Donors in Semiconductors - are they Understood in Electronic Era?

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Abstract. The physics of semiconductors and contemporary electronics cannot be understood without impurities. The hydrogen-like shallow donor (and acceptor) state of electron (hole) bound by Coulomb electrostatic force of excess charge of impurity is used to control conductivity of semiconductors and construct semiconductor diodes, transistors and numerous types of semiconductor electronic and optoelectronic devices, including lasers. Recently, surprisingly, the physics of impurity donors appeared to be much richer. Experimental evidence has been provided for universal existence of other types of electronic states of the same donor impurity:
i) mysterious, deep, DX-type state resulting in metastability – slow hysteresis phenomena - understood as two-electron, acceptor-like state of donor impurity, formed upon large lattice distortion or rearrangement around impurity and accompanying capture of second electron, resulting in negative electron correlation energy U;
ii) deep, localized, fully symmetric, A1, one-electron donor state of substitutional impurity.
The latter state can be formed from the "ordinary" shallow hydrogen-like state in the process of strong localization of electron by short range, local potential of impurity core, preserving full (A1) symmetry of the substitutional impurity in the host lattice.
The "anticrossing" of the two A1 (shallow hydrogenic and deep localized) energy levels upon transformation is observed.
All types of electronic states of impurity can be universally observed for the same donor impurity and mutual transformation between different states occur upon changing experimental conditions.
The knowledge about existence and properties of these "new", molecular type, donor states in semiconductors seems still await general recognition and positive application in contemporary material and device science and engineering.

1. Introduction
The role of impurities in controlling the conductivity of semiconductors was recognized at the very beginning of the history of semiconductors and semiconductor electronics. A.H.Wilson in his report on "The Theory of Electronic Semi-Conductors" [1], considered conductivity of intrinsic semiconductor, the perfectly pure cubic crystal with, at T=0K, fully filled valence band and empty conduction band, separated by energy band gap $\Delta W=W_2-W_1$. Upon comparing the theoretical results with experiment he found that experiment could be hardly assigned to intrinsic parameter, $\Delta W$, of the crystal: Gruneisen, in his article on conductivity in the "Handbuch der Physik,"[2] cites...
a number of elements as semi-conductors. Unfortunately, the resistance curves are often completely changed by the presence of small quantities of impurities...Gudden[3] is inclined to the view that no pure substance is ever a semi-conductor”. Thus, Wilson concludes that: „Theoretically there is no reason why semi-conductors should not exist...”, „Experimentally, however, the only substances which show undoubted semi-conducting properties are very impure, and it may be that they have no intrinsic conductivity. If this is so, the theory would have to be extended to take into account of the effects of impurities in increasing the conductivity of poor conductors.”.

2. Extrinsic Semi-conductors

Further theoretical considerations led to the conclusion, that the number and properties of impurities govern the semi-conducting properties of otherwise intrinsic semi-conductor or insulator. The simplest illustration on the role of impurities in changing property of the host crystal can be found in the book of Herbert Fröhlich „Elektronentheorie der Metalle” in chapter IV. „Halbleiter”[4] (Fig.1)

Fig.1 Logarithm of the number of free electrons in extrinsic (impure) semiconductor as a function of inverse temperature 1/T for different number of impurities: n_a>n_a'>n_a'' – theory [4]

One can see on the picture that for large temperature range, 1/T>1/T_c, the conductivity, proportional to the number of free electrons n, is governed by the number of impurities n_a, and the activation energy of impurity level, E_a, whereas the intrinsic properties of semiconductor can be observed at high temperatures, 1/T<1/T_c, with intrinsic gap energy, E_g, responsible for temperature dependence of n in this temperature regime.

The experimental verification of theoretical prediction of Fig.1 required vast experimental efforts in purification of germanium [5,6] and silicon [7], allowing for intentional doping with group V, (phosphorus, antimony, arsenic) and group III (boron, aluminum) impurities: Lark-Horovitz et al [5] report: „Germanium samples purified by high vacuum treatment have been alloyed by adding from 0.001 percent to 1.0 percent of metallic impurities. Plotting log ρ (resistivity) and log R (Hall constant) against 1/T shows that the resistivity at low temperatures decreases with increasing temperature, increases around room temperature and then drops sharply with a slope identical for various samples...indicating that germanium behaves at low temperatures as an impurity semiconductor, but is at high temperatures an intrinsic semiconductor with energy level separation of about 0.76 volt.”. Pearson and Bardeen [7]: „X-ray measurements indicate that both elements (boron and phosphorus) replace silicon in the lattice...each added boron contributes one acceptor level, and it is likely that each added phosphorus contributes a donor level...In the intrinsic range, at high temperatures conductivity results from electrons thermally excited from the filled band to conduction band. The energy gap is about 1.12 eV. The energy, E_a, required to ionize an acceptor by exciting an electron from the filled band, as determined from the temperature variation of concentration at lower temperatures...at high dilution, 0.08 eV, is about what is expected for a hole moving in a hydrogen-like orbit about a substitutional B⁻ ion...The ionization energy of
donors is less than that of acceptors, probably because conduction electrons have a smaller effective mass than holes.”[7].

3. Hydrogenic-like impurity donors and acceptors in germanium and silicon

Theoretical elucidation of ionization energy of impurity resulted from analogy of impurity-in-the-lattice to hydrogen atom[7]: „A substitutional impurity atom from the fifth group has one more valence electron than is required to fill the four valence bonds with neighbouring silicon atoms. In its lowest energy state, this extra electron is weakly bound by the extra charge on the nucleus of the impurity atom. The electron moves in a hydrogen-like orbit [8], but electrostatic force is reduced by the dielectric constant, \( \kappa \), of the crystal, the effect is to reduce the binding energy by a factor \( \kappa^2 \), which brings it down to the range of thermal energies (~0.08eV).” The original formula for the energy of electron having effective mass \( m^* \), in electronic state with quantum number \( n \), comes from N.F. Mott and R.W Gurney [8]:

\[
E - E_\alpha = -\frac{e^2 m^*}{2\hbar^2 n^2 \kappa^2} = -\frac{1}{n^2 \kappa^2} \cdot 13.53 eV
\]

One should mention that exact application of the formula to estimate hydrogenic donor and acceptor binding energies in silicon was not possible at that time, 1949, since effective mass \( m^* \) parameters of conduction and valence bands, as well as detailed structure of these bands were not known. Without that knowledge the authors found that transport activation energy in phosphorus doped silicon, \( E_\alpha = 0.045 eV \) is „in reasonable agreement” with hydrogenic-like model with \( \kappa = 13 \) and \( m^* = 0.67 m \) for electrons, and \( E_\alpha = 0.08 eV \) well corresponds to hydrogenic model for acceptor with effective mass of a hole \( m^* = m \).

Although the theoretical description of impurity donors and acceptors was very simple and intuitive (though far from accuracy of „exact” effective mass models accounting for real structure of conduction and valence bands developed later for germanium and silicon) the engineering of n- and p-type germanium and silicon doped with group-V and group-III elements allowed for constructing first diodes and transistors and starting contemporary semiconductor electronics.

Further detailed theoretical [9,10] and experimental studies, especially optical infrared spectroscopy [11] of donor and acceptor impurities in germanium and silicon demonstrated quite complicated structure of electronic levels of these hydrogenic-like donors due to „non-spherical” tensor properties of effective mass of electron and hole in indirect, many-valley band structure of germanium and silicon, not allowing for direct using of simple hydrogenic formula for the study of detailed structure of these impurities. However, the general idea of „effective mass” model, assuming that electrons and holes are bound by the Coulomb potential of excess charge of impurity on the states extending over many lattice constants remained valid and allowed for easy „intuitive” understanding of electronic processes governing conductivity and optical properties of these semiconductors.

4. Hydrogenic-like impurities in direct gap III-V and II-VI semiconductors

The full beauty and simplicity of hydrogenic-like model was fully exploited for direct-gap, III-V semiconductors, like GaAs, InP or II-VI semiconductors, like CdTe, CdSe with direct gap and spherical and low-mass conduction band minimum: \( m^*/m = 0.0665 \) for GaAs, 0.0803 for InP, 0.0965 for CdTe and 0.118 for CdSe [12-14]. The smaller is the effective mass of the electron in particular host semiconductor the larger is the Bohr radius of bound electrons, making assumptions of effective mass theory well fulfilled.

5. Small deviations from hydrogenic model - „chemical shifts”

The deviations from simple hydrogenic-like model for shallow donors in III-V and II-VI semiconductors appeared to be very small. For GaAs the energies of ground, \( n=1 \), state of different donor impurities deviated by 0.1-0.3 meV accounting for 2-6 % of the full value of ionization energy of the ground state. The theory assigned these small shift, within perturbation approach, to be equal to the strength of local potential of impurity core times the probability of the electron on
hydrogen-like orbit to be at the impurity core, the latter quantity being very small. This small but specific for different species changes of ground state energy allowed for very precise diagnostics of ultra-pure materials, e.g. for determining relative abundance of different residual impurities. Studies of undoped and low intentionally doped samples facilitated precise spectroscopic identification of most abundant impurities observed in far-infrared spectroscopy experiments [12-15]. Similar techniques have been used also for elementary, group IV, semiconductors with much success [16]. One can say that the spectroscopic techniques applied for diagnostics of ultra-pure semiconductors are among the most sensitive diagnostic techniques humanity ever invented. They can detect the impurity with abundance as low as 1 atom of impurity per 10¹⁰ atoms of host semiconductor!

6. Hydrogenic-like impurity levels associated with multi-conduction bands

The spectacular successes in predicting the properties of substitutional donor impurities within hydrogen-like approach and small deviations from the model observed, easily handled with small perturbation theories, pointed to the end of adventure with impurity donors as scientific and technological subject. Most of technologies applied for semiconductor materials like germanium, silicon, III-V, II-VI, undoped, intrinsic, as well as doped, extrinsic, matured and everything seemed to be well predictable. The non-trivial donor impurity related phenomena observed in some system, especially upon crossing of different multi-valley conduction bands, have been associated to complexity of solving hydrogenic-like impurity problem in these circumstances[17]. The experimental evidence for hydrogenicity of impurity levels was elucidated from pressure- and alloying- dependence of impurity levels. If hydrogenic, these levels should follow the band minimum from which the impurity level wave function originates [17].

5. Non-hydrogenic behaviour of donor impurities in semiconductors – DX Centres.

Surprisingly, by the end of 70-ies, much rumour appeared with „discovery” by Lang and Logan[17] and Nelson [18] of very unusual behaviour of donor impurities in AlxGa1-xAs alloys for 0.2<x<0.4, i.e. for III-V semiconductor alloys with direct band gap with simple non-degenerate spherical conduction band minimum at Γ point of Brillouin zone, for which one could expect the donor impurities should be hydrogenic-like shallow donors. The strange behaviour could be described as „persistent photoconductivity”.

![Fig.2 Example of „chemical shifts” structure on the 1s-2p(+) shallow-Γ- donor line observed in magneto-optical far infrared laser magneto-spectroscopy experiment for two high-purity samples of GaAs grown with two, LPE and MOCVD, techniques [15]]
At low temperatures the conductivity of the doped samples could be changed upon illumination with light which "persisted" as long as hours and days if sample was kept at low temperatures, below about 77K. The excess conductivity could be quenched by heating the sample above some characteristic temperature. This was due to extremely low (less than $10^{-30}$ cm$^2$), thermally activated capture cross section for conducting electrons.

One should mention that strange effects have been observed for other compositions x of Al$_x$Ga$_{1-x}$As, and for other semiconductor systems like GaP:As$_{1-x}$[19], GaSb[20], InSb[21], CdTe[22], Cd$_{1-x}$Zn$_x$Te[23], CdS[24], CdF$_2$[25] under specific experimental conditions e.g. at high hydrostatic pressures.

The donor state responsible for such strange behaviour had other bizarre properties: the thermal ionization energy ($0<E_t<0.2$ eV) was an order of magnitude lower than the threshold energy of the photon ($0.6<E_0~1.2$eV) required to ionize donor center. This phenomenon was called "large Stokes shift".

To explain these phenomena Lang and Logan proposed that the donor center is extremely strongly coupled to the lattice. The configuration coordinate CC diagram was proposed to describe the processes observed: large optical excitation energy, barriers responsible for slow thermal processes and large displacement of the lattice coordinate to switch off radiative recombination after optical excitation.

Those properties could not be explained by no means by simple models of hydrogen-like substitutional donor impurities. In particular the strongly delocalized electronic wavefunction of loosely bound electron of shallow, hydrogenic-like donor could not produce significant electron-
phonon coupling in covalent semiconductors with small Fröhlich electron-phonon coupling constant $\alpha$.

The complex consisting of donor D and unknown another constituent X, most likely anion, arsenic, vacancy on nearest neighbour site, V$_{As}$, called „DX” center, was later proposed by Lang Logan and Jaros[17] to be responsible for these phenomena.

The properties of DX centres were characteristic of defect centres with highly localized electrons, e.g. some parameters were strongly dependent on particular dopant [26].

One should mention at this point that similar models were proposed earlier by Porowski et al [21] and Langer et al [25] to explain similar phenomena observed in InSb under pressure and in CdF$_2$:In, respectively.

The unwanted slow-transient phenomena observed in operation of Field Effect Transistors made of GaAs/AlGaAs heterojunction structures were assigned to be related to deep donor traps in AlGaAs exhibiting phenomena described as „DX-centers” [27].

7. Nature of the X – was it necessary?

Investigations into the nature of DX- like state imposed following question: what X could be? Is it thermodynamically stable object? Is anion vacancy a good candidate for X? The answer was not simple, but doubts about X as an stable object „introduced to the host lattice” appeared from very beginning. Why different conditions of growing samples with different techniques have no significant influence on the number of DX centres observed? Why so different systems like donors in III-V compounds and In donor in CdF$_2$ have so many similarities? The answer came from the analogy with CdF$_2$:In. For this peculiar system it was possible to show that the In donor can possess two faces: it is bistable; it can bind electron either in deep state similar to DX state in III-V’s or in hydrogen-like shallow effective mass state[25]. Both states can be mutually transformed: upon ionization of deep states the shallow states are populated and the number of both states must be the same.

8. Bistability of DX-center: Shallow and DX states are different states of the same donor.

To check how DX centres in Al$_x$Ga$_{1-x}$As relate to ordinary shallow donor states the attempt has been made to transform DX centres into ordinary shallow donors. To demonstrate this possibility it was necessary to have shallow states deep enough to distinguish between two processes:

(i) ionization process of DX in which electrons are transferred to the conduction band and remain free

(ii) the process in which after ionization of DX-like state the shallow donor states are populated.

First attempt with observing population of effective-mass state was successful with Al$_x$Ga$_{1-x}$As:Te samples in composition x range corresponding to shallow donor originating from X minimum and, thus, relatively deep[28-31]. The population of shallow states could be observed optically[30] but final proof on the shallow-deep bistability came from carefully designed transport measurements [28,31]with results shown on Fig.5. The experimental results and careful analysis within two-level donor model (as distinguished from the model of two different objects with different concentrations) proved one-to-one relation of DX and shallow donor as two different states of the same donor.

Independent confirmation came from the theory. At the same time Chadi and Chang published the theoretical local density calculations [32]: they proposed that DX is a defect center resulting from the „reaction”: $2d^0\rightarrow d^- + DX^-$ where $d^0$ and $d^-$ are neutral and ionized donors in substitutional position and $DX^-$ indicate large dopant-dependent relaxation leading to threefold-coordinated interstitial sites, Fig.6. Moreover the result of their calculation was that $DX^-$ is a negatively charged defect which captures two electrons, i.e. relaxation leads to negative correlation energy U for two captured electrons.
Fig. 5 Transport measurement in indirect-band gap n-type Al$_{0.67}$Ga$_{0.33}$As:Te and analysis within two-level donor model demonstrating bistability of DX-Shallow donor [31]; closed symbols: cooling in darkness, open symbols: heating up after illumination at low temperatures.

![Graph of mobility and concentration vs. inverse temperature](image)

Fig. 6 Microscopic models for Si and Te donors in substitutional position $d$ and relaxed configuration DX$^-$ related to Chadi and Chang model for Al$_{0.67}$Ga$_{0.33}$As [32]

9. The negative-U, acceptor properties of DX center

Further experimental verification of the theoretical model of Chadi and Chang required cross-checking of the issue of possible negative-U character of the center. The transport data was tested for consistency with the model. Modification of the two-level donor model towards accommodation of acceptor-like DX$^-$ state resulted in application of new statistics. As a results reasonable agreement with experiment was obtained [33]. Although the experiment could not exclude either model it confirmed that both models are possible i.e. assumption on acceptor-like DX$^-$ is consistent with experiment. The discussion on the issue, regarding more complicated models and
further tests of the idea was also positive towards negative-U system [34,35]

![Fig.7 Temperature dependence of the Hall electron concentration for AlGaAs:Te, x=0.57. The solid line represents two equally well fitting curves: positive U model and weak compensation and negative U model with arbitrary compensation. Broken line represents positive U model with strong compensation fitted at high temperatures][33]

**10. Deep localized fully symmetric, A₁, state of substitutional donor impurity**

Further developments towards understanding the nature of donor impurities followed from the discussion on the alternative models, so-called small lattice relaxation model of DX centres. The authors of these models tried to understand behaviour of DX-like state assuming that strong localization of the electron on the substitutional impurity, without invoking large rearrangements of the donor neighbourhood, is sufficient for creating bizarre DX properties [36,37].

Another impulse to further study was observation of bizarre behaviour of shallow donor states observed under high hydrostatic pressure in InSb and GaAs which "anticrossed" with some unknown deep level and quenched the population of the shallow donor upon entering the gap[38].

![Fig.8 The deep level anticrossing shallow level at about 9 kbar for the "deepest" shallow donor abundant in GaAs (most likely Ge) observed by Wasilewski [38,39]]

The attempt has been made to unravel the nature of these unknown deep states and "make peace" in discussion on DX-centers by answering the question: "Localized Electronic States with A₁ Symmetry of Substitutional Donors- Are They DX-centres?"[39]

To answer the question, the experiment has been performed in which the behaviour of shallow donor under high hydrostatic pressure for well characterized Si donor in GaAs in high purity GaAs was observed. The Diamond Anvil Cell high pressure technique was applied to go for
pressure high enough to see expected phenomena of Si donor. It was assumed that „chemical shifts” for deep states for different residual impurities must be scaled up in comparison with those observed for shallow donors as much more „density” of electron at impurity is expected, see Fig.9

Fig.9 Properties of deep A₁ localized states: A₁(Ge): extrapolated from experiment of Fig.8
A₁ - expected behaviour of deep A₁ level for another donor impurity, e.g. Si.

Fig 10 Observed positions of Donor-Acceptor photoluminescence lines for Si doped GaAs
Transitions from Γ-shallow and deep Si donor states to two acceptors are seen [40]

The far-infrared absorption, luminescence and transport experiments unraveled that localized states of A₁ symmetry are generally observed for different donor species and have similar properties to the bizarre unknown deep states observed for unknown residual species: there is no barrier for capture of electrons to these states at low temperatures, they can be observed in luminescence experiments upon entering the gap of GaAs under pressure, they quench population of shallow state upon „anti-crossing” with shallow states, and it is not possible to populate again shallow states upon shining light at low temperature on the sample. Thus, they are NOT DX-centres, and they have all attributes of levels described theoretically as strongly localized states of A₁ symmetry of substitutional impurity[37]

The experimental results on GaAs:Si under pressure are in good qualitative agreement with theory of Dabrowski et al [41]. In this theory Chadi and Chang model was supplemented, including localized one-electron localized state of donor impurity.

The detailed reports for Si donors, as well as for other species, Sn, S, Se, Te in GaAs and Al,Ga₁₋ₓAs have been reported [40]. The observed dependence of energy levels on pressure and alloying and on the impurity species well conform the theory of deep localized A₁ states[37].
The magneto-optical spectra at high pressures of $1s-2p^+$ transition for different donor species in three different samples. Above 30 kbar the shallow donor lines disappear and deep donor-related luminescence lines, like those seen in Fig.10, can be observed [40].

These results, the knowledge of existence and properties of localized, molecular-like states of impurity donors seems generally not to be known and recognized among semiconductor and solid state community and awaits future positive exploitation.

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