 2005 to about 20% only, the rest being replaced with new thin-film technologies. Among them CdTe is one of the three most serious candidates. Similarly, present use of II-VI photo-detectors is very small (limited to photoresistors in some cameras), although II-VI detectors are ideally suited for the visible region, and have a potential for high quantum efficiency[3,4]. First ZnSe *p-i-n* photo-diode, reported recently, had before any optimization the quantum efficiency of 8%, with the potential of about 60%[4]. Still the most common light detectors in visible range are silicon photodiodes. Since the E_g of Si falls in the infrared region, the quantum efficiency of Si detectors is very low for the blue-green light. Thus, for this range the Si detectors have to use special layers to convert visible light into infrared, resulting in complicated and expensive devices, which still have low quantum efficiency of about 10%. These examples best illustrate promising possibilities for the substantial increase of applications for II-VI's – providing that basic and technological knowledge keeps improving, so that the current technical problems get solved at a more satisfactory level. The other, very exciting area of applications for II-VI's are green, blue or higher energy lasers, where there also exists an enormous potential for high volume applications: These are: full color displays and white light emitting devices (two other needed colors, red and green have been available for some time), optical communications, laser printers, numerous sensor applications, compact discs, etc. (Shifting from presently used red to blue light would enable better focusing due to a smaller diffraction, thus, recording density can be increased by a factor of three). The first II-VI laser-diode based on ZnSe was demonstrated in 1991[5], emitting coherent light at a wavelength of 490-nm, in pulsed current regime (at 77 K) and lasting very short time. Since then, many improvements have been made: In 1993, a pulsed operation at RT was announced, and soon afterwards also the RT continuous-wave (CW) operation[6]. Lifetime of such devices, which was for the first laser diodes measured in seconds, now has been improved to over 100 h[7]. ZnSe lasers have been already used for a prototype demonstration in high-density CD players[8]. The mechanisms responsible for the degradation and short lifetime seem to be better understood[9-13], rising hopes for better solutions in the future. Particularly exciting is the development of laser diode with Be-reinforced crystal lattice[14], which is expected to prolong laser lifetime significantly. Despite considerable progress in this field, the future of the ZnSe based blue laser is not quite clear at the moment. Lately, spectacular advances of competing blue lasers based on Indium gallium nitride have been made[15], in which the lifetime of CW blue lasers was improved to ca. 30 h by 1997, with the announcement of the 10,000 hours lifetime extrapolated from the latest devices[15]. On the other hand, even if the InGaN lasers are first to be fully commercialized, the wide implementation of the blue lasers can give the boost to the whole field, II-VI based lasers inclusive. Besides, the GaN-based laser diodes seem to be most suitable to the violet spectral range, whereas the ZnSe based devices with the emission in the green and blue-green range can be realized more readily[16]. Other important applications of II-VI's cover optical processing, their use as detectors in the X-ray and γ-ray energy regions and as refractory materials (high electro-optic coefficient allows the creation phase holograms in the crystal, which can be used to store, process or transfer optically-coded information), etc.

In all these and some other applications of wide band-gap II-VI's, it is essential to achieve good bipolar electrical conductivity, i.e. to be able to perform efficient doping both with donors and acceptors up to very high concentrations (above $10^{18}/cm^3$, desirably above $10^{19}/cm^3$). However, until nineties only CdTe could be doped to both sides, whereas ZnSe, CdSe and CdS could be easily doped only to *n*-side, and ZnTe (and newly rediscovered Be-VI and Mg-VI compounds) only to *p*-side. Persevering difficulties in achieving efficient doping of the wide-band-gap II-VI compounds of both *p*- and/or *n*-type still remain main obstacles in applications and a continuous puzzle about this whole class of materials, not yet fully solved. The analysis of fundamental causes of these difficulties, as well as finding the ways to overcome them is the main subject of this paper.

1.3. Basics, definitions and scope

To obtain good electrical conductivity, a number of requirements have to be fulfilled: First, an adequate concentration of doping atoms has to be incorporated into the crystal. For equilibrium conditions, this corresponds to reasonable solubility of the dopant; in non-equilibrium conditions it assumes the ability to place dopant atoms into a desired, in general, substitutional position in the lattice. Second, energy levels of these dopants have to be close enough to the corresponding band edge ('shallow levels'). Thus the dopants are easily ionized at RT (or any other device working temperature) providing free carriers in the respective bands. Third, the incorporation of dopants must not provoke spontaneous formation of some oppositely charged defects which would de-activate them, either directly, by pairing with dopants or by compensating their electrical activity from the distance. Efficient doping, hence, means that free carrier concentration is equal or at least comparable to dopant concentration, i.e. $n \cong [N_D]$, or $p \cong [N_A]$. n denotes free electron concentration and p free hole concentration. N_D and N_A stands for foreign donors and acceptors, respectively, whereas brackets, [], denote their concentration. Here it is assumed that the concentration of residual acceptors, $[N_A]$, is negligible in comparison with the intentionally added donors, otherwise $n = [N_D]_{eff} \equiv [N_D] - [N_A]$. In this paper, term *self-compensation* will be used to describe spontaneous formation of a native defect or spontaneous change of the position of dopant atoms which would compensate electrical activity of the 'normal' dopant in perfect substitutional position, where it has a shallow level. Mutual compensation of dopant atoms (for example due to the incorporation into different lattice sites with different electrical activity) is sometimes also termed auto-compensation, whereas direct de-activation of dopant due to pairing with a native defect is sometimes called passivation.

Some early attempts to avoid compensation problems in II-VI's were made by changing pressures of M and X constituents which were in equilibrium with MX crystal at high T. Here M stands for a metal and X for a chalcogenide component of a II-VI compound. By quenching from high T, quasi-equilibrium conditions are obtained at RT ('frozen equilibrium'). In contrast, non-equilibrium conditions assume that kinetic factors dominate during material preparation already. Hence, in cases such as low-T growth or processing, thermodynamic requirements of minimal equilibrium total energy can be avoided, at least to some extent.

Following the title, only wide-band-gap II-VI's are treated in this paper, in which the 'wide band gap' limit is assumed to be $E_g \geq 1.5$ eV at RT, as it is customary (*e.g.* Ref. 17). The analysis of doping limits deals mostly with the IIB-VI binary compounds (*i.e.* Cd-VI, and Zn-VI compounds), since at present barely basic properties of IIA-VI's are known, even less known are their doping limits. However, IIA-VI's are recognized as very promising in improving some relevant properties of II-VI crystals, particularly the rigidity and thermal stability of the lattice in IIA-IIB-VI alloys and of the devices based on them (Section 3.4). In many applications ternary and quaternary II-VI alloys are needed to satisfy simultaneously various, often adverse, requirements. Typical structure of ZnSe-based laser diode consists of almost ten such layers. ZnSeTe quantum wells (QW) are most often used as active layers, and the depth of such QW is sometimes further increased both in the conduction band (by adding Mn) and in the valence band (by adding S) in the alloy. Light confinement is obtained by sandwiching the active layer with materials with lower index of refraction such as ZnMgSSe allows. These alloys not only have very large E_g (thus being ideal for the cladding layer) but also can be tailored to match the lattice constant with ZnSe. There is a substantial literature dealing with many aspects of growth and characterization of these multi-component alloys, but here only the aspects concerning doping problems/limits will be covered. Novelties related to the inclusion of beryllium in these structures are presented in a separate section (3.4).

1.4. Overview of most important methods for identification of compensating defects and quantitative evaluation of their concentrations

The core of the problem is to determine positively and quantitatively the involvement of particular defects in doping problems. The appropriate methods should be able to identify on an atomic scale the chemical nature, local structure, and dynamic properties of defects which are (or suspected to be) responsible for the electrical compensation of dopants, and they should offer the possibility to correlate them quantitatively with electrical measurements. Still, there is a very limited number of such experimental techniques. Methods of choice in identifying point defects and obtaining structural information are as follows: paramagnetic or spin resonance (EPR or ESR), optically detected magnetic resonance (ODMR), and two rather new methods, positron annihilation (PA) and perturbed angular correlation (PAC)[17].

Where applicable, EPR (*e.g.* Ref. 18) gives exceptionally valuable information regarding detailed structural properties of defect, particularly its symmetry and the nature of its surrounding. Good theoretical understanding of interactions of microwaves with bonding electrons in the magnetic field makes possible numerical testing of a number of proposed/assumed defect configurations, thus enabling clear identification of particular defect configuration by a good fit of experimental results. Both isolated vacancies and some point-defect complexes, such as vacancy-dopant pairs, can be observed either by means of ordinary EPR or photo-EPR (in the latter case the unpaired electron is produced by photo-ionizing the defect). There are a number of review papers summarizing both early[19-21], and some new[22-24] EPR studies of the II-VI compounds. When wavelength dependence of the excitation of the signal is measured, EPR can also give information on electronic properties (photo-ionization energies) of the observed defects (photo-EPR, *e.g.* Ref. 25). By measuring the change of luminescence intensity with magnetic field, another powerful technique, optically detected magnetic resonance (ODMR) is obtained. ODMR thus associates luminescence bands with a particular defect center (*e.g.* Ref. 26 or 27).

The efficiency of PA for investigating lattice defects has been first established in metals, soon to be applied in III-V's and II-VI compounds (*e.g.* Ref. 28). In solids, energetic positrons from radioactive sources rapidly slow down to thermal velocities, and after diffusion of typically 200-500 ps eventually annihilate, and emit the γ-rays in the process. Lattice defects, particularly open-volume defects of negative charge, are potential wells that can trap positrons, which then have a longer lifetime. Experimentally, either the measurement of the positron lifetime[29,30] or of Doppler broadening of the positron annihilation line-shape[31] can be carried out. PA can give positive identification of a negatively charged vacancy, as well as its concentration, providing that the so-called specific positron trapping rate has been at least once determined by an independent method[32]. It can distinguish between vacancy, divacancy and multivacancy and it is sensitive to the charge of the vacancy. Measurements at low T can also detect positron trapping at negatively charged substitutional atoms, and even interstitial atoms were claimed to be identified[33]. At present, PA practically can not distinguish whether a vacancy is isolated or it is a part of a complex, but it seems that such determination with PA is becoming increasingly feasible[31,34,35]. However, PA can not detect positively charged vacancies.

Perturbed angular correlation is a nuclear hyperfine technique[36,37] which gives a detailed and quantitative information about immediate surroundings of the probe atom. The PAC spectroscopy detects the interaction of quadrupole moment of a nuclear probe with local electric field gradient (EFG) induced by close surroundings of the probe atom[36]. From the fit of the PAC spectrum, $R(t)$, set of two PAC parameters, ν_Q and η, is obtained that unambiguously labels each particular probe-atom-defect configuration, and gives their relative fractions. After the first thorough treatment of the PAC theory[38], a number of distinct PAC signals were identified for specific defect configurations first in metals and then in silicon and in the III-V compounds. In II-VI's PAC was first applied to CdTe[39] in early eighties, followed by detection and identification of a number of specific dopant-defect interactions in other II-VI compounds[36-44]. In particular, there is a full consensus about identification of ($\mathrm{In_{Cd}}$-$\mathrm{V_{Cd}}$) pairs (A center), in all IIB-VI's[36,44], obtained with the ^{111}In probe atom. ^{111}In is an especially convenient PAC isotope for Cd-VI's, since it is a shallow donor at cation site, and decays into ^{111}Cd becoming just one of host atoms. Where applicable, PAC seems to be an excellent choice for confirming or excluding various mechanisms for electrical de-activation of dopants. Namely, any fraction of misplaced dopant atoms, such as dopant atoms in intrinsic, antisite or irregular positions, would be visible as a new signal in the PAC spectrum. Similarly, some other compensation/de-activation mechanisms like possible lattice relaxation around doping atom, formation of new phase containing a fraction of the In atoms, etc., would also be observable by creating additional characteristic PAC 'fingerprint'. The combination of

PAC and electrical measurements enables quantitative correlation between concentration of dopants, free carriers, and compensating defects detected at the microscopic level[45-47]. Unfortunately, since a limited number of species are both interesting as dopants in II-VI's and in the same time have the isotopes usable for PAC, this narrows the applicability of this extraordinary method. Furthermore, PAC obviously cannot detect isolated point defects (or other compensating species) which are spatially remote from the dopant probe atoms.

Shallow electronic levels are usually inferred from photoluminescence, PL, and other methods based on optical spectroscopies, and deep levels from ODMR, photo-EPR, Deep Level Transient Spectroscopy, DLTS, and other methods based on capacitive or current determination of energy levels. Spectrum of 'ordinary' PL of a good-quality undoped material is generally dominated by sharp lines closest to the excitation (above-the-gap) energy, related to excitons bound to neutral donors, D^oX, and acceptors, A^oX, and, possibly, ionized donor D^+X (I_2, I_1, and I_3 respectively; according to the generally accepted nomenclature Deeper and broader lines appear (DAP's) in doped materials, and they are connected with either shallow donor-acceptors pair transitions (D^sAP) or deep donor-acceptor pairs (D^dAP). The appearance and, particularly, increase of intensity and broadening of D^dAP's is regularly connected with the onset and increase of electrical compensation. Hence the PL measurements, which are relatively easy to perform, have been often used for quick and convenient estimate of the efficiency of doping and of the overall crystal quality even if the origin of DAP is not identified.

Using tunable dye laser excitation in the PL measurements, the possibilities of PL are considerably increased[48,49]. In the photoluminescence excitation technique (PLE), the intensity of a particular emission is monitored, while the excitation source is energy scanned[50-55]. This mode of excitation allows one to isolate absorption processes preferentially for a given luminescence transition. In selective photoluminescence (SPL), the PL spectra are recorded using different wavelengths for excitation. Then certain luminescence transitions become resonantly excited allowing their separation from the background, which consists of overlapping luminescence bands. With these techniques typically four to eight excited states of shallow dopants can be detected. By comparing values of excited states with the ones calculated for hydrogenic shallow dopant, a great number of donors[54,56-67] and acceptors[54,68-84] had been identified. It has been proven in both CdTe[56] and ZnSe[57] that donor ionization energies, even if they extend to ≈45 meV (in ZnSe), obey Haynes's rule (i.e. a linear dependence of exciton energy on the depth of the donor at which the exciton is localized). These precise findings proved to be extremely important in the analysis of what governs the electrical properties of undoped compounds treated under different external vapor pressures (Section 2.1.1.). Ionization energies of donors and acceptors are summarized in Section 2.5.

By selective excitation with tunable dye laser a signal resonant with the specific electronic transitions can be also enhanced considerably (several hundred times) in Raman spectroscopy (RS) as well[64]. An addition of magnetic field (B) in resonant RS[57,67,85,86] brings a new advantage: the energy levels split into two, according to the spin quantum number of the electron. RS involving spin-flips of such electrons can be easily observed by measuring both Stokes and anti-Stokes Raman signal. By changing excitation laser energies, various donor-related lines become resonantly enhanced and visible in the RS spectrum. Hence results of spin-flip Raman (SFRS) spectroscopy become comparable and complementary to the results obtained with ODMR, as well as with PL. The drawback of PL and Raman related techniques are that they are not quantitative regarding concentrations of investigated defects.

It seems particularly promising to combine some of methods providing structural information on defects in a quantitative manner with some of methods providing, again quantitatively, information on electronic properties. For example, by combining PAC with DLTS, a direct connection between microscopic structural and electronic properties can be made[87]. The other very interesting possibility is to use a radioactive isotope as a marker-dopant, the decay of which can then be used to identify isotope-associated PL signal[88]. Most of these thrilling possibilities, tested first to column IV or III-V compounds, are just at their beginnings in II-VI's.

Rapid development of characterization techniques, of which only a part is summarized in this section, gives hopes for even faster progress in our understanding of various, often interrelated, causes of doping difficulties, which are the subject of the following sections, 2.1.-2.9.

2. MECHANISMS LIMITING EFFICIENT DOPING IN II-VI COMPOUNDS

2.1. Doping limits due to compensation by native point defects and defect complexes

In the original self-compensation studies[89-92] as well as in many studies up to early eighties, it was assumed that the spontaneous generation of compensating native point defects (vacancies, interstitials....) was the main cause of experimentally observed doping problems. This basic compensating mechanism, with some variation, was the most widely accepted as a primary cause for dopant deactivation and hence intensively studied for decades[56,89,92,93]. These simple species were assumed to neutralize dopants electrically by trapping their free carriers; the compensating vacancy not necessarily being generated in the vicinity of the dopant atoms. It was also believed that the concentration of these native defects could be introduced into the crystal in appreciable concentration during the crystal growth or by thermal treatments at high T under controlled vapor pressure of constituents[92,93]. Furthermore, it was assumed that by manipulating with gas pressures of the M and X constituents one could induce the departure of stoichiometry, and thus provoke the formation of high concentration of vacancies (and/or interstitials). These native defects, when frozen by rapid cooling (quenching) of the crystal to RT, would control the electrical properties. Since the density of atomic sites in II-VI's is in the $10^{22}/cm^3$ range, a deviation of stoichiometry as small as 10^{-4} implies the defect concentration in the $10^{18}/cm^3$ range.

A wide band-gap, generally, gives a strong incentive for the introduction of compensating defects (native defects or even mobile contaminants) since the recombination of free carriers from dopants with oppositely charged compensating defects would lower the total energy of the crystal. For example, if a material is doped with donors, their electrons will occupy the energy levels close to the conductive band minimum (CBM, or E_C), Fig 1a.

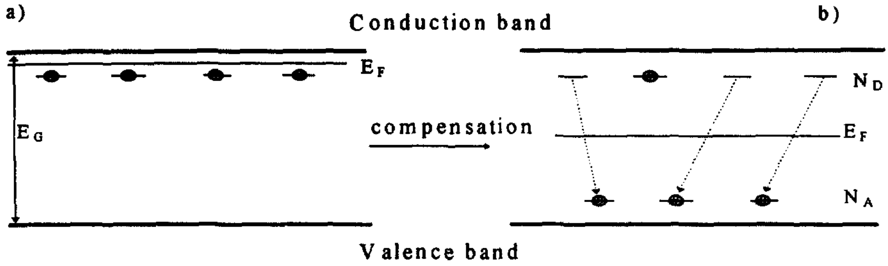


Fig. 1. Energy changes due to compensation. In uncompensated n-type material E_F is close to the conduction band (Fig. 1.a), while in a compensated material (Fig. 1b) E_F is close to the intrinsic Fermi level, located at about $E_g/2$. The electronic energy difference is given by the difference in Fermi levels.

If some acceptor-type compensating species are now introduced (Fig. 1b), electrons will have a lower energy state available (since acceptors are missing an electron with respect to the host), and electrons will lower their energy by dropping down into the acceptor state. In this process the free carrier concentration will be reduced, lowering the conductivity of semiconductors. An equal number of compensating acceptors would lead to a Fermi level (E_F) at approximately mid-gap, $E_g/2$. Hence, the system gains energy of about $E_g/2$ per electron, and that gain increases for larger E_g. To obtain that gain, the crystal must spend some energy - the formation energy of defect, $E_{form.}$- to create such compensating native acceptors - vacancies, interstitials, antisites or complexes. A classical suggestion[92] is that the process of spontaneous formation of native compensating defects would proceed along with the dopant incorporation provided the energy gained by compensation is higher than the energy needed to create a compensating defect ($\approx E_g/2 > E_{form.}$), thus resulting in completely inefficient doping. It is important to note, however, that large E_g is by no means a sufficient reason to have doping problems – if it were so, any wide band gap compound would be similarly difficult to dope from both *p*- and *n*- side, which is definitely not the case.

2.1.1. Self-compensation by native vacancies

Basic concept and the identification of vacancies.

The principles of self-compensation of dopants by spontaneously created native vacancies, were first given by Mandel and co-workers[89-91]. Mandel calculated the tendency toward self-compensation by comparing band-gaps and vacancy formation energies of a number of compounds, evaluated from then available cohesive energies[89]. He predicted, even for optimally selected experimental parameters, a complete spontaneous compensation of dopants with oppositely charged native vacancies for KCl (as a representative of I-VII compounds), a considerable compensation for *n*-ZnTe, a lower compensation for *n*-CdTe and practically no compensation for *n*-GaAs, which is well in agreement with the general experimentally observed trends. Available experimental results seemed to confirm – or at least did not seem to contradict – the notion of the stoichiometry-departing-related abundance of isolated point defects in II-VI compounds. Isolated metal (cation) vacancies have indeed been observed (*via* EPR/photo-EPR, and ODMR) in ZnSe[22,94-98], ZnS[95,99], CdS[100], and CdTe[101] - hence in all the II-VI's except in ZnTe and CdSe. These vacancies are generally doubly negatively charged (except for those in CdTe, where V_{Cd} is singly negatively charged), being mostly deep acceptors. Cation vacancies (negatively charged) were also observed in a number of the PA studies, particularly in CdTe[102-104], and ZnSe[33,105]. (This identification is less definite, since with PA it is difficult to distinguish the isolated from the bound vacancies). Chalcogenide vacancies also having deep levels, were observed in ZnS[20,106-8], ZnSe[109] and CdTe[110]. Recent surveys of identified isolated native vacancies in the II-VI's were given in Refs. 22-24. Energy levels associated with isolated vacancies are shown as a part of Table I.

Are isolated vacancies a dominant species that compensate dopants and control conductivity? First doubt in the all-decisive role of vacancies surfaced with the discussions of the question what governs the electrical conductivity in the undoped II-VI's[82,111]. Based on detailed investigation of donors and acceptors in CdTe and ZnTe and their evolution during treatment under different conditions[56,60,82,111-114], it had become increasingly evident that the residual impurities were the ones that controled the electrical properties. For the intrinsic defects, however, it was found that they influenced electrical properties only by changing the solubility of these residual impurities, making them either active or inactive. Hence the observed shallow levels obtained from the Hall-effect measurements and previously attributed to the isolated native vacancies, were then re-assigned to residual impurities (un-intentional dopants). A considerable number of shallow levels was detected in ZnSe, CdS, CdSe, ZnTe and CdTe and assigned to substitutional donor and acceptor impurities. They were convincingly identified, primarily with SPL, PLE and ODMR (Section 1.4.), despite their very close ionization energies (see Tables 2 and 3 inSection 2.5.). Should the point defects govern the conductivity, a much lower number of conductivity-governing levels would be observed, since the number of possible different native point defects is much smaller. Several more recent quantitative PA studies of undoped crystals confirmed that the concentration of cation vacancies was low, even when experimental conditions were optimized to create metal vacancies. Concentration remained at best in the $10^{16}/cm^3$ range, *i.e.* at or below the range of concentrations of residual impurities[102-104]. The concentration of anion vacancies was also found to be rather low even after thermal treatment[110].

As for the doped II-VI's, higher concentrations of vacancies were sometimes either observed by PA[31,105,115-117] or deduced from some less direct methods. (For example, in ZnSe:N from the shift in the LO phonon frequency or a decrease of the lattice parameter in ZnSe in high resolution X-ray measurements[118]). However, a detailed analysis of all vacancy-related results shows that detected vacancies were not the isolated ones. For example, when larger concentrations of vacancies were observed with PA (like in references cited above), they were almost regularly parts of dopant-vacancy pairs (Section 2.4), not isolated vacancies. Namely, PA at present, as discussed in 1.4., cannot differentiate between single vacancies and those paired with dopants, and the experimental conditions in those studies were stimulating for the formation of pairs.

The strongest argument against the importance of isolated native vacancies as significant compensating centers is the fact that they were at the microscopic level regularly observed only after some special treatments (electron irradiation, neutron irradiation, stress, quenching after high T heating, *etc.*). The reports, which would

	ZnTe	ZnSe	ZnS	CdTe	CdSe	CdS
A-center D_M -V_M or D_X-V_M	155(Cl)^{1,2} 160(Cl)^{3,4} 188(Al)^{7,8} 190(Al)^{2}	450(Al)^{1} 500(Cl)^{2,5} 600^{4,9}	850(Cl)^{1} 950(Cl)^{4} 1000(I)^{2,5}	116(F)^{2} 125(Cl)^{2,6} 120(Cl)^{4,8,10} 127(Cl)^{2} 119(Br)^{2} 128(I)^{2} 131(Ga)^{2} 142(In)^{2} 140(In)^{4,11}		
V_M $^{2-/-}$level or $^{-/0}$		660^{4} 700^{1,15} E_c- 2000^{8}	1100^{1,4,12} 1620^{8} 1250^{8a} $V^{-/0}$ 600^{1}	≤470^{1,4,13} 470^{8} 230^{16} 780^{17}		identified^{14}
V_X $^{2+/+}$level or $^{+/0}$		E_c-1750^{4} 1000^{8}	E_c-~2800^{4,18} 700^{8a} 1500^{1}	$V^{+/0}$ 200^{1,6,19}		
A_X-V_X		E_c-44^{20,20a,21} E_c-45$^{22, 22a}$ E_c-45.2±.3^{23} E_c-55^{24} E_c-56^{25} E_c-43-55^{26,26a}				

^{1}Ref. 24	photo EPR
^{2}Ref. 65	ODMR+PL
^{3}Ref. 367	ODMR
^{4}Ref. 62	ODMR, ^{4a}REf.62: PL-DAP
^{5}Ref. 370	ODMR
^{6}Ref. 151	EPR, ODMR
^{7}Ref. 149	ODMR+PL
^{8}Ref. 23	ODMR,
^{8a}Ref 23, ESR, difference in E_A indicates strong lattice relaxation	
^{9}Ref. 371	ODMR
^{10}Ref. 150	EPR, ODMR
^{11}Ref. 378	ODMR
^{12}Ref. 99	ODMR
^{13}Ref. 101	photo-EPR
^{14}Ref.100	EPR
^{15}Ref. 98	ODMR
^{16}Ref.372	PAC+Adm.Spectr.
^{17}Ref. 368	PICTS
^{18}Ref. 20	photo-EPR
^{19}Ref. 110	photoEPR
^{20}Ref.75	ODMR, ^{20a}Ref.75 V_{Se}-Zn-N_{Se}
^{21}Ref.163	PL
^{22}Ref. 57	SFRaman, ^{22a}Ref.57, N-dop.
^{23}Ref. 53	SPL
^{24}Ref. 67	Raman
^{25}Ref. 373	SPL,
^{26}Ref. 52	Raman, PLE,
^{26a}Ref. 52	N-related

Table I: Energy levels connected with vacancy-related native defects. Values are given above the valence band maximum, E_V (in meV), unless stated otherwise.

positively confirm the isolated native vacancies obtained from the as-grown material are quite rare, and in fact non-existent, when only strongly proven cases are taken into account (*e.g.* Ref. 17.)

Theoretical considerations underwent a similar circle of emphasis and denial of the importance of isolated point defects as a direct cause of self-compensation and doping problems. All-pervasive importance of vacancies was assumed in early theoretical works. Even some more recent thermodynamic calculations for *p*-ZnSe[119,120] predicted a practically complete electrical compensation of N acceptors in ZnSe by doubly charged native vacancies, V_{Se}^{2+}. However, after a free hole concentration up to $2{\cdot}10^{18}/m^3$ was experimentally obtained in ZnSe:N, the validity of such calculations was called into question[121]. A calculation of the minimal expected degree of self-compensation by ionized native vacancy in practically all III-V and II-VI compounds (22 cases) was presented in Ref. 122). The part referring to II-VI's[46] is shown in Fig. 2.

Maximal predicted efficiency of doping is shown as a function of the relative size of constituents in order to emphasize the importance of the relative sizes of M and X atoms (and hence of M and X vacancies) for self-compensation, to be discussed later (Section 2.9.). In this calculation vacancy formation energies and enthalpies were calculated using Phillips-Van Vechten's two-band theory[123,124], and chemical potentials were calculated from dissociation pressures of the compounds and partial pressures of the constituents. Neither explicit lattice relaxation nor other possible corrections were incorporated into these calculations, hence one should expect the results to show rather qualitative than quantitative effects. Still the calculated minimal compensation factors and maximal calculated $n/[N_D]$, and $p/[N_A]$ ratios, limited by a spontaneous vacancy self-compensation, exactly follow the trends observed experimentally for all these compounds (see Section 4. or Fig. 11. in Section 2.9 for comparison). Calculations predicted no compensation in CdTe nor in Si, Ga, and III-V's (except in the case of *p*-GaN, where a strong self-compensation was predicted), a moderate to considerable tendency towards self-compensation of acceptors in most II-VI compounds, (CdS, CdSe, ZnSe, CdSe) as well as for donors in ZnTe. However, in any of the 'problem' cases a calculated vacancy self-compensation is insufficient to explain the extent of experimentally observed doping problems. Surprisingly, no similar comparative study for larger number of compounds was performed with more precise calculation methods developed later, which seems necessary before a definite judgement is made. Among particular calculated cases, acceptor doping of ZnSe attracted almost all the attention[125-136], and was studied in most details. Formation energies of all native defects in ZnSe were predicted using *ab initio* potentials in first-principle calculations of super-cell, which represents the crystal containing a particular defect[126]. One of the conclusions of this one and of additional calculations[127] was that the concentrations of all native defects were too low to compensate dopants significantly. Later calculations[134], which included lattice relaxation in more detail, yielded lower energy for the formation of V_{Se}^{2+} (with the consequent higher equilibrium concentration for this defect). Still the formation energy of single V_{Se}^{2+} remained higher than the formation energy of a competing defect (A center), particularly at higher dopant concentrations[134].

Hence a consensus is growing[17,46,121,127,137], based both on experimental and theoretical results, that the isolated vacancies are not a direct cause of electrical self-

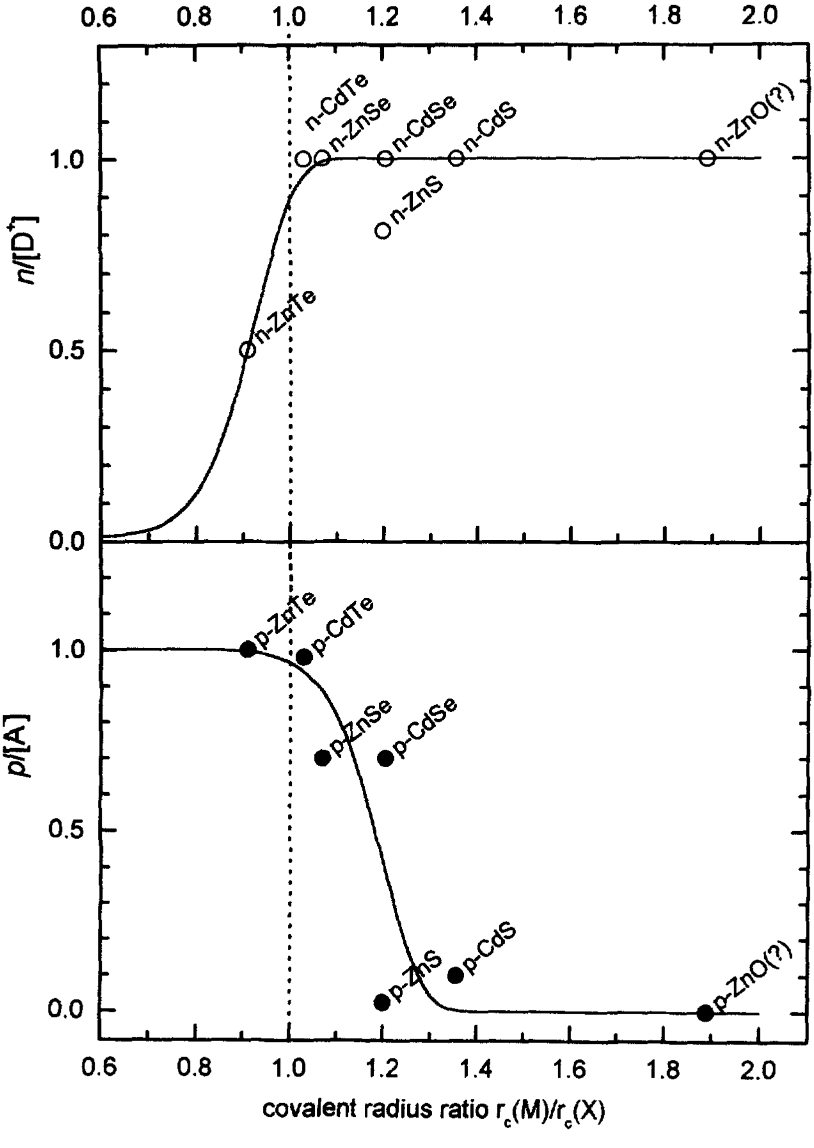


Figure 2: Maximum doping efficiency with donors, $n/[D^+]$, and acceptors, $p/[A^-]$, limited by self-compensation with native vacancy, calculated for conditions of thermodynamic equilibrium. Results are presented in dependence of relative atom (vacancy) size of each compound. (?) denotes that some input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

compensation and doping problems and appears that they are never a dominant native defect[138].

Indirect influence of vacancies on doping efficiency. Having said that, however, the indirect role of vacancies has to be examined as well. The equilibrium concentration of each dopant or defect, $[N_j]$, is defined by its formation energy, and can be expressed (neglecting the entropy term, which is estimated to be small[125]) as[126]:

$$[N_j] = [N_{sites}]\cdot\exp(-E_{form.}(j)/kT) \qquad (2.1.1.)$$

where $E_{form.}(j)$ is the energy of formation for the j-th defect or dopant, whereas $[N_{sites}]$ is the concentration of possible site incorporation, which is obviously the same for both sublattices. For example, the formation energy needed to incorporate one (negatively charged) A^- atom into M place, and thus form an acceptor A^-, in the MX semiconductor is[129]:

$$E_{form.}(A_M^-) = E(A_M^-) - \mu_A + \mu_M - E_F \qquad (2.1.2.)$$

where $E(A_M^-)$ denotes basic energy of formation (incorporation), E_F is the Fermi level position relative to the valence band minimum, VBM (E_V), μ_A and μ_M denote chemical potentials[139] of the acceptor A and of the component M in the MX compound, respectively. On the right side of Eq. 2.1.2., the terms from the second to the fourth one say that the incorporation of A_M^- acceptor will be favored if more A atoms are available (higher μ_A), if the position of E_F is higher (more energy is liberated due to the transfer of an electron from E_F to A) and if more M places are available (lower μ_M).

From the Eq. 2.1.1., it is evident that the relative concentration of native vacancies V_M and V_X will depend on the ratio of their formation energies:

$$kT \ln([V_M]/ [V_X]) = E_{form.}(V_X)/ E_{form.}(V_M) \qquad (2.1.3)$$

Since formation energies depend directly on the size of vacancies, as stressed out particularly by van Vechten[123,124] a long time ago, relative concentrations of vacancies depend basically on their size. Although the vacancies, as just elaborated in this section, do not directly determine electrical conductivity, and although the vacancy-formation energies appear to be considerably higher than those of many dopants[126,127], the vacancies indirectly play an extremely important role, in which their relative sizes (and relative values of their formation energies) seem to be decisive. This conclusion does not follow only from the calculations shown in Fig. 2, but, more importantly, from the analysis of experimentally determined values for maximal *n*- and *p*-doping in the IIB-VI compounds, elaborated later (Section 2.9.). Only CdTe, which has practically equally sized atoms can be doped easily both *p*-and *n*-type. Wherever the ratio of metal to chalcogenide atoms (and hence also metal to chalcogenide vacancy) is larger, it appears that the *n*-doping is facilitated, whereas the *p*-type doping is made more difficult, and *vice versa*.

In conclusion, it seems that isolated native vacancies do not play any direct role in compensation, either as a compensating defect nor as a dominant defect whose energy level directly controls the conductivity. However, the dopability with foreign atoms is strongly influenced by the fact whether native vacancy can be more easily formed at M or X place in the MX lattice.

2.1.2. Self-compensation by native interstitials

In the thermodynamic approach and calculations, interstitials are equivalent to vacancies[92], and they went through a similar circle as vacancies (previous section) regarding their possible role for self-compensation and doping problems. Although in first-principle total energy (*ab initio*) calculation of undoped and doped ZnSe[126,127] the interstitials were calculated to be the most abundant among native defects, their concentrations were estimated to be insufficient to prevent successful doping. Not less important, native interstitials were seldom observed experimentally, and even when detected, it was, in general, only after some specific low-temperature treatment. For example, the Zn interstitials (Zn_i) were observed in ZnSe by EPR[96] after low-T electron irradiation, but were readily annihilated at temperatures even below RT. The formation of interstitials or interstitial-related complexes was proposed in several papers based on indirect experimental evidence: Se interstitials, Se_i, were proposed to be responsible for a specific PA signal in ZnSe[33]. Furthermore, complex (Zn_i–Zn_{Zn}-N_{Se}) in ZnSe:N was recently proposed[140] - instead of or along with the usual (V_{Se}-N_{Se}) complex - to be the deep-donor part of the observed D^dAP in PL spectra. Again based on the interpretation of PL spectra, the formation of Te_i complexes in CdTe:Cl was proposed[141]. At present, there is no additional or independent confirmation for any of these assignments. Particularly relevant for the evaluation of the role of interstitials appear to be the experiments in which ion beam analysis techniques are used, since they are particularly sensitive to interstitials. Namely, the interstitials block the channels between rows of atoms in a perfect crystalline lattice and deflect the probing particles (protons, γ-rays or α particles) in channeling techniques like channeling Rutherford Back Scattering (channeling RBS), Particle Induced X-rays Emission (channeling PIXE) or in channeling nuclear reaction analysis (channeling NRA). In such studies[142-145], all performed on ZnSe lightly to heavily doped with N, and moderately to strongly electrically compensated, no Zn_i's were observed, which indicated that native interstitials did not play a role of any significance as compensating donors in the compensation of N_{Se} acceptors. In contrast, a considerable fraction of N_i was observed in most of these works[143-145] (Section 2.3).

All above results indicate that native interstitials are probably of no importance, particularly as isolated point defects, for the observed doping problems.

2.1.3. Self-compensation by native antisites

Antisite defects should not form easily in II-VI's, due to a large difference in number of valence electrons and a large difference in electronegativity as well as due to a high ionicity of the inter-atomic bonds in II-VI's. Theoretical studies based on first-principles total-energy calculations indicated that in stoichiometrically grown ZnSe and ZnTe the formation energies of antisites (like of other native defects) are too high in both places and in any charge state[126,127] to explain the observed compensation phenomena. For instance, the concentration of Se_{Zn}^{2+} (energetically most favorable among the antisites in ZnSe) is calculated to be more than ten times lower than, say, $[Zn_i^{2+}]$ or $[V_{Zn}]$[126]. In contrast, based on an earlier calculation[146], the formation of Zn_{Te} antisite was calculated to be energetically favorable in ZnTe. According to the proposed model Zn_{Te} antisite should have an energy level within the valence band only in ZnTe, thus explaining the proneness of ZnTe to *p*-type doping. In all other II-VI's, Zn_{Te} would be a deep trap. It seems that experiments did not prove this model. For example, one of the consequences of the model would be a sharp drop of *p*-type proclivity in $ZnTe_{1-x}Te_x$ alloys above a certain x, while a graded transition is actually observed instead.

Experimentally, in several occasions the formation of either antisites or antisite pairs was mentioned as one of the possibilities compatible with experimental results, but without a further positive proof. Hence, at present it does not look likely that this type of defects would play any important role in observed limits of doping. Still, particularly due to the lack of some differential technique to detect antisites, such claim has to be made with caution.

2.1.4. Self-compensation by dopant-vacancy pairs (A center)

Experimental detection of A centers. As mentioned in the section 2.1.1, a number of experimental results in II-VI compounds indicates the existence of complexes which include native vacancies. Particularly, a self-compensation *via* formation of dopant-native vacancy pairs (so called A center) was often proposed to explain the de-activation of dopants. Namely, the metal vacancy - donor pairs have been observed in all IIB-VI's, i.e. in CdS[44], CdSe, CdTe, ZnTe, ZnSe and ZnS[36] with PAC, and long before that with EPR in ZnS and ZnSe[22,95,98,147,148] in ZnTe[149] and CdTe[150,151]. Vacancy-related signal in PA in CdTe[23,24,31,35,104,117,152], ZnSe[115,116,153] and ZnSSe[105] was also assigned to A center. (Problem of discerning PA signals belonging to isolated vacancies from paired vacancies is discussed in Section 1.4.) The quantitative correlation between concentration of A centers and electrical properties are, however, much, much scarcer. At present, most data from which concentrations of A center were derived came from PA measurements. In several reports (still a very limited number) authors looked for possible correlations between a concentration of A centers (derived from PA), a carrier concentration (from Hall effect or from C-V profiling) and/or a dopant concentrations (from SIMS). Such correlations were observed, in electrically compensated CdTe doped either with In or Cl[31,24,117,152], dopant concentration varying from $5 \cdot 10^{15}/cm^3$ up to $10^{18}/cm^3$ [31] and in Ga doped ZnSe (for Ga concentrations from below $10^{16}/cm^3$ till above $10^{19}/cm^3$)[115,116], and in several other cases. Some experiments are easy to interpret since chemical potentials (Eq. 2.1.1. and 2.1.2.) during thermal treatment were selected to stimulate the formation of A centers[104]. It is much more difficult to discern and interpret cases in which the formation of A center and its increase with dopant concentration was observed despite experimental conditions, aimed to reduce compensation and obtain optimal doping.

Connection between external chemical potentials and the formation of an A center. It is well known that thermal treatment of doped, conductive II-VI crystal under conditions that enhance creation of native defects with opposite charge can drastically reduce its conductivity. Spontaneous creation of vacancies and formation of an A center was one of the plausible explanations even before any microscopic and quantitative proof was available[154]. A model case is In doped CdS, for which it has been known for ages that the conversion from highly n-type to semi-insulating material can be obtained by thermal treatment under sulfur pressure, even if In concentration is very high[155,156]. What is precisely occurring at the microscopic level in CdS:In was recently clarified by a combination of PAC and Hall-effect measurements[45-47].

If In implated CdS samples are annealed under conditions of high Cd potential all In atoms get incorporated in substitutional In_{Cd} sites (Fig. 3a, and configuration 3e.) The

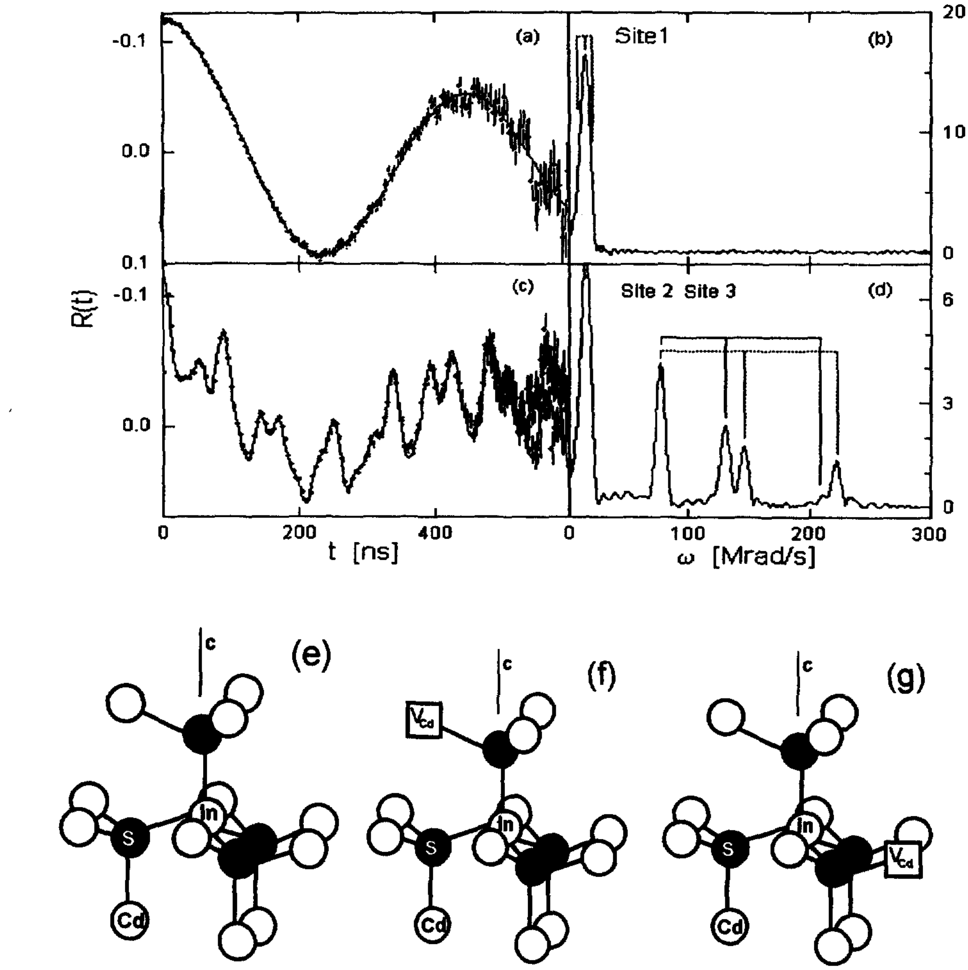


Fig. 3. The PAC time spectra R(t), their Fourier transforms F(ω), and respective atomic configurations. Spectrum (a), obtained after annealing of In implanted CdS under Cd pressure, reflects configuration (e) - all ^{111}In probe atoms at Cd sites in undisturbed surroundings. Spectrum c), obtained after annealing of implanted CdS under S pressure, reflects comparable fractions of In_{Cd} and (In_{Cd}-V_{Cd}) pairs. Being a hexagonal crystal CdS has two slightly different A center configurations, shown in (f) and (g), in which (In_{Cd}-V_{Cd}) pairs are positioned in or out of the basal plane.

same can be done up to In concentrations of $\approx 10^{20}/cm^3$, explaining why free carrier concentration equal to [In] (n ≈ [In]) can be obtained under analogous experimental conditions[155-158]. In contrast, when the same samples were annealed under S pressure, a matching concentration of V_{Cd} and resulting (In_{Cd}-V_{Cd}) pairs was formed. (Fig 3b,c configurations e, f, g.). This process is accompanied with a complete electrical compensation of the sample, which was obtained in the $10^{16}/cm^3$ - $10^{20}/cm^3$ range of In concentrations. Results represent direct microscopic and fully quantitative experimental evidence of the basic principle of self-compensation: in a very wide range of dopant concentrations crystal spontaneously creates the exact matching concentration of native point defects needed to completely electrically compensate foreign doping atoms (Fig. 4.).

Combination of electrical and PAC measurements on the same set of samples have shown how this doping mechanism works at the atomic level: approximately half of In_{Cd}^+ donors were directly passivated by pairing and creating A centers, $(In_{Cd}^+\text{-}V_{Cd}^{2-})^-$. These A centers are singly negatively charged acceptors, which electrically compensate the other half of In_{Cd}^+ donors. Still, in In:CdS, the A center does not pose a limit to doping, since formation of A centers can be completely prevented even at very high In concentration (up to $10^{20}/cm^3$) by thermal treatment under Cd pressure. It probably occurs also in many other analogous dopant/compound combinations (although in a not so wide dopant concentration range), but we will not attempt to make a comprehensive list of these cases, since they are not of particular technological interest.

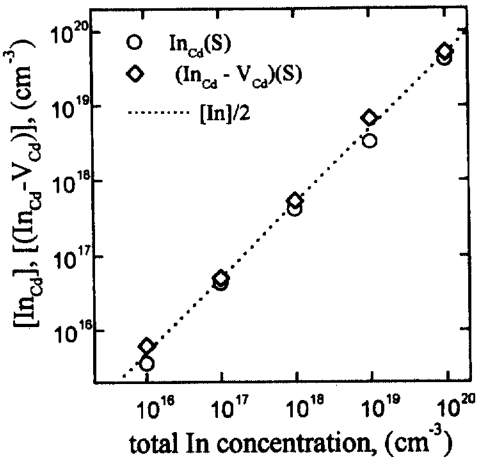


Fig. 4. Concentrations of free substitutional In atoms (In_{Cd}^+, O) and paired In atoms ((In_{Cd}^+-V_{Cd}^{2-})$^-$, ◇) as a function of total In concentration after implantation and annealing under S pressure. Dashed line depicts y=[In]/2 function.

'Unavoidable' formation of A centers. It seems certain, however, that the formation of A centers cannot always be prevented, even when optimal experimental conditions are chosen, i.e. the conditions which minimize the formation of native defects with opposite charge of the dopants during the processing (growth or thermal treatment). It seems quite probable that the mechanism may be responsible for compensation in a number of cases, which will be presented and analyzed in the rest of this section.

A-centers in p-ZnSe. It is a well documented experimental fact that *p* in ZnSe:N saturates at about *p* $10^{18}/cm^3$ when [N] exceeded $10^{18}/cm^3$, and then even drops dramatically when [N] reaches $10^{19}/cm^3$ or higher[159-161]. In a number of methods considerable changes are observed close to or at the saturation concentrations: in PL spectra, a characteristic deep donor-acceptor (D^dAP) line appears, at 44-55 meV below the conduction band[162,163]. This D^dAP band has a characteristic red-shift with the increase of [N], and the blue-shift with the increase of excitation intensity, which have been well explained by the potential fluctuations of CBM and VBM, caused by a very strong compensation for higher[N][164-168]. Additionally, the LO phonon line in Raman spectra shifts with the increase of [N], in the way one would expect if native defects were present[118]. Moreover, in high resolution X-ray measurements the lattice constant of ZnSe decreases with [N] far more rapidly than one would expect from the contribution from shorter Zn-N bonds alone[118], which indicates the presence of vacancies. Furthermore, optically detected magnetic resonance (ODMR)[75,121] and spin-flip Raman scattering[85,86,67,169] detected a deep donor (with g= 1.38) in the similarly N doped ZnSe crystals. The connection between signals from these various methods, particularly ODMR, SFRS and PL, was convincingly established[65,67,75,121]. All these observations were consistent with the existence of a compensating complex defect involving V_{Se} in ZnSe, which was concluded to be (N_{Se}-V_{Se}) pair, *i.e.* A center. Finally, V_{Se}-related complex, assumed to be just (N_{Se}-V_{Se}) was indeed observed with PA in highly doped ([N] over $10^{18}/cm^3$) but highly compensated (n = $2\cdot10^{17}/cm^3$) ZnSSe:N[105].

Theoretical investigations also support the notion that dopant-vacancy pairs may be very important for observed doping limits in N doped ZnSe. Total energy calculations[134] give strong support to the model of formation of an A-center. The difference from previous similar *ab initio* calculations[127] is that the strong lattice relaxation around V_{Se}, when doubly negatively charged, is taken into account, which effectively reduces its formation energy, and allows its formation in large concentrations. When the V_{Se}^{2+} makes pair with a singly ionized dopant acceptor (N_{Se}^-) it not only neutralizes this acceptor but this pair $(V_{Se}^{2+}\text{-}N_{Se}^-)^+$ acts as s (singly ionized) donor, which compensates one more single acceptor. This leads to a complete compensation and saturation of free carrier concentration. Similar conclusions were reached in another total-energy calculation study[132], although in this study the complexes of N with Zn interstitials, as well as the formation of large point defects clusters were also found to be energetically quite favorable. Recent thermodynamic calculation[137], which takes into account the same pair as a dominant charged defect in neutrality equation has come to the same conclusion.

A-centers in n-ZnSe. It seems that the self-compensation *via* formation of an A center is also an important mechanism in n-ZnSe, although at considerably higher doping levels than in *p*-ZnSe. In uniformly doped ZnSe layers net electron concentration increased linearly with [Cl] up to $10^{19}/cm^3$ range, but became saturated for higher [Cl] and eventually started to decrease for even higher doping levels[170]. A recent total energy calculation indicated that the Cl incorporated well in Se lattice sites, where it was an effective donor[133]. However, the 'softness' of the ZnSe lattice manifests itself as a large distortion, which then leads to the formation of (Cl_{Se}-V_{Zn}) complex. This acceptor is predicted to be the most important source for compensation of Cl_{Se} donors[133]. These calculations are in agreement with a PA study in Cl doped ZnSe-ZnS crystals[105], in which (assumingly) paired Zn vacancies have been observed. Similarly, heavy doping of ZnSe with Iodine provoked spontaneous formation of PA-detected compensating V_{Zn} (and then A centers)[153], although no electrical measurements were reported, and hence no quantitative correlation could be made. In addition, in heavily doped Ga-ZnSe the formation of A centers (Ga_{Zn}-V_{Se}) could be inferred from the analysis of ion-channeling spectra[171]. Furthermore, the formation of the (Ga_{Zn}-V_{Zn}) A center was blamed for compensation and saturation of Ga donors in Ga-implanted ZnSe[172], which was concluded from the characteristic DAP in PL spectrum.

A-centers in CdTe:In. Numerous, strong and convincing arguments for the de-activation of donors due to self-compensation with an A-center were offered also for In-doped CdTe. Saturation of *n* at high [In] in CdTe:In was observed directly by means of high temperature Hall effect measurements (in the range 973-1173 K)[173]. In samples doped up to ≈ $10^{18}/cm^3$, In donors were uncompensated, resulting in $n \cong$ [In]. However, for higher [In], *n* saturated and became independent on [In][173]. Similarly, in MBE growth under optimal conditions for n-doping which minimize the formation of [V_{Cd}], *n* remained saturated at ~1-2·10^{18}/cm^3 even when [In] exceeded 10^{19}/cm^3 [174,175]. These optimal conditions proved to be thermal treatment under Cd pressure in high-T processes and growth under Cd over-pressure or growth with additional Cd flux during low-T MBE growth[173,175]. It appears that at high enough [In] spontaneous formation of V_{Cd} occurs, resulting in (In_{Cd}-V_{Cd}) acceptor pairs, which then compensate the remaining In_{Cd} donors[154,173,175,176]. The arguments for A-center compensation mechanism were derived both from experimental measurements (high temperature Hall effect and DLTS[173,176] and PL in combination with several other methods[175]), and theoretical considerations (thermodynamic calculations)[154,173,176]. Just as it happens in ZnSe:N (previous paragraphs), the saturation of *n* at high [In] in CdTe:In is accompanied by the appearance of DAP band at about 1.4 – 1.5 eV in PL spectra, the intensity of which increases with [In][174,175]. This PL signal is assigned to the A center[175], in analogy with the interpretation of corresponding DAP's in PL spectrum in CdTe and ZnTe. These DAP's were identified to belong to the A center in CdTe:Cl by ODMR[110,150] and with PA[117], as well as to A centers in ZnTe:Cl and ZnTe:Al[149] (also identified by ODMR). In the same study[175] a strong increase of migration of In atoms was observed when [In] had become critically high, despite of the fact that T was as low as 220°C. (Strong migration of In at high [In] was confirmed by X-ray photoelectron spectroscopy, XPS, and by SIMS). This is again in perfect agreement with the notion that at high enough [In] the [V_{Cd}] spontaneously strongly increased, although the growth parameters remained identical. In another study[177], in MB- grown CdTe:In, the delta-layer of Mn was incorporated in some samples, in order to study the diffusivity of Mn as a function of Cd/Te beam pressure ratios during growth. It has been found that for growth at stoichiometric conditions Mn diffusivity (determined by SIMS) has a minimum, while *n* has a maximum. With the departure from stoichiometry the Mn diffusivity increases while *n* decreases, both being apparently the consequence of the increase of [V_{Cd}] for insufficiently high Cd/Te ratio[177]. The correlation between [In] and the concentration of V_{Cd}-related complex (presumably (V_{Cd}-In_{Cd}) was also observed by PA[31], but the detailed experiment in critical In concentration range and under optimal regime to minimize V_{Cd} formation still has to be performed. The other critical experiment which could address the question of the role of A center in de-activation of In_{Cd} donors at high [In], is also still waiting to be done. It would comprise a parallel study using Hall-effect and PAC study on series of samples being doped in an optimal way (i.e. [V_{Cd}] formation minimized) in a wide range of [In]. Namely, the PAC signal belonging to (In_{Cd}-V_{Cd}) A center in CdTe is well known[36]. The occurrence of this signal in PAC spectrum for higher [In], where *n* starts to stagnate, and in particular a possible correlation of intensity of this PAC signal with [In] at even higher In concentrations would be a positive and fully quantitative proof for this self-compensation mechanism in CdTe:In.

A-centers in CdTe:I. In iodine-doped CdTe the carrier concentration was limited to just under 10^{19}/cm^3, although over 10^{20}/cm^3 iodine atoms were incorporated[178]. When [I] was below 10^{18}/cm^3, *n* was proportional to [I] and no sign of compensating V_{Cd} was observed in the PA spectrum. However at, and particularly above [I] =10^{18}/cm^3, *n* started to saturate accompanied with a strong increase of V_{Cd}-related PAC signal, although growth conditions remained the same[178]. It seems quite convincing that the spontaneous formation of V_{Cd} (and hence of A center) limits the doping in this case as well.

Arguments are given that dopant-vacancy pair formation limits the doping also in acceptor-doped CdTe and in donor-doped ZnSe, CdS and CdSe[137], although there is a new evidence that (at least) in CdS an other mechanism, (the formation of a new phase, i.e. the solubility) limits the n-doping[46,47]. There are also a number of other dopant/compound combinations in which theoretical arguments for doping limits were offered *via* formation of compensating DX or AX centers (next section), but for which neither this nor any other mechanism has been as yet experimentally proven. In all these cases the compensation *via* formation of A centers, hence, remains a possible and even plausible alternative. Note however, that even for the two most analyzed cases (ZnSe:N and CdTe:In, the later one being offered as a model case for A-center compensation mechanism[137]) alternative compensation mechanisms continue to be proposed, as analyzed in sections 2.2 and 2.3. Obviously more work and more direct experimental proofs are needed.

In conclusion, self-compensation by A center seems to be a very important mechanism that limits efficient doping of most (perhaps all) donors in CdTe, most donors in ZnSe, and possibly in CdSe, and at least some of the acceptors in ZnSe. It is probably also important in many other cases, including those where the mechanism of doping limits is questionable or unknown.

2.2. Self-compensation due to lattice relaxation and related formation of deep levels

Theoretical considerations. Generally speaking, dopant atoms have a different size and a different charge-state than host atoms. Therefore, the incorporation of some dopants into the lattice can induce relaxation of surrounding atoms, which influences the total energy of the crystal. If such relaxation is strong, a bond in the vicinity of the foreign atom can break, leading to the formation of a charged, compensating defect center[135,136,179-188]. Electrically, this process results in the 'conversion' of the standard substitutional atom (expected to behave as a dopant with a shallow hydrogenic level), into the dopant

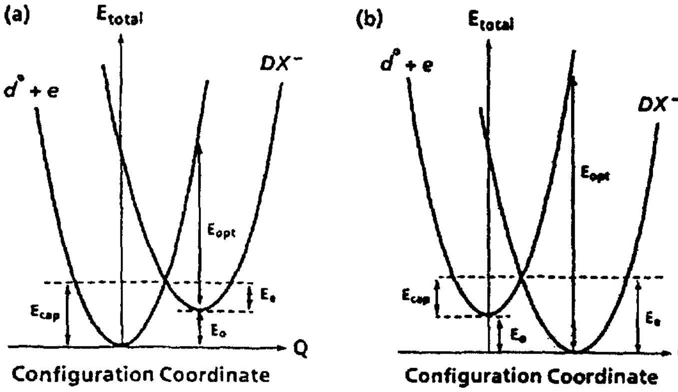


Fig. 5. Configuration coordinate diagrams for donor DX centers (e.g. Al, Ga) in ZnSe and ZnTe are shown in (a) and (b) respectively. The DX center is a metastable resonance state above the conduction-band minimum in ZnSe but is more stable than the shallow donor state in ZnTe. The optical (E_{opt}) and thermal (E_0) ionization energies and the capture (E_{cap}) and emission (E_e) barriers are shown. (Fig. 2. in Ref. 183)

displaced from its lattice site, where it forms a deep level. The mechanism is analogous to the formation of DX center[189] observed in GaAs and Ga-Al-As system[190]. The model is usually presented through the configuration coordinate picture with a shallow metastable state and a deep ground state (Fig. 5.a and b).

The idea was first applied to explain why As and P dopants in ZnSe do not behave as substitutional shallow acceptors, as it was expected. Total energy calculations[180,181] examined stability of the AX center by examining the energies of the following reaction:

$$2a^{o} \rightarrow a^{-} + A^{+} \qquad 2.2.1$$

where a^{o}, a^{-}, and A^{+} denote structural states associated with the neutral, negative and positive charge state of an acceptor. The two neutral acceptors are not assumed to be close to each other. For As in ZnSe the calculation predicted that the AX^{+} structural state (AX center), would be energetically more favorable than a 'normal' substitutional position. In 'relaxed' configuration the As atom has shortened bonds with 3 neighboring Zn atoms, and a broken bond with the forth Zn. Strong relaxation was predicted for P dopant as well, but the result was less decisive. The same type of calculations show that small and strongly electronegative dopants like N and Li (and also isoelectronic O) do not produce large relaxation, which was used to explain relative successes in obtaining *p*-type doping with these dopants and also stimulated their further study.

The doping efficiency for a number of donors was also investigated by analyzing a reaction analogous to Eq. 2.2.1 . The possibility of a large impurity displacement in the lattice leading to a deep state and a donor de-activation was first suggested for Cl in CdTe[179]. More recent calculations for CdTe[185] predicted considerable lattice relaxation and formation of DX centers with deep levels for In, Ga, Al and Cl donors. A DX state in CdTe doped with column III donors (In, Ga and Al) leads to a broken-bond geometry with trigonal C_{3v} symmetry, where incorporated donors are being considerably displaced toward an 'interstitial' position. For column VII donors in CdTe (Cl, Br and I) three types of large lattice relaxations have been found, also with trigonal symmetry[187]. For Ga in CdTe, the DX state was calculated to be more stable (i.e. to have lower formation energy) than the shallow hydrogenic donor state. As for Al, In and Cl dopants the DX state is found to be metastable, but it becomes favorable either in case the crystal is exposed to the hydrostatic pressure (HP), or at high dopant concentrations. The predicted doping limits for CdTe were then estimated[185] to be $1.8 \cdot 10^{18}/cm^{3}$ for In and $6 \cdot 10^{18}/cm^{3}$ for Cl, in good agreement with experimental data[175,191]. From the same calculation the critical HP pressure for the shallow-deep transition was calculated to be 3 and 14 kbar for In and Cl atoms, respectively. The formation of DX centers is predicted also in CdTe alloyed with ZnTe, MgTe and MgSe[187]. In ZnSe the calculations predicted that the shallow donor configuration is energetically more favorable, in particular for Ga and Al donors[183,188] (as well as for In and Tl[188]) so that DX center should be a metastable defect configuration (Figure 5a). In contrast, in ZnTe, for the same Ga and Al donors, the relaxed DX states, having deep donor levels, should be energetically more favorable[183]. (Fig. 5b). This strong tendency toward relaxation and formation of a DX center for donors in ZnTe (and MgTe) was then used to explain the difficulties or even inability of *n*-type doping in these compounds. Subsequent calculations also suggested that the relaxation around the dopant atom which produces deep compensating levels, might be even more complex and might result in the breakage of two host bonds ('DBB') and the creation of VI-VI dimer bond[186].

Experimental confirmation of DX and AX centers. The most important experimental sign indicating the presence of DX (or AX) center is the observations of persistent photoconductivity, PPC[192], where both the deep level and the shallow metastable level can be detected at lower temperatures, due to optically induced deep-shallow transition. Furthermore, a large difference between the thermal and the optical ionization level is indicative of a large lattice relaxation. The presence of persistent photo-EPR signal[193] was observed as well.

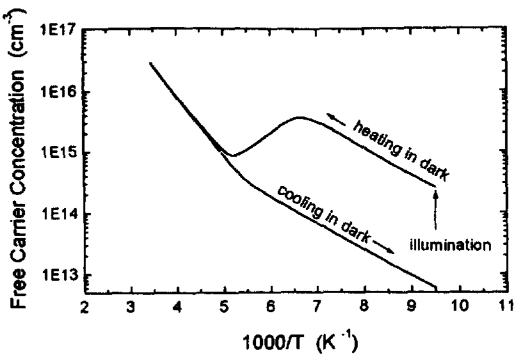


Fig. 6. The temperature dependence of free carrier concentration measured in dark (cooling) and after illumination at low temperature (heating, with light turned off).

Illustration of the temperature dependence of PPC on T is shown in Fig. 6, while the results of measurements in specific cases can be found in Refs[137,194-200].

In the ground state the DX center is a deep donor that governs conductivity. Illumination at low T can excite it into a shallow state, which persists even after the illumination is turned off. 'Quenching' of PPC will occur at higher T, when thermal energy becomes large enough to overcome the capture barrier, E_{cap} (Fig 5b), allowing the thermally activated transition into the relaxed, ground state.

If observation of PPC is taken as the main criterion[192], at present the formation of a DX center can be taken as experimentally confirmed in n-CdTe-based alloys CdMgTe[202,201], CdZnTe[193,196,199], CdMnTe[200,202,203], and Ga doped ZnSe[197]. The AX center has been found up to now only in *p*-ZnMgSSe[194,204]. This is obviously considerably less than the above-mentioned calculations predicted. One possible reason might be the difficulty in proving the existence of the DX center in cases where doping efficiency is very low and one cannot perceive both the shallow and the deep states through the observation of PPC. This might easily be the case in ZnTe, for example, where despite strong *n*-doping, usually a very deep level controls the conductivity, which, in principle, can be explained by several compensating mechanisms. From the observation of both shallow and DX states in CdZnTe:Cl it can be most probably concluded on the relevance of DX center in ZnTe as well. Namely, the photo-transport properties exhibit a smooth, systematic dependence on the Zn content, starting from pure CdTe up to 35% Zn in the cation sites (after that the electron concentration becomes too low), indicating that the same mechanism is responsible in the whole range of the Zn fraction in alloys[199]. Furthermore, in a recent study by EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near-Edge Structure) analysis[205], Cl atoms in ZnTe were found displaced from Te lattice sites in [111] direction, having trigonal C_{3v} symmetry. In contrast to ZnTe, the same study[205] found that in ZnSe all Cl atoms were incorporated into regular four-coordinated Se lattice sites. Both findings appear nicely compatible with the expected difference between ZnSe and ZnTe (Figure 5). However, there are still certain doubts: ZnTe has recently been doped with either Cl[206] or Al[207-209] up to relatively high concentrations, with shallow levels governing the conductivity (Section 4.2). The successes in *n*- doping of ZnTe appears to speak against the DX model, at least up to the achieved concentrations: if the relaxed DX state is the energetically favorable configuration for et least Al atoms in ZnTe[187], these atoms should relax upon incorporation, despite the fact that they were incorporated by non-equilibrium growth/doping conditions. Namely, the capture barrier, E_{cap}, is expected to be low, as it was in all cases were the DX center was observed[193,196,197,199-204]. So obviously further experimental work is needed on the subject.

The problems in identifying the role of the DX (AX) center can also be illustrated by the example of P dopant in ZnSe, where substitutional P does not behave as an hydrogenic acceptor, but gives a 0.6-0.7 eV deep level above the valence band[94], and consequently a poor doping efficiency. ODMR measurements have shown that it also does not have the expected T(d) symmetry, but a distorted C_{3v}, presumably due to Jan-Teller effect[79]. All that seems compatible with an AX-type dopant. Nevertheless, recent first-principles calculations[136] required a reinterpretation of the experimental data, claming that the P interstitial (near hexagonal site) should be the deep acceptor. To complicate the problem even more, both EPR[210] and ODMR measurements[211] suggest that P in ZnSe sometimes agglomerates into clusters containing 4P atoms.

In CdTe the DX center was observed under hydrostatic pressure for a number of different dopants from both column III and column VII[195,198,212]. For In doped CdTe ([In] in the $10^{18}/cm^3$ range) the DX state was found to be located within the conduction band, 110-130 meV above the conduction band minimum, E_C. The DX level can be lowered below E_C by applying hydrostatic pressure (HP). When HP rose above 7-8 kbar, a typical PPC behavior was noticed[195,212].

The discrepancies between predictions and reported experiments still remain unclear. One of the reasons could be the role of dopant concentration, which is quite uncertain, especially at extremely high concentrations. For example, for very high [In] in CdTe (5 and 8 at.% of In), an analysis of EXAFS measurements[213] suggests strong lattice relaxation around Cd lattice sites, already at ambient pressure, generated by the introduction of high concentration of In. Similarly, a detailed analysis of T dependence of Hall-effect data also points to the existence of DX centers even without the application of HP[214]. The apparent contradiction to reports from Refs. 195 and 212, may be solved by considering the increase of Fermi level along with dopant concentration. At high enough [In] the position of Fermi level might cross over the DX level position making DX center energetically favorable also without application of external pressure, but In concentrations needed for that seem to be much higher than estimated in Ref. 187. The effect might be analogous with the activation of DX center in GaAs that take place at extremely high Si concentration[215], while otherwise it can be observed only in GaAlAs alloys.

Besides Chadi's single broken bond model for DX center, a triple-broken-bond model, also based on first-principles calculation, has recently been proposed[216]. It implies an antisite incorporation of dopant and even lower formation energy than 'classical' DX center. It has the same C_{3v} symmetry, but implies that dopant atom moves in opposite direction along [111] direction than it does in single-broken-bond configuration. Another DX model has been proposed[217], in which the electron-phonon coupling is the driving force for the undistorted-distorted transition. It gives a somewhat different distortion geometry around the dopant atom. All of these models offer (albeit a somewhat different) explanation for normal/relaxed state transformations, for the existence of two different charge states in two configurations, for the absence of a paramagnetic signal in the ground DX state, the existence of PPC and its dynamics, as well as the trends in changes of the depth of thermal and emission barriers in ternary alloys due to the change of the ratio of constituent elements. The experimental check of these models might hopefully become more accessible through precise measurements of atom position and bond lengths *via* EXAFS studies[205,218].

It can be concluded that a DX center is difficult to identify positively, so that its existence is proven in only a limited number of cases. It is argued that it might be effective in many other dopant/compound combinations, particularly at very high dopant doses. Generally, prime candidates are among donor-doped telurides and acceptor-doped selenides and sulfides.

2.3. Self-compensation by amphoteric dopant incorporation (auto-compensation)

Some dopants/impurities tend to incorporate into different places in the crystal and consequently assume different charge states, which results in mutual electrical compensation. The best documented case is Lithium in ZnSe[66,127,130,219,220, 222-227]. Being the atom from the row I, Li was considered to be an excellent candidate for *p*-type doping in ZnSe. The energy of formation (incorporation) of Li_{Zn} is relatively low (0.51 eV[222]) and it produces negligible distortion[222], and lattice relaxation[127,130,180] in its substitutional surroundings. Li_{Zn} also gives a relatively shallow level, 114 meV above the valence band[228], which can be considered quite acceptable. Many attempts, however, to obtain efficient *p*-type doping of ZnSe with Li remained unsuccessful, and very often poorly reproducible. Li doping either by a temperature-difference growth method[229], by MOCVD[230,231,232] or MBE growth[224], by ion implantation[233] resulted in more or less compensated material, so that up to very recently the maximal hole concentration achieved in Li:ZnSe has remained relatively low ($p \approx 10^{17}/cm^3$). The reason lies in the fact that a fraction of Li atoms goes into tetrahedral interstitial sites, Li_i, where they act as donors[219,223]. The formation energy of Li_i has been found to be also very low, 0.64 eV[222], just slightly higher that the one of Li_{Zn}, and to depend on stoichiometry (it decreases for Zn-rich crystal[222]). This leads to a competition between substitutional and interstitial incorporation of Li, and strong sensitivity on Fermi level position, where Li_i incorporation becomes favored as the Fermi level is closer to the valence band (stronger *p*-type)[128]. Since the diffusion coefficient of Li is large, Li_i readily migrates through the crystal even at relatively low T, facilitating the formation of neutral pairs Li_{Zn}-Li_i. For lower total Li concentrations Li_{Zn} incorporation is preferred and p increases with [Li][228]. That decreases the Fermi level, and Li_i incorporation starts to prevail, resulting in saturation and then even decrease of p, although the parameters of crystal growth remain unchanged[228]. Li_{Zn}-Li_i pairing was observed more directly in PL spectra[69]. The doping of ZnSe with Na faces exactly the same problem[127,219], since the formation energy for Na_i is also low (1.0 eV)[219].

The same mechanism of auto-compensation of Li (and Na) is also observed in other II-VI's. Amphoteric incorporation, dependent on Fermi-level-position, was also established when Li was diffused in (initially) *n*- and initially *p*-CdTe. In both cases

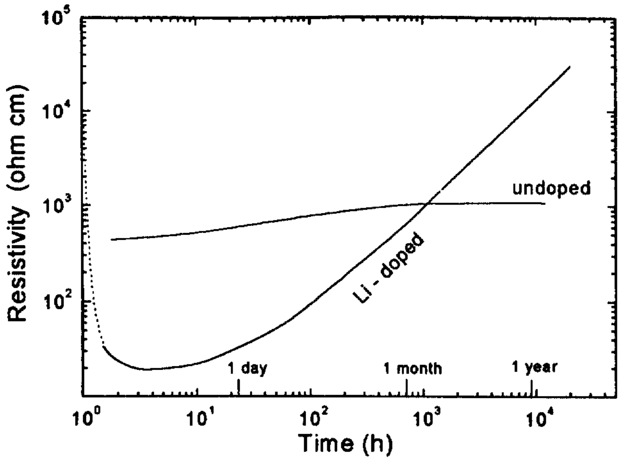


Fig. 7. Room temperature changes in resistivity of Lithium-doped and undoped CdTe samples after quenching from 600° C to RT. After Fig. 5 in Ref. [135].

highly compensated, highly resistive material was obtained[234]. An example of the influence that amphoterically incorporated Li atoms have on electrical properties of CdTe during 1 year of RT aging[235] are shown in Fig. 7. Li was introduced by thermal treatment at 600-750°C, under Cd overpressure which favors the incorporation of Li at both sites, and hence compensation. After quenching, due to a much lower solubility of Li at RT, Li starts to out-diffuse and segregate into a second phase. Since Li_i donors migrate considerably faster than Li_{Cd} acceptors, CdTe becomes an electrically de-compensated *p*-type. Once all Li_i are gone, the effects of much slower out-diffusion of Li_{Cd} become also visible, resulting in a steadfast decrease of acceptors.

Changes in electrical properties at RT due to Li (and other light and fast-migrating atoms) have been observed in a number of occasions. For example, electrical conductivity and the net carrier concentration in Li- and Na-doped CdTe samples have decreased significantly after aging at RT for several months[234]. Thermal instability of Ag in CdTe was also well documented. In the PL study of CdTe samples doped with Ag a considerable changes occurred already at RT[236]. PL results were interpreted as spontaneous release of Ag_{Cd} into interstitial sites. Since Ag_i atoms have a rather high mobility and are donors with a charge opposite to Ag_{Cd}, the formation of Ag_{Cd}-Ag_i pairs seems to occur, just as with Li or Na doped samples. Similarly, in another CdTe:Ag study[237] the PL (A_0X) line known to be related to Ag_{Cd}[82] was also found to decrease steadily after doping, which was then interpreted in the same way. It is interesting that although in this study Li and Na were not intentionally co-doped, the substitutional Li (and/or Na)-related (A_0X) line, still observable in PL spectra due to the presence of these atoms in CdTe as residual impurities, also decreased with RT annealing and became practically unidentifiable after one year.

The amphoteric incorporation of N in ZnSe:N is one of the alternative mechanisms proposed[182] to explain *p*-doping limits and de-activation of acceptors N_{Se}. N_i is a shallow donor in ZnSe; besides, its inclination towards making N-N pairs is well known since the binding energy of N_2 molecule is very high. However, in an ion beam analysis study of the lattice location of N, utilizing the nuclear reaction $^{15}N(p, \alpha\gamma)^{12}C$ and channeling PIXE, no N interstitials were found in MBE grown samples even when [N] was above $10^{20}/cm^3$ [142]. The same analysis also suggested that N atoms were located at substitutional sites. It prompted the belief that N_i are unimportant as compensating species in ZnSe:N[46,121], particularly since a well-documented self-compensation mechanism *via* A center (Section 2.1.4) seemed sufficient to explain the observed *p*-doping limit. However, newer measurements with improved sensitivity (using nuclear reaction $^{15}N(p, \alpha)^{12}C$ and detecting α particles) resulted in a considerably different picture regarding site-selection of N atoms in ZnSe[143]. The MBE-grown samples, doped with N in $2\text{-}6\times10^{18}/cm^3$ range were studied. It was shown that a large fraction of N was distributed randomly making probably N-N pairs, while another N fraction was placed in pure interstitial (tetrahedral) sites, either as isolated interstitial or as a part of the N_{Se}-N_i complex. Both non-substitutional fractions increased with [N], well in agreement with experimentally observed decrease of doping efficiency with the increase of [N][143]. The same authors also investigated MBE grown ZnSe:N films, in which N was introduced *via* ion implantation[144]. In as-implanted samples 2/3 of N atoms were out of substitutional sites, and annealing only increased the fraction of tetrahedrally sited N atoms (*i.e.* compensating donors) offering a plausible microscopic explanation why the implantation is generally unsuccessful for obtaining efficiently doped ZnSe:N. In another study[145] both N and N_2 were implanted into ZnSe, in order to get insight into the location of N_2 in the ZnSe lattice, again using ion beam analysis. Although the number of N atoms incorporated in the lattice was the same, and the crystallinity of both samples similarly recovered after annealing, in the N implanted sample prevailed the incorporation into sites N_{Se}, while in the N_2 implanted sample a random distribution was dominant. All these results give support, at the microscopic level, to the notion that amphoteric behavior of N, including the formation of a N_2 molecule, can contribute to de-activation of N_{Se} acceptors. The problem with stable N_2 is also known from doping of ZnSe with N from plasma: much better doping efficiencies are achieved when high -power RF plasma source is used[238,239], which produces mostly N ions, instead of classical sources, which produce mostly N_2 molecules.

A nice support to the model of the deactivation due to N pairing inside the ZnSe crystal is given by a Monte Carlo simulation of the nitrogen-pair formation *via* diffusion[159,240]. The simulation assumes the existence of two compensating nitrogen complexes, one containing only one N atom and the other two N atoms. The probability for the migrating N atom to come upon another N atom increases with [N], since the distance between N atoms in the crystal becomes smaller. As a consequence, it has been calculated that the saturation of *p* occurs when [N] exceeds $10^{18}/cm^3$, and then *p* strongly decreases with the increase of [N]. (Fig. 8).

Finally, the compensation which includes N-N pairs was also supported by one of recent total energy calculations on mechanisms which compensate N acceptors in ZnSe:N[135]. It was concluded that the formation of N_2 molecule is favored for Se-rich conditions, while in Se rich conditions the formation of a split-interstitial N-N complex, occupying Se sites, pose a limit to N doping. It is safe to conclude that the amphoteric incorporation of N (either as N_i-complex, or as N_2 molecule or both) is also one of the well documented mechanisms which hampers *p*-doping in ZnSe:N.

The amphoteric behavior might occur also for column IV dopants in II-VI's (which can be important since Si is a technologically introduced contaminant as a constituent of quartz vessel) and for transitional metals (Cu, Ag, Fe..), which is particularly inconvenient since these species are fast diffusers and contaminants that are especially difficult to avoid.

There are isolated reports about some other dopants behaving amphoterically. The examples include a possible amphoteric incorporation of In antisites in ZnTe:In[242], and complexes involving interstitial In in the CdTe:In[243]. Very recently, antisite Cl_{Zn} was proposed as a very efficient DX centar in ZnTe:Cl[216]. There is also a total energy calculation[136] suggesting that the formation of antisite P_{Zn} in ZnSe:P may be a favorable way to compensate P_{Se} acceptors. P_{Cd} antisite (where it would be triple donor) was also proposed to form in CdTe:P[244] in an effort to explain the difficulties of CdTe doping with P. However, any of these assignments still need some more positive experimental confirmation.

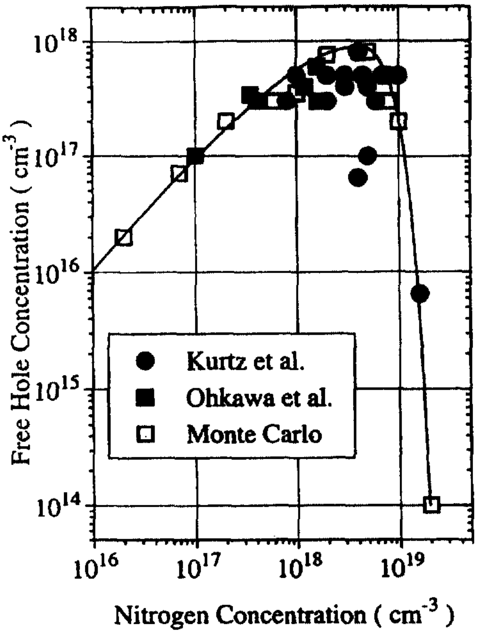


Fig. 8. Free-hole concentration in ZnSe doped with RF nitrogen plasma as a function of the total nitrogen concentration (solid symbols from Refs. 374&375) together with results of a Monte Carlo simulation (open simbols) The solid curve is a guide for the eye. (Fig. 8 from Ref. 240).

Self-compensation of doping atoms by its own species in other configurations (auto-compensation) offers at present one of the best documented examples of a self-compensation mechanism. The crystal chooses this type of compensation instead of the formation of native defects, when the formation energy of the amphoteric defect is lower than the formation energy of the native one. That seems to be the reason why the auto-compensation has been found exclusively in cases of light dopants like Li, Na and N, and transitional metals.

2.4. Solubility limits of dopants (formation of a second phase)

All previously proposed mechanisms assumed that a) incorporation of dopants in sufficient concentrations is not a problem, and b) that these donors/acceptors are shallow enough so that they are readily ionized at RT. There are, however, serious arguments that these requirements might not be easy to meet. Namely, the wide band gap also poses a fundamental problem in achieving the high equilibrium solubility, due to the resulting high energy of incorporation for most dopants. Furthermore, the solubility depends on Fermi level position[130,245] in a way that for a Fermi level close to the bands (and that is a desirable position in successful doping) the solubility becomes much lower than it would be for the middle-of-the-gap position. Generally, the conditions that are optimal for the suppression of compensating defects, are at the same time the worst from the standpoint of solubility. For example, if one adjusts experimental conditions to maximize concentration of metal vacancies so as to ease the incorporation of group III-donors (low chemical potential of external metal gas phase), the solubility will be indeed increased. However, the provoked shift in stoichiometry toward chalcogenide-rich side will also create favorable conditions for the formation of compensating V_{Cd} vacancies. These problems were analyzed in a number of experimental and theoretical papers[127,137,165,194,219,245-247]. A fully self-consistent total energy calculation, was performed for Na, Li, and N in ZnSe[127,130] and ZnTe[128]. Calculation yielded solubility limits for ZnSe grown/doped at 250°C, to be $4 \cdot 10^{15}/cm^3$, $6 \cdot 10^{18}/cm^3$ and $2 \cdot 10^{19}/cm^3$ for Na, Li and N, respectively, and much higher solubilities (for Li 10-10^3 times higher) in ZnTe. The successes of these calculations were predictions that the solubility of these acceptors would be considerably higher in ZnTe than in ZnSe, and that N had a higher solubility than Li and much higher than Na; all of these are consistent with the available experimental data. For example, doping of ZnSe and ZnTe with N during MBE growth under identical conditions resulted in an order of magnitude higher concentration of N in ZnTe than in ZnSe[246]. The calculations explained why ZnTe was much more easily *p*-dopable than ZnSe; they also clarified the lack of success of Na doping of ZnSe[225] and gave an alternative explanation for the doping limit for Li as an acceptor dopant. The solubility of Li, Na and N in ZnSe was calculated to be limited by the formation of a new phase, Li_2Se, Na_2Se and N_3Se_4, respectively[127]. Theory has not yet been applied to other dopants and other compounds to determine whether and where solubility problems can be expected.

X-ray diffraction is a classical method to determine the possible presence of a new phase in a compound but it has limitations concerning the thickness of the layer. PAC spectroscopy is a particularly convenient method for positive identification of the solubility limit *via* observation of the characteristic new PAC signal in the spectrum with the onset of a new phase. Namely, a suspected new alloy (in case its PAC signal is not known) can be synthesized in such a way that a small fraction of constituent atoms is replaced by radioactive PAC isotope. The obtained PAC signal can then be compared with the PAC signal of the highly doped compound enabling a positive identification of a new phase. For example, the solubility in indium implanted CdS[46,47] was found to be limited by the formation of a second phase, $CdIn_2S_4$, (for the annealing condition comprising high chemical potential of S), or In clusters (for the annealing conditions maximizing chemical potential of Cd). These limits appear at very high In concentrations, around $10^{20}/cm^3$, for former experimental conditions and around $10^{19}/cm^3$, for the latter ones.

The presence of precipitates or voids is the sign of probable solubility problems - any mechanism that includes native defects or DX center is not expected to give a second phase. For example, precipitates were observed after high T treatments in ZnSe highly doped with In[248], Ga[248,249] and Li[250]. In a study of N-implanted ZnSe electrical and TEM results were compared: whereas a highly resistive or even semi-insulating material was obtained after annealing for all N doses, TEM revealed voids for high N doses[251]. It is plausible to assume that the voids are the consequence of the formation of N_2 gas phase[252]. Doping in non-equilibrium conditions considerably alleviates the problems connected with solubility, since then the incorporation of atoms is governed more by kinetics than by thermodynamic requirements. The solubility limit is the ultimate doping limit, which will always finally become operative, unless some other mechanism has limited the efficient doping at lower concentrations. Besides the above mentioned example of In-doped CdS, other cases of solubility limits at very high doses include *n*-doping of CdS with other donors, and *p*-type doping of ZnTe.

2.5. Insufficient ionizability of some prospective dopants at RT

To donate free carrier into conductive (valence) band at the working temperature of a device (RT, in general), the dopant must have a level close enough to the respective band ('shallow level'). At times when doping with a number of dopants proved completely unsuccessful, there was a doubt whether some of potential dopants had a shallow level at all. Along with the availability of II-VI monocrystalline material of considerably improved quality, with the ability to better control the incorporation of a desired dopant on the 'right' site in the lattice, and particularly with the availability of fine spectroscopic techniques (partly described in Section 1.4), a much more complete picture is obtained. Presently identified levels of potential dopants in IIB-VI compounds are shown in Table 2, presenting ionization energies for donors, and Table 3, presenting ionization energies for acceptors.

A glance at the Tables and a comparison among different compounds shows that the lack of appropriately shallow donors (acceptors) cannot be a sufficient reason to explain doping problems, not even to explain the very different propensity toward *n*- or *p*-doping in various compounds. For example, comparison of acceptors in CdTe and ZnTe shows that despite a much stronger inclination of ZnTe for *p*-type doping, the ionization energies of potential acceptors are practically the same. Or, an other example: it has been established recently[68] that doping of ZnSe with a very small concentration of phosphorus, will result in a clean incorporation of P into the substitutional site, where it has a quite low ionization energy, just 85.3 meV above E_v[68]. Yet *p*-doping of ZnSe with P is known to be stubbornly difficult. Obviously, some other reasons (Sections 2.1-2.4.) must be much more important than the lack of 'good' dopants with shallow levels.

2.6 Phenomenological model for predicting doping limits

All of the approaches presented in Sections 2.1-2.5. start from some specific mechanism which could potentially affect doping and then try to evaluate its absolute and relative importance in hindering efficient doping through various calculational and experimental efforts. There is also a phenomenological approach, the so-called *amphoteric defect model*[253,255,258] which aims at predicting the doping limitations in semiconductors without requiring any knowledge of mechanisms leading to the introduction of electrically active compensating species. The model was first developed for III-V compounds[253-256]. This phenomenological treatment has only recently been applied[257,258] and further developed[159,259] in II-VI compounds[246,258,260-262,263]. Its applicability has been further extended to I-III-VI compounds as well[263]. The model uses the energetic positions of the compound band edges, E_C and E_V, with respect to an absolute reference energy level (usually vacuum), and determines Fermi stabilization

	ZnTe	ZnSe	ZnS	CdTe	CdSe	CdS
B		25.6[1] 26[2]				
Al	18.5[1] 18.3[4] 18[7]	25.6[1] 26.3[5] 26[2]	100[1] 74[6]	14.05[3]		
Ga		27.2[1] 27.0[8] 27.9[5]	400[6]	13.88[3]		33.1[1]
In		28.2[1,9] 28.1[8] 28.9[5]	400-600[6]	14.5[1] 14.15[3]		33.8[1]
F		28.2[1] 28.8[9] 29.3[5]	13.67[3]			35.1[1]
Cl	20.1[1,7]	26.2[1,] 26.1[4,8] 26.9[5]		14.1[1] 14.48[3] 14.0[5,10]		32.7[1]
Br		26.8[11]				32.5[1]
I		23.95[8] 30.4[8]	600[6]			32.1[1]
Li_i		≈21[1] 17[2] 20±2[12]		13.9[1]		28[1]
Na_i		20[2,12]				
N_i		29.1±.1[13] 26[14]				
?		E_c-900[6,6a]		14.3[1]	19.5[1]	

[1] Ref. 58	Opt. spectr., PL
[2] Ref. 59	DAP-PL
[3] Ref. 56	PL, SPL
[4] Ref. 60	SPL, PLE
[5] Ref. 61	PL
[6] Ref. 62	photo-EPR
[6a] Ref. 62: metal interstitial	
[7] Ref. 23	ODMR, PL
[8] Ref. 64	SPL, ES, Raman
[9] Ref. 54	PLE, SPL
[10] Ref. 65	ODMR, PL
[11] Ref. 55	PLE, SPL
[12] Ref. 66	DAP-PL
[13] Ref. 51	PLE, SPL
[14] Ref. 67	Raman, SF-Raman

Table II: Ionization energies E_D (in meV) of various foreign donors in different Zn- and Cd-chalcogenides. Methods are indicated with references.

	ZnTe	ZnSe	ZnS	CdTe	CdSe	CdS
$\mathrm{Li_M}$	60.5[1] 61[4]	114[1,2] 113[5] 111[6]	150[1]	57.8[1] 58[4]	109±8[3]	165±6[3]
$\mathrm{Na_M}$	62.8[1] 62.8[4]	126[1] 128[2]	190[1]	58.8[1] 58.7[4]		196±6[1]
$\mathrm{Cu_M}$	148[1] 149[4] 146[7] 140[7a]	650[1]	1250[1]	147[1] 146[4,7,8] 140[7a]		1100[3] 860[9]
$\mathrm{Ag_M}$	121[1] 123[4,7]	430[1] 113[10]	720[1] 113[10]	108[1] 107.5[8] 92[10] 123[7]		260[1]
$\mathrm{Au_M}$	277[1]	~550[1]		263[4]		
$\mathrm{N_X}$		100±15[1] 110[2,13,14] 111[6]		56[4,10,11]	21-31[12]	
O	isoel.trap[15]	80[15]	110[15]	46[15]		116[15]
$\mathrm{P_X}$	63.5[1,4]	~85[1] 85.3[2] 550[1] 600-700[16,17]		60[1] 68.2[4] 50[7]	83±6[3]	120[1] 600[1]
$\mathrm{As_X}$	79[1] 78.5[4]	~110[1] 113[18]		92[4,11]		750[1]
?	48[4] 181[4] 113[4]					

[1]Ref. 58	opt. spectr.,PL	[10]Ref. 52	Ram., PLE
[2]Ref. 68	PL, PLE	[11]Ref. 73	PL,SPL
[3]Ref. 69	PL	[12]Ref. 74	Hall, PL-DAP
[4]Ref. 60	SPL,PLE	[13]Ref. 75	ODMR
[5]Ref. 70	PL,I-V,C-V	[14]Ref. 76	DLTS
[6]Ref. 67	SF-Raman	[15]Ref. 77	PL
[7]Ref. 65	PL, [7a]Ref. 65: IR	[16]Ref. 62	ODMR
[8]Ref. 71	PL, reson.exc.PL	[17]Ref. 79	ODMR
[9]Ref. 72	Laser ablation, PL	[18]Ref. 80	PL

Table III: Ionization energies E_A (in meV) of various foreign acceptors in different Zn- and Cd- chalcogenides. Methods are indicated with references.

levels $E_{SI,p,n}$ ('defect-creation' reference energy levels) at which the creation of a new defect does not change the free energy of the crystal. The maximal achievable *n*-doping for each compound is then estimated through the maximal attainable E_F, which cannot exceed the calculated $E_{SI,n}$, while the maximal *p*-doping is estimated in the same way through the minimal E_F, which cannot be lowered below $E_{SI,p}$. Relative band edge positions of various II-VI compounds as well as calculated 'pinning' levels for *n*-doping, $E_{SI,n}$ and for *p*-doping, $E_{SI,p}$ are shown in Fig. 9.[159,259].

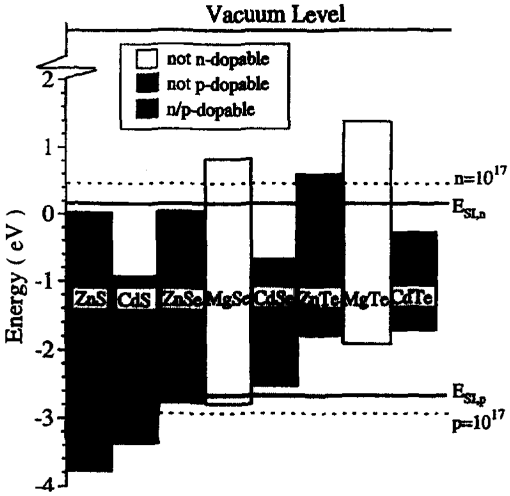


Fig. 9. Relative band edge positions of various II-VI compounds. The experimentally obtained dopability is indicated by different shadings. (Fig. 1 from Ref. 259)

Essentially the same results, (although numerical values somewhat differ) were reported in Ref. 263. Obvious predictions are that a material with highly positioned CBM (E_C) (in respect to $E_{SI,p}$) will be difficult to dope *n*-type, while the materials having low E_V (in respect to $E_{SI,n}$) will be difficult to dope *p*-type. Hence, small work function will ease the *p*-doping, while large positive electron affinity will help the *n*-doping.

The model states that a ratio of concentrations between compensating species, E_{comp} and intentionally added active donor or acceptor, $D_{A,D}$, is given by[137,254]:

$$[E_{comp}]/[D_{A,D}] = \exp(-2(E_F - E_{SI,p,n})/kT)) \qquad (2.6.1)$$

where $E_{SI,p,n}$ (*i.e.*, $E_{SI,p}$ or $E_{SI,n}$) are - according to the model - constants with respect to the vacuum level for all compounds as long as the compensation mechanism is the same. The model implies that when E_F approaches $E_{SI,p,n}$ an abrupt reduction of the formation energy of some charged defects increases their concentration and ensures a strong compensation[256]. One of experimental supports for the model is frequently observed stabilization ('pinning') of E_F at the mid-gap after the introduction of a (generally unknown) native defect by electron irradiation[253] regardless of whether the starting material was a strong *n*-type or a *p*-type i.e. regardless of whether the starting E_F was close to E_C or the starting E_F was on the opposite side of the gap.

The up to now reported successes of this model in II-VI's are excellent predictions of the decrease of (experimentally observed) maximal *p* and of the increase of maximal *n* in ZnSeTe alloys as a function of Te/Se ratio in the alloy[258], and equally well predicted doping limits in ZnMgSe, CdMgTe, ZnMgSTe and ZnMgSSe alloys and the way they depend on the ratios of the constituents[159,259]. Although this method does not provide (nor attempts to specify) any information about the nature of the compensating defect(s), it seems that it can very well reproduce experimentally obtained doping limits (as long as the mechanism of compensation remains unchanged). Hence, it can be of great practical value, particularly for predicting viability and limitations of *n*- and *p*-type doping of complex new multi-component compounds, and can offer valuable hints on how to avoid or alleviate doping problems.

Marfaing[137] showed *via* quasi-chemical analysis that a natural and meaningful interpretation could be provided for the $E_{SI,p,n}$. He modeled Eq. 2.6.1 for ZnSe doped in nitrogen, and calculated the maximal *p*-doping under the assumption that the doping was limited due to the spontaneous formation of Se vacancies which enable the formation of compensating (N_{Se}-V_{Se}) donors (A centers). The defect-creation reference energy level was then identified to be:

$$E_{SI,p} = (E_{D1}+E_{D2})+k\cdot T\cdot \ln[\surd(K_p\cdot[V_{Se}])] \qquad (2.6.2)$$

where E_{D1} and E_{D2} refer to the first and second ionization levels of Se vacancy, while K_p refers to temperature-dependent pair-formation constant. This analysis established the way how to connect the phenomenologically determined parameter $E_{SI,p}$ with the specific material and defect properties, but also showed that, in general, $E_{SI,p}$ (or $E_{SI,n}$) cannot be taken as constants independent on the material properties and the mechanism of compensation.

2.7. 'Softness' of the lattice and other aspects potentially important for the doping of II-VI's

'Weakness' of the lattice of II-VI compounds is reflected in relatively high native defect concentrations and the high mobility of these defects (as well as of some foreign impurities or even dopants) at processing temperatures. All self-compensation problems related to native defects become, evidently, more difficult to cope with if a large concentration of native defects is available, and if the mobility (diffusivity) of these defects is relatively high. Although at high T defects and impurities are separated (binding energies of complexes like A centers are generally low), they still interact electronically, i.e. indirectly, through the neutrality equation. A clear experimental proof for such notion, and how high concentrations of native defects can be induced by the presence of dopants, is demonstrated, for example, in Fig.4: observation of large concentrations of (In_{Cd}-V_{Cd}) pairs measured at RT, obviously required that large concentration of V_{Cd} be present at high-T before quenching, and the concentration of [V_{Cd}] be higher when [In] was higher, despite the fact that they were separated at high-T.

Self-diffusion experiments are a relatively direct probe and measure of the presence of isolated native defects, both interstitials and vacancies. A self-diffusion coefficient is a product of a defect concentration and a diffusivity coefficient, which is proportional to the defect mobility (e.g. Ref. 154). Self-diffusion coefficients of both metal and chalcogenide components in II-VI's are relatively very high, as shown, for example, in Ref.154, where values experimentally determined in II-VI compounds were compared with those of III-V compounds. The self-diffusion coefficients in II-VI compounds are orders of magnitude higher, which elucidates part of the reasons why self-compensation is a much bigger problem in II-VI's than in III-V's, even when the band-gaps are comparable. Part of the difference reflects higher defect mobilities and part higher defect concentrations, but both aspects increase the probability of defect-impurity interaction, and hence of self-compensation[154].

The instability of Li dopants in CdTe at RT has already been shown in Fig. 7 (Section

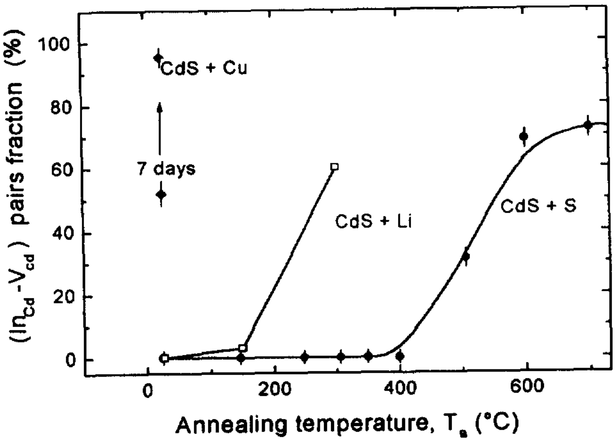


Fig. 10. Change of fraction of (In$_{Cd}$-V$_{Cd}$) pairs with annealing: ◆ - CdS with evaporated Cu layer; □– CdS with Li diffused from Li$_2$S under S pressure, ● - undoped CdS annealed under S pressure.

2.3.). Figure 10 demonstrates, (also at RT), the dopant-interaction-enhanced creation and mobility of native defect V$_{Cd}$ in CdS. For 'normal' thermal creation of V$_{Cd}$ in CdS temperatures above 400°C are needed[36,44,45,264]. However, if Cu is available (in this experiment Cu reservoir was supplied by the evaporation of a Cu layer on a CdS surface at RT) fast in-diffusion of Cu from the surface takes place, resulting in compensation of donors and consequently in highly resistive material[265-269]. Microscopic mechanism of this process was recently elucidated using PAC spectroscopy[264]: Cu causes the compensation of donors indirectly, by provoking fast in-diffusion of cadmium vacancies from the surface, which actually do the compensation of donors which are present in CdS. Figure 10. also demonstrates that the same effect is taking place due to in-diffusion of Li donors (although it occurs at somewhat higher T than with Cu). Cadmium vacancies appear again only after Li in-diffusion becomes significant, at temperatures which are considerably lower than those needed for the thermal creation of V$_{Cd}$. A similar effect was also observed when Li was introduced in ZnTe[270], CdS[271] and ZnSe[272], also by PAC. (Possible additional formation of auto-compensating Li$_M$-Li$_i$ pairs is not observable by PAC). Other examples of RT instabilities due to the migration of Li, Na, Ag and other fast diffusers in various II-VI's were analyzed in section 2.3.

There are reports about changes of properties in strongly N doped ZnSe also already at RT: After a 6 months storage at RT a region extending 100 nm from the surface was formed, showing an increase in compensating-donors-related transitions (D^{d}AP's) in PL spectra[121,163]. Furthermore, ZnSe:N thermally treated at 300°C for not more than 0.5-1.5 hours showed a significant compensation[121]. All that indicates considerable in-diffusion of Se vacancies already at RT, possibly enhanced by the strong thermodynamic driving force for the incorporation of compensating centers. In a PL, SIMS and C-V profiling study of the migration of compensating defects in ZnSe:N it was confirmed that the effective decrease in [N$_{Se}$] upon annealing stemed from the compensation by defects that originated from the surface[273]. The defect was argued to be V$_{Se}^{2+}$ since Zn$_i$ is quite mobile even at RT[274] and could not maintain the observed concentration gradient from the surface. The migration energy of this defect was measured to be 4.0 eV, unusually high for vacancy, which was ascribed to a large relaxation associated with V_{se}^{2+}. The diffusivity prefactor was also found to be unusually high (10^{14} cm^2/s), but it is compatible with large relaxation energy, and also explains a still high mobility of V_{se}^{2+} already at moderate T.

Doping-related increase of diffusivity in II-VI alloys, grown at low to moderate temperatures, were observed in a number of cases[175,275-278], indicating the (spontaneous and unwanted) formation of native vacancies. For example, in ZnCdSe/ZnSe structure the doping-enhanced self-diffusion of Cd became significant at 360°C and even more at higher T[277]. The diffusion coefficient of Cd increased up to three orders of magnitude as compared to the undoped material[277,278].

PAC investigations also clearly proved the mobility of metal vacancies in several II-VI's at RT, particularly in CdTe[279], and CdS[36,44,46]. In these experiments vacancies were introduced by quenching from high to RT, and the trapping of V_{Cd}^{2-} by ^{111}In probe atoms, and formation of A centers was monitored at RT[279] or at temperatures just above RT[36]. Migration energy for V_{Cd} in CdS was determined to be only 1.0 eV, while binding energies with In were 0.15 eV in CdTe[279] and 0.35eV in CdS[36], respectively.

A relatively easy formation of native defects and particularly their mobility already at low to moderate temperatures makes efficient doping more difficult, independently of the particular mechanism which is most detrimental to the particular dopant/compound combination.

2.8 Relative importance of various mechanisms

The magnitude of the problem in discerning both the relative and absolute importance of a particular mechanism is best illustrated by examples of two (most studied) dopant/compound combinations, N dopant in ZnSe and In dopant in CdTe. Suggested mechanisms for explaining doping limits of N in ZnSe have up to now included: self-compensation by native V_{Se}[89], or by A center (V_{Se} - N_{Se}) pair[121,134,137,163], or by N_i[182], or by (V_{Se} - N_i) pair[280], or by antisites N_{Zn}[143], or by (N_{Zn} - N_{Se}) antisite pairs[142,143], or by (N_{Se}-Zn_i) pairs[140], or due to the solubility limit of N[127], or by formation of N_2 molecule either in interstitial[135,145] or in Se place[135], or by clustering of N atoms[132,143], or, finally, by the relaxation-related bond breaking model[186]. Only after decades of tedious research we have come close to sorting out these possibilities. Two of the mechanisms which seem to be the most important (neutralization of N_{Se} acceptors by self-compensation *via* (V_{Se} - N_{Se}) pairs, and auto-compensation *via* formation of N-N pairs) were analyzed in detail in Sections 2.1.4 and 2.3, respectively. At the calculational level it seems that difficulty in differentiation arises primarily due to quite similar energies of the formation of most mentioned defects or complexes. Total energy calculations at best (with a proper consideration of d-electrons and proper evaluation of reliability and consistency of calculations) are accurate to about 0.4 eV for charged defects and 0.2 eV for neutral defects[126]. Furthermore, various approximations[127,132,134-136] bring additional discrepancies even in basically same approach, which results in different conclusions regarding which defect(s) has the lowest formation energy. At the experimental level it is extremely difficult to decidedly identify the 'culprit' unless, for the particular dopant/compound combination some positive and quantitative method can be put to its best use. For example, if there is a nice EPR or ODMR signal, or if there is an appropriate PAC isotope, etc. For the particular case of ZnSe:N it is safe to say that more than one mechanism is operative, and their relative importance can be dependent on [N] as well as on the method of growth/doping. For example, in growth/doping with plasma having high N_2 fraction, almost certainly a part of N atoms won't be incorporated into acceptor N_{Se} sites. For the CdTe:In, the dependence of an operative mechanism on [In] can perhaps clarify different assignments (formation of A center (In_{Cd}-V_{Cd}) or/and DX center), with the former mechanism starting to limit doping efficiency already at medium/high [In], and the latter becoming operative only at extremely high [In].

Various dopant/compound combinations for which the doping-limiting mechanism is quite convincingly determined are summarized in Table IV. It is clear that what is unknown greatly surpasses what is known and much more work has to be done before a more complete picture can be composed.

In CdTe most donors (possibly all) and probably some acceptors seem to be limited with A center, although at high doses the DX center can become important. By analogy a similar thing can be expected for donors in CdSe. Donor doping in CdS is limited by solubility (at a very high level). For ZnSe, acceptor N provokes the formation of a compensating A center, although auto-compensation probably also occurs, just as with other light atoms such as Li and Na. The incorporation of all three species in equilibrium conditions, however, is limited by the solubility and formation of a second phase. Solubility probably also limits (at a very high level) the acceptor doping of ZnTe, while for donors in ZnTe the formation of a DX center plays an important role despite some doubts and insufficient experimental support. A DX center has to be suspected wherever severe doping problems occur already at lower doses, like in acceptor-doped sulfides, and possibly also in selenides. It may also be indicative that in *n*-CdTe-based alloys the DX center becomes operative when compounds with highly positioned VBM (see Fig. 9) are added, i.e. MgSe, MgTe and ZnTe. Similarly, an AX center is activated in *p*-ZnSe when alloyed into ZnMgSSe, where both ZnS and MgSe have low-lying CBM. Evidently much additional experimental and theoretical work is needed before final conclusion is reached about the extent of various mechanisms and their relative importance in explaining ultimate doping limits.

Considering small number of clear cases, all general conclusions are inevitably somewhat speculative. Still we are tempted to conclude that in IIB-VI's the susceptibility to particular doping-limiting mechanism can be connected with relative size of constituent atoms (i.e. relative formation energies of native vacancies). It appears that in compounds having similarly sized atoms (CdTe and ZnSe; Fig. 2 or Fig. 11) the spontaneous formation of native defects (and A centers) is the prime cause of doping limits for most donor and acceptor dopants. For II-VI's having differently sized atoms, the doping on the 'easy' side (i.e. *p*-side for ZnTe and n-side for CdS, for example) seems to be limited by the formation of a new phase (solubility limit). For doping on 'difficult' side, the formation of a DX (AX) center is a prime suspect, although other mechanisms cannot be ruled out.

2.9. Common origin of doping-limiting mechanisms in IIB-VI compounds and alloys

In spite of differences among the mechanisms which de-activate dopants in specific dopant/II-VI combinations, they all stem from the common roots - from basic

Donors Dopants	**Doping-limiting mechanism**	**References**
CdTe:In	A center: $(In_{Cd}-V_{Cd})$ pairs	31, 154, 176, 173, 174, 175, 177
CdTe:In	DX center (for very high doses)	183, 213, 214
CdTe:I	A center: $(I_{Cd}-V_{Cd})$	178
CdTe:Cl	A center: $(Cl_{Cd}-V_{Cd})$ pairs	110
CdTe:Cl	DX center (for very high doses)	179, 185
n-CdTe	native defects (A center)	137
ZnSe:Cl	A center: $(Cl_{Cd}-V_{Zn})$ pairs	105, 133, 170
ZnSe:I	A center: $(I_{Cd}-V_{Zn})$ pairs	153
ZnSe:Ga	A center: $(Ga_{Cd}-V_{Zn})$ pairs	137, 171, 172
ZnSe:Ga	DX center	197
CdS:In	new phase (solubility)	46, 47, 156, 376
CdS:Ga	new phase (solubility)	376
CdS:Cl	new phase (solubility)	156
ZnTe:Al or Ga or In	DX center	183, 187
ZnTe:Cl	DX center	199, 205
n-CdMgTe		201, 202
n-CdZnTe		193, 196, 199
n-CdMnTe		200, 202, 203

Acceptors Dopants	**Doping-limiting mechanism**	**References**
CdTe:Li	auto-compensation, $(Li_{Cd}-Li_i)$ pairs	233, 234, 235
CdTe:Ag	auto-compensation, $(Ag_{Cd}-Agi_i)$ pairs	236, 237
p-CdTe	native defects (A center)	137
ZnSe:N	A center $(N_{Se}-V_{Se})$	65, 67, 75, 105, 118, 119, 121, 162,163
ZnSe:N	auto-compensation (N_i, N-N, N_2, .)	135,144, 145, 240
ZnSe:Li or Na	auto-compensation	69, 219, 222, 223, 245, 228, 227
same	solubility	127, 130, 250, 251
ZnSe:P or As	DX	180, 181
ZnTe	solubility, (Zn_3N_2)	128, 130, 137
p-ZnMgSSe	AX center	194, 204

TABLE IV. Well-documented mechanisms limiting doping of particular donors and acceptors in II-VI compounds thermodynamic requirements for minimum energy of the system. These requirements pose strong limitations on doping in equilibrium (and quasi-equilibrium) conditions, but also, to a lesser extent, in non-equilibrium conditions. In this section we will attempt to prove that the common origin of these basic thermodynamic requirements can be determined more specifically.

Figure 11 presents a summary of doping results of IIB-VI compounds and ternary IIB-VI alloys. Fig. 11.a refers to free carrier concentrations obtained by doping with donors, while Fig. 11.b refers to acceptors. Most successful doping obtained both under quasi-equilibrium conditions and under non-equilibrium conditions are presented. Cases of traditionally 'difficult' doping, where *p*-or *n*- doping was practically impossible to obtain under quasi-equilibrium conditions were included as well (full squares). The results are presented as a function of ratio R of atomic covalent radii of M and X constituents of each compound, just as in Fig. 2. Ratios for alloys were calculated using a mean value of the radius assuming linear extrapolation. The results for maximum *n*-doping obtained in IIB-VI compounds under conditions of thermodynamic quasi-equilibrium, as well as results of doping limits in alloys were fitted by the function:

$$n_{\max} = n_{\mathrm{o,max}} \cdot [1 - \exp(-\mathrm{A} \cdot \mathrm{R}^{\mathrm{B}})] + n_{\mathrm{background}} \qquad 2.9.1$$

where R denotes ratio of covalent radii, $\mathrm{R} = r_c(\mathrm{M})/r_c(\mathrm{X})$,either of a compound or an alloy, and A and B are parameters, fixed for all compounds/alloys. $n_{\mathrm{o,max}}$ denotes maximal concentration for any of the compounds obtained under optimal conditions, here selected as $10^{20}/\mathrm{cm}^3$, while $n_{\mathrm{background}}$ denotes the lowest value, ascribed, in fact, to situations where doping is not effective. In Fig. 11.a, $n_{\mathrm{background}}$ is (somewhat arbitrarily) chosen as $10^{15}/\mathrm{cm}^3$, just to avoid showing pointlessly low values obtained when doping is completely ineffective, which would the obscure meaningful range of *n* and *p* concentrations, from 10^{15}-$10^{16}/\mathrm{cm}^3$, (a background level) up to excellent doping ($10^{20}/\mathrm{cm}^3$ or even higher).

It is obvious that this very simple equation, with only one variable, describes reasonably well maximal electron concentrations obtained under different conditions. Especially taking into account that here collected data represent different growth techniques, dopants, optimizations, authors, etc. The fitting curve follows the variance of $n_{\max}$ along at least 4 orders of magnitude, and approximates equally well different $n_{\max}$ values for various compounds and alloys whose maximal equilibrium carrier concentrations are limited by supposedly very different mechanisms (self-compensation for CdTe and ZnSe, DX center for most of the ranges in ZnCdSe and CdZnTe alloys, solubility limit for CdS, ...).

A similarly simple relation appropriately describes *p*-doping limits:

$$p = p_{\mathrm{0,max}} \cdot \exp[-(\mathrm{C} \cdot \mathrm{R}^{\mathrm{D}})] + p_{\mathrm{background}} \qquad 2.9.2$$

where C and D are parameters, fixed for all compounds/alloys. It connects reasonably well the maximal attained hole concentrations in various compounds, where the conductivity once more has been limited by different mechanisms limiting *p*-doping.

Results suggest that all these mechanisms have a common denominator and possibly common origin. Some particularity of various mechanisms might be responsible for differences in the slope ranging from fully activated to more and more de-activated dopants.

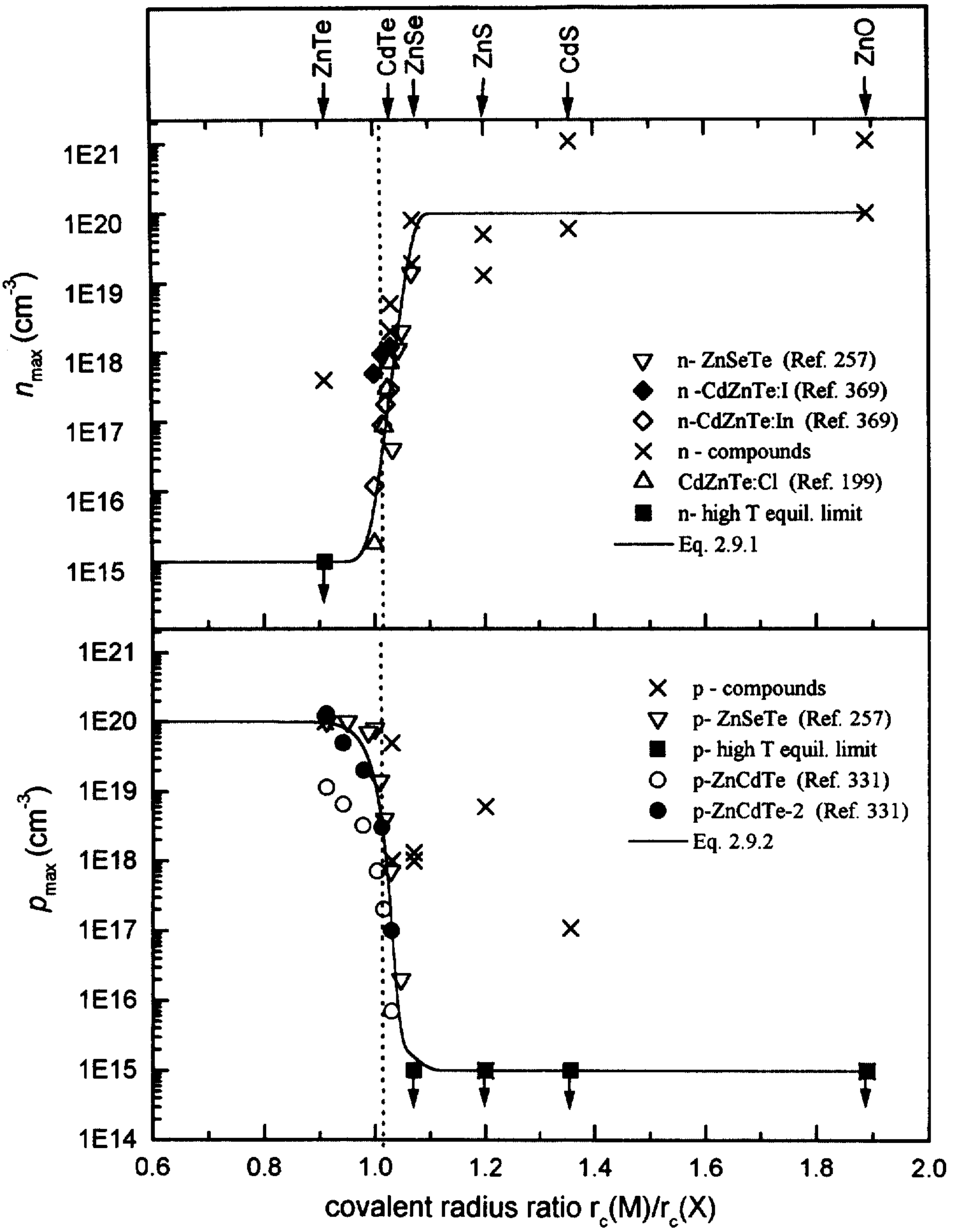


Figure 11. Maximum experimental free carrier concentrations achieved for doping with donors, n_{max}, and acceptors, p_{max}, in IIB-VI compounds and alloys obtained for growth/doping in the equilibrium and non-equilibrium conditions. Results are presented in a dependence on the relative atom (vacancy) size of each compound or alloy. The high T equilibrium limits (full squares with a downward pointed arrows) are also included in the Figure as 10^{15}/cm^{-3} values of n and p - for a discussion, see the text.

The relative size of atoms matters, as predicted by Van Vechten a long time ago[123], irrespective of the particular mechanism that limits dopability. The single variable in Eqs. 2.9.1 and 2.9.2, the ratio of atoms covalent radii, appears to be sufficient to describe and to predict *n*- and *p*-type dopability of IIB-VI compounds as well as their ternary alloys. As discussed in Section 2.1.1. the importance of the sizes of M and X atom lies in the fact that their size determines the sizes of their respective vacancies[281]. Since the formation energy of a vacancy is proportional to its size[123], the ratio of M to X atom radii, actually, determines the ratio of the formation energies for vacancies at M and X sites. It means that, according to the Eq. 2.1.3., the larger the ratio R, the larger is the ratio of concentrations of the donor-like native vacancies V_X to the acceptor-like native vacancies V_M, $[V_X]/[V_M]$. Experimental results presented in Figs. 11a and 11.b clearly demonstrate the importance of ratio R on dopability. Above discussion shows that the ratio $[V_X]/[V_M]$ is the factor that predominantly influences the success of dopability in IIB-VI binary or ternary compounds.

Furthermore, a glance at the Eq. 2.6.2. tells us that the relative positions of $E_{SI,n}$ and $E_{SI,p}$ will also depend, in essence, on the $[V_X]/[V_M]$ ratio, indicating that the dopability evaluated from the phenomenological model might be also connected to the ratio of M and X atomic (covalent) sizes.

This leads us to the conclusion that, although isolated native vacancies do not directly govern the electrical properties of IIB-VI's (Section 2.1.1), the relative easiness of formation of vacancies in one or the other sublattice bears a crucial significance. It determines the natural tendency of nominally 'undoped' crystal to have *p*- or *n*-type conductivity or both, and it is also very important in either helping or inhibiting the possibility of reaching very high doping levels in IIB-VI compounds and alloys.

3. EQUILIBRIUM AND NON-EQUILIBRIUM APPROACHES IN OBTAINING HIGHER AND MORE EFFICIENT DOPING

Since 'normal' doping in quasi-equilibrium conditions does not yield efficient doping due to reasons elaborated in Chapter 2, a number of different approaches has been devised. The presently 'best' doping results of these efforts were already presented in Fig. 11, while details and present status of dopability for each II-VI compound is presented in Chapter 4. Approaches that enabled these successes in overcoming doping difficulties, as well as some future prospects, are the subjects of this chapter.

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

An analysis of doping-limiting mechanisms, reviewed in Chapter 2 of this paper, reveals that different approaches have to be followed in order to avoid different mechanisms. Non-equilibrium growth/doping or processing seems particularly appropriate in reducing some, but not all, of these problems. A non-equilibrium approach appears to be excellent to minimize self-compensation, auto-compensation and problems related to the limited solubility, since manipulation at lower T reduces the formation of (potentially) compensating native defects, and supplies less thermal energy for the migration of dopants. Both factors reduce the probability of formation of self-compensating defects or the formation of a second phase, whichever happens to be thermodynamically most favorable. However, non-equilibrium processes are not expected to be similarly helpful in reducing probability of formation of a DX center, neither can they solve all problems caused by the 'softness' of the lattice, which allows the diffusivity of some defects and particular dopants already at RT.

3.1. Low-temperature methods of crystal growth and doping

A number of methods have been developed which enable the growth and doping in non-equilibrium conditions. So far, the best results in obtaining good *n*- and *p*- type dopability have been achieved now with molecular beam epitaxy (MBE)[282]. The method, extensively used in manufacturing of III-V epitaxial devices (including 3-5 million lasers/month for compact discs), have also proved to be very useful for the low-T growth of II-VI compounds. The first II-VI blue laser was produced by MBE(Ref. 5). Although even at temperatures used in MBE 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 a likelihood to mitigate restrains of thermodynamic equilibrium and to surpass the limitations it poses. The manipulations *via* chemical potentials in high-T treatments have in MBE been replaced by the manipulations with flux ratio of constituents, thus enabling better influence on the incorporation of dopant into desired lattice location.

I will start this short overview of MBE successes in doping of II-VI's with a classically 'difficult' case: *p*-type doping of ZnSe. The *p*-type conversion with MBE has been obtained with several dopants, nitrogen being the best. Up to $p = 1.2 \cdot 10^{18}/\mathrm{cm}^3$ has been achieved with practically full doping efficiency, using improved high-power plasma source, at growth temperature of 250 °C[239,283]. The high activation has been obtained thanks to the generation of predominantly atomic nitrogen in the plasma. Despite this relatively high *p*, the compensation was successfully kept at a very low level. Ratio p/[N], derived from parallel C-V and SIMS measurements, was close to 1, with high reproducibility. PL spectroscopy also confirmed low compensation, since I_1 line remained visible, and D^dDAP spectra showed still well resolved phonon spectra. The result established - at least at that doping level - that the self-compensation could be almost eliminated with optimally selected non-equilibrium conditions. The results also proved that the somewhat lower doping efficiency, *p*/[N]= 0.6, which was obtained earlier[238] was caused by auto-compensation (probably N_2 molecule) and not by the compensation with V_{Se}. The *p* level around $18^{18}/\mathrm{cm}^3$, but not substantially higher, was also obtained by several other groups'[160,161,246,284], but generally with a lower doping efficiency (i.e. higher [N]). Incorporation of N even above $10^{20}/\mathrm{cm}^3$ was achieved[142], but then with substantially lower doping efficiency (*p* again maximally in the $10^{18}/\mathrm{cm}^3$ range). Possible reasons for deactivation of N were discussed in Sections 2.1.4. and 2.3. MBE also produced the highest doping of ZnSe on *n*-side, with Cl as a dopant: *n* above $10^{20}/\mathrm{cm}^3$ was obtained by means of selective doping, and well above $10^{19}/\mathrm{cm}^3$ with non-selective doping[285]. n-ZnS was also successfully grown by MBE, with n above $10^{19}/cm^3$, using Al as a dopant. The highest reported p values in p-ZnTe were once again obtained with N dopant in MBE growth/doping, achieving $p = 1 \cdot 10^{20}/cm^3$ [206]. Instead of usual (100) surface, the growth was performed on (311)B plane. It was argued that the growth in this plane made more difficult for N atoms to migrate across the surface and produced N-N pairs, with the net result being higher nitrogen doping. Similarly high p-doping of ZnTe:N, were also obtained by several other groups, even without the substrate tilting[258,261,286]. MBE growth and doping with N also yielded the first successful conversion of CdSe to p-type conductivity with $p \approx 10^{17}/cm^3$ [74]. The shallow level with $E_A \approx 21\text{-}31$ above E_V was attributed to N. In CdTe, the maximum n-type doping was obtained with iodine, resulting in maximum electron concentrations of $5 \cdot 10^{18}/cm^3$ [178], while doping on p-side has resulted up to now in $p = 2\text{-}3 \cdot 10^{17}/cm^3$ for N doping[80,287]. Evidently, most of the efforts with MBE have been directed toward p-ZnSe (particularly with N as a dopant), while much less work has been done on other II-VI binary compounds. Finally, MBE has proven exceptionally successful in growing ternary and quaternary II-VI alloys[194,288], including those containing IIA constituents[14,16,257,260,262,289,290], whose importance and role is presented in the Section 3.4. Taking also into account the convenience of MBE for growing II-VI compounds, alloys, heterojuctions and multilayers which can be used to optimize band gap and lattice constant matching, MBE seems to be the most prospective method for the production of commercial II-VI based devices, including blue/green II-VI lasers. It will be so particularly once the doping limitations and other problems (like thermal stability at least around RT, good contacts, etc.) have been fully understood and put under control.

Blue laser diodes have been also obtained recently with somewhat less expensive growth methods like metalorganic vapor phase epitaxy (MOVPE), and metalorganic chemical vapor deposition (MOCVD). MOVPE has been commonly understood as a promising technique for fabrication of practical and high performance devices, but in contrast to MBE, it is still struggling to achieve reliable p-type doping[291-293]. Doping with P and As of ZnSe has resulted in compensated material, with characteristic D^dAP's in PL spectra[291]. Doping with Li or Na resulted in a substitutional incorporation of dopants and in the formation of shallow acceptors[231], but again the compensation was strong and a low $p \approx 10^{14}/cm^3$ was obtained[291]. In contrast, co-doping with Li and N *via* Li_3N, either by diffusion[291,294,295] or excimer laser doping[296] yielded hole concentrations of about $10^{18}/cm^3$. Due to the lack of appropriate precursors, doping with N requires higher temperatures to get rid of the co-incorporated hydrogen. This in turn interferes the general requirements for low-T growth. Photo-assisted MOVPE[297] can effectively lower the growth temperatures for ZnSe:N[293], still obtaining p close to $10^{18}/cm^3$, since the above-the-gap illumination during the growth changes the position of the Fermi level, thus reducing the formation of native defects[298,299]. It seems that N acceptors can also be activated by an electron beam, supposedly due to the destruction of H-N complexes followed by the removal of free H atoms from the epilayer[300]. However, as in other growth methods for ZnSe:N, it seems that for the present $p \approx 10^{18}/cm^3$ limit cannot be surpassed. In contrast to p-doping, MOVPE can produce a carrier concentration above $10^{19}/cm^3$ in n-ZnSe by doping with I[301], and other halogens, while doping with group III elements is more affected by compensation. MOVPE is successfully used to fabricate

ZnSe-based laser diode structures[291,302,303] and light emitting diodes[292]. Thanks to the progress in *p*-type doping, a successful device applications are expected in the near future[291].

MOCVD is also a very promising method for growing doped II-VI layers in non-equilibrium conditions. It can produce a very high *n*- doping of ZnSe, particularly with I, where n as high as $8 \cdot 10^{19}/\text{cm}^3$ was obtained[304]. It also succeeded in converting ZnSe into *p*-type with growth in the 330-480°C range, again by N as a dopant, but maximal obtained p was still only just above $10^{16}/\text{cm}^3$ [302].

3.2. Ion implantation

Ion implantation allows introduction of dopants at as low a temperature as desired. First type conversions were obtained by means of 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[305]. However, this method has two serious drawbacks. First, thermal processing to some moderate temperature is still needed (at least 400°C but usually higher) in order to anneal the implantation-induced damage. Secondly, implantation creates a lot of lattice defects, which can react with implanted atoms or between themselves and form relatively stable compensating defects. Recent study on Zn implanted ZnSe study showed that some point defects are mobile already at RT and that they migrate rapidly under ion implantation[306]. Cl doped ZnSe showed high level of compensation of Cl_{Se} donors, presumably with Cl_{Se}-V_{Zn} pairs, which are acceptors, as concluded from results of RBS, PIXE, Raman and electrical measurements[307].

A positive example of the usefulness of implantation towards increasing doping efficiency is a very high concentration of holes, up to the $p = 5 \cdot 10^{19}/\text{cm}^3$ (a maximum achieved till now by any method), obtained in CdTe by implantation of P and subsequently by pulsed electron beam annealing[308,309]. The sensitivity of the obtained results to the subtleties of annealing procedure is indicative: in several other studies the implantation of CdTe with P resulted in much lower p[310,311]. In CdS implanted with Indium[46,47] In atoms can be placed into a perfect donor site, In_{Cd} close to ~100%, up to concentrations of $[\text{In}] \approx 10^{20}/\text{cm}^3$, as determined by PAC. The doping efficiency could not be determined, however, since the substrate also become highly conductive under these annealing conditions.

In general, a better understanding of implantation induced disorder is needed in order to fully unleash potentials of this method.

3.3 Growth/doping by ultra-fast processes

Despite ever-improving trends and enormous advancements achieved by means of relatively low-T growth/doping techniques, the general trends in doping efficiency are still influenced to a certain degree by basic thermodynamic limitations (see Chapter 4 or Fig.11). This indicates that presently used non-equilibrium conditions may still be too close to the equilibrium ones.

Several original approaches have emerged recently, where unprecedentedly high doping was obtained by super-fast processes. For example, high-power lasers were applied in some cases of 'difficult' dopings, like *p*-doping of ZnSe[296] and *n*-doping of ZnTe[209]. The excimer UV lasers, such as ArF, KrF or XeCl are known in industrial use for surface modification. Since semiconductors have a very high absorption coefficient in UV range, light is absorbed only near the surface. As the pulse duration time is only 10-30 ns, the heated region is limited to 100 nm, or so. During the laser pulse the near-surface T is likely to exceed the melting point, followed by a very rapid re-crystallization. If a dopant material is put on the surface of the crystal, the dopant will be injected into the crystal during the laser irradiation process. The UV laser annealing technique was recently applied to ZnSe, after a layer of K_2S or Na_2Se was deposited on the ZnSe surface[312]. It appears that during the laser pulse K and Na were introduced at the Zn site. Resistivity decreased for 7 orders of magnitude and the hole concentration increased above $10^{19}/cm^3$. Although many details of this complicated process still have to be understood, the technique obviously has a potential at least for making contacts to the wide-gap materials. In a different technique, but with a similar goal, Nd-glass IR laser (wavelength 1.06 μm) was used to irradiate ZnTe crystal coated with Al film[208,209]. During a 20 ns pulse duration Al was injected into a *p*-ZnTe:P substrate (*p* close to $10^{17}/cm^3$). The electron concentration in the first ≈150 nm of the ZnTe crystal was measured to be above $10^{18}/cm^3$, with a *p-n* junction at 300 nm. A previously unknown band in electro-luminescence spectra was attributed to the radiative transition between Al donor and valence band. Again, it is too early to evaluate the full potential of the method.

Furthermore, *p*-type CdS films have been prepared by laser ablation using Nd:YAG laser. The beam of the laser was guided on the target, and the ablated material was deposited to the nearby glass substrate[72,313]. The target was made of a cold-pressed mixture of pure powders of CdS and Cu. The *p*-type conductivity is derived from PL spectroscopy, the ionization energy of the acceptor was found to be $E_A = 0.86$ eV, in accordance with the known Cu_{Cd} acceptor level 1.1-1.2 eV above E_V[314], and Cu content of 3% in the film. Obviously, much more research is needed to understand the process and to explore the possible applications in the preparation of solar cells and light emitting devices.

Laser ablation was also used to dope ZnTe films with nitrogen[315]. ZnTe films were grown on GaAs substrate by pulsed laser ablation of soichiometric ZnTe target in a high-purity N_2 ambient. Hole concentrations close to $10^{20}/cm^3$ were obtained, although the mechanism of doping is not clear.

All of these new approaches are obviously opening new and promising possibilities.

3.4 Reinforcement of the lattice in IIB-VI compounds

Several years ago Vèrié[316-318] conducted a thorough examination of the covalency/ionicity of all semiconductor materials and the relation of these parameters with lattice rigidity, i.e. with energies of formation of point defects and energies associated with creation of dislocations. He identified the shear modulus $C_s = (C_{11}-C_{12})/2$ as a simple indicator of lattice strength. Namely, C_s can be directly related to the formation energy of a vacancy in any tetrahedrally coordinated material through the equation[319]:

$$E_V = (1/5)\, C_s\, d^3 \qquad 3.4.1.$$

where d is the nearest-neighbor distance in the crystal.

Similarly, the energy of the creation of a unit length of dislocation has been also found to be directly proportional to C_s[317,320].

Following the bond orbital model (BOM) developed by Harrison[321,322] as well as a wealth of experimental data on C_s, Verie has shown that in a whole range of tetrahedrally coordinated structures (diamond-like, zinc blende and wurcite), C_s can be fairly well described by a semi-empirical law expressed as[318,323]:

$$C_s = e^2\,[1.715\,(\alpha_c)^3]\,/\,d^5 \qquad 3.4.2.$$

The covalency parameter, $(\alpha_c)^3$ derived from BOM in Harrisson's theory[321,322], linearly corresponds[318] to the Phillips's[324] covalency parameter. This relation covers the whole range of materials, from practically ionic crystals like AgI, CuCl, to fully covalent column-IV elements. A straightforward conclusion emerges from this relation: the higher the shear modulus is, the more rigid the lattice and less prone to formation of both point and linear defects. From the relation it is clear why the II-VI's have many more problems with defects creation and migration (and all the unwanted consequences) then the III-V compounds: short bonds and weak ionicity, generally lacking in IIB-VI compounds, are crucial for the lattice stability.

Relation 3.4.2. also gives the possibility to predict bond strength in new alloys. Analysis of data[318] shows that Be-VI compounds should exhibit strong covalencies and a stable zinc blende structure with short bonds (Be has a very small covalent radius, 0.975Å[325], leading to C_s values which are substantially higher than in ZnSe and other IIB-VI compounds). Thus Be-based bonding should substantially enhance the crystal elastic rigidity in (Be,IIB)-VI alloys. Contrary to Be, the Mg- based compounds, although Mg is also an element from the IIA column, have even lower C_s values than ZnSe, which might explain the problems observed in (Mg,IIb-VI) compounds, related to native defect creation/migration[275]. In addition, all IIA-VI compounds should have very large band gaps (although mostly still experimentally undetermined). Considering that BeSe and BeTe have a smaller lattice constant than GaAs and even smaller than Si, the possibilities for gap engineering and lattice engineering seem extraordinary.

All these optimistic theoretical prospects were, and in a great extent still are, contrasted to the almost unexisting knowledge of basic material properties of IIA-VI's. Even the question of the band gap character (direct or indirect) is still open. BeTe has been the first and for long time the only one to be obtained in a single crystalline form[326]. With prospects of such exquisite properties, however, this situation is changing rapidly. Very recently BeSe[288] and ZnBeSe[327,289] have also been produced as single crystals. Measurements of Vickers microhardness, MH, confirmed that MH increases with Be content in ZnBeSe, as well as the band gap E_g, (from the absorption measurements). MH actually almost tripled when the Be fraction was increased from 0 to 17%. Binding energies were calculated to be high in Be-VI's[290], in fact higher than in GaAs, and comparable to Si (as well as to GaN). Experimentally, the high bond energy was demonstrated by measuring desorption (change in growth rate) in vacuum as a function of substrate temperature[290].

Particularly systematic efforts were directed toward growth, (almost exclusively with MBE) and characterization of structures important in laser-diode devices[14,16,288,290,327]. Be alloys promise important improvements in all elements of an opto-electronic device. Starting from a *p*-contact side (on GaAs) of a ZnSe-based laser diode structure: BeTe/ZnSe seems to be superior to ZnTe/ZnSe for the graded lattice-matched *p*-contact[14,290,328], since BeTe has a much lower lattice mismatch with GaAs than ZnTe, and still has excellent *p*-type dopability (*p* above $10^{20}/cm^3$) and a small valence band offset. Furthermore, BeTe seems to be an ideal candidate as a buffer layer to passivate the GaAs surface by blocking the reaction of Se and S with GaAs. BeTe can also be used to correct lattice matching to GaAs of ZnSeTe or ZnMgSeTe cladding layers. Namely, ZnTe is used in cladding layers to increase *p*-doping, but its presence increases the mismatch as well. Quaternary (BeMgZn)Se has also been grown with excellent quality[14] (the rocking curve width was only 17 arcsec., which is at the theoretical limit). Strongly doped both *n*- and *p*-BeZnSe have been grown on GaAs substrate with high structural perfection[14,327]. Recently, the growth of a BeZnSe layer was realized on a Si(001) surface as well[288]. Finally, bearing in mind the active region of the laser diode, BeZnCdSe quantum well and several other structures - ZnCdSe QW, BeZnSeTe epilayer and BeTe/ZnSe superlattice - have been successfully grown[290]. Although only the feasibility studies and basic characterization were done up to now, practically without any optimizations, results are very encouraging. The first Be-containing light emitting diode had an extrapolated half-life of 4,000 h at moderate current densities ($15 A/cm^2$) [290]. The first Be-containing laser diode was reported at the end of 1997[329] and a laser diode having a lifetime of 57 h under CW operation at RT was announced[329] to be reported soon. There is a worldwide activity in this field and fast progress in various directions. Considering the very optimistic theoretical predictions and excellent realization of these prediction till now, the considerably reinforced II-VI lattice and better protection from uncontrolled activities of native defects - as well as practical benefits from that - seem to be within reach.

3.5. Effects of co-doping and indirect doping

3.5.1 Co-doping with two different dopants

Effects of co-doping with more than one specie in order to obtain higher free carrier concentration have not yet been systematically investigated, but there are both theoretical arguments as well as some (although very limited) experimental indications that co-doping could result in an increase of dopant concentrations. First, there are conceptual arguments that the 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 replaced host atom. Co-doping with two atoms of different sizes (e.g. Na and Li at M site in ZnSe), one larger and the other smaller than the host atom, might counterbalance the size mismatch and be beneficial (in comparison with single-specie doping) in reducing total strain in the lattice. It seems even more favorable if these two dopants, with larger/smaller sizes than the host atoms, would be co-doped into different lattice sites (e.g. Na at M and N at X sites in ZnSe). In this case, besides the size compensation effect, the co-doping at opposite lattice sites should reduce the drive for the departure from stoichiometry, which becomes stronger as the concentrations are higher and which introduces native defects in large concentrations[127,137].

There are only a few experiments on that subject. For example, the diffusion of the

Li_3N into ZnSe layer[294,295] resulted in hole concentrations of up to $10^{18}/cm^3$, - a range of p which is otherwise difficult to obtain with N and close to impossible with Li. Obviously co-doping with two different acceptors (Li_{Zn} and N_{Se}), in opposite sublattices resulted in the increased p-dopability. Best results were obtained with lower-T diffusion of Li_3N (470°C), while at higher diffusion temperatures p decreases – most likely Li atoms started to occupy the donor-like interstitial site as well[62,219,235], as discussed in section 2.3. SIMS analysis of Li and N profiles after different annealing times, showed that Li and N atoms diffuse in cooperation, each helping the lattice incorporation of the other. It is seems as if the substitutional Li somehow - probably through local strain effects - stabilizes the substitutional configuration of N and *vice versa*[183]. The use of Na instead of Li would perhaps be even more effective, considering that the Na atom is larger and possibly would be less prone to convert into an interstitial position. In another experiment[379], ZnSe epitaxial layers were grown by photo-assisted MOVPE with co-doping of cadmium and chlorine. Although Cd is an isoelectronic atom in II-VI's, the cadmium co-doping consistently enhanced the incorporation of Cl donors when compared with control samples, which were not co-doped with Cd. This effect was explained by the concept of a tetrahedral misfit. Since Cd has a larger covalent radius than Zn, the resulted strain makes the incorporation of a Cl atom, which has a smaller covalent radius than Te, energetically more favorable. Essentially, the local mutual compensation of misfit strain apparently resulted in lower free energy of the system, so that the incorporation of Cl was increased. In another attempt, the co-doping of ZnSe with acceptor N and isoelectronic Te was also performed[247], having in mind better solubility of N in ZnTe than in ZnSe[127,247]. The increase of total N concentration was indeed achieved, as detected by SIMS. However, the goal of increasing free hole concentration was not reached in this particular case, since some (unidentified) compensating donors were introduced as well. Furthermore, an analysis of the difference in p-type dopability of ZnTe and CdTe might be helpful for the assessment of potentials of co-doping. While ZnTe can be easily p-doped as high as $10^{20}/cm^3$, the dopability in p-CdTe is typically 2-3 orders of magnitude lower[330,331]. In p-ZnCdTe:N alloys even a small fraction of Zn dramatically increases p[331]. It seems that the presence of Zn atoms stabilizes the substitutional N_{Te} configuration and/or increases its solubility. One can compare the near-neighbor distances: the CdTe bond length is 2.81 Å[325], while that of Cd-N is only 2.10 Å, which should induce strong local strain in the lattice. In contrast, the Zn-Te bond length is shorter (2.62 Å) hence the presence of the Zn atom should lower the local strain. Thus, the higher the number of Zn atoms in the nearest neighbor position, the lower the energy of substitutional configuration of nitrogen. From these examples it is apparent that the fine balance in the immediate vicinity of the dopant atom is crucial, and that matching the sizes is one of the most important factors, - a conclusion which radiates also from Fig. 11 and the discussion in Section 2.9.

In addition, there are also several more subtle examples of unintended co-doping. The first successful strong n-type doping of bulk ZnSe was obtained by the use of excess Zn during the growth, doping or annealing(*e.g.* Ref. 332). It was shown later 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 gettering into the excess Zinc[219,245,332]. Namely, the presence of oppositely charged atoms/defects increases the solubility of the desired dopant. A similar effect seems to have happened in the famous breakthrough success of *p*-doping of GaN with Mg. The high-enough solubility of Mg was obtained thanks to parallel (unintentional) incorporation of H during MOCVD growth. When H was removed by post-growth annealing[333], Mg remained 'frozen' in the lattice, not being sufficiently mobile to out-diffuse. The first *intentional* attempt to use co-doping with fast-slow diffusing species was the use of the amphoteric dopant Li in ZnSe[250]. The Li doped crystal was heated to high T (where electrically neutral (Li_{Zn}-Li_i) pairs are expected to form), and then quenched, in the hope that the more mobile Li_i would out-diffuse first, leaving Li_{Zn} acceptors uncompensated. Quenching indeed changed resistivity for several orders of magnitude, but type conversion to *p*-ZnSe was not obtained. Apparently not only Li_i but also Li_{Zn} atoms were mobile at higher T. Anther attempt[334] involved MOCVD grown ZnSe:N, in which N_{se} is presumably compensated with H (from NH_3 precursor). An excimer laser was used for an ultra-fast annealing of the sample surface. It was expected that H has higher diffusivity (ionic mobility) than N, and that H could be removed preferentially. More than 90% of H was indeed removed (judging from the observed de-compensation of acceptors N_{Se}) with 20 sec.-long pulses, but not all. It was concluded that the pulse length was too short, so that part of the N and H atoms remained close enough to re-bond after re-solidification.

The concept of co-doping recently received a strong theoretical support[335]. Based on *ab-inito* calculations of the electronic band structure the co-doping with *n*- and *p*-dopants (in unequal concentrations) was proposed. Calculations were concentrated on the changes of electrostatic energy, called Madelung energy, (ME), caused by the incorporation of various dopants. Specifically, N doping of ZnSe causes a shift of N 2p and Se 4p orbitals toward higher energy regions. This leads to de-stabilization of ionic charge distribution in *p*-ZnSe, which pushes nitrogen to preferentially adopt the interstitial sites at high-enough concentrations. The similar increase of ME and the same destabilization was calculated to occur in Li doped *p*-ZnSe. Conversely, calculations predicted the decrease of ME for Al, Ga or In doped *n*-ZnSe. In particular, doping with In leads to an exceptionally large decrease of ME due to the strong interaction between In 5s and Se 4p states. Hence, the co-doping of N and In (in a small controlled quantity) should be advantageous for the stabilization of the ionic charge distribution and would enable the increase of net *p*-type carrier density in comparison with simple *p*-doping. The analogous calculations where done for some other semiconductors, including GaN[336], leading to similar recommendations for improving the dopability. The recently reported successful *p*-type doping of GaN by co-doping with Be and O[337] coincides well with these calculations. It would be interesting to calculate the influence of other combinations analyzed in the previous two paragraphs (co-doping with two acceptors at the same or different lattice sites, or with a dopant and an isoelectronic atom, etc.) on ME and on the destabilization of ionic charge distribution and dopability.

3.5.2 Indirect doping

Indirect doping presumes the use of a radioactive isotope for doping, so that the time of incorporation of the dopant can be separated from the time when the dopant attains its desirable electrical activity. The concept was proposed with the idea to trick the self-compensation and achieve *p*-doping of GaN[338] by using small fraction of ^{67}Ga isotope instead of stable Ga. The introduction of ^{67}Ga during growth, or doping of GaN would not provoke any self-compensating reaction of the crystal. However, after the decay of ^{67}Ga to ^{67}Zn, new acceptors would be created which would remain uncompensated, since RT does not provide enough thermal energy for the generation of new compensating donors. At the time it was proposed, the 'indirect doping' could not be proven, since considerable isotope activity is needed for bulk doping. However, for doping structures as small as QW radioactive activity would be acceptably small[339]. Another version of 'indirect doping' includes co-doping with two oppositely charged dopants, one of them being a temporary dopant[122,338,340]. Radioactive atoms, selected to have the opposite charge than the desired dopants, would cause temporary electrical neutralization, eliminating the need for the formation of compensating native defects during the critical time at high T, during growth and/or doping. An example of such a temporary dopant is ^{111}In, which is donor in II-VI's, but after decaying to ^{111}Cd (lifetime 2.8 days) becomes just an ordinary host atom in Cd-VI compounds or an isoelectronic atom in Zn-II's. *p*-doping of CdS, for example[340], would be obtained by co-doping of ^{111}In and an acceptor (Na, Li or N) which would, during growth or thermal treatment, compensate each other (and also mutually ensure higher solubility). After decay temporary donors would become just ordinary host atoms, while acceptors would remain uncompensated. Indirect doping should be equally applicable for other 'difficult' dopings.

The concept of 'indirect doping' was recently confirmed experimentally[341,342]. Radioactive ^{107}Cd was implanted into CdTe. It acted as a host atom during high-T treatment (annealing of implantation-induced damage), but transformed into an acceptor after decay into a stable Ag isotope. Since compensated vacancies were not formed, practically 100% doping efficiency was obtained. In contrast, the implantation directly with Ag resulted in compensation already during implantation at RT. Similarly, the doping of *p*-ZnTe with radioactive ^{115}Cd (which decays into a stable In isotope) resulted in ≈ 100% efficiency doping with In, although the dose was not high enough to obtain conversion to *n*-ZnTe[342].

Furthermore, the 'indirect doping' idea can be used for positive identification of a signal (in practically any method) which is suspected to belong to a donor-acceptor pair. Namely, the isotope-related signal changes in time in a predictable way determined by the radioactive-atom decay. The feasibility of this concept was recently demonstrated in GaAs[88], where radioactive ^{111}In were used. During its decay to ^{111}Cd all those PL peaks increased in which Cd acceptors were involved. Similarly, in CdTe the $^{107}\mathrm{Cd}\rightarrow\mathrm{Ag}$-related increase of *p* enabled the identification of the $\mathrm{Ag_{Cd}}$ shallow level[341,343].

Very little of the abundance of interesting possibilities which co-doping offers was adequately explored hitherto, neither on the theoretical nor experimental level. Co-doping is particularly interesting since it also addresses the problem of local lattice strains and lattice relaxation. Hence it could possibly prevent the formation of DX (AX) centers. - a doping-limiting mechanism which seemingly cannot be remedied by non-equilibrium dopant incorporation.

4. PRESENT STATUS OF DOPABILITY OF II-VI COMPOUNDS

4.1. ZnSe

Both group VII halogenides and group III metals can be used to obtain very high *n*-doping of ZnSe. The highest *n* in ZnSe was obtained up to now with I, (with MOCVD), up to $8.2\cdot10^{19}$/cm^3(304), but values well above10^{19}/cm^3 were also obtained with MOVPE[301], as well as with MBE[344]. Extremely high *n* values were also obtained with Cl, where *n* above10^{20}/cm^3 was obtained with MBE selective doping, and above 10^{19}/cm^3, with non-selective doping[285]. Other authors have also successfully realized Cl doping with *n* above 10^{19}/cm^3, some by MBE[258], others with Hot-Wall Epitaxy[345].

High *n*-type conductivity was also obtained with In and particularly Al doping[346].

As elaborated in section 2.1.4., the best *p*-doping at present has been obtained with N, where $p \approx 10^{18}$/cm^3 was reported by a number of authors[214,239,283,347-349]. Li was the first dopant to yield reproducible *p*-doping of ZnSe[220,350], although not at a satisfactory high level. Li yielded *p* doping typically around $(1\text{-}2)\cdot10^{17}$/cm^3(223,351), or lower (*e.g.* Ref. 5. The problem with Li is its tendency toward auto-compensation (section 2.3.), not very high solubility (section 2.4.) and high diffusivity, even at relatively low temperatures. For example, the uniform distribution of Li was observed (by SIMS) in epitaxial films, even when they were delta-doped with Li[350]. Electro-migration of Li was observed as well[351]. The best Na doping of ZnSe was obtained with liquid phase epitaxy from a Se solution under controlled Zn vapor pressure, ($p_{max} \cong 10^{18}$cm^3), with Na_2Se as a dopant[352]. Co-doping of Li and N also yielded *p* at 10^{18}cm^3 or even slightly above[294,295].Other *p*-dopants produce a substantially lower *p* at present[352]. However, one has to be aware that N has quite a deep level in ZnSe. Should one succeed to incorporate *e.g.* P, which has a shallower level (Table 3), into a ZnSe lattice at the same concentration level as N - and without self-compensation - the *p*-type conductivity could be substantially better.

As mentioned in the introduction, successful *p*-doping of ZnSe prompted a flurry of activities aimed at applications, and the first[5] and presently the longest living blue-green laser diodes[7] are based on ZnSe.

4.2. ZnTe

In contrast to other IIB-VI's, in ZnTe it was impossible to obtain *n*-doping for a long time. Attempts to diffuse any expected donor would, at best, end up in a very highly resistive material. As elaborated in Chapter 2, a number of mechanisms - self-compensation[92], insufficient solubility[219] and formation of DX center[187,216] - were invoked to explain the lack of success. Non-equilibrium doping during growth at relatively low temperatures changed that considerably. The first *n*-type doping of ZnTe with electron concentrations reaching $3\cdot10^{16}$/cm^3 was obtained by MBE growth at 260°C with Cl doping using a $ZnCl_2$ effusion cell[206]. An interesting aspect of that experiment is that for low Zn/Cl ratios of beam fluxes, ZnTe remained *p*-type despite Cl doping. By increasing the Zn/Cl ratio, ZnTe became *n*-type, and with even further increase of Zn/Cl ratio electron concentration grew. The increase of *n* was attributed to an increase of Cl atoms occupying tellurium sites. Considerable sensibility to stoichiometry manipulation *via* the change of Zn/Te flux ratio perhaps indicates that the uncontrolled concentration of compensating V_{Zn} might be the main cause of doping problems in *n*-ZnTe, rather than formation of DX centers or limited solubility. Even higher *n*-doping was obtained by group III atom doping into M site, using Al as a dopant during MOVPE growth[207]. *n*-type ZnTe layers with an electron concentration in a range of $1\text{-}4\cdot10^{17}/\text{cm}^3$ and a resistivity as low as 0.1-0.3 Ω·cm have been obtained. It has been indicated by the PL measurement that Al was incorporated in the epitaxial layer. In particular, no Zn vacancy-related peak (2.369 eV) could be detected and the 2.15 eV band due to a transition between Al_{Zn} and (Al_{Zn}-V_{Zn}) pairs, which would indicate compensation, was relatively weak. The decrease of compensation of Al dopants was also observed in Al doped ZnTe grown by MOVPE, particularly at lower substrate temperature, but conversion to *n*-type was not achieved[353]. Al doping up to $n \approx 10^{18}/\text{cm}^3$ was obtained using a laser-doping technique (section 3.3), in which Al atoms were injected and incorporated into ZnTe lattice, apparently without compensation[208,209].

In contrast to numerous problems with *n*-type doping, ZnTe is naturally *p*-type. In MBE growth using nitrogen plasma, hole concentrations of up to at least $10^{19}/\text{cm}^3$ were obtained[247,354,355], but more often up to $\approx 1\cdot10^{20}/\text{cm}^3$ [206,258,261,286,330,331]. Comparison of N doping of ZnTe and ZnSe showed much higher solubility of N in ZnTe[247], in accordance with theoretical predictions[128,131]. These calculations predicted a lower incorporation energy of N into ZnTe (0.27 eV)[131] than into ZnSe (0.38 eV)[130] (see also sections 2.4. and 3.5.). *n*- and *p*-doping of ZnTe enabled fabrication of first ZnTe p-n junctions[209].

4.3. CdTe

Maximum *n*-type doping reported to date has been $n = 5\cdot10^{18}/\text{cm}^3$ [178]. It was achieved in MOCVD growth with iodine as a dopant. Indium doping resulted hitherto in *n* not higher than $2\cdot10^{18}/\text{cm}^3$ [173] or close to this value[175]. Hence the non-equilibrium methods haven't yet delivered much of an improvement over quasi-equilibrium (high-T+quenching) processing, where similar values were obtained. For example, a full ≈100% activation of In was obtained for In content $2\cdot10^{18}/\text{cm}^3$ [356]. In several other studies the doping of CdTe with In resulted in $n = 1\text{-}\ 3\cdot10^{18}/\text{cm}^3$ [155,176], while diffusion of Cl resulted in slightly lower *n*, in accordance with the estimated solubility of Cl of about $10^{18}/\text{cm}^3$ at processing temperature (800°C)[156].

As already mentioned, the highest *p*-doping was obtained with implantation of P and pulsed electron beam annealing[308], with *p* up to $5\cdot10^{19}/\text{cm}^3$. *p*-doping obtained during growth is at present much lower, with hole concentration up to $10^{18}/\text{cm}^3$, obtained for doping with N. However, typically even lower values are reported, $p = 1\text{-}3\cdot10^{17}/\text{cm}^3$, also for doping with N[80,287,330], and one order of magnitude lower for As doping[80]. In doping with P under high-T equilibrium conditions, hole concentrations of up to $3\cdot10^{17}/\text{cm}^3$ were obtained[357].

The most efficient solar cells till now (16% efficiency) were produced by depositing *p*-CdTe, by close-space sublimation technique, on *n*-CdS, which was obtained by MOCVD[1]. Both techniques are considered cost-effective and easily scaleable.

4.4. CdS

CdS is naturally n-type and extremely high electron concentrations were readily attainable. The highest *n* reported was as high as $10^{21}/\text{cm}^3$ [263,358], but values of *n* of about $10^{20}/\text{cm}^3$ are more common[155-158]. Indium doping by high-T diffusion resulted in $n =$

$6\cdot10^{19}/cm^3$, in excellent agreement with In concentration, limited by the In solubility at processing temperatures[156]. Doping with Cl and Br can also ensure doping above $10^{19}/cm^3$, if compensation is prevented, by processing under conditions of high chemical potential of Cd. The obtained n coincides roughly with the solubility of these dopants, indicating that it is the solubility which finally limits the doping, just as with In[156].

p-doping was traditionally assumed to be hampered by the formation of compensating V_{Se} acceptors. However, it has been found that at very high concentrations of Cu (order of 1% or more) - if it is somehow successfully introduced into the CdS - results in the conversion into p-type[72,359-362]. Although Cu_{Cd} is an acceptor in CdS[314], the microscopic mechanism of doping is not clear, since the p is orders of magnitude lower than the Cu content, and there is no evidence of a formation of a Cu-related second phase[359,362].

4.5. CdSe and ZnS

CdSe and particularly ZnS received much less attention than other II-VI's, except when being a part of ternary or quaternary alloys. They were traditionally considered n-dopable but not p- dopable, just as CdS and ZnSe. Growth under non-equilibrium conditions and with improved control over stoichiometry changed this perception for these compounds as well. p concentration in ZnS as high as $8\cdot10^{18}/cm^3$ was achieved[363]. On the n-side, Al-doped ZnS grown by MBE resulted with n higher than $10^{19}/cm^3$ [263,364].

p-CdSe with a hole concentration of $10^{17}/cm^3$ was obtained for the first time using MBE and N plasma source[74]. It is deduced from PL measurements that the ionization energy of the shallow acceptor is 21-31 meV above the E_V. On the n-side, electron concentration in the range of $10^{19}/cm^3$ was achieved[269,365]. The detailed investigation was not done yet for any of these dopant/II-VI's combinations, which would reveal the microscopic mechanism which finally enabled successful doping, nor the mechanism(s) which ultimately limited doping to reach even higher levels.

n-CdSe has been used to form a heterojunction with p-CdS(Cu) having solar cells in mind[359]. Light emitters in the visible range of the spectra were successfully realized using n-CdSe and p-ZnTe to form heterojunction structures[286,366]

4.6. IIA-VI compounds

IIA-VI compounds tend to be p-type, but their doping properties still have to be studied in detail. For BeTe it was proven that it can be heavily doped using plasma activated nitrogen, up to $p = 10^{18}/cm^3$, as determined by means of the Hall effect and IR reflection[14].

5. SUMMARY AND CONCLUSIONS

Revived interest for II-VI compounds in this decade inspired numerous theoretical and experimental studies of these materials leading to the identification of doping problems which are responsible for the low applicability of these materials, which is still far bellow their potential. Specifically, these problems are:

- self-compensation by spontaneously generated native defects having opposite charge than dopants, particularly by making compensating pairs with dopants (A centers),

- auto-compensation by some dopants, in particular light dopants like Li, Na, N, etc.,

- self-compensation caused by strong relaxation of the lattice around some doping atoms resulting in the breakage of bonds with host atoms and formation of deep levels,

- the problems with insufficient solubility, resulting in the inadequately high concentration of many dopants,

- the insufficiently shallow level of some dopants, which makes them only partly ionized at RT.

The relative size of atoms in IIb-VI compounds (which translates in preference to form relatively more vacancies in M or X sublattice) was found as a common underlying factor irrespective of the mechanism which actually limits doping in particular dopant/compound combination.

In addition, insufficient rigidity of the lattice in IIB-VI's (as compared to III-V's), which results in higher self-diffusion of host atoms, dopants and native defects, and a lower formation energy for both point defects and dislocations, makes most of the identified doping-limiting mechanisms more effective.

Although there is no consensus yet about the relative importance of these doping-limiting mechanisms, it has become clear that the question of successful doping of the II-VI compounds is indeed a very difficult one, since almost all of the potentially ‘good’ dopants have one or several serious drawbacks.

However, the greatly extended theoretical and practical understanding of the mechanisms that cause doping problems is opening ways toward their solution. A number of possibilities to reduce or circumvent doping problems, including some new ideas, were discussed and analyzed:

- Doping in non-equilibrium conditions, far enough from the thermodynamic equilibrium, proved to be particularly successful. Kinetic processes then prevail, so that limits given by equilibrium requirements can be (at least partly) surpassed. The doping/growth at low temperatures, particularly using MBE, but also MOVPE and MOVCD (and some other growth/doping techniques in particular cases) showed excellent results. They also offer better control over stoichiometry, through the external manipulation of component beam fluxes. With these techniques all II-VI compounds can now be doped both from *n*- and *p*-sides, although not always up to technologically satisfying levels.

- Ion implantation also succeeded in obtaining exceptionally high doping levels in some cases.

- Several ultra-fast processes, like laser doping or laser ablation also yielded some excellent doping results. The impact and the possibilities of these recently developed techniques are still difficult to judge.

- Recent inclusion of little known Be-VI compounds into II-VI alloys, brought the much-needed reinforcement of the II-VI lattice, reducing problems related with the 'soft' lattices of IIb-VI compounds, and ensuring better protection from uncontrolled activities of native defects. Since Be-VI compounds also have a large band gap and a small lattice constant, excellent possibilities for both gap engineering and lattice engineering were opened. Considering the very optimistic theoretical predictions, and excellent realization of these predictions, many applications, including the realization of a green-blue laser diode with long lifetime seems realistic in the near future.

- Co-doping with different sized atoms or co-doping into both lattice sites can increase dopability, which was recently proven experimentally. It might also be the only method which can prevent formation of DX center, since such doping should reduce internal strains around doping atoms - the question generally not addressed with non-equilibrium methods.
- 'Indirect doping' method, where radioactive dopants change their electrical activity only after transmutation, tricking the compensation or even using it to increase solubility. This idea although proposed a long time ago, only recently got the experimental confirmation.

Numerous recent successes and the fast improvement of dopability achieved with the above approaches seem to announce a much wider applications of II-VI compounds in the near future, in accordance with the huge technological potential of these materials.

REFERENCES

1. T. Aramoto, S. Kumazawa, H. Higuchi, T. Arita, S. Shibutani, T. Nishio, J. Nakajima, M. Tsuji, A. Hanafusa, T Hibini, K. Omura, H. Ohyama and M. Murozono, *Jpn. J. Appl. Phys.* 36, 6304 (1997).
2. Final Report of '*Thin Film Solar Cell Study*' for 'MUSICFM' APAS RENA CT94) 8, Oct. (1996)
3. W. Fashinger, W. Spahn, J. Nürnberger, A. Gerhard, M. Korn, K. Schüll, D. Albert, H. Reis, R. Ebel, R. Schmit, B. Olszowi, M. Ehinger and G. Landwehr, *phys. stat. sol.* (b) 202, 695 (1997).
4. A. Gerhard, J. Nürnberger, K. Schüll, V. Hock, C. Schumacher, M. Ehinger and W. Fashinger, *J. Cryst. Growth,* 184/185, 1319 (1998).
5. M. A. Haase, J. Qiu, J.M. Depydt and H. Cheng, *J. Appl. Phys.* 59, 1272 (1991).
6. S. Itoh, H. Okuyama, S. Matsumoto, N. Nakayama, T. Otaha, T. Miyajma, A. Ishibashi and K. Akimoto, *Electron. Lett.* 29, 766 (1993).
7. S. Taniguchi, T. Hino, S. Itoh, K. Nakano, N. Nakayama, A. Ishibashi and M. Ikeda, *Electron. Lett.* 32, 552 (1966).
8 K.W. Haberem, P.F. Baude, S.J. Flamholtz; M. Buijs, J.J. Horikx; K.K. Law, M.A. Haase; T.J. Miller; G.M. Haugen, *Proc. SPIE - Int. Soc. Opt. Eng.* 3001, 101 (1997).
9. The initial dark spots - held to be responsible for laser degradation- are believed to be connected with stacking faults, where these intersect active area of the laser. During the laser operation these defects become mobile (their mobility enhanced by the electron-hole recombination) and create first the dark lines and then the dark patches until overall laser failure occurs (Refs.[10,11,12]). Still, it has been shown recently, that this explanation was not sufficient to explain laser degradation. When a laser was fabricated with a very small density of pre-existing structural defects[13], a degradation (albeit much slower) still occured, and after aprox. 350 h of operation rapid ('chatastrofic') degradation occured in few hours. No characteristic dark patches (characteristic feature in a material which before the laser illumination had a high stacking fault density) were present in this improved material, which indicates that the active layer degraded through some other mechanisms. They include recombination enhanced defect generation and/or recombination enhanced defect reaction, i.e. processes which are not related to the extended crystalline defects, but probably to the point defects.
10. J. Petruzello, K.W. Haberem, S.P. Herko, T. Marshall, J.M. Gaines, S. Guha G.D. U'Ren and G.M. Haugen, *J. Cryst. Growth* 159, 373 (1996).
11. G.M. Haugen, S. Guha, H. Cheng, J.M. Depydt, M.A. Haase, G.E. Höfler, J. Qui and B.J. Wu, *Appl. Phys. Lett.* 66, 358 (1995).
12. M. Hovinen, J. Ding, A.W. Nurmikko, G.C.Hua, D.C.Grillo, L. He, J. Han and R.L. Gunshor, *Appl. Phys. Lett.* 66, 2013 (1995).
13. Y.K. Song, A.V. Nurmikko, C.-C. Chu, J. Han, T.B. Ng and R.L. Gunshor, *Electron. Lett.* 32,

1829 (1996)

14. A. Waag, Th. Litz, F. Fisher, H.-J. Lugauer, T. Baron, K. Schüll, U. Zehnder, T. Gerhard, U. Lunz, M. Keim, G. Reuscher and G. Landwehr, *J. Cryst. Growth* 184/185, 1 (1998).
15. S. Nakamura, *Phys. World*, Feb., pp. 31 (1998).
16. G. Landwehr, F. Fisher, T. Baron, T. Lutz, A. Waag, K. Schüll, H. Lugauer, T. Gerhard, M. Keim and U. Lunz, *phys. stat. sol. (b)* 202, 645 (1997).
17. G.F. Neumark, *Mat. Sci. Eng.* R21, 1 (1997).
18. J. Bourgoin, M. Lannoo, *Point Defects in Semiconductors*, Ed. , Springer-Verlag, (1992).
19. R.S. Title, Paramagnetic resonance studies, in: *Physics and Chemistry of II-VI Compounds*, Eds. M. Aven and J.S. Prener, North-Holland, Amsterdam, (1967).
20. J. Schneider, in *II-VI Semiconducting Compounds*, ed. D.G. Thomas, W.A. Benjamin, New York, pp. 40 (1967).
21. G.D. Watkins, *Lattice Defects in II-VI compounds*, In *Inst. Phys. Conf. Ser. 31*, London, (1977)
22. G.D. Watkins, *J. Cryst. Growth* 159, 338 (1996).
23. J.W. Allen, *Semicond. Sci. Technol.* 10, 1049 (1995).
24. B.K. Meyer and W. Stadler, *J. Cryst. Growth* 161, 119 (1996).
25. W. Jantsch and G. Hendorfer, *J. Cryst. Growth* 101, 404 (1990)
26. B.C. Cavenett, *Adv. in Phys.* 30, 475 (1981).
27. J.-M. Spaeth, J.R. Niklas, R.H. Bartram, *Structural Analysis of Point defects in Solids*, Solid State Sciences 43, Ed. by H.J. Queisser, Springer-Verlag (1992).
28. F. Plazaola, A.P. Seitsonen, M.J. Puska, *J. Phys.: Condens. Matter* 6, 8809 (1994).
29. S. Dannefaer, *J. Phys. C: Solid State Phys.* 15, 999 (1982).
30. R. Pareja, R.M. de la Cruz and P. Moser, *J. Phys. Condens. Matter* 4, 7153 (1992).
31. H. Kauppinen, L. Baroux, K. Saarinen, C. Corbel and P. Hautojärvi, *J. Phys.: Condens. Matter* 9, 5495 (1997).
32. R. Krause, A. Klimanov, F. Kiessling, A. Polity, P. Gille and A. Schenk, *J. Cryst. Growth* 101, 512 (1990).
33. K. Terashima, E. Tokizaki, A. Uedono and S. Tanigava, *Jpn. J. Appl. Phys.* 32, 736 (1993).
34. L. Wei,Y.-K. Cho, C. Dosho, S. Tanigawa, T. Yodo, K. Yamashita, *Jpn. J. Appl. Phys.* 30, 2442 (1991).
35. R. Krause-Rehberg, H.S. Leipner, T. Abgarjan and A. Politi, *Appl. Phys.* A 66, 599 (1998).
36. Th. Wichert, Th. Krings and H. Wolf, *Physica* B, 185, 297 (1993).
37. Th. Wichert, *Hyperf. Interact.* 97-98, 135 (1996).
38. A. Abragam and R.V. Pound, *Phys. Rev.* 92, 943 (1953).
39. R. Kalish, M. Deicher and G. Schatz, *J. Appl. Phys.* 53, 4793 (1982).
40. N. Achtziger, J Bollmann, Th. Licht, B. Reinhold, U. Reislohner, J Rohrich, M. Rub, M. Wienecke and W Witthuhn, *Semicond. Sci. Techn.* 11, 947, (1996).
41. Th. Wichert, *Appl. Phys.* A, A61, 207 (1995).
42. E. Bertholdt, M. Frank, F. Gubitz, W. Kreische, Ch. Ott, B. Röseler, F. Schwab, K. Stamler and G. Weeske *Appl. Phys. Lett.* 58, 461 (1991).
43. S. Unterricker and F. Schneider, *Hyperf. Int.* 39, 39 (1988).
44. R. Magerle, M. Deicher, U. Desnica, R. Keller, W. Pfeiffer, F. Pleiter, H. Skudlik, and Th. Wichert, *Appl. Surf. Sci.* 50, 169 (1991).
45. U.V. Desnica, *J. Cryst. Growth* (1998), in press.
46. U.V. Desnica, *Vacuum* 50, 471 (1998).
47. R. Magerle, M. Deicher, A. Burchard, U.V. Desnica, and I.D. Desnica-Franković, to be published.
48. P.J. Dean, *Prog. Cryst. Growth Charact.* 5, 89 (1982).
49. Y. Zhang, B.J. Skromme, H. Cheng, *Phys. Rev.* B 47, 2107 (1993).
50. E. Tournie, C. Morhain, G. Neu and J.-P. Faurie, *Phys. Rev. B* 56, R1657 (1997).
51. E. Tournie, C. Morhain, G. Neu and J.-P. Faurie, *J. Cryst. Growth* 184/185, 520 (1998).
52. J. Kraus, E. Kurtz, S. Einfeldt, D. Hommel, H. Lugauer and A. Waag, *Semicond. Sci. Technol.* 11, 1255 (1996).
53. C. Morhain, E. Tournie, C. Neu, C. Ongaretto and J.P. Faurie, *Phys. Rev. B* 54 4714 (1996).
54. P.J. Dean, D.C. Herbert, C.J. Werkhoven, B.J. Fitzpatrick and R.N. Bhargava, *Phys. Rev.* B 23,

4888 (1981).

55. P.J. Dean, W. Stutius, G.F. Neumark, B.J. Fitzpatrick and R.N. Bhargava, *Phys. Rev.* B 27, 2419 (1983).
56. J.M. Francou, K. Saminadayar, J. Pautrat, *Phys. Rev.* B, 41, 12035 (1990).
57. C.M. Townsley, J.J. Davies, D. Wolverson, P.J. Boyce, G. Horsburgh, T.A.Steele, K.A. Prior and B.C. Cavenett, *Phys. Rev. B* 53, 10983 (1996).
58. R.N. Bhargava, *J. Cryst. Growth.* 59, 15 (1982).
59. G.F. Neumark, *Phys. Rev. B* 37, 4778 (1988).
60. J. Pautrat, J.M. Francou, N. Magnea, E. Molva and K. Saminadayar, *J. Cryst. Growth* 72, 194 (1985).
61. J.L. Merz, H. Kukimoto K. Nassau and J.W. Shiever, *Phys. Rev.* B 6, 545 (1972).
62. G.F. Neumark, *Mat. Lett.* 30, 131 (1997).
63. C.H. Henry, K. Nassau and J.W. Shiever, *Phys. Rev.*B 2, 545 (1970).
64. P. Blanconnier, J.-F. Horgel, F.-M. Jean Louis and B. Sermage, *J. Appl. Phys.* 52, 6895 (1981).
65. W. Stadler, D.M. Hofmann, H.C. Alt, T. Muschik, B.K. Meyer, E. Weigel, G. Müller-Wogt, M. Salk, E. Rupp and K.W. Benz, *Phys. Rev B* 51, 10619 (1995).
66. G.F. Neumark and C.R.A Catlow, *J. Phys. C* 17, 6087 (1984).
67. J.J. Davies, D. Wolverson and P.J. Boyce, *phys. stat. sol.* (b) 187, 407 (1995).
68. G. Neu, C. Morhain, E. Tournie and J.P. Faurie, *J. Cryst. Growth* 184/185, 515 (1998).
69. C.H. Henry, K. Nassau and J.W. Shiever, *Phys. Rev.* 4, 2453 (1971).
70. K. Hingerl, H. Sitter, J. Lilja, E. Kuusisto, K. Imai, M. Pessa, G. Kudlek and J. Guttowski, *Semicond. Sci. Technol.* 6, A72 (1991).
71. E. Molva, J.P. Chamonal, G. Milchberg, K. Saminadayar, B. Pajot and G. Neu, *Solid State Comm.* 44, 351 (1982).
72. B. Ullrich, H. Enzumi, S. Keitoku and T. Kobayashi, *Mat. Sci. Eng.* B35, 117 (1995).
73. E. Molva, K. Saminadayar, J. Pautrat and E. Ligeon, *Solid State Comm.* 48, 955 (1983).
74. T. Ohtsuka, J. Kawamata, Z. Zhu and T. Yao, *Appl.Phys. Lett.* 65, 466 (1994).
75. B.N. Murdin, B.C. Cavenett, C.R. Pidgeon, J. Simson, I.S. Hauksson, and K.K. Prior, *Appl. Phys. Lett.* 63, 2411 (1993).
76. I.S. Hauksson, D. Seghier, H.P. Gislason, G.D. Brownilie, K.A. Prior and B.C. Cavenett, *J. Cryst. Growth* 184/185, 490 (1998).
77. K.Akimoto, .H. Okuyama, M. Ikeda and Y. Mori, *Appl. Phys. Lett.* 60, 91 (1992).
78. E. Molva, J.M. Francou, J.L. Pautrat, K. Saminadayar and Le Si Dang, *J. Appl. Phys.* 56, 2241 (1994).
79. J.E. Nicholls and J.J. Davis, *J. Phys.C.* 12, 1917 (1979).
80. H.J. Lugauer, A. Waag, L. Worschech, W. Ossau, G. Landwehr, *J. Cryst. Growth.* 161, 86 (1996).
81. G. Neu, Y. Marfaing, R. Legros, R. Triboulet and L. Svob, *J. Lumin.* 21, 1596 (1980).
82. E. Molva, J. Pautrat, K. Saminadayar, G. Milchberg, *Phys. Rev.* B 41, 12035 (1990).
83. N. Magnea, E. Molva, D. Bensahel and R. Romestain, *Phys. Rev.* B 22, 11240 (1980).
84. H. Venghaus and P.J. Dean, *Phys. Rev.* B 21 1596 (1980).
85. C.L. Orange, D. Wolverson, B. Schilchtherle, J.J. Davis, K. Ogata and S. Fujita, *Semicon. Sci. Technol.* 12, 1609 (1997).
86. P.J. Bojce, J.J. Davis, D. Wolverson, K. Ohawa, and T. Mitsuyu, *Appl. Phys. Lett.* 65, 2063 (1994).
87. C. Zistl, R. Sielemann, H. Haesslein, S. Gall, D. Braeunig and J. Bollmann, *Mater. Sci. Forum* 258-263, 53 (1997).
88. R. Magerle, A. Burchard, M. Deicher, T. Kerle, W. Pfeiffer and E. Recknagel, *Phys. Rev. Lett.* 75, 1594 (1995).
89. G. Mandel, *Phys. Rev.* 134A, 1073 (1964).
90 R.S. Title, G. Mandel and F.F. Morehead, *Phys. Rev.* 136A, 300 (1964).
91 G. Mandel, F.F. Morehead and P.R. Wagner, *Phys. Rev.* 136A, 826 (1964).
92. F.A. Kröger, *The Chemistry of Imperfect Crystals*, Nort-Holland, Amsterdam, (1964), second edition (1967).

93. T. Taguchi and B. Ray, *Prog. Cryst. Growth and Charact.* 6, 103 (1983).

94. G.D. Watkins, *Radiation Effects* 9, 105 (1971).

95. G.D. Watkins, *Intrinsic Defects in II-VI compounds*, (ARL T 75-011), (Springfield, VA: National Technical Information Service)

96. G.D. Watkins, in *Defect Control in Semiconductors*, Ed. K. Sumino, Elsevier, Amsterdam, pp.933 (1990).

97. D.Z. Jeon, H.P. Gislason and G.D. Watkins, *Phys. Rev.* B 48, 7872 (1993).

98. K.M. Lee, L.S. Dang and G.D. Watkins, *Solid State Comm.* 35, 527 (1980).

99. K.M. Lee, K.P. O'Donnell and G.D. Watkins, *Solid State Comm.* 41, 881 (1982).

100. A.L. Taylor, G. Filipovich and G.K. Lindberg, *Solid State Comm.* 9, 945 (1971).

101. P. Emanuelsson, P. Omling, B.K. Meyer, M. Wienecke and M. Schenk, *Phys. Rev.* B 47, 15578 (1993).

102. C. Corbel, F.M. Kiessling, C. Gély-Sykes and R. Triboulet, *Mater. Sci. Eng. B* 16, 134 (1993).

103. H. Zimmerman, R. Boyn, B.K. Meyer, M. Winecke and M. Schenk, *Mater. Sci. Eng.* B 16, 139 (1993).

104. R. Krause-Rehberg, H. Zimmerman, A. Klimakow and Th. Dorst, *phys. stat. solidi* (a) 134, K45 (1992).

105. K. Saarinen, T. Laine, K. Skog, J. Mäkinen and P. Hautojärvi, *Phys. Rev. Lett.* 77, 3407 (1996).

106. J. Schneider and A. Räuber, *Solid State Comm.* 5, 779 (1967).

107. Y. Shono, *J. Phys. Soc. Japan* 47, 590 (1979).

108. K. Leutwein, A. Räuber and J. Schneider, *Solid State Comm.* 5, 783 (1967).

109. I.A. Gorn, V.N. Martinov, E.S. Volkova and V.I. Griner, *Sov. Phys. Semicond.* 24, 336 (1990).

110. B.K. Meyer, P. Omling, P. Weigel and G. Müller-Vogt, *Phys. Rev.* B 46, 15135 (1992).

111. P.J. Dean, H. Venghous, J.C. Pfister, B. Schaub and J. Marine, *J. Lumin.* 16, 363 (1978).

112. P.J. Dean, *J. Lumin.* 18-19, 363 (1978).

113. J. Pautrat, N. Magnea and J.P. Faurie, *J. Appl. Phys.* 53, 8668 (1982)

114. E. Simmonds, R.A. Stradling , J.R. Birch and C.C. Bradley, *phys. stat. solidi* (b) 187, 387 (1995).

115. T. Miyajima, H. Okuyama, K. Akimoto, Y. Mory, L. Wei and S. Tanigawa, *Appl. Phys. Lett.* 59, 1482 (1991).

116. T. Miyujima, H. Okuyama, K. Akimoto, Y. Mori, L. Wei and S. Tanigawa, *J. Cryst. Growth* 117, 694 (1992).

117. W. Stadler, D.M. Hofmann, B.K. Meyer, R. Krause-Rehberg, A. Polity, Th. Abgarjan, M. Salk, K.W. Benz and M. Azoulay, *Acta Phys. Polon.* 88, 921 (1995).

118. J. Petruzello, J.M. Gaines, P. Van der Sluis, D. Olego and D. Ponzoni, *Appl. Phys. Lett.* 62, 1496 (1993).

119. K.A. Prior, B.N. Murdin, C.R. Pidgeon, S.Y. Wang, S. Hauksson, J.T. Mullins, G. Horstburg and B.C. Cavenett, *J. Cryst. Growth* 138, 94 (1994).

120. M. Ichimura, T. Wada, Sz. Fujita, and Sg. Fujita, *Japn. J. Appl. Phys.*, 30, 3475 (1991).

121. K.A. Prior, *J. Cryst. Growth* 187, 379 (1995).

122. Desnica, U.V., *Radiation Physics of Semiconductors and Related Materials*, Ed. G.P. Kekelidze, and V.J. Shakovtsov, Tbilisi Univ. Press, Tbilisi, p. 667, (1980).

123. J.A. van Vechten, in *Handbook on Semiconductors*, Vol. 3, Ed. S. P. Keller, North-Holland Publ. Co. (1982).

124. J.A. van Vechten, *J. Electrochem. Soc.* 122, 419 (1975).

125. D.B. Laks, C.G. Van de Walle, G.F. Neumark, and S.T. Pantelides, *Phys. Rev. Lett.* 66, 468 (1991).

126. D.B. Laks, C.G. Van de Walle, G.F. Neumark, P.E. Bloech and S.T. Pantelides, *Phys. Rev.* B 45, 10965 (1992).

127. D.B. Laks and C.G. Van de Walle, *Physica B* 185, 118 (1993).

128. D.B. Laks, C.G. Van de Walle, G.F. Neumark and S.T. Pantelides, *Appl. Phys. Lett.* 63 1375 (1993).

129. C.G. Van de Walle, D.B. Laks, G.F. Neumark and S.T. Pantelides, *J. Cryst. Growth* 117, 704 (1992).

130. C.G. Van de Walle, D.B. Laks, G.F. Neumark and S.T. Pantelides, *Phys. Rev. B* 47, 9425 (1993).

131. C.G. Van de Walle and D.B. Laks, *Solid State Comm.* 93, 447 (1995).
132. S. Pöykkö, M.J. Puska and R.M. Nieminen, *Phys. Rev.* B 57,12174 (1998).
133. S. Pöykkö, M.J. Puska and R.M. Nieminen, *Phys. Rev.* B 57,12164 (1998).
134. A. Garcia, and J.E. Northrup, *Phys. Rev. Lett.* 74, 1131 (1995).
135. B.H. Cheong, C.H. Park and K.J. Chang, *Phys. Rev.* B 51, 10610 (1995).
136. K.W. Kwak, D. Vanderbilt and R.D. King-Smith, *Phys. Rev.* B 50, 2711 (1994).
137. Y. Marfaing, *J. Cryst. Growth* 161, 205 (1996).
138. Before completely discarding this possibility, which was a favorite explanation for decades and which then seemed compatible with results obtained by a large number of experimental methods and calculations, several words of caution are in place. Lack of positive experimental proof in fawor is not an absolute proof against it, especially since the number of appropriated methods for identification and study of point defects is so limited. The use of the EPR as one of the most reliable methods, is in decline, especially in industrial laboratories, due to its slowness and impracticality to follow. As a consequence, detailed studies which would give a fully quantitative comparison of dopand concentration, free carrier concentration and concentration of (potentially compensating) isolated native vacancies, on samples treated under a variety of conditions, are generally very rare. Furthermore, in theoretical considerations a detailed comparative study, using present state-of-the-art first principle calculations (large enough 'super-cell', proper inclusion of d-electrons into calculation, as well as the proper treatment of the dependence of the defect formation energies on chemical potential, on Fermi level position, on charge state of the defect and – particularly tricky – on stoichiometry) of a wider numbers different dopant/compound combinations is still lacking. Additionally, there are still fresh reports (*e.g.* A. Savitsky, O. Parfenyuk, M. Illashchuk P. Fochouk and V. Buranchek, *J. Cryst. Growth* 184/185, 1155 (1998).) in which arguments are offered claiming that in the same particular experimental conditions large quantities of native point defects - up to $10^{18}/cm^3$ - are present in nominally undoped material and that these defects govern electrical properties.
139. The chemical potential μ_M is the energy of a reservoir of M atoms in equilibrium with the system. M atom states with an energy of more than few kT below μ_M will be filled, while those more than a few kT above μ_M will be empty. Thus the high μ_M corresponds to M-rich environment, while a low value refers to a M-poor environment. The analogous relation holds for μ_A. For an element in thermal equilibrium with a gas phase, the chemical potential can be related to the partial pressure. For an ideal gas with partial pressure p one has $\mu = \mu_o - kT \ln p$.
140. A.N. Krasnov, Yu.F. Vaksman, and Yu.N. Purtov, *J. Mater. Lett.* 17, 133 (1998).
141. V. Valdna, *Phys. Scripta* T69, 315 (1997).
142. T. Yao, T. Masumito, S. Sasari, C.K. Chung, Z. Zhu and F. Nishiyama, *J. Cryst. Growth* 138, 290 (1994).
143. H. Kobayashi, K. Kimura, F. Nishiyama, S. Miwa and T. Yao, *J. Cryst. Growth* 184/185, 475 (1998).
144. H. Kobayashi, K. Kimura, F. Nishiyama, S. Miwa and T. Yao, *Nucl. Instr. Meth.* B 132, 142 (1997).
145. T. Yao, Z. Zhu, Y.H. Wu, C.D. Song, F. Nishiyama, K. Kimura, H. Kajiyama, S. Miwa and T. Yasuda, *J. Cryst. Growth* 159, 214 (1996).
146. J.D. Dow, R.-D. Hong, S. Klemm, S.Y. Ren, M.-H. Tsai, O.F. Sankey and R.V. Kasowski, *Phys. Rev. B* 43, 4396 (1991).
147. J. Schneider and A. Räuber, *J. Chem. Phys.* 42, 1839 (1965).
148. J. Schneider, B. Dischler and A. Räuber, *J. Phys. Chem. Solids* 31, 337 (1970).
149. J. Bittebiere and R.T. Fox, *Phys. Rev.* B 34, 2360 (1986).
150. D. M. Hofmann, P. Omling, H.G. Grimmeiss, B.K. Meyer, K.W. Benz, D. Sinerius, *Phys. Rev.* B 45, 6247 (1992).
151. D. M. Hofmann, W. Stadler, P. Christmann, B.K. Meyer, *Nuc. Instr. Methods Phys. Res.* A 380, 117 (1996).
152. C. Gély-Sykes, C. Corbel and R. Triboulet, *Solid State Comm.* 80, 79 (1991).
153. L. Liszkay, C.Corbel, P. Hautojärvi, R. Aulombard, T. Cloitre, J. Griesche and F. Kiessling, *Appl.*

Phys. Lett. 70, 2723 (1997).

154. Y. Marfaing, *Prog. Cryst. Growth Charact.* 4, 317 (1981).
155. H.W. Woodbury, *Phys. Rev.* **134**, A492 (1964) ,
156. H.W. Woodbury, In: *II-VI semiconductor compunds*, Ed. by D. G.Thomas, North Holand, Amsterdam (1967).
157. I Broser, R. Broser and E. Birkicht, *J. Cryst. Growth* **101**, 497 (1990)
158. Ch. Fricke, R. Heitz, A. Hoffmann and I. Broser, *Phys. Rev.* **B 49**, 5313 (1994)
159. W. Faschinger, *J. Cryst. Growth* in press (1998).
160. K. Ohkawa, T. Karasawa and T.J. Mitsuyo, *J. Cryst. Growth* 111, 797 (1991).
161. E. Kurtz, J. Nimberger, B. Jobst, H. Baumann, M. Kuttler, S. Eimfeldt, D. Hommel, G. Ladwehr, K. Bethge and D. Bimberg, *J. Cryst. Growth* 159, 289 (1996).
162. A.L. Chen, W. Walukiewicz, and E.E. Haller, *Appl. Phys. Lett*, 65, 1006 (1994).
163. I.S. Hauksson, J. Simpson, S.Y. Wang, K.A. Prior and B.C. Cavenett, *Appl. Phys. Lett.* 61, 2208 (1992).
164. C. Kothandaraman, G.F. Neumark and R.M. Park, *J. Cryst. Growth* 159, 298 (1996).
165. Y. Marfaing, *J. Cryst. Growth* 138, 305 (1994).
166. M. Behringer, P. Bäume, J. Gutowski and D. Hommel, *Phys. Rev.* B 57, 12869 (1998).
167. P. Bäume, J. Gutowski, E. Kurtz, D. Hommel and G. Landweher, *J. Cryst. Growth* 159, 252 (1996).
168. R. Heitz, E. Moll, V. Kutzer, D. Wiesmann, B. Lummer, A. Hoffmann, I. Broser, P. Bäume, W. Taudt, J. Söllner and M. Heuken, *J. Cryst. Growth* 159, 307 (1996).
169. T.A. Kennedy, E.R. Glaser, B.N. Murdin, C.R. Pidgeon, K.A. Prior and B.C. Cavenett, *Appl. Phys. Lett.* 65, 1112 (1994).
170. K. Ohkawa, T.J. Mitsuyo and O. Yamazaki, *J. Appl. Phys.* 62, 3216 (1987).
171. K. Hirano, I.Suemune and G. Sato, *Jpn. J. Appl. Phys.* 36, L37 (1997).
172. H. Gleitsmann, N. Amman, J. Hermans, A. Schneider, J. Geurts, P. Karduck and M. Heuken, *J. Cryst. Growth* 138, 324 (1994)
173. L. Shcherbak, P. Feichouk, P. Fochouk and O. Panchouk, *J. Cryst. Growth* 161, 219 (1996).
174 F. Bassani, S. Tattarenko, K. Saminadayar, J. Bleuse, N. Magnea, and J.L. Pautrat, *Appl. Phys. Lett.* 58, 2651 (1991).
175. F. Bassani, S. Tattarenko, K. Saminadayar, N. Magnea, R.T. Cox, A. Tardot and C. Grattepain, *J. Appl. Phys.* 72, 2927 (1992).
176. T. Ido, A. Heurtel, R. Tribulet and Y. Marfaing, *J. Phys. Chem. Solids* 48, 781 (1987).
177. G. Karczewski, T. Wojtowicz, *Acta Phys. Pol.* 90, 635 (1996).
178. F. Fischer, A. Waag, L. Worscheck, W. Ossau, S. Scholl, G. Landwehr, J. Mäkinen, P. Hautojärvi and C. Corbel, *J. Cryst. Growth* 161, 214 (1996).
179. R. Legros, Y. Marfaing and R. Triboulet, *J. Phys. Chem. Solids* 39, 179 (1978).
180. D.J. Chadi, and K.J. Chang, *Appl. Phys. Lett.* 55, 575 (1989).
181. D.J. Chadi, *Appl. Phys. Lett.* 59, 3589 (1991).
182. D.J. Chadi, *Physica B* 185,128 (1993).
183. D.J Chadi, *Phys. Rev. Lett.* 72, 534 (1994).
184. D.J Chadi, *J. Cryst. Growth* 138, 295 (1994).
185. C.H. Park and D.J. Chadi, *Appl. Phys. Lett.* 66, 3167 (1995).
186. C.H. Park and D.J. Chadi, *Phys. Rev. Lett.* 75, 1134 (1995).
187. C.H. Park and D.J. Chadi, *Phys. Rev.* B 52, 11884 (1995).
188. D.E. Onopko and A.I. Ryskin, *Phys. Lett.* A 208, 244 (1955).
189. D.V Lang, R.A.Logan, M. Jaros, *Phys. Rev.* B 19, 1015 (1979).
190. P.J. Mooni, *J. Appl. Phys.* 67, R1 (1990).
191. A. Waag, Th. Litz, F. Fisher, H. Heinke, S. Scholl, D. Hommel, G. Landwehr and G. Bilger, *J. Chryst. Growth* 138, 437 (1994).
192. The observation of PPC is a necessary but not a sufficient condition for concluding the exsistence of DX centers (L.J. Malloy and Khatchaturyan,In: *Semiconductors and Semmimetals*, Ed. by R.K. Willardson, A.C. Beer and E.R. Weber, Academic, NY Vol. 38 235 (1993)). PPC can also result from potential fluctations, which appear at least in some strongly compensated systems. It seems,

however, that it can be possible to differentiate between these two different causes of PPC; see: H.X. Jiang and J.Y. Lin, *Appl. Phys. Lett.* 64, 2547 (1990)

193. K. Khachaturyan, M. Kaminska, E.R. Weber, P. Becla and R.A. Street, *Phys. Rev.* B 40, 6304 (1989).
194. R.L. Gunshor, J. Han, G.C. Hua, A.V. Nurmirko and H. Jeon, *J. Cryst. Growth*, 159, 1 (1966).
195. C. Skierbiszewski, P. Wisniewski, E. Litwin-Staszewska, T. Suski, Z. Wiliamowski, A.K. Zakrzewski, G. Karczewski and W. Jantsch, *Acta Phys. Polon.* 90, 927 (1996).
196. T. Thio, J.W. Bennett, D.J. Chadi, R.A. Linke and M.C. Tamargo, *J. Electron. Mat.* 25, 229 (1996).
197. T. Thio, J.W. Bennett, and P. Becla, *Phys. Rev.* B 54, 1754 (1996).
198. G.W. Iseler, J.A. Kafalas, A.J. Straus, H.F. MacMillan and R.H. Bube, *Solid State Comm.* 10, 619 (1972).
199. B.C. Burkey, R.P. Khosla, J.R. Fisher and D.L. Losee, *J. Appl. Phys.* 47, 1095 (1976).
200. I. Terry, T. Penny, S. von Molnár, J.M. Rigotty and P. Becla, *Solid State Comm.* 84, 235 (1992).
201. A. Waag, F. Fisher, J. Gershuetz, S. Scholl and G. Landwehr, *J. Appl. Phys.* 75, 1368 (1994).
202. S. Scholl, J. Gershuetz, H. Schäfer, F. Fisher, A. Waag and G. Landwehr, *Solid State Comm.* 91, 491 (1994).
203. I. Terry, S. von Molnár, A.M. Torrssen and P. Becla, *Sphylos. Mag.* B 65, 1245 (1992)
204. NJ. Han, M.D. Rigle, Y. Fan and R.L. Gunshor and A.V. Nurmikko, *Appl. Phys. Lett.* 65, 3230 (1994)
205. K.Akimoto, T. Kobayashi, T. Ogawa, W.Ohtsuka, T. Maruyama andY. Kitajima, *J. Cryst. Growth,* 184/185, 398 (1998).
206. I.W. Tao, M. Jurkovic and W.I. Wang, *Appl. Phys. Lett.* 64, 1848 (1994).
207. H. Ogawa, G. Irfan, H. Nakayuma, M. Nishio and A. Yoshida, *Jpn. J. Appl. Phys.* 33, L980 (1994).
208. V.N. Iodko and A.K. Belayeva, *Mat. Sci Forum* 182-184, 353 (1995).
209. V.N. Iodko, V.P. Gribkovskii, A.K. Belyaeva, Yu.R. Spurun-Belevich and Zh. A. Ketko, *J. Cryst. Growth* 184/185, 1170 (1998).
210. R.K. Watts and W.C. Holton, *Phys. Rev.* B 2, 4882 (1970).
211. D. Verity, J.J. Davies and J.E. Nicholls, *J. Phys. C* 14,1485 (1981).
212. D. Wasik, J. Przybytek, M. Baj, G. Karczewski, T. Wojtowicz, and J. Kossut, *J. Crys. Growth,* 159, 392 (1996).
213. F.J. Espinosa, J. Mustre de Leon, M. Zapata-Torres, R. Castro-Rodrigez, J.L.Pena, S.D. Condradson and N.J. Hess, *Phys. Rev.* B 55, 7629 (1997).
214. T. Suski, P. Wisniewski, E. Litwin-Staszewska, D. Wasik, J. Przybytek, M. Baj, G. Karczewski, T. Wojtowicz, A.K. Zakrzewski and J. Kossut, *J. Cryst. Growth* 159, 380 (1996).
215. T.N. Theis, P.M. Mooney and S.L. Wright, *Phys. Rev. Lett.* 60, 361 (1988).
216. Sun-Ghil Lee and K. Chang, *Phys. Rev.* B 57, 6239 (1998).
217. S.W. Biernacki, *Sol. State Comm.* 88, 365 (1993).
218. T. Kobayashi, T. Ogawa, W. Otsuka, T. Maruyama, K. Akimoto and Y. Kitajima (unpublished)
219. G.F. Neumark, *J. Appl. Phys.* 51, 3383 (1980).
220. T. Marchall and D.A. Cammack, *J. Appl. Phys.* 69, 4149 (1991).
221. M. A. Haase, J.M. Depydt, H. Cheng and J.E. Potts, *J. Appl. Phys.* 58, 1173 (1991).
222. A.N. Krasnov, *J. Cryst. Growth* 141, 89 (1994).
223. H. Katayama-Yoshida, T. Sasaki and T. Oguchi, *J. Cryst. Growth* 117, 625 (1992).
224. H. Cheng, J.M. DePuydt, J.E. Potts and T.L. Smith, *Appl. Phys. Lett.* 52 147 (1988).
225. H. Cheng, J.M. DePuydt, J.E. Potts and M.A. Haase, *J. Cryst. Growth* 95, 512 (1989).
226. K. Hingerl, H. Sitter, J. Lilja, E. Kuusisto, K. Imai, M. Pessa, G. Kudlek and J. Guttowski, *Semicond. Sci. Technol.* 6, A72 (1991).
227. G.F. Neumark, S.P Herko and B.J. Fitzpatrick, In: *Proc. 13 Int. Conf. Defects in Semicond.*, Ed. L.C. Kimerling and J.M. Parsey, p.1205 (1984).
228. J.L. Merz, K. Nassau and J.W. Shiever, *Phys. Rev.* B 8, 1444 (1973).
229. J. Nishizava, R. Suzuki and Y. Okuno, *J. Appl. Phys.* 59, 2256 (1986).
230. T. Yasuda, I. Mitshuishi and H. Kukimoto, *Appl. Phys. Lett.* 52 57 (1987).

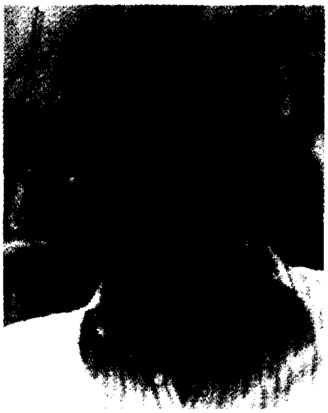
321. A. Yoshikava, S. Muto, S. Yamaga and H. Kasai, *Jpn. J. Appl. Phys.* 27, L260 (1988).
232. A. Yahata, H. Mitsuhashi, K. Hirahara and T. Beppu, *Jpn. J. Appl. Phys.* 29 L4 (1989).
233. T. Yodo and K. Yamashita, *Appl. Phys. Lett.* 53 2403 (1989).
234. E.N. Arkad'eva, O.A. Matveev and V.A. Sladkova, *Sov. Phys. Semicond.* 2, 1264 (1969).
235. U.V. Desnica, and N.B. Urli, *Phys. Rev.* B 6, 3044 (1972).
236. B. Monemar, W.M. Chen, P.O. Holtz and H.P. Gislason, *Phys. Rev.* B 36, 4831 (1987)
237. B. Yang, Y. Ishikawa, T. Miki, Y. Doumae and M. Isshiki, *J. Cryst. Growth* 179, 410 (1997).
238. K. Kimura, S. Miwa, T. Yasuda, L.H. Kuo, C.G. Jin, K. Tanaka and T. Yao, *Appl. Phys. Lett.* 70, 81 (1997).
239. K. Kimura, S. Miwa, C.G. Jin, L.H. Kuo, T. Yasuda, A. Ohtake, K. Tanaka, T. Yao and H. Kobayashi, *Appl. Phys. Lett.* 71, 1077 (1997).
240. W. Faschinger, *Semicond. Sci. Technol.* 12, 1291 (1977)
241. S.N. Maksimovski and S.P. Kobeleva, *Inorg. Mater.* 22, 815 (1986)
242. F.V. Wald, *phys. st. sol.* (a) 38, 253 (1976)
243. H. Zimmerman, R. Boyn, M.U. Lehr, H.-J. Schulz, P. Rudolph and J.-Th. Kornack, *Semicond. Sci. Technol.* 9, (1994).
244. D. Kim, A.L. Fahrenbruch and R.H. Bube, 20th *IEEE PV Spec. Conf.,Rept. No. 0160-8371/88/0000-1487*, (1988)
245. G.F. Neumark, *Phys. Rev. Lett.* 62, 1800 (1989).
246. Y. Fan, J. Han, L. He, R.L. Gunshor, M.S. Brandt, J. Walker, N.M. Johnson, and A.V. Nurmikko, *Appl. Phys. Lett.* 65, 1001 (1994).
247. Y. Fan, J. Han, R.L. Gunshor, J. Walker, N.M. Johnson, and A.V. Nurmikko, *J. Electron. Mat.* 24, 131 (1995).
248. G. Jones and J. Woods, *J. Phys. D.* 9, 799 (1976).
249. A.K. Ray and F.A. Kröger, *J. Electrochem. Soc.* 125, 1355 (1978).
250. G.F. Neumark and S.P Herko, *J. Cryst. Growth* 59, 189 (1982).
251. J.S. Vermaak and J. Petruzzello, *J. Electron. Mater.* 12, 29 (1983)
252. It is interesting that, in contrast to very high N doses, at a very low dose practically all implanted N atoms could be positioned into a substitutional Se places (B. Itterman, K. Marbach, G. Welker, E. Diehl, M. Füllgrabe, M. Heemeier, F. Kroll, F. Mai, P. Meier, D. Peters, H. Thiess, H. Ackermann, H-J. Stöckmann, W.-D. Zeitz, H. Wenisch, D. Hommel, G. Landwehr, *J. Cryst. Growth,* 184/185, 485 (1998)). Spin-polarized ^{12}N probe nuclei were implanted into ZnSe and from the β-radiation detected nuclear magnetic resonance measurements it was conlcuded that about half N atoms lends on Se site even before annealing. Almost complete incorporation of N into a N_{Se} substitutional sites was obtained with annealings at temperatures as low as 120°C. In N_{Se} sites, N should be unperturbed electrically active acceptor.
253. W. Walukiewicz, *Phys. Rev.* B 37 , 4760 (1988)
254. W. Walukiewicz, *J. Vac. Sci. Technol.* B6 1257 (1988).
255. W. Walukiewicz, *Appl. Phys. Lett.* 54, 2094 (1989).
256. W. Walukiewicz, *Phys. Rev.* B 50, 5221 (1994).
257. W. Fashinger, R. Krump, G. Brunhaler, S. Ferreira and H. Sitter, *Appl. Phys. Lett.* 65, 3215 (1994).
258. W. Fashinger, S. Ferreira and H. Sitter, *Appl. Phys. Lett.* 64, 2682 (1994).
259. W. Faschinger, *J. Cryst. Growth* 159, 221 (1996).
260. W. Fashinger, S. Ferreira and H. Sitter, *Appl. Phys. Lett.* 66, 2516 (1995).
261. (FE94) S.O. Ferreira, H. Sitter, W. Faschinger and G. Brunthaler, *J. Cryst. Growth.* 140, 282 (1994).
262. S.O. Ferreira, H. Sitter and W. Faschinger, *Appl. Phys. Lett.* 66, 1518 (1995).
263. S.B. Zhang, S.-H. Wei and A. Zunger, . *Appl. Phys.* 83, 3192 (1998).
264. U.V. Desnica, I.D. Desnica-Franković, R. Magerle, A. Burchard and M. Deicher, Mat.Sci. Forum, 258-263, 1347 (1997)
265. T. Lukaszewicz, *phys. st. sol. (a)*, 78, 611, (1982)
266. J.L. Sullivan, *IEEE Trans. son. ultason.* SU-32, 71 (1985).

267. J.L. Sullivan, *J. Phys D: Appl. Phys.* 6, 552 (1973)268.
268. J.L. Sullivan, *Phys. Rev. B* 184, 796, (1969)
269. T. Yamagami, *Jpn. J. Appl. Phys.* 33, 3237 (1994)
270. H. Wolf, U. Hornauer, R. Lermen, Y. Endalamow, T. Filz, Th. Krings, St. Lauer, U. Ott, E. Singer, M. Tsige and Th. Wichert, ICDS 18, . Ed. M. Suezawa and H. Katayama-Yoshida, *Materials Science Forum* 143-147 (Trans Tech Publications, p. 459 (1994).
271. H. Wolf, Th. Krings and Th. Wichert, *Nucl. Instrum. Methods Phys. Res.* B 63, 240 (1992).
272. H. Wolf, A. Jost, R. Lermen, T. Filz, V. Ostheimer and Th. Wichert, ICDS 18, . Ed. M. Suezawa and H. Katayama-Yoshida, *Materials Science Forum* 196-201 (Trans Tech Publications, p. 321 (1995).
273. A.L. Chen, W. Walukiewicz, K. Duxtand and E.E. Haller, *Appl. Phys. Lett,* 68, 1522 (1996)
274. F. Rong and G.D. Watkins, *Phys.Rev. Lett.* 58, 1486 (1987)
275. M. Straßburg, M. Kuttler, O. Stier, U.W. Pohl, D. Bimberg, M. Behringer and D. Hommel, *J. Cryst. Growth* 184/185, 465 (1998).
276. M. Behringer, K. Ohkawa, V. Grossmann, H. Heinke, K. Leonardi, M. Fehrer, D. Hommel, M. Kuttler, M. Strassburg and D. Bimberg, *J. Cryst. Growth* 184/185, 580 (1998)2.
277. M. Kuttler, M. Strassburg, V. Türck, R. Heitz, U.W. Pohl, D. Bimberg, E. Kurtz, G. Landwehr and D. Hommel, *Appl. Phys. Lett.* 69, 2647 (1996)
278. M. Kuttler, M. Strassburg, O. Stier, U.W. Pohl, D. Bimberg, E. Kurtz, J. Nürnberg, G. Landwehr, M.Behringer and D. Hommel, *Appl. Phys. Lett.* 71, 243 (1997)
279. J.W. Griffith, R. Lundquist, R. Platzer, J.A. Gardner, G. Karczewski and J.K. Fudyna, *Mat. Sci. Forum* 143-147, 405 (1994)
280. M. Suzuki, T. Ueonama and A.Yanase, in: *Extended Abstracts of 1993 Int. Conf. Sol. State Develop. Materials*, Chiba, p.74. (1993).
281. J. Friedl, *Dislocations*, Addison-Wesley, Reading, Massachussetts, U.S.A., 1967, p.74
282. A.J. Cho, *J. Cryst. Growth* 150, 1 (1995).
283. K. Kimura, S. Miwa, C.G. Jin, L.H. Kuo, T. Yasuda, A. Ohtake, K. Tanaka, T. Yao and H. Kobayashi, *J. Cryst. Growth* 184/185, 411 (1998).
284. H. Jeon, J. Ding, W. Patterson, A.V. Nurmikko, W. Xie, D.C. Grillo, M. Kobayashi and R, Gunshor, *Appl. Phys. Lett.* 59, 3619 (1991)
285. T. Yao, Z. Zhu, *phys. stat. sol.* (b) 187, 387 (1995).
286. J.F. Swenberg, M.W. Wang, R.J. Miles, M.C. Phillips, A.T. Hunter, J.O. McCaldin and T.C. McGill, *J. Cryst. Growth* 138, (692 (1994).
287. S. Oehling, H.J. Lugauer, M. Schmitt, H. Heinke, U. Zehnder, A. Waag, C. R. Becker and G. Landwehr, *J. Appl. Phys.* 79, 2343 (1995).
288. J.P. Faurie, V. Bousquet, P. Brunet and E. Tournie, *J. Cryst. Growth* 184/185, 11 (1998).
289. F. Firszt, S. Legowski, H. Meczynska, J. Szatkowski, W. Paszkowicz and K. Godwod, *J. Cryst. Growth,* 184/185, 1335 (1998).
290. F. Fischer, G. Landwehr, Th. Litz, H.J. Lugauer, U. Zehnder, Th. Gerhard, W. Ossau and A. Waag, *J. Cryst. Growth* 175/176, 532 (1997).
291. Sz. Fujita and Sg. Fujita, *J. Cryst. Growth,* 184/185, 398 (1998).
292. W. Gebhardt, B. Hahn, H. Stanzl and M. Deufel, *J. Cryst. Growth* 159, 238 (1996).
293. M.U. Ahmed, P. Prete, .S.J.C. Irvine, A. Stafford, L.M. Smith, A.C. Jones and S.A. Rusworth, *J. Cryst. Growth* 184/185, 429 (1998).
294. T. Honda, S.W. Lim, K. Yanashima, K. Inoue, K. Hara, H. Munekata, H. Kukimoto, F. Koyama and K. Iga, *Jpn. J. Appl. Phys.* 35, 3878 (1996).
295. T. Honda, S.W. Lim, K. Inoue, K. Hara, H. Munekata, H. Kukimoto, F. Koyama and K. Iga, *J. Cryst. Growth* 170, 503 (1997).
296. Y. Hatanaka, T. Aoki, T. Arakava, D. Noda and Y. Nakanishi, *J. Cryst. Growth* 184/185, 425 (1998).
297. S.J.C. Irvine, A. Stafford, M.U. Ahmed, A. Brown and H. Kheyrandish, *J. Electron. Mat.* 26, 723 (1997).
298. N.C. Giles, R.L. Harper, J.W. Han and J.F. Schetzina, In: *Mat. Res. Soc. Symp. Proc.,* 161, 227 (1990).

299. M. Ichimura, T. Wada, Sz. Fujita, and Sg. Fujita, *J. Cryst. Growth* 117, 689 (1992).
300. V.I. Kozlovsky, A.B. Krysa, W. Taudt and M. Heuken, *J. Cryst. Growth* 184/185, 435 (1998)
301. N. Shibata, A. Ohki and A. Katsui, *J. Cryst. Growth* 93, 703 (1988)
302. A. Toda, F. Nakamura, Y. Namashima and A. Ishibashi, *J. Cryst. Growth* 170, 461 (1997).
303. K. Ogata, D. Kawaguchi, N. Nishiyama, Sz. Fujita and Sg. Fujita, *J. Cryst. Growth* 184/185, 554 (1998).
304. D. Noda, T. Aoki, Y. Nakanishi and Y. Hatanaka, *Jpn. J. Appl. Phys.* 36, 6302 (1997)
305. F.J. Bryant, *Prog. Cryst. Growth and Charact.* 6, 191(1983).
306. Kin Man Yu and E.D. Bourret-Courchesne, *Appl. Phys. Lett.* 69, 2062 (1996).
307. Kin Man Yu, J.W. Ager, III, E.D. Bourret, J. Walker, and W. Walukiewicz, *J. Appl.*
308. H.L. Hwang, K.Y.J. Hsu, H.Y. Ueng, *J. Cryst. Growth* 161, 73 (1996).
309. H. Quyang, M.L. Peng, Y.M. Lin, M.H. Yang and H.L. Hwang, *J. Cryst. Growth,* 72, 232 (1985)
310. M. Chu, R.H. Bube and J.F. Gibbsons, *J. Electrochem. Soc.* 127, 483 (1980)
311. C. Uzan, R. Legros and Y. Marfaing, *J. Cryst. Growth* 72, 252 (1985)
312. W.P. Shen ahd H.S. Kwok, *J. Appl. Phys.* 65, 2162 (1994)
313. S. Keitoku, H. Ezumi, H. Osono and M. Ohta *Jpn. J. Appl. Phys.* 34, L138 (1995)
314. 11. R. Heitz, A. Hoffman, P. Thurian and I. Broser, *J. Phys. C.: Condens. Matter* 4, 157 (1992)
315. C.M. Rouleau, D.H. Lowndes, J.W. McCamy, J.D. Budai, D.B. Poker, D.B. Geohegaan, A.A. Puretzky and S. Zhu, *Appl. Phys. Lett.* 67, 1545 (1995).
316. C. Verie, In: *Proc. Int. Conf. Semicond. Heteroepitaxy,* Ed. B. Gil and R.L. Aulombard, World Scientific, Singapoore, p.73 (1995).
317. C. Verie, *Mat. Sci. Eng.* B43, 60 (1997).
318. C. Verie, *J. Cryst. Growth* 184/185, 1061 (1998).
319. J. Friedl, In: G. DeWitt, B. Dreifus, P.G. De Gennes, Eds.,*Physique des Basses Temperatures,* Gordon and Breach, N.Y., p. 561 (1962).
320. J.Y. Marzin, J.M. Gerard, P. Voisin and J.A. Brum, in: T.P. Pearsall Ed., *Strained-Layer Superlattices: Physics,* Academic Press, San Diego, p. 59 (1990)
321. W.A. Harrison, *Electronic Structure and Properties of Solids,* ch. 7, p. 175, W.H. Freeman and Co., San Francisco, (1980).
322. W.A. Harrison, *Phys. Rev.* B 24, 5835 (1981).
323. In Ref. [316] a slightly different relation was devised, but with the same basic approach.
324. J.C. Phyllips, *Rev. Modern Phys.* 42, 317 (1970)
325. J.A. Van Vechten and J.C. Phyllips, *Phys. Rev.* B 2, 2160 (1970)
326. W.M. Yim, J.P. Dismukes, E.J. Stafko and R.J. Paff, *J. Phys. Chem. Solids* 33, 501 (1972)
327. B. Bousket, E. Tournié, M. Laüght, P. Vannégučs and J.P. Faurie, *Appl. Phys. Lett.* 70, 3564 (1997)
328. P.M. Mensz, *Appl.Phys. Lett.* 64, 2148 (1994)
329. A. Waag, F. Fisher, K. Schüll, T. Baron, H.-J. Lugauer, Th. Litz, U. Zehnder, W. Ossau, T. Gerhard, M. Keim, G. Reuscher and G. Landwehr, *Appl. Phys. Lett.* 70, 280 (1997).
330. T. Baron, S. Tatarenko, K. Saminadayar, N. Magnea and J. Fontenille, *Appl. Phys. Lett.* 65, 1284 (1994).
331. T. Baron, K. Saminadayar and N. Magnea, *J. Appl. Phys.* 83, 1354 (1998).
332. M. Aven and H.H. Woodbory, *Appl. Phys. Lett.* 1, 53 (1962)
333. S. Nakamura, N. Inasa, M. Senok and T. Mukai, *Jpn. J. Appl. Phys,* 31, 1258 (1992).
334. G.F. Neumark and N.C. Padmani, *Mat. Sci. Eng.* B 45, 213 (1997).
335. H. Katajama-Yoshida and T. Yamamoto, phys.stat.sol. (b) 202 763 (1997).
336. T. Yamamoto and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.* 36, L180 (1997).
337. O. Brandt, H.H. Yang, A. Kostial and K.H. Ploog, *Appl. Phis. Lett.* 36, 2707 (1996)
338. U.V., Desnica, Urli, N. and Etlinger, B. *Phys. Rev.* B 15, 4119 (1977).
339. In order to remain in its lattice site after decay the radiactive isotope has to have a recoil energy smaller than the displacement energy. Isotopes decaying *via* electron capture process satisfy this requirement, in particular ^{111}In, ^{71}Ge, ^{125}I, ^{67}Ga, but some others isotopes as well (U.V. Desnica, *Inst. Phys. Conf.* 43, 521 (1979)).
340. U.V. Desnica, *Phys. Stat. Solidi* (a) 39, K33 (1977).

341. J. Bollmann, M. Wienecke, J.Röhrih and H. Kerkow, *J. Crystal Growth* 159, 384 (1996).
342. M. Wienecke, J. Bollmann, J. Röhrich, K. Maass, B. Reinhold, D. Forkel-Wirth, The ISOLDE Collaboration, *J. Cryst. growth* 161, 82 (1996).
343. The method is successful because oppositely charged dopants/defects do tend to make pairs. It was concluded from PL measurements, but it was also demonstrated recently with PAC,(Ref. [272] and H. Wolf, T. Filz, St. Lauer, A. Jost, V. Ostheimer, Th. Wichert, M. Deicher, R. Magerle, A. Burchard, D. Forkel-Wirth and H. Haas, *Int. Conf. Hyperfine Interactions*, Leuven, (1995).) for ^{111}In donor pairing with N, P, As and Sb acceptors in ZnSe, ZnTe and CdTe. Similarly, donor-native acceptor pairing is also confirmed in all II-VI compounds^{436,44}, particularly complex In - V_M, as well as analogous donor-acceptor pairs with other PAC probing atoms , ^{77}Br as donor placed in VI substitutional place, and ^{79}Rb as acceptors placed in II substitutional place.
344. J.M. Wallace, J. Simpson, S.Y. Wang, H. Stewart, J.J. Hunter, S.J.A. Adams, K.A. Prior and B.C. Cavenett, *J. Cryst. Growth,* 117, 320 (1992).
345. S. Sakakibara, K. Fujimoto, N. amano, K. Ishino A. Ishida and H. Fujiyasu, *Jap. J. Appl. Phys.* 33, 2008 (1994).
346. A.N. Georgobiani, U.A. Aminov, Yu. V. Korostelin, V.I. Kozlovsky, A.S. Nasibov and P.V. Shapkin, *J. Cryst. Growth,*184/185, 470 (1998).
347. K. Ogata, D. Kawaguchi, T. Kera, Sz. Fujita and Sg. Fujita, *J. Cryst. Growth* 159, 312 (1996).
348. K. Ogata, D. Kawaguchi, T. Kera, Sz. Fujita and Sg. Fujita, *Mater. Sci. Eng.* B 43 (1997).
349. N.R. Tasker, B.A. Khan, D.R. Dorman and K. Shahzad, *Appl. Phys. Lett.* 62, 270 (1993).
350. M. A. Haase, H. Cheng, J.M. Depydt and J.E. Pots, *J. Appl. Phys.* 67, 448 (1990).
351. M. Yoneta, M. Ohishi, H. Saito, N. Junnai and T. Ohno, *J. Cryst. Growth* 184/185, 455 (1998).
351. M. A. Haase, J.M. Depydt, H. Cheng and J.E. Potts, *Appl. Phys. Lett.* 58, 1173 (1991).
352. F. Sakurai, M. Motozawa, K. Suto and J.-i. Nishizava, *J. Cryst. Growth* 172, 75 (1997).
353. S.I. Gheyas, S. Hirano, M. Nishio and H. Ogawa, *Appl. Surf. Sci.* 100/101, 634 (1996).
354. N.J. Duddles, K.A. Dhese, P. Devine, D.E. Ashenford, C.G. Scott, J.E. Nicholls and B. Lunn, *J. Appl. Phys.* 76, 5214 (1994).
355. J. Han, T.S. Stavrinedes, M. Kobayashi, R.L. Gunshor, M.M. Hagerott and A.V. Nurmikko, *Appl. Phys. Lett.* 62, 840 (1993)
356. F.A. Selim, V. Swaminathan and F.A. Kröger, *phys. st. sol.* (a) 29, 465 (1975)
357. R.B. Hall and H.H. Woodbury, *J. Appl. Phys.* 39, 5361 (1968)
358. W.P. Shen and H.S. Kwok, *Mater. Res. Soc. Symp. Proc.* 340, 457 (1994)
359. Y. Kashiwaba, A. Tada and T. Ikeda, *Jpn. J. Appl. Phys.* 33, L1613 (1994).
360. P.J. Sebastian, *Appl. Phys. Lett.*, 62, 2956 (1993).
361. P.J. Sebastian and M. Ocampo, *J. Appl. Phys.* 77, 4548 (1995).
362. S. Mathew, P.S. Mukerjee and K.P. Vijayakumar, *Jpn. J. Appl. Phys.* 34, 4940 (1995).
363. S.Iida T.Yataabe and H. Kinto, *Jpn. J. Appl. Phys.* 128, PL535 (1989).
364. I.K. Sou, Z. Yang, J. Mao, Z.H. Ma, P.Yu and G.K.L. Wong, *Appl. Phys. Lett.* 69, 2519 (1996).
365. H. Wyands and M. Cocivera, J. Electrochem. Soc, 139, 2025 (1992)
366. M.C. Phillips, M.W. Wang, J.F. Swenberg, J.O. McCaldin and T.C. McGill, *Appl. Phys. Lett.* 61, 1962 (1992).
367. D.M. Hofmann, W. Stadler, K. Oettinger, B.K. Meyer,P. Omling, M. Salk, K. Benz, E. Weigel; G. Muller Vogt, *Mater. Sci. Eng.* B, 16, 128 (1993).
368. K. Zanio, in *Cadmium Teluride,* eds. R.K. Willardson and A.C. Beer, *Semiconductors and Semmimetals,* Vol. 13, Academic Press, NY (1972).
369. D. Brun-Le-Cunff, T. Baron, B. Daudin, S. Tatarenko and B. Blanchard, *Appl. Phys. Lett.* 67, 965 (1995).
370. J.E. Nicholls J.J. Davis, N.R. Polton, R. Mach and G.O. Müller, *J. Phys.C.* 18, 455 (1985).
371. D.J. Dunstan, J.E. Nicholls, B.C. Csvenett and J.J. Daavies, *J. Phys.* C 13, 6409 (1980).
372. U. Reislöhner, J. Grillenberger and W. Witthuhn, *J. Cryst. Growth* 184/185, 1160 (1998).
373. P. Blanconnier, J.-F. Horgel, F.-M. Jean Louis and B. Sermage, *J. Appl. Phys.* 52, 6895 (1981).
374. E. Kurtz, D. Albert, J. Kraus, D. Hommel, and G. Ladwehr, *Proc. Int. Symp. on Blue Lasers and LEDs (Chiba 1996)* ed. Yoshikava et al. p. 429 (1996).
375. K. Ohkawa, A. Tsujimura, S. Hayashi, Y. Yoshii and T. Mitsuyu, *Extended Abstracts of the Int.*

Conf. on Solid State Devices and materials, (Tsukuba 1992) p. 330, 1992.
376. A.N. Georgobiani, A. N. Gruzintsev, A.V. Spitsyn and I.M. Tiginyanu, *phys. stat. sol.* (a) 111, 301 (1989)
378. W. Stadler B.K. Meyer, D.M. Hofmann, B. Kowalski, P. Emanuelsson, P. Omling, E. Weigel, G. Müller-Vogt and R.T. Cox, *Mater. Sci. Forum* 143-147, 399 (1994).
379. K. Bao, P.D. Healey, M. Gokhale, J.E. Ayers and F.C. Jain, *Appl. Phys. Lett.* 67, 1098 (1995).



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