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PROPOSAL TO THE ISOLDE COMMITTEE

THE ELECTRONIC STRUCTURE OF IMPURITIES IN SEMICONDUCTORS.

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SUMMARY

The electronic structure of isolated substitutional or interstitial impurities in group IV, IV-IV, and III-V compound semiconductors will be studied. Mossbauer spectroscopy will be used to investigate the incorporation of the implanted isotopes on the proper lattice sites. High resolution conversion electron spectroscopy yields unique information on the local density of electron states around the probe atom. The data can be directly compared to theoretical calculations using the LMTO scheme. Deep level transient spectroscopy will be used to identify the band gap levels introduced by metallic impurities.

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The electrical - and partly the optical - properties of semiconductors are governed by the concentration and chemical nature of wanted or unwanted impurity atoms. This dominance is manifest in very pure semiconductors for concentrations down to or below the 10^{10} cm^{-3} range. Most conventional techniques are either unable to cope with such low concentrations or are "chemically blind". Some of these shortcomings can be overcome by the techniques proposed here, which allow for a thorough characterization of the electronic structure of impurities in semiconductors well below their solid solubility. For certain - mainly metallic - impurities, producing deep levels in the band gap, this is done by Deep Level Transient Spectroscopy (DLTS). For others a more detailed investigation of the electronic density of states can be carried out using High Resolution Conversion Electron Spectroscopy (CESVEC). Mossbauer Spectroscopy (MS) can in several cases be used to prove the proper lattice site incorporation after the ion implantation and annealing processes.

ISOLDE is a unique tool for these investigations for several reasons: Firstly, most of the ion beams are free from contaminations by stable isotopes. This is the essential feature for the DLTS measurements. Secondly, rather strong, short lived sources can be produced. This is essential for the CESVEC program. Thirdly, a broad range of isotopes of one or more elements is available simultaneously.

Besides the technologically stimulated interest of being able to manipulate the properties of semiconductors, the study of impurities - and particularly their electronic properties - has profound basic interest. The theoretical methods developed over the last two decades are among the most sophisticated many-body schemes in existence. However, many aspects of these theoretical schemes have not been tested critically against experimental results, since these have only been scarcely available.

The semiconductors discussed here all crystallize in the diamond structure and are characterized by an average number of valence electrons per atom of four: the group IV (Si, Ge, alfa tin, diamond), the IV-IV compounds (Si_xC_{1-x}, Si_xGe_{1-x}, Sn_xGe_{1-x} and $Si_xGe_ySn_{1-x-y}$) and the III-V compounds (GaP, GaAs, GaSb, InP, InAs, and InSb). The appropriate part of the periodic system is shown in Fig. 1. The electronic structure can be described by the valence bands, which are filled, the band gap, and the empty conduction bands. When a host atom is replaced by an atom of the same valence (e.g. Ge in Si) the perturbations of the electronic structure is in most cases confined to the valence bands. When replaced by an atom with a higher valence (e.g. P in Si), the most dramatic effect is the introduction of levels in the otherwise forbidden band gap, close to the conduction band. These states containing the so-called donor electrons are sources of electrons for the conduction bands. The replacement also leads to modifications of the valence bands. Analogously, replacing a host atom with an impurity with a lower valence (e.g. Al

in Si) introduces levels in the band gap, close to the valence band, which can act as a source of holes. When the valence difference between host and impurity is greater than one, complex level schemes in the band gap can occur together with modifications of the valence band structure.

Using CESVEC the modifications of the valence band structures can be monitored spectroscopically. The method relies on the fact that internal conversion can take place also in the valence shells - albeit with a very low probability. The energy of an outgoing conversion electron is given by:

(1) $E_{ce} = E_N - E_B(n,l) - W_{sp}$

where E_N is the nuclear transition energy, $E_B(n,l)$ is the binding energy of the electron with quantum numbers n,l, and W_{sp} is the spectrometer work function. The conversion electrons emerging with the highest energies (close to E_N) originate from the valence shells of the probe atom. When their energy is analyzed with sufficiently high resolution, from theer intensity a mapping of the occupied electron states at the probe atom. Conversion electron spectroscopy is thus principally similar to other electron spectroscopies, e.g. X-ray photo electron spectroscopy, except for the fact that the conversion electron emission process is localized to the probe atom. First results have been obtained and partly published within the project IS240 [1,2,3]. Fig.1 shows an example of the results obtained: Part a) shows an LMTO calculation of the local density of states around an As atom in GaAs (lower half), and around a Sn atom replacing an As host atom (upper half). The full lines represent the s-like states and the stippled lines the p-like states. Part b) of the figure shows a comparison between the broadened theoretical results and the experimental conversion electron spectrum of the 23874 eV M1 transition in ^{119}Sn incorporated on As sites in GaAs. The s- and p-parts of the calculation have been weigthed according to the known conversion coefficients, which are strongly angular momentum dependent. The theory predicts that the incorporation of a Sn atom in several III-V compounds leeds to the creation of a highly localized s-like state some 9 eV below the Fermi level. This is clearly reflected by the experimental results shown here [2], and has been shown to be a more general phenomena [3]. The LMTO scheme has thus been thoroughly tested for these rather complicated systems (amphoteric donors and acceptors in several III-V compounds). This work has also led to the conclusion that the next step in the theoretical development should be the incorporation of lattice relaxation around the over-sized impurities. We propose here to follow up on these first exploratory measurements and conduct an investigation of probe isotopes of the elements Zn, Ga, Ge, As, Se, Sn, Sb, and Te incorporated in the group IV elements, in IV-IV and in III-III compounds. Here we take advantage of the fact that isotopes of the 4sp elements (Zn, Ga, Ge, As, Se) have become available at ISOLDE with good

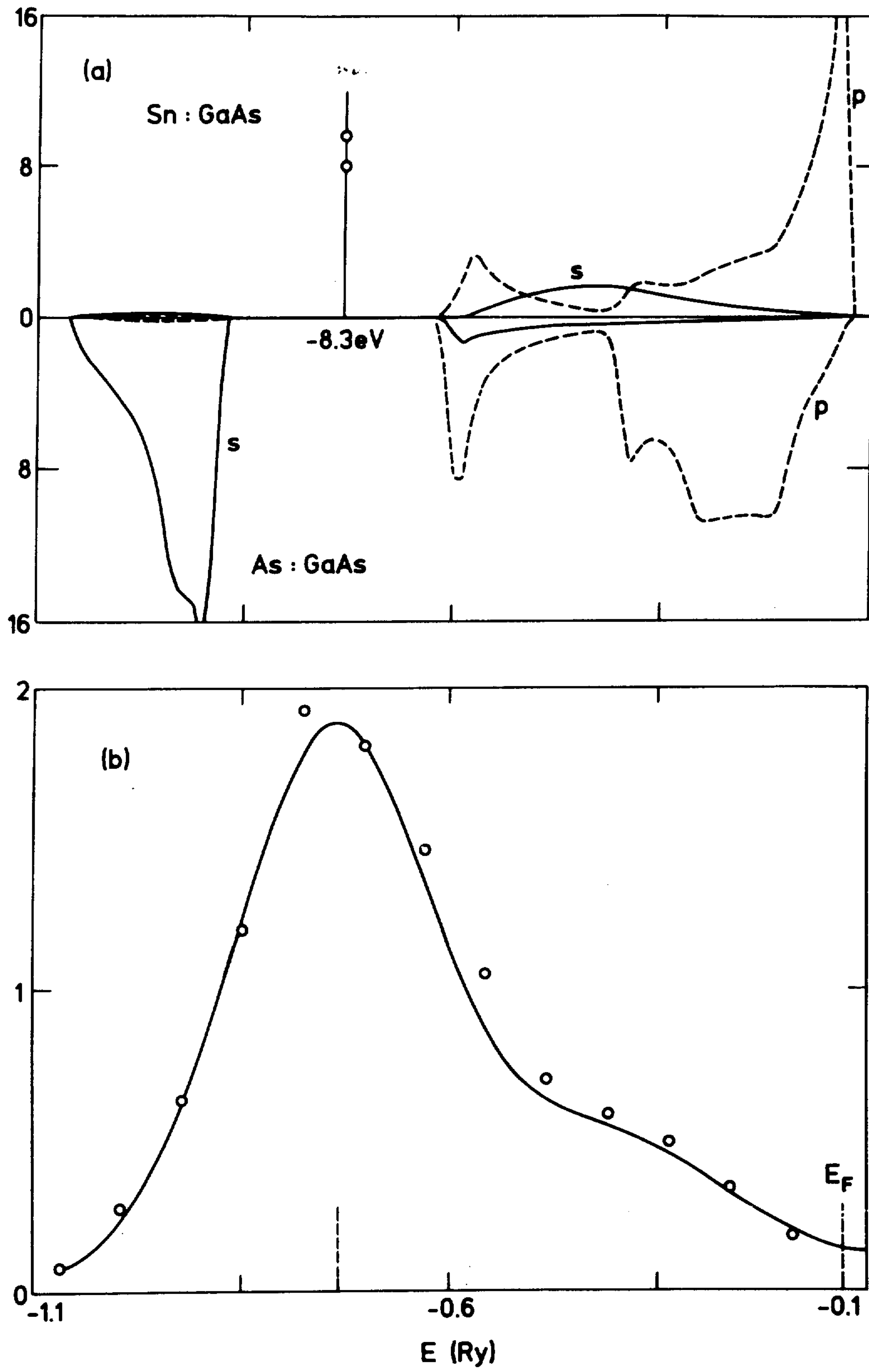

Fig.1

yields. Furthermore in the case of the 5sp elements Sb and Te, experiments have become possible by an upgrade to higher energies of the Zurich beta spectrometer, originally built for neutrino mass experiments. Theoretical calculations using the state-of-the-art LMTO scheme will be carried out on the same systems and possible improvements implemented as justified by the experimental results.

When the valence difference between an impurity and the host lattice atoms becomes sufficiently large, the most important modification of the electronic structure of the system is the introduction of complicated level schemes in the band gap. Especially metallic impurities constitute a source of wanted and unwanted donor and acceptor levels in the band gap of most semiconductors. Technologically, this can be beneficial in some cases - the growing field of band gap engineering - but in most cases it creates severe problems. Theoretically, these impurities are interesting since their choice of lattice site (generally interstitial versus substitutional) depends critically on their valence in a non-understood way. However, to solve these problems, the levels introduced by a given metallic impurity have to be identified. These impurities have very low solubilities so sensitive methods (e.g. DLTS) have been developed to detect their presence and the associated band gap levels. However, the identification has proven very cumbersome due to the "chemical blindness" of these methods. We have shown that this problem can be partly overcome by doping the semiconductors with radioactive impurities (IS01-39). This results in time dependent DLTS signals as the radionuclei transmute thus leading to an unambigous identification of the involved impurities [4,5]. Fig.2 shows the DLTS signal from an n-type Si sample doped with ^{189}Ir decaying with a halflife of 13 days to ^{189}Os. Fig.3 shows the disappearence of the two main peaks in this spectrum during the decay of ^{189}Ir.

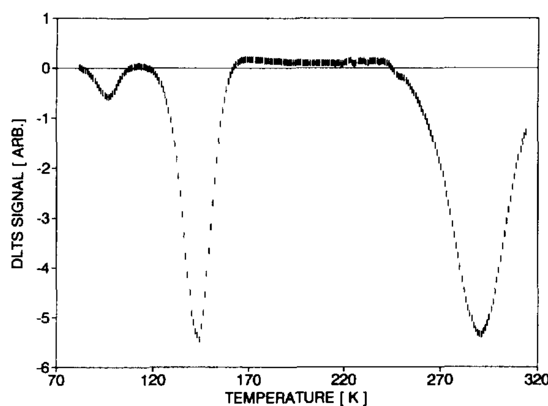

Fig.2

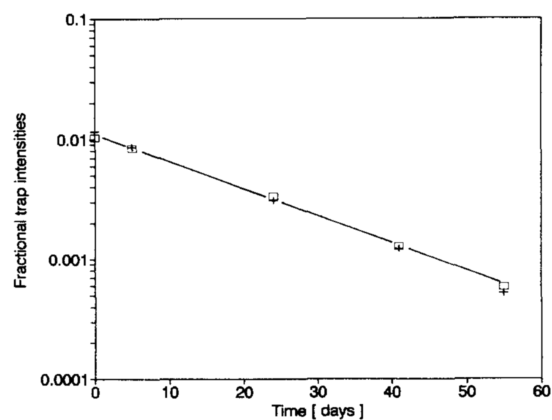

Fig.3

This proves beyond any doubt that Ir is involved in the center giving rise to these levels [5]. Likewise it was shown that both levels originate from the same defect, which we believe is substitutional Ir. In a similar manner we were able to identify the levels introduced by Pt and Au impurities in Si and to prove indirectly that these levels all originate from undisturbed, substitutional impurities. This has settled a dispute which has gone on for more than thirty years [4]. We propose to study the levels introduced by the 3d, 4d and 5d elements in Si, Ge, and Si_xGe_{1-x} compounds. The IV-IV compounds are likely to be the materials of the future, both in basic physics but even more in electronics providing the basis for the next generation of fast integrated optical and electronic components. The Institute of Physics and Astronomy in Aarhus has just aquired an MBE sytem to be able to grow high quality epitaxial films of these new materials. The materials should be available by the time of the start of the new ISOLDE facility.

For the period of 1992 to 1994 we request 50 shifts of beam time on existing target / ion source combinations. The rather large request is mainly due to the fact that the CESVEC experiments are very beam time consuming; often requiring three shifts of beam time per measurement. On the other hand, the information coming out is outstanding and cannot be obtained by any other experimental method currently avaliable. With respect to space requirements, the implantations can be carried out on the stationary collection positions requested by the solid state physics user groups. Likewise sample treatment prior to and after the implantation can be performed in the solid state physics laboratory.

References.

1.J.W.Petersen, G.Weyer, E.Holzschuh, W.Kündig, Phys. Letters A 146, 226 (1990).
2.J.W.Petersen, G.Weyer, A.Svane, E.Holzschuh, W.Kündig, Invited talk at the E-MRS spring meeting, Strassbourg, 1991, to be published shortly in Nucl.Instrum. Methods.B.
3.J.W.Petersen, A.Svane, E.Holzschuh, to be published.
4.J.W.Petersen, J.Nielsen, Appl.Phys.Lett. 56, 1122 (1990)
5.J.W.Petersen, J.Nielsen, To be published in the proceedings of the 16 th. International Conference on Defects in Semiconductors, Bethlehem, PA, July 1991.