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Shallow-level centers in semiconductors – 2000

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Abstract

A synopsis of papers presented at the 9th International Conference on Shallow-Level Centers in Semiconductors (SLCS-9), held in Yumebutai, Awaji Island, Japan, from 24 to 27 September 2000, is given. Recent achievements in the fields of donor and acceptor identification and characterization, majority doping enhancement and co-doping processes, the role of special impurities such as oxygen, hydrogen, nitrogen and carbon, special features revealed by spectroscopy and some technical applications, are summarized.

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Keywords: Semiconductors; Donors; Acceptors; Doping

1. Introduction

The Ninth International Conference on Shallow-Level Centers in Semiconductors took place in a magnificent setting in Yumebutai, Awaji Island, Japan, from 24 to 27 September 2000. In the present report a summary, reflecting strongly the author's personal impression, of the scientific papers presented is given. The contents are organized in sections under the headings donors, acceptors, (co-)doping, special impurities, spectroscopy and applications, with an additional paragraph dealing with some papers on related impurity effects. The meeting was the ninth in a series of meetings, proceeding under slightly varying names, focussing on the properties of defects and impurities which introduce shallow donor or acceptor electronic levels in the band gap of semiconductors and as such have an import impact on electron and hole concentrations, particularly under room-temperature conditions. The scientific output of all the meetings is well documented in the conference proceedings to which references can be found in Table 1.

2. Donors

A primary task in the issue of shallow-level centers in semiconductors is the thorough exploration of donor and acceptor states of single impurities or complexes, with particular challenges being offered by new materials or new structures of materials. In the category of n-type doping several impurities with donor activity were uncovered. In magnesium-doped Czochralski silicon Ho observed the room-temperature formation of MgO pairs. Similar to the well-known isolated interstitial Mg double donor, the Mg_iO_i complex is also

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Table 1
Conferences on Shallow-Level Centers in Semiconductors and their proceedings

Year	Site	Chairperson(s)	Proceedings
1984	Berkeley, USA	E.E.Haller, A.K. Ramdas, K.K. Bajaj	Solid State Communications 53 (1985) 1033–1149
1986	Trieste, Italy	A. Baldereschi	Shallow Impurity Centers in Semiconductors, A. Baldereschi and R. Resta (Eds.), Physica B+C 146 (1987) 1–305
1988	Linköping, Sweden	B. Monemar	Shallow Impurities in Semiconductors 1988, B. Monemar (Ed.), Institute of Physics, Bristol, 1989, pp. 1–579
1990	London, England	M. Skolnick, G. Davies, L. Canham E. Lightowlers, M. Brozel	Shallow Impurities in Semiconductors IV, G. Davies (Ed.), Materials Science Forum 65–66 (1991) 1–480
1992	Kobe, Japan	T. Nishino	Shallow Impurities in Semiconductors V, T. Taguchi (Ed.), Materials Science Forum 117–118 (1993) 1–535
1994	Berkeley, USA	E.E. Haller, A.K. Ramdas	Solid State Communications 93 (1995) 341–470
1996	Amsterdam, The Netherlands	C.A.J. Ammerlaan, B. Pajot	Shallow-Level Centers in Semiconductors, C.A.J. Ammerlaan and B. Pajot (Eds.), World Scientific, Singapore, 1997, pp. 1–534
1998	Montpellier, France	W. Knap, S. Huant	Shallow-Level Centers in Semiconductors, W. Knap, S. Huant and E. Frayssinet (Eds.), Physica Status Solidi B 210 (1998) 251–900
2000	Awaji Island, Japan	H. Katayama–Yoshida	M. Suezawa (Ed.), Physica B, this volume

an interstitial (double?) donor, with an ionization energy of 124.66 meV. Also in silicon, Kolomoets et al. report formation of new donors by heat treatment, 2 h at 800°C, in neutron-transmutation doped material. For the more classical donor of substitutional antimony in silicon, Fujimoto et al. compared the magneto-conductivity in bulk and delta-doped layers in the regime of weak localization. It is concluded that spin–orbit interaction has an anti-localization effect. For III–V materials, the shallow-donor activity of oxygen in the wide-gap semiconductor GaN was uncovered by Wetzel et al. At hydrostatic pressures of 18 GPa, the shallow state converts to a deep DX-like donor state. This serves as a simulation of the AlGaN alloy with a 40% Al content. Another study of metal–insulator transition, on the hydrogenic-donor impurity band in n-type GaAs, was carried out by Kobori et al. A wide range of dopant concentrations, from 10^{14} to $10^{18}\,cm^{-3}$, was used. Zeeman magneto-optical absorption was measured in fields up to 9 T. The linewidth of the $1s–2p_+$ absorption was monitored and a drastic increase with donor concentration was observed. Numerical theoretical estimates of energy-band widths were made to account for the observations. In the description of donor states in lower-dimensional III–V systems a large, all South-American, effort is made by Oliveira, Latgé, Duque, Porras-Montenegro, and others. One expects the electronic states of shallow-level impurities with their extended wave functions to be especially sensitive to the confinement imposed by spaces of mesoscopic size and of lower dimension. The theoretical studies, in the GaAs/$Al_xGa_{1-x}As$ system include single and multiple quantum wells, quantum wires and quantum dots. An effective fractional-dimensional space scheme is adopted to represent the real anisotropic system of a shallow donor in confined environment. Binding energies of 1s donor states are calculated for various well and barrier thicknesses, and for various donor positions in the wells. In the calculations effects of electric, magnetic and laser fields are also treated. As regards II–VI compounds, a new donor Al_{Zn} in ZnSe was reported by Neu et al. From the spectroscopic data in the photoluminescence experiment, i.e., the absence of 2s–2p splitting, it is concluded that the donor is free of central-cell correction. More tentatively, a shallow donor level due to lithium and a moderately deep donor level from Na, both impurities residing on interstitial sites, are reported. An interesting spectroscopic feature is the identification in the spectra of two-electron transitions, reminiscent of such transitions reported for NO

complexes and thermal donors in silicon [1,2]. Also on the issue of II–VI doping, Uplane et al. found boron to be an efficient shallow donor in hexagonal ZnO films. Interactions between donors in n-type CdTe were investigated by Karpierz et al. The line width of the optical 1s–2p transitions were studied by photoconductivity and magneto-spectroscopy for the shallow donors In_{Cd} and I_{Te}, occupying substitutional sites on the different sublattices of CdTe. A spatially fluctuating potential leads to narrow peaks for small and broad peaks for strong fluctuations. Similar detailed information on the technological process of doping was obtained by Kato et al. for germanium. In this case, the interaction between the common column-V donor As and column-III compensating acceptor Ga was monitored by the line width of As $1s–2p_{\pm}$ far-infrared absorption. A correlated distribution of ionized impurities is found if the total concentration of donors and acceptors exceeds $10^{14}\,cm^{-3}$. Such a correlation might also be reflected in the spectra of donor–acceptor pair luminescence [3–6].

3. Acceptors

In spite of their description in disparaging terms, defects and impurities are by no means entities to be avoided in semiconductors. As an illustrious example, boron as an impurity in diamond creates one of the most precious gemstones. Obeying an effective-mass description, the electronic structure of the shallow acceptor boron reflects the complexity of the diamond valence band maxima at the Brillouin zone center. A magneto-spectroscopy study by Hyunjung Kim has provided the quantitative parametrization of the boron-bound holes. The spin–orbit splitting between the $p_{3/2}$ and $p_{1/2}$ valence band maxima, $\Delta' = 16.7\,cm^{-1}$ for ^{12}C and $\Delta' = 16.1\,cm^{-1}$ for ^{13}C, is small compared to the splitting in the heavier elements Si and Ge. The Luttinger parameters γ_1, γ_2 and γ_3 characterizing the dispersion of these bands near their maxima were determined, the value $\gamma_2/\gamma_3 = 0.08$ revealing a strong mass anisotropy for the light- and heavy-hole bands. Applying a magnetic field, the Zeeman splitting factors g_1 and g_2 were determined in magnitude and sign. An even more complex situation of acceptor states in the lower-dimensional system of cubic InGaN/GaN multiple quantum wells (MQW) was treated theoretically by Sipahi et al. A modified $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian for the kinetic energy is implemented in a multiband (6×6) Luttinger–Kohn effective-mass equation. Spin–orbit split-off bands are included, as well as strain energies due to lattice mismatch at the interfaces of the wells. Valence band states are calculated self-consistently for undoped MQWs. Conditions of acceptor doping to obtain a two-dimensional hole gas are investigated. Unambiguous identification of common acceptor impurities in InP still shows controversies in the literature. The first optical absorption spectra of an acceptor in InP are reported by Causley and Lewis. Zeeman measurements in magnetic fields from 0.5 to 6.5 T are reported for the $1s_{3/2}(\Gamma_8^+)$ to $2p_{3/2}(\Gamma_8^-)$ transition (G line) at wave number $241.7\,cm^{-1}$. The splitting of the line in highest fields permits the determination of the g factor allowing further characterization of the acceptor. A new acceptor state related to an anti-site defect was observed by Lany et al. who implanted radioactive ^{71}As into CdTe. Following the nuclear decay scheme ^{71}As (65.3 h)$\rightarrow$ ^{71}Ge (11.2 d)$\rightarrow$$^{71}Ga$ (stable) the presence of As steadily decreases, in correspondence with its lifetime, the concentration of Ge as an intermediate product first rises and then decays, whereas the concentration of Ga grows in the last stages of the nuclear decay and rises to a saturation level. Defect identification is based on these distinct time dependencies. As recoil energies in the nuclear reactions are small, the basic defect structures do not change. Immediately upon implantation the known As_{Te} acceptor with a binding energy of 92 meV is observed through the donor–acceptor pair (DAP) luminescence at $\lambda = 819$ meV. A new DAP emission revealing an acceptor level at 42 meV appearing in the final stages of the experiment is ascribed to a Ga_{Te} anti-site center. This is similar to the Ga_{Se} anti-site center in ZnSe. Based on valency arguments the configuration corresponds to a triple acceptor. With its binding energy 42 meV smaller than the effective-mass value of 57 meV, the center has a repulsive

central-cell potential. Another application of nuclear solid state techniques was reported by Sielemann and Haesslein. The method of perturbed angular correlation (PAC) of gamma emission, allowing the determination of defect symmetries, was applied to study the trapping of interstitial atoms in germanium by indium acceptor impurities, with the isotope ^{111}In as the radioactive probe. A remarkable difference was found between In^- and Sb^+ trapping efficiencies for neutral interstitials. Although both atoms are similarly oversized impurities, the In traps interstitials, while Sb preferentially captures vacancies. A model is proposed in which a positive charge core of the interstitial accounts for the different capture behavior. Conversion of the double acceptors Be and Zn in silicon into monovalent acceptors by binding hydrogen was reported by Fukata et al. Binding one hydrogen atom, forming the BeH or ZnH centers, results in partial passivation. Full passivation occurs with the addition of two hydrogen atoms to the acceptor and formation of the BeH_2 and ZnH_2 complexes. Centers are identified by optical absorption related to electronic or vibrational excitations. With binding energies of 2–3 eV the centers have a remarkable thermal stability, possibly related to stronger forces of the double acceptor impurities. In the best traditions of the conference, the motional effects of the light hydrogen atom around its binding center and the effect on spectra were also investigated [7].

4. (Co-)doping

Intersolubility relations, when two different foreign impurities are present, have attracted the attention of semiconductor crystal growers since the early days [8]. For the specific case of two impurities interacting via long-range electrostatic forces, the effects on solubility were found to be negligibly small [9]. However, new opportunities in the subject are created by the computational power available nowadays which enable the prediction of properties of small impurity complexes with a hetero-nuclear internal structure. Modern crystal-growth techniques allow the creation of centers while avoiding the establishing of global thermodynamic equilibrium. Hence, new activity is employed to either enhance the maximum concentration of a particular common dopant or to introduce p- or n-type dopants which are normally rejected by the crystal. Theoretical work has developed the basic concepts to describe doping limits. In his Amphoteric Defect Model (ADM) Walukiewicz introduces the Fermi level stabilization energy E_{FS}, located at 4.9 eV below the vacuum level. On the basis of this ADM model, the difficulties encountered with n-type doping of diamond and p-type doping of ZnO are understood. Zhang et al. introduce pinning levels for both n- and p-type doping, governing maximum attainable electron and hole concentrations. On a microscopic level doping limitations are ascribed to the formation of the so-called killer defects. These can consist of spontaneously formed compensating defects, such as the acceptor-type cation vacancy in GaAs, GaN and InP. Alternatively, the transformation of a donor into an acceptor, such as the DX^- center in GaP, may limit the maximum electron concentration. It is left to the experimentalist to implement the proposed solutions and turn them into practical tools. The most notorious case is the problem of n-type doping of diamond. In theoretical studies by Nishimatsu et al. the substitutional group V or VI impurities P, N and S are found to give deep donor levels, at $E_{cb}-0.47$ eV, $E_{cb}-1.92$ eV and $E_{cb}-1.63$ eV, respectively. The center P_s distorts to a C_{3v} trigonal symmetry, possibly experimentally observed in magnetic resonance by the MA1 spectrum [10]. The parallel with the pseudo-Jahn–Teller trigonally distorted substitutional nitrogen center is apparent [11]. The introduction of hydrogen produces PH complexes with H on an antibonding interstitial site. The presence of H pushes up the P level to form a PH impurity band with electron conductivity. The p-type conductivity of the II–VI compound ZnSe was achieved by co-doping with acceptor N and donor Ga. Using nitrogen from an N_2O source, Tabata et al. report hole concentrations as high as $5\times10^{19}\,cm^{-3}$ for ZnO films on a glass substrate and $10^{21}\,cm^{-3}$ on a sapphire substrate. In theoretical work on the same system by Yamamoto et al., N is found to be

a deep acceptor, at $E_{vb} + 0.79\,eV$, whereas the N–Ga–N complex has a more shallow ground state. Experimental work of Yoneta et al. on co-doping of ZnSe by donor Cl and acceptor Li has demonstrated a reduced ionization energy for the acceptor dopant. Enhancement of the p-type conductivity of silicon can be obtained by co-doping and partial compensation by donor phosphorus, for the concentration ratio $n_B : n_P = 2 : 1$ (Kawasaki et al.). Formation of a stable acceptor complex with the structure B–P–Si–B enhances the boron solubility and the shallowness of the ionization level. A practical demonstration of the ADM model is provided by nitrogen doping of GaAs which shifts the conduction band towards the E_{FS} level. In Se-doped $Ga_{0.92}In_{0.08}N_{0.02}As_{0.98}$ an electron concentration of $n = 7 \times 10^{19}\,cm^{-3}$ was achieved, representing an increase by an order of magnitude over GaAs.

5. Special impurities: O, N, H, muon, C, Au, Pt, P

Heat treatment of silicon in a temperature range between roughly 300°C and 550°C is known to produce centers with shallow donor nature. Although the precise description of the donor formation process and donor structures is still lacking, it is related to impurity complex formation in which the light impurities H, C, N and O are involved. Species of the shallow thermal donor (STD) family as originally detected by photothermal ionization spectroscopy [12] have ionization energies from 35 to 37 meV. In the experiments of Yang et al. equal spectra were observed in nitrogen-doped Czochralski silicon. In the corresponding local vibrational modes an oxygen isotope effect ^{16}O versus ^{18}O was established. It is suggested that STDs have an N–O pair structure. In research by Langhanki et al. on hydrogenated Czochralski silicon the relation between optical centers D1–D3 and the NL10(H) and STD(H) centers was further investigated. The presence of hydrogen and oxygen in the centers was confirmed by isotope effects in ENDOR and LVM spectroscopy. In passing, it can be mentioned that no such evidence was ever reported for nitrogen. Magnetic resonance on the D1–D3 donors gave spectra with an isotropic g tensor for D1, an orthorhombic tensor for D2, similar to NL10, and confirmed participation of H in ENDOR. A model of a $C_i-H-(O_i)_2$ complex as a single donor is proposed. As illustrated by these papers, defect modeling is still in a stage of speculation. An abundance of models related to the shallow thermal donors observed as STD(A,...,G), NL10(H,Al,X), N–O(1,...,5), D1, D2, D3 or AA1 stresses the need to refer to centers by their carefully identified high-resolution spectroscopic fingerprints, as obtained in electronic or vibrational optical spectroscopy (FTIR) and magnetic resonance. The high-field magnetic resonance, with microwave frequencies of 90 GHz and more, presently enjoys rapid development and will improve spectral resolution. Also, the advent of crystalline mono-isotopic silicon (^{28}Si) holds great promise. Oxygen being the key impurity in most of these donor formation processes, its properties are of particular relevance. In the theoretical studies of Yamada–Kaneta the vibrations of oxygen in silicon, considered as an Si–O–Si center, coupling to the A_{2u} and A_{1g} local phonon modes is included. The spectrum of the low-energy anharmonic excitations of local phonon states could be consistently determined. Studies by local vibrational mode (LVM) spectroscopy, a field of more recent strong activity, have proven to be very fruitful. In LVM, using frequency shifts induced by isotope substitution, atoms can be chemically identified and for this reason LVM has been referred to as the ENDOR of optical spectroscopy [13]. In contrast to magnetic resonance, the LVM spectroscopy can be applied to all defect charge states. Murin et al. presented a new assignment as an $(Si_i)_2O_i$ complex for the LVM at $936\,cm^{-1}$. A previous identification as Si_iO_i complex, based on EPR studies of the A18, AA13 and AA14 centers, correlated with a DLTS level at $E_{vb} + 0.13\,eV$, was questioned. In germanium, an enhanced formation of oxygen-related thermal double donors (TDD) following MeV-electron irradiation is reported by Murin et al. for the earliest species TDD1–TDD4. An equivalent effect is absent in the silicon case. It indicates an alternative mechanism of TDD formation, such as a transformation of radiation-induced defects into thermal double donors. Also,

further studies were carried out by Murin et al. on the known phenomenon of hydrogen-enhanced migration in silicon. The identification of lines in LVM spectroscopy with particular defects has allowed detailed studies of defect generation sequences. A spectacular enhancement of diffusion rates of oxygen and small oxygen aggregates, by factors of 10^5–10^6, can occur, especially at temperatures below 300°C. In a microscopic model, the interaction of hydrogen with oxygen results in a substantial lowering of the migration barrier, from a standard 2.53 eV to typically 1.6–2.0 eV. The hydrogen-assisted motion of defects is a more general phenomenon, as demonstrated by Mukashev et al. Applying magnetic resonance as the experimental tool, the hydrogen-assisted formation of self-interstitial complexes, was detected and monitored through the AA1 spectrum. The AA1 center is an interstitial-type defect, a shallow double donor, similar to the NL8 TDD, but with a distinctly different structure. Formation of vacancy aggregates is observed via the AA17 spectrum, corresponding to a more exotic structure of a hydrogen-passivated ring-hexavacancy. Formation of the interstitial aluminum pair, EPR spectrum AA15, at the low temperature of 200 K gives evidence of hydrogen-enhanced aluminum migration. In view of the stable bonding of hydrogen into its molecule H_2, the presence of H_2 in silicon is expected, but is difficult to observe. Applying Raman spectroscopy, Mori et al. concluded that H_2 molecules can stay as molecules on T_d interstitial sites, can be trapped as platelets or be trapped at multivacancies. For the divacancy, specifically, having trapped three molecules the V_2H_6 center is assigned in Raman-shift spectroscopy to an absorption at 3815 cm^{-1}. The center is stable, in 30-min isochronal thermal anneal studies, up to 200–250°C. The formation and structure of hydrogen platelets in silicon was the subject of theoretical studies by Kim and Chang. In their energetically most favorable model hydrogen saturates internal (1 1 1) surfaces with H_2 molecules at interstitial sites in between. The positive muon can be considered as a light-mass radioactive proton analogue. Observation of muon spin rotation is a useful tool for the study of defect structures and dynamics. Applying the technique to GaAs, Shimomura et al. concluded that the muon on the anomalous bond-centered site is an active electron–hole recombination center. In contrast, the muon on the normal T_d site does not have a strong interaction with photo-excited carriers. Generally, hydrogen is found and employed to partially or fully passivate electronic centers. The opposite effect can also happen, as exemplified by the hydrogen interaction with the iso-electronic carbon impurity in silicon. The C_s-H_i complex has a donor level at $E_{cb}-0.15$ eV, as observed by Fukuda et al. in DLTS studies. By observation of uniaxial stress-induced splitting of the spectra, the defect symmetry was determined to be trigonal. Hydrogen is considered to occupy a bond-centered position. A related $C_s-(H_i)_2^*$ complex, also with a trigonal structure, but with a pair of symmetry-inequivalent hydrogen atoms, was reported by Markevich et al. The defect structure was determined with LVM spectroscopy, using isotope substitutions $^1H/^2H$ and $^{12}C/^{13}C$ and application of uniaxial stress. Carbon–carbon pairs with both carbon atoms on substitutional sites have been studied quite extensively by magnetic resonance, either direct or via the ODMR of the 0.97 eV zero-phonon luminescence. They are observed, in different charge and motional states, by the EPR spectra G11, G11*, L7, WL1 and PT1. Pairs of C_s–Si_i–C_s are formed upon irradiation when a C_s–C_i pair traps a vacancy. Lavrov et al. have observed the local vibrational modes at 527 cm^{-1} for the neutral and at 749 cm^{-1} for the negatively charged C_s–C_s pair. Upon hydrogenation new LVMs are observed arising from the trigonal axial complex C_s–H H–C_s, with both C atoms and H atoms on equivalent places. Complexes are stable up to 700°C. Partial passivation of the 5d transition metals gold and platinum is reported by Huy and Ammerlaan. A new EPR spectrum NL64 corresponds to a triclinic AuH_2 complex, with a structure similar to an earlier described PtH_2 center. Platinum is partially passivated by the formation of trigonal PtH_3 centers. In theoretical studies, Caldas and Baierle could show that for interstitial phosphorus in silicon the split-interstitial configuration $(PSi)_i$ is the most favorable one, in an analogy to the silicon self-interstitial. The P donor can be de-activated

by the self-compensation process of formation of P_s–P_i pairs. It is remarkable that some 175 years after the discovery of the element silicon, new basic information on the most common form of its n-type doping is presented at a frontiers-of-physics conference. Good news for those among us who wish the defects-in-semiconductors field a lasting future [14].

6. Spectroscopy

Traditionally, optical spectroscopy has been the main experimental tool for in-depth characterization of centers with shallow levels. By applying external perturbations on the shallow-bound electron states, such as by magnetic fields or by hydrostatic or uniaxial strain fields, the information on energy spectra can be enhanced, e.g., by lifting degeneracies. Observation of polarization effects in absorbed or emitted light can be very informative. With the theoretical effective-mass description available, interpretations can be made on a high level of scientific sophistication. As an example the study by Fisher et al. on germanium doped with donor P and compensating acceptor Ga can serve. The effect of surface strain, caused by abrading of samples, is manifested in the hydrogenic spectra of the bulk shallow donors and acceptors. The observed splitting of the $p_\pm$ lines of P indicates a splitting induced by a uniform uniaxial compressive force, which is well-known both in theory and experiment. Therefore, from the observed splitting of about $1\,cm^{-1}$ the acting strain can be calculated. The resulting value is then used in the quantitative analysis of splittings in the gallium acceptor states. New improved values for the deformation potentials of Ga are derived. Subsequent relaxation of the strain by treatment in an ultrasonic cleaning bath could be followed. Investigations by Alt et al. have given structural information on the nitrogen accommodation in GaAs and $In_yGa_{1-y}As$, both for bulk material and in the form of multiple quantum wells. Following the implantation of nitrogen, local vibrational modes are observed at $473\,cm^{-1}$ for ^{14}N and at $458\,cm^{-1}$ for ^{15}N. From simultaneous implantation of both isotopes the structure is established as an isolated single nitrogen center. This is the nitrogen species active in formation of ternary $GaAs_{1-x}N_x$ or quaternary $In_yGa_{1-y}As_{1-x}N_x$, alloys. Intrinsic properties of wurtzite-GaN using high-quality crystals grown by the lateral epitaxial overgrowth (LEO) method were investigated by Chichibu et al. In the specimens free excitons are observable at room temperature. From the analysis of optical spectra observed in free-standing GaN at 10 K the exciton-polariton dispersion relationship and polariton lifetimes were determined for the three fundamental excitons A, B and C. Neu et al. derived selection rules for optical phonon-assisted transitions, involving neutral donors or acceptors in hexagonal (wurtzite) GaN. Based on site symmetry and using the methods of group theory, a classification is given of optical absorption and emission processes, involving free or impurity-bound carriers, with or without spin–orbit interaction. Lines in published optical spectra are assigned to one- or multi-phonon-assisted transitions. A new manifestation of two-electron transitions (TET) is reported by Nakata et al. for lithium-doped ZnSe. Li_{Zn} is an acceptor with the binding energy 110 meV; Li_i is a shallow donor with ionization energy 15 meV. In the optical absorption spectrum some additional lines replicating the main transitions are observed. One of these, at around 100–102 meV, is interpreted as reflecting the simultaneous excitation of acceptor Li_{Zn} from $1s_{3/2}$ to the $2p_{5/2}$ doublet and an adjoining donor Li_i from 1s to 2s, by 6.4 meV. Information on the distance in this $Li_{Zn}-Li_i$ donor–acceptor pair and its influence on the absorption is not yet available. Yoshino et al. have continued their exploration of native non-radiative centers in ZnSe which affect blue light emission. The piezoelectric photoacoustic signal was used to directly detect non-radiative carrier recombination processes, to complement the observation of radiative transitions in the photoluminescence (PL) spectra. A new deep level related to aluminum defects is observed in ZnSe : Al substrate. A study of exciton dynamics in CdTe was made by Seto et al. Donor-bound excitons D^0X were observed by their photoluminescence around 1594 meV, and acceptor-bound

excitons A^0X near 1590 meV. In the time-resolved experiment, with a system response time of 15 ps, a trapping time of order 1 ns was measured for D^0X, shorter than for A^0X. It is concluded that the neutral donor interacts with excitons through long-range Coulomb-like forces. The full time evolution of the bound-exciton states is analyzed by a set of rate equations. Fujii et al. performed time-resolved photoluminescence measurements of manganese-doped superlattices of CdS, CdSe and CdTe with a ZnS barrier layer. The forbidden intrashell d–d transitions acquire transition probability through interaction with host crystal atoms. Time dependency studies of the Mn luminescence around 600 nm indicated shorter lifetimes for the superlattices than for bulk material. Analysis of the luminescence decay requires two time constants both of which are correlated with the spin–orbit interaction constants ζ_{LS} of S, Se and Te.

7. Applications

Laser action can arise from population inversion of light- and heavy-hole bands in germanium. By excitation in crossed electric and magnetic fields holes can be accumulated in the light-hole band, with a typical lifetime of 10^{-11} s. Far-infrared emission is obtained by stimulated inter-sub-band transitions to the heavy-hole band, with a typical lifetime of 10^{-12} s. The spectrum of emission spans a wavelength range from 50 to 500 μm, in the region of a few THz. It was found that the gain is reduced by group-III shallow acceptors, such as Ga, causing self-absorption at the lasing wavelength, a disturbing effect which does not occur for group-II elements. The effect of intra-center absorption on the gain and the emission spectrum of p-type Ge lasers was investigated by Hübers et al. The absence of self-absorption of the far-infrared emission inside the Ge : Be lasers gave an amplification twice that of Ge : Ga lasers. New mechanisms for laser action in the mid- and far-infrared are based on donor states in n-type silicon and use an occupation inversion between longer-living higher and shorter-living lower states of photo-excited neutral donor spectra. For Si : P the stimulated emission by the transition from $2p_0$ to 1s(E) states at wavelength $\lambda = 59$ μm was observed by Orlova et al. A second system employs the longer lifetimes of the higher electronic states compared to the $2p_0$ state in Si : Bi to obtain lasing conditions. The range of spontaneous emission is from 100 to 300 μm. Ternary semiconductors of I–III–VI_2 composition, with chalcopyrite structure, are suitable materials for photo-voltaic applications. With a high absorption coefficient above $10^5\,cm^{-1}$ over the entire range of visible light, only 1 μm thin films are required for full energy conversion. Extensive optical and electrical measurements on the compounds $AgIn(S_xSe_{1-x})_2$ and $CuGaSe_2$ were performed by Yoshino et al. with the aim of detailed materials characterization. In the former material, the band gap is adjustable from 1.2 to 1.9 eV. In the photoluminescence spectra the free-exciton emission is observed indicating high purity and low intrinsic defect concentration in the samples. In solar cells of these materials conversion efficiencies of 18.8% are reached, comparable to the performance of polycrystalline silicon devices. Besides these examples of laser and solar cell fundamentals and development, the topic of doping limits and co-doping and the process of hydrogen passivation, as mentioned in other sections of this paper, have a clear relevance in applications as well.

8. Related topics

In addition, papers were contributed dealing with related defect issues, with more indirect effect on semiconductor doping. In response to the growing interest in SiGe alloys new investigations were made on the structure of native defects in germanium by da Silva et al. For the vacancy four charge states within the band gap were found distorting the same way as the silicon vacancy. Contrary to silicon, however, V^+ is also a stable state. Due to small E-mode coupling no negative-U effect occurs. The stable configuration for the self-interstitial is a split $\langle 1\,1\,0\rangle$ dumbbell with four neighbor atoms involved, forming a structure referred to as kite defect. Due to a different covalent radius from the host, dopant atoms

induce strain fields in the host crystal around their site. To relieve such strains voids and dislocation loops are generated. For the case of nitrogen doping of silicon, Harada et al. considered the configurations N_s, interstitial N_i, the N_i pair and N_2V. The strain energy associated with the N_2V complex was found to be smallest. This will result in reducing free-vacancy concentration and void formation. Dislocation mobility in non-polar silicon is considerably lower in comparison to the III–V and II–VI zinc-blende polar semiconductors. Fazzio et al. considering the energies involved in core reconstruction of 30° partial dislocations were able to correlate the reconstruction energy with activation energies for dislocation velocity. In addition, a new model for the electronic band structure associated with the dislocation core is proposed. An understanding of the detrimental effects of extended defects, either by themselves or through interaction with dopant point defects, is crucial for the development of better semiconductor devices. Calculations by Fazzio et al. show that dopant atoms segregate towards stacking faults in Si and GaAs. A silicon impurity in GaAs finds itself on a more stable position both on a Ga site and on a metastable interstitial site near Ga in the core of a stacking fault than in the crystalline environment. The silicon impurity exhibits a DX-like behavior with an associated small lattice relaxation. Investigation of impact ionization of neutral-donor-bound excitons (D^0, X) in n-type GaAs is reported by Aoki. By applying voltage pulses over contacts on the sample surface a strong brightening of the He–Ne laser generated photoluminescence is observed as the result of current-induced ionization of the bound excitons, converting (D^0, X) into (D^+, X). Dynamics of hot carriers in n-type InGaAs films were studied by the resonant photo-electromagnetic effect by Okashita et al. Studies of the improvement of Bridgman-grown n-type ZnSe crystal quality by annealing in Zn atmosphere are reported by Yoneta et al. By deep-level transient spectroscopy (DLTS) an electron trap at 0.3 eV was measured. The density of this trap was reduced upon prolonged annealing at 800°C. Electron transport in the amorphous semiconductor SnO_2, heavily doped with native oxygen vacancies, was measured by Mukashev et al. A model to explain the temperature effect of the conductivity near the metal–insulator transition is proposed. Applying photo-thermal excitation CVD, Nakayama et al. were able to grow silicon layers at low-temperatures super-doped with the 3d transition metal Mn to the concentration of 10%. In this new silicon-based dilute magnetic semiconductor, the ferromagnetic state is controlled by a double exchange mechanism via spin-polarized carriers and can therefore be influenced by doping, carrier injection or illumination. The properties of this novel material were studied. Mn atoms preferably occupy interstitial sites. Valence states form a 3d electron band by sp–d hybridization. At low-temperatures carrier scattering by Mn magnetic moments is observed in an anomalous Hall effect.

9. Conclusion

Though the subject of shallow-level states is not sharply delimitated, a coherent set of lectures was presented at SLCS-9. Looking at the meeting from an alternative point of view, the scientific and technological information discussed can be summarized on the common denominator of semiconductor doping. As doping is the foremost process required for the transformation of intrinsic semiconductor materials into bulk samples, structures or devices offering numerous opportunities for innovative research and application, the dopings issue is of an indisputable relevance. At SLCS-9 progress in the identification and characterization of shallow dopant impurities in fundamental physico-chemical terms has been thoroughly discussed. In a natural way, special attention has gone to newer materials, such as the wide band gap semiconductor GaN, and to newer structures, for instance in the form of lower-dimensional configurations. An understanding of the doping process leads to control over application as reflected in this meeting on control of doping, hydrogen passivation, solar cell optimization or implementation of advanced laser principles. Yumebutai, the stage of dreams, has been, through the research efforts of physicists, a stage of dreams that came to fulfilment during the few

days of SLCS-9. For the next meeting, the 10th in the series, scheduled for the year 2002, new progress can be anticipated.

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