EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

CERN/ISC 96-15
ISC/P81
22. APRIL 1996

PROPOSAL TO THE ISOLDE COMMITTEE

GOLD AND PLATINUM IN SILICON - ISOLATED IMPURITIES AND IMPURITY COMPLEXES

Aarhus[1] - Dublin[2] - Konstanz[3] - Lisboa[4] - CERN[5] Collaboration

A. Burchard[3], J. Correia[4], M. Deicher[3], M. Fanciulli[1], D. Forkel-Wirth[5], M. Henry[2],
R. Magerle[3], and G. Weyer[1]

Spokesperson: M. Henry
Contactperson: D. Forkel-Wirth

Geneva 1996

ISC/P81/S

GOLD AND PLATINUM IN SILICON - ISOLATED IMPURITIES AND IMPURITY COMPLEXES

Aarhus[1] - Dublin[2] - Konstanz[3] - Lisboa[4] - CERN[5] Collaboration

A. Burchard[3], J. Correia[4], M. Deicher[3], M. Fanciulli[1], D. Forkel-Wirth[5], M. Henry[2], R. Magerle[3], and G. Weyer[1]

Spokesperson: M. Henry
Contactperson: D. Forkel-Wirth

Summary

Gold and platinum impurities in silicon are exploited for the control of minority carrier lifetimes, and this important feature has resulted in sustained research interest over several decades. Although the properties of isolated substitutional Au atoms are well understood, this is not the case for Pt. Considerable uncertainty exists regarding the nature of several Pt related defects observed in electron paramagnetic resonance (EPR) and photoluminescence (PL). One of the objectives of this experiment is to exploit the transformation of radioactive Au isotopes as a means of producing specific Pt centres, and to use our thorough knowledge of Au in silicon to guide us in the interpretation of data obtained for the centres when they transform to Pt.

In addition to isolated impurities, the experiment also addresses the question of pairs of atoms formed by Au and Pt with Fe and Li. Several separate studies of these impurity pairs have been reported, but the benefits of a direct comparison of the defects in both the Au and Pt forms should be substantial. A special case of impurity pairing is provided by pairs of identical atoms. Au-pairs in silicon have been cited as the source of both EPR and optical spectra, but for Pt-pairs no evidence of any optical effects has been reported. The use of radioactive Au provides the opportunity of not only producing Pt pairs but also Au-Pt pairs as an intermediate species. These issues will be addressed by means of photoluminescence and deep level transient spectroscopy and substantial progress in the understanding of these impurities in silicon is expected to result from the work.

1. Introduction and Motivation

Transition metal impurities in semiconductors are of common scientific and technical interest. Most of these impurities create energy levels deep in the band gap, providing effective recombination centres for free charge carriers. Therefore, dopants like gold or platinum are widely used in silicon device technology to increase transistor switching speed by reducing minority carrier lifetime and diffusion length. On the other hand, the semiconducting material can be easily contaminated with these fast diffusers during device processing steps. In successive phases of microelectronic technology, *ad-hoc* solutions have been found for such metal contamination. The most common approach is to precipitate the metal atoms beneath the region of the silicon wafer in which the integrated circuits are produced. This procedure has been successful, but it imposes extremely stringent requirements on chemical purity of materials and processing techniques. It is becoming apparent, however, that as devices get smaller and the level of integration increases, the tolerance level for residual metal impurities will decrease further. The only viable approach in the long term is to fully suppress the detrimental effects of such contaminants, or, in a benign scenario, to exploit their properties to advantage. In either case, a fundamental knowledge of the impurity metal properties, and the interactions between impurities, will be essential.

In this proposal, we address some of the fundamental issues regarding a selection of the elements of importance in silicon technology. Au and Pt are among those of most importance, as pointed out above. Au is commonly used in producing metal contacts to devices also and will inevitably be one focus of attention. The elements from Mn to Cu, notably Fe, are among the fast diffusing impurities which enter the silicon wafer during high temperature processing. The quartz tubes used for furnace annealing also contain significant traces of lithium, which not only diffuses rapidly at high temperatures but which is also mobile at room temperature. It is not surprising that considerable attention has been devoted to these impurities in silicon over the years. Despite that, the subject is recognised as one of the most intractable in silicon research, mainly due to the difficulty of identifying specific defects with specific elements. The exploitation of radioactive transformation should provide special insights in this respect.

2. Au and Pt in silicon

The details of the electronic and optical properties of isolated Au atoms in silicon appear to be finally established approximately forty years after the earliest studies [1,2]. Specifically, the donor and acceptor levels in the band gap and the corresponding optical absorption signatures are now known to high accuracy [2]. In the course of the forty years of study, many other Au-related defects were uncovered by a variety of techniques, especially electron paramagnetic resonance (EPR) [3, 4]. Generally, the pairing of the Au with trace metal contaminants is believed to account for these defects [5]. The role that Au might play as an unintentional metal contaminant in the production of defects in other studies has not been as widely accepted. We show below that this is indeed an important consideration.

The experimental study of Au in silicon has frequently involved comparison with Pt, its neighbouring element. Much success has been achieved by exploring the similarities expected for Au^0 and Pt^- which have the same electronic configuration, for example [6]. A particularly useful example is that described by Petersen et al. [7] in a study using radioactive isotopes whereby the association of a DLTS (deep level transient spectroscopy) peak with substitutional Au was confirmed via comparison with Pt. With respect to complexes involving other impurities in silicon, Pt shows some of the same trends as Au. One of the most recent publications on this subject concerns Au-Li and Pt-Li [8]. These parallel studies of Au and Pt are obviously significant for establishing the true nature of the defects, their structures and energy levels.

Reference has been made above to the use of EPR, optical absorption and DLTS in the study of defects. EPR and DLTS are both "ground state" techniques in that only the defect ground state may normally be studied. Optical absorption has all the benefits of spectroscopic techniques, especially high specificity and high accuracy, with the advantage of providing both ground state and excited state data. However, path lengths of several mm and defect concentrations of typically 10^{14} - 10^{15} cm^{-3} are necessary. Accordingly, the technique would require samples containing unacceptably high amounts of radioactive isotopes. The inverse of optical absorption - luminescence - does not have this disadvantage. The most common means employed for generating luminescence is to use an optical pump (usually a laser) to produce electrons and holes in the semiconductor. When these carriers become bound and recombine at defects or impurities, the spectrum of the recombination radiation-line energies, vibrational sidebands, temperature dependence of the intensities, etc. - contains a wealth information on the defect or impurity. The term photoluminescence (PL) is used to denote such optically-generated luminescence. PL is employed widely in all classes of semiconductor (and other) research and is recognised as one of the most important and powerful techniques available [8]. The principal advantage it offers, in addition to the usual advantages pertaining to spectroscopy, is the potential for very high sensitivity. For semiconductors, the penetration depth of the laser radiation and the diffusion length of electrons and holes are generally of the order of 100 μm, often less. A typical laser beam has a cross-sectional area of ~10 mm^2. Accordingly, the effective sample volume for PL is of the order of 10^{-4} cm^3. The detection limit can be as low as 10^{13} cm^{-3} in favourable cases, so that a total of 10^9 atoms can be sufficient to produce detectable PL signals. This can be lowered further by focusing the laser to a spot, for example. To get the full benefits from PL it is usually necessary to operate at liquid helium temperatures, thereby minimising vibrational effects and enabling weakly bound electrons and holes to remain bound at defects/impurities so that the optical transitions occur. One consequence of this high sensitivity is the capability of detecting trace contaminants in nominally intrinsic semiconductors. During the course of PL studies of transition metals in silicon, many investigators have been unable to determine with confidence the chemical identity of impurities giving rise to particular PL signals [9]. Combining PL with radioactive atoms, however, allows direct identification. Provided the radioactive decay causes a chemical transformation (normally a β-decay), the strength of the PL signal will change with the typical time constant of the radioactive decay, which then can be taken as the impurity's fingerprint.

The feasibility of using luminescence with radioactive isotopes has been confirmed independently by the Dublin and Konstanz groups using ^{111}In in both silicon [10] and gallium arsenide [11]. In our proposed experiments we intend to perform studies on radioactive Au and Pt isotopes in Silicon. There exist several isotopes decaying from Au to Pt, which provides the perfect means of comparing corresponding defects involving the two elements, unambiguously labelled via the radioactive decay constant.

3. Current status of research

3.1 Feasibility Studies

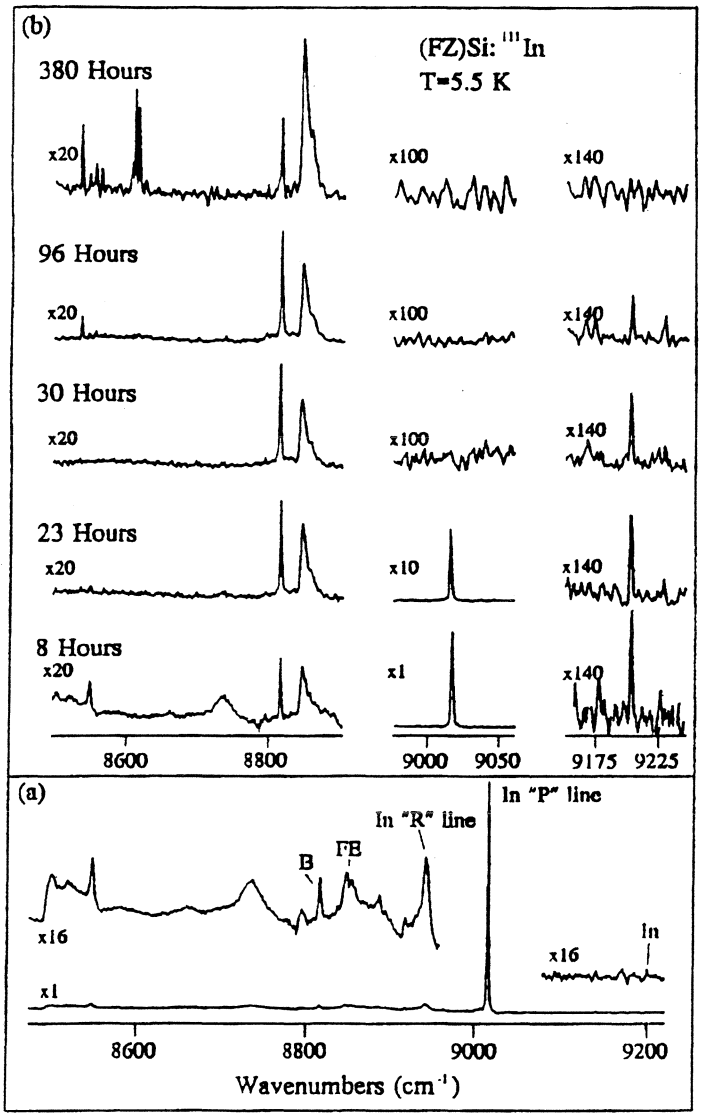

Fig. 1: PL spectra of Si:^{111}In recorded at 5.5 K and different times after doping (b). The In acceptor bound exciton line occurs at 9200 cm^{-1}. The P-line (a) is due to an isoelectronic centre, features 'B' and 'FE' are due to residual boron acceptors and free excitons, respectively.

The first PL experiments using implanted radioactive isotopes were performed during 1994 using ^{111}In decaying to ^{111}Cd in both silicon and GaAs [10,11]. The samples were prepared in Bonn and Konstanz. In the case of silicon, the substitutional In acceptor centre and another well-known (but not yet fully identified) isoelectronic centre were observed. The data are presented in Figure 1. The loss of intensity in the In acceptor bound exciton line at ~ 9200 cm^{-1} follows closely the expected trend. For the isoelectronic ('P') centre, the decay rate was found to be much faster than expected. Subsequent measurements revealed that this rapid loss of signal was due to cycling the sample to room temperature in the intervals between making PL measurements [12]. After several days and weeks, new features appear in the spectra. These previously unknown lines have been confirmed using stable Cd implantation as being due to Cd, the daughter of the ^{111}In decay.

The data for ^{111}In in GaAs are summarised in Figure 2 [11]. In this case, the evidence lies in the growth of a Cd-related band. The intensity changes, normalised to a common feature in all spectra, have been fitted successfully and are found to be in agreement with the 2.8 day half-life of ^{111}In.

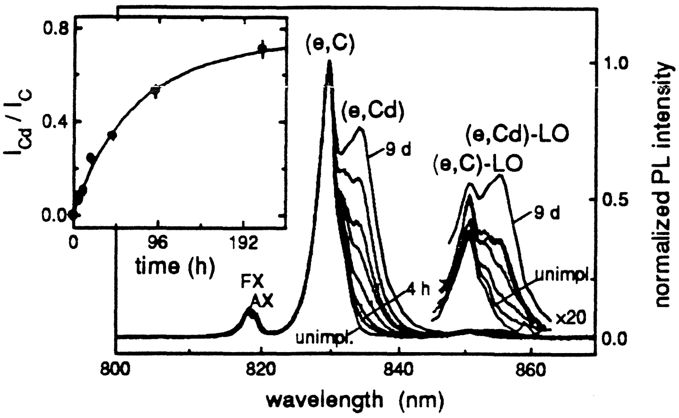

Fig. 2: PL spectra of undoped and ^{111}In doped GaAs taken 4 h, 12 h, 22 h, 2 d, 4 d, and 9 d after doping. All spectra are normalised to the intensity of the (e,C) peak. The inset shows the height I_{Cd}/I_C of the (e,Cd) peak as function of time after doping [11].

3.2 Experiments at ISOLDE

The success achieved in the feasibility experiments prompted new experiments using other isotopes. The availability of Hg beams in 1995 provided the opportunity to perform one exploratory experiment regarding Au-related defects. The outcome of these measurements was very revealing and examples of the data obtained are shown in Figure 3. Two isotopes, mass 191 and mass 195, were used:

$$^{191}Au \xrightarrow{3.2h} {}^{191}Pt \xrightarrow{2.9d} {}^{191}Ir$$

$$^{195}Au \xrightarrow{183d} {}^{195}Pt$$

The data obtained for mass 195 are shown in Figure 3(a). The spectrum in Figure 3(a) is typical of those produced by many transition metals in silicon. The sharpest lines on the high energy (or wavenumber) side of the spectrum are caused by electron-hole recombination without any phonon involvement. For defects which have significant electron-phonon coupling, some of the recombination energy goes into the production of phonons, and the energy of the emitted photon is reduced accordingly. Thus, PL spectra usually contain a structured phonon sideband of the sharp (purely electronic or zero-phonon) lines extending to lower energies. Where a particular mode of vibration is favoured by the defect, a prominent peak occurs in the sideband shifted from the zero-phonon line by the energy of the mode. Thus, PL can also provide data on the vibrational properties of defects.

The group of lines labelled A in Figure 3(a) is observed in the early stages of the decay. A new group of lines, labelled B, appears and dominates in the spectrum after ~200 days. The A group is a well-studied spectrum attributed to Fe [13]. Here, however, we see that it appears to be related to Au. We observe another Fe-related spectrum in the sample (outside the range shown in Figure 3) and we believe that the A group of lines is due to a defect involving *both* Fe and Au.

The appearance of group B as Au decays to Pt suggests that B is due to Pt. Furthermore, the details of the spectrum - line separations and relative intensities - show quite strong similarities to the A group. We strongly suspect that B is in fact the direct analogue of A a Pt-Fe defect being the luminescence centre. Such centres have been reported in EPR [14].

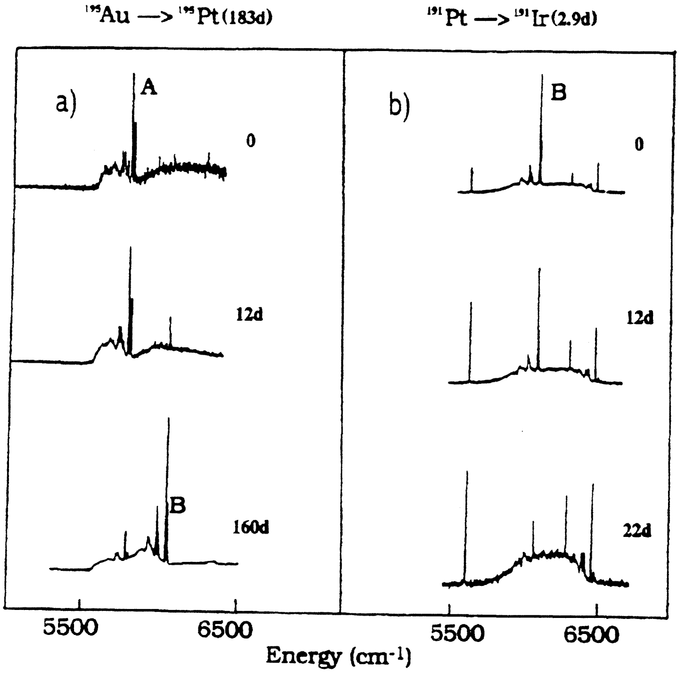

Fig. 3: Pl spectra recorded for Si samples implanted with radioactives isotopes derived from Hg parents. Part (a) shows the results for ^{195}Au → ^{195}Pt, part (b) for ^{191}Pt → ^{191}Ir.

We now turn to the data in Figure 3(b) obtained for mass 191. The samples were first studied six days following implantation, by which time roughly 75% of the implanted atoms had transformed to ^{191}Ir, the remaining 25% being ^{191}Pt. The B group of Figure 3(a) is dominant in the spectrum, and it decays in accordance with the 2.9 day half life of ^{191}Pt. Of the other lines in the spectra of Figure 3(b), there are no reports in the literature. It is highly likely that the final stable product of the decay, Ir, is the source of these new features.

In summary, the preliminary measurements we have made have revealed the following:

- A luminescence spectrum commonly believed to be due to Fe is found to be Au-related and most probably is due to a Au-Fe pair defect.
- A new Pt-related luminescence spectrum is observed, most probably due to Pt-Fe pair defects in the samples.
- The presence of Ir in silicon results in the occurrence of several previously unknown luminescence spectra.

These experiments were conducted on a very limited set of samples due to the time constraint as parasitic user. Only one type of starting material was used. The isotopes chosen were those with reasonably long half-life values - several days minimum - to enable the samples to be transported to Dublin for the measurements.

4. Proposed Experiments

4.1 Isolated impurities

The experiments for which we request beam-time concern both un-resolved long-standing problems and new issues recently raised in the literature. The case of isolated substitutional Au^0 defects is now well understood [2], as is the electronically equivalent Pt^- defect [6]. For Pt^0, characteristic acceptor-like absorption spectra are observed and attributed to substitutional Pt [15]. The PL data for Si:Au corroborate the absorption data in the case of the Au donor defect [16]. No reports of PL for the Au acceptor defect have appeared, probably due to the unfavourable spectral region in which the PL is likely to occur. For Pt, however, there is complete mismatch between the absorption and PL data. The reported PL spectra show sharp lines at 805 meV and 811 meV [17]. Absorption, on the other hand, occurs at 916 meV and 989 meV [15,18]. The 805 meV PL is attributed to interstitial Pt, whereas substitutional Pt is cited as the origin of the 811 meV PL spectrum [17].

One of our experiments will involve the preparation of samples treated so that the radioactive Au occupies substitutional sites. The effect of the Au → Pt transformation on the details of the PL should enable the identifications of the Pt-related PL to be confirmed or refused.

4.2 Au and Pt pairing with Fe

These experiments are required in order to confirm the significant results obtained in the preliminary measurements described above. The presence of Fe in the samples used in that original study was inadvertent. Next, we propose to undertake comparisons of samples free of Fe-doping and samples which are co-doped with Fe. If, as we suspect, Au-Fe and Pt-Fe pairs are produced, then we can address several questions by using radioactive Au. The first question is whether the Pt-Fe defects produced by the decay of Au → Pt are the same as those formed when Pt is introduced directly. It is possible also to examine the relative PL efficiencies of Au-Fe and Pt-Fe defects if both are present in the same sample. This issue emerged in the preliminary measurements reported above - the PL due to Pt-related defects appears to be disproportionately intense. The reason for this is not known and the explanation is likely to include details of carrier capture mechanisms at the defects in addition to the relative importance of radiative and non-radiative transitions.

4.3 Au and Pt pairing with Li

The question of Au-Li and Pt-Li pair formation has emerged in the literature recently. The significant result reported to date is that accidental trace Li contamination in samples may account for hitherto unidentified defects observed in EPR [19]. Although these defects have not yet been reported as relevant to the PL properties of either Si:Au or Si:Pt, the issue merits investigation in view of the uncertainties regarding the nature of the defects which produce the PL spectra observed for Si:Pt.

4.4 Au and Pt pair defects

Defects involving pairs of Au atoms have been advanced as the source of both optical absorption [20] and EPR spectra in Si:Au [21]. For Si:Pt, EPR data consistent with a defect containing two equivalent Pt atoms in a centre of C_{2V} symmetry have also been reported [22], but in this case there are no reports of associated optical spectra. The Si:Au absorption spectra consist of a complex series of at least four groups of sharp optical transitions and vibrational sidebands. In theory, at least one group of these lines should be observable in PL. We will attempt to observe these transitions initially using stable Au ion implantations and, if successful, the experiment will be repeated using radioactive Au which decays to Pt. For pair defects, the departure of the measured decay rates from the rates consistent with the half-life will enable the involvement of two atoms in the defects to be confirmed. This experiment would also enable Au-Pt pair centres to be investigated - an intriguing prospect.

For all the experiments proposed above, the principal techniques to be employed are PL and DLTS, both of which have been proved to be feasible with radioactive isotopes. As a general rule, DLTS data (being very well known for both Au and Pt in silicon) will enable samples to be well characterised thereby providing crucial information for the interpretation of PL data. Several of the defects which we expect to produce - particularly those associated with Fe and Li - will, however, require detailed DLTS measurements in addition to PL for full analysis.

5. Beam-time Request

Of the techniques to be employed, some of the DLTS measurements will be performed on site. For PL, samples will be transported to the laboratories. The following Hg isotopes are requested:

$$^{189}Hg \xrightarrow{8m} Au \xrightarrow{28m} Pt \xrightarrow{10.9h} Ir \xrightarrow{13.1d} Os$$

$$^{191}Hg \xrightarrow{49min} Au \xrightarrow{3.2h} Pt \xrightarrow{2.9d} Ir$$

$$^{193}Hg \xrightarrow{4h} Au \xrightarrow{17.5h} Pt^{*} \xrightarrow{4.3d} Pt$$

$$^{195}Hg \xrightarrow{10h} Au \xrightarrow{183d} Pt$$

In the case of mass 189, the effective starting point of the samples will be Pt with the final product being Os. For mass 191 the sequence Au → Pt → Ir will be accessible, while mass 193 will provide Au → Pt only. By comparison of the data, it should be possible to unequivocally identify observed spectra with specific elements. For mass 195, the Au half-life of

183 days will enable long-term storage effects (essentially prolonged room-temperature annealing) to be examined.

In all cases, doses of 10^{12} atoms at 60 keV will be suitable. The availability of the high-voltage platform would be a decided advantage, but 60 keV is sufficient for PL as shown by the feasibility studies. Intrinsic, n-type and p-type materials will be used and sets of samples implanted with the radioactive isotopes only, and sets co-doped with Fe and with Li, will be required. The total estimated beam-time requirement is 12 shifts during liquid Pb runs. It will be possible, however, for other users to have access in the course of these shifts.

References

[1] C.B. Collins, R.O. Carlson and C.J. Gallagher, Phys. Rev. **105**, 1168 (1957)

[2] G.D. Watkins, M. Kleverman, A. Thilderkvist, and H.G. Grimmeiss, Phys. Rev. Lett. **67**, 1149 (1991)

[3] H.H. Woodbury and G.W. Ludwig, Phys. Rev. **117**, 1287 (1960)

[4] R.L. Kleinhenz, Y.H. Lee, J.W. Corbett, E.G. Sieverts, S.H. Muller and C.A.J. Amerlaan, Phys. Status Solidi B **108**, 3363 (1981)

[5] G.W. Ludwig and H.H. Woodbury, in *Solid State Physics*, ed. by F. Seitz and D. Turnbull (Academic, New York 1962) Vol 13, p 223.

[6] G. D. Watkins, Physica **117/118**, 9 (1983)

[7] W. Petersen and J. Nielsen, Appl. Phys. Lett. **56**, 1122 (1990)

[8] E.C. Lightowlers in *Growth and Characterisation of Semiconductors* ed. by R.A Stradling and P.C. Klipstein (Adam Kilger, Bristol 1990) p. 135

[9] H. Conzelmann, Appl. Phys. A **42**, 1(1987)

[10] S.E. Daly, M.O. Henry, K. Freitag and R. Vianden, J. Phys,: Condens. Matter **6**, L643 (1994)

[11] R. Magerle, A. Burchard, M.Deicher, T. Kerle, W. Pfeiffer and E. Recknagel, Phys. Rev. Lett. **75**, 1594 (1995)

[12] S.E. Daly, M.O. Henry, C.A. Frehill, K. Freitag, R. Vianden, G. Rohrlack and D. Forkel, in *Defects in Semiconductors 18*, ed. by M: Suezawa and H. Katayama-Yoshida (Trans Tech Publications, Zurich-Uetikon 1995) p. 1497

[13] M.C. doCarmo, M.I. Calao, G. Davies and E.C. Lightowlers, in *Defects in Semiconductors 15*, ed. by G. Ferenczi (Trans Tech Publications, Aedermannsdorf 1989) p. 421

[14] A.B. van Oosten, Nguyen Tien Sou, L.S. Vlasenko and C.A.J. Ammerlaan, in *Defects in Semiconductors 15*, ed. by G. Ferenczi (Trans Tech Publications, Aedermannsdorf 1989) p. 355

[15] G. Armelles, J. Barrau, M. Brousseau, B. Pajot and C. Naud, Solid State Commun. **56**, 303 (1985)

[16] D. Thebault, J. Barran, M. Brousseau, Do Xuan Zhang, J.C. Brabant and F. Voillot, Solid State Commun. **45**, 645 (1983)

[17] G. Armelles, J. Barrau, V. Thomas and M. Brousseau, J. Phys. C: Solid State Phys. **19**, 2593 (1986)

[18] G. Davies, E.C. Lightowlers, P. Izard and M. Brosseau, Mater. Sci. Eng. B **4**, 173 (1989)

[19] P. Alteheld, S. Greulich-Weber, J.-M. Spaeth, H. Weihrich, H. Overhof and M. Hohne, Phys. Rev. B **52**, 4998 (1995)

[20] A. Theilderkvist, S. Ghatnekar Nilsson, M. Kleverman, and H.G. Grimmeiss, Phys. Rev. B **49**, 16926 (1994)

[21] H. Hohne, Phys. Status. Solidi B **109**, 525 (1982)

[22] H.J. Von Bardeleben, D. Stievenard, M. Brousseau, J. Barrau, Phys. Rev. B **38**, 6308 (1988)