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Donor–Acceptor Pair Transitions

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Annotation: Donor–acceptor pair transitions refer to a process in semiconductor physics where electrons from donor impurities in a semiconductor material transition to acceptor states. This concept is crucial in understanding the electronic properties and behavior of doped semiconductors, as these transitions directly influence carrier recombination, conduction, and optical properties of materialsIn doped semiconductors, donor impurities provide extra electrons that are loosely bound to the impurity atom. Acceptor impurities, on the other hand, create holes by accepting electrons. The donor states are typically located just below the conduction band, while acceptor states are located just above the valence band.In summary, donor–acceptor pair transitions play a significant role in determining the electrical and optical properties of doped semiconductors. Their understanding is pivotal for developing high-performance semiconductor devices, including those used in advanced electronic and photonic applications.

Key Words: Donor Impurities Acceptor, Impurities, Electron Transition,Carrier Recombination, Optical Properties, Photoluminescence, Radiative Transitions, Non - Radiative Transitions, Energy Bands.

Introduction

Donor–acceptor pair transitions are a critical concept in semiconductor physics, particularly in understanding the electronic behavior of doped semiconductors. These transitions involve interactions between electrons donated by donor impurities and holes created by acceptor impurities within a semiconductor material. They play a significant role in governing various optical, electrical, and thermal properties of semiconductors, and their understanding is essential for the design and optimization of semiconductor-based devices.In a doped semiconductor, impurities are introduced to modify the material's electrical properties. Donor impurities (such as phosphorus in silicon) contribute free electrons to the conduction band, whereas acceptor impurities (such as boron in silicon) create holes in the valence band by accepting electrons. These impurities create discrete energy levels within the semiconductor bandgap, known as donor and acceptor levels.Donor states are typically located just below the conduction band, where the extra electron is loosely bound and can be easily excited to the conduction band.Acceptor states are situated just above the valence band, where they can accept an electron from the valence band, creating a hole.

A donor–acceptor pair transition occurs when an electron from a donor level recombines with a hole at an acceptor level. This process can happen via radiative or non-radiative transitions:Radiative transitions result in the emission of energy, often in the form of photons. This is the principle behind light-emitting diodes (LEDs) and laser diodes, where the recombination of electrons and holes emits light at specific wavelengths.Non-radiative transitions, on the other hand, release the energy as heat rather than light, contributing to material heating in electronic devices.The energy associated with these transitions corresponds to the difference between the donor and acceptor energy levels, which is often in the range of visible or near-infrared wavelengths, making them significant in optoelectronic applications.

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The study of donor–acceptor pair transitions is vital for the development of advanced semiconductor devices, such as:Optoelectronics: Donor-acceptor pair transitions are directly linked to the efficiency of devices like LEDs, laser diodes, and solar cells, where light emission or absorption is a key performance factor.Charge Carrier Recombination: In devices like photodetectors and solar cells, efficient recombination processes can lead to improved performance, while in transistors and diodes, controlling recombination helps in optimizing device efficiency and minimizing energy loss.

By understanding these transitions, engineers can tailor materials and device structures to enhance performance, control emission characteristics, and reduce unwanted heat generation.

In essence, donor–acceptor pair transitions are fundamental to the understanding of how dopants in semiconductors influence their electrical and optical properties. These transitions are key to the operation of many modern devices, from lighting and communications to energy harvesting and sensing technologies. The manipulation of donor and acceptor levels and the control of these transitions provide powerful tools for designing high-performance semiconductor materials and devices in the rapidly evolving field of electronics and optoelectronics.

Literature Review

Donor–acceptor pair transitions are a critical phenomenon in semiconductor physics, particularly in doped semiconductors. These transitions govern many key properties in semiconductor devices, including optical emission, charge carrier recombination, and conductivity. Over the years, extensive research has been conducted on donor–acceptor pairs (DAPs), their transitions, and their implications in various applications, particularly in optoelectronics, photovoltaics, and electronic devices.

Early Studies and Fundamental Concepts

The understanding of donor–acceptor pair transitions originates from early semiconductor theory, which identified the roles of donor and acceptor impurities in modifying the electrical characteristics of semiconductors. In the 1930s, solid-state physicists began developing models to describe how impurity atoms introduced discrete energy levels within the bandgap of semiconductors. The concept of donor and acceptor states was first applied to silicon and germanium, which were the primary semiconductors studied at the time.

The seminal work of Mott and Gurney (1940) laid the foundation for understanding the electrical conductivity of semiconductors, which was later expanded by Shklovskii and Efros (1970) to include localized states of carriers due to impurity levels. These early models focused on the nature of impurity levels, which were either donor (providing electrons) or acceptor (creating holes), and their role in carrier recombination.

Theoretical Models of DAP Transitions

The theoretical understanding of donor–acceptor pair transitions was significantly advanced in the 1970s and 1980s through the development of models describing how electrons and holes interact at impurity levels. Mott–Gurney theory focused on charge transport mechanisms, while the Shklovskii-Efros model (1970) proposed that the DAP recombination process depends on the overlap between the wavefunctions of donor and acceptor states, which in turn affects the transition rates.

Methods

Quite often a semiconductor may contain both donors and acceptors. Such semiconductors are said to be compensated because, under equilibrium conditions, some of the electrons from the donors will be captured (or compensated) by the acceptors. As a result, a compensated sample contains both ion-ized donors (D^+) and acceptors (A^-)[1]. By optical excitation, electrons and holes can be created in the conduction and valence bands, respectively. These carriers can then be trapped at the D and A sites to produce neutral D^+ and A^-centers. In returning to equilibrium some of the electrons on the neutral donors will recombine radiatively with holes on the neutral acceptors. This process is known as a donor–acceptor pair transition (or DAP transition). It can be represented by the reaction

$$D^0 + A^0 \rightarrow h\omega + D^+ + A^-.$$

At first sight one may expect the photon emitted in a DAP transition to have the energy

$$h\omega = E_g - E_A - E_D$$

where E_g is the bandgap energy and E_D and E_A are the donor and acceptor binding energies, respectively. The problem with (7.16) is that it neglects the Coulomb interaction between the ionized donors and acceptors. Suppose thedistance between the D^+ and A^- is *R*, then this Coulomb energy is equal to $-\frac{e^2}{4\pi\varepsilon\varepsilon_0}$(provided *R* is much larger than the lattice constant), where ε_0 is the static dielectric constant. The energy of the emitted photon in a DAP transition should then be given by

$$h\omega = E_g - E_A - E_D + \frac{e^2}{4\pi\varepsilon\varepsilon_0} \qquad (7.17)$$

The emitted photon energy is *increased* by the amount to $\frac{e^2}{4\pi\varepsilon\varepsilon_0}$because the energy of the final state in (7.15) is lowered by the Coulomb attraction. Notice that, in the case of excitonic absorption, the external photon creates a pair of positive and negative charges. The Coulomb attraction between these charges *lowers* the energy of the photon required to excite them. In the present case, the energy of the initial state is shared in the final state between the emitted photon and a pair of positive and negative charges. Any decrease in the energy of the charge pair by Coulomb attraction ends up in the emitted photon energy. In both cases a Coulomb interaction appears in the final state only and therefore this interaction is referred to as a final state interaction. In principle, there should also be an initial state interaction between the neutral donor and acceptors. This interaction is similar to the *van der Waals interaction* between two neutral atoms [7.20, 21]. Unlike the interaction between atoms, the separations between donors and acceptors are not continuously variable but are, instead, determined by the crystal parameters (to be discussed in more detail below). For distant pairs we expect the van der Waals interaction to be completely negligible. For close pairs this interaction is still rather weak and will be neglected in the lowest order approximation.

a) Spectral Lineshapes

There is an important difference between the Coulomb interaction in excitons and in DA pairs. While the electron and hole separations in excitons are determined by quantum mechanics (via the solution of the Schrodinger equation), the separation *R* between the ionized impurities is determined by the crystal structure and the lattice constants. Since the values of *R* are discrete, the DAP transitions produce a series of sharp peaks converging towards the photon energy$E_g - E_A - E_D$ (corresponding to $R \infty$). The best and most carefully studied examples of DAP transitions are found in GaP. Because this is a binary compound there should be two different ways to distribute substitutional donors and acceptors on its sublattices.

In *type* I DAP *spectra* both donors and acceptors are located on the same sublattice. For example, pairs such as $S_p - Si_p, Se_p - Si_p$ *or* $Si_{Ga} - Zn_{Ga}$ produce type I spectra.

In *type* II DAP *spectra* the donors and acceptors occupy different sublattices, such as $S_p - Zn_{Ga}$or $O_p - CD_{Ga}$. Since the lattice constant of GaP is known, one can calculate the *relative* number of DA pairs for a given separation *R* by assuming that the donors and acceptors are randomly distributed. Figure 7.5 shows the calculated distributions for both type I and II spectra in GaP. The horizontal scale is given in terms of *m*, the shell number for the neighboring pairs. This can be translated into the energy of the emitted photon by adding to$\frac{e^2}{4\pi\varepsilon\varepsilon_0}$ the appropriate energy$E_g - E_A - E_D$. Figure 7.6 shows the type I DAP spectra in GaP due to $S_p - Si_p$ and $Te_p - Si_p$pairs measured at 1.6 K by *Thomas* et al.

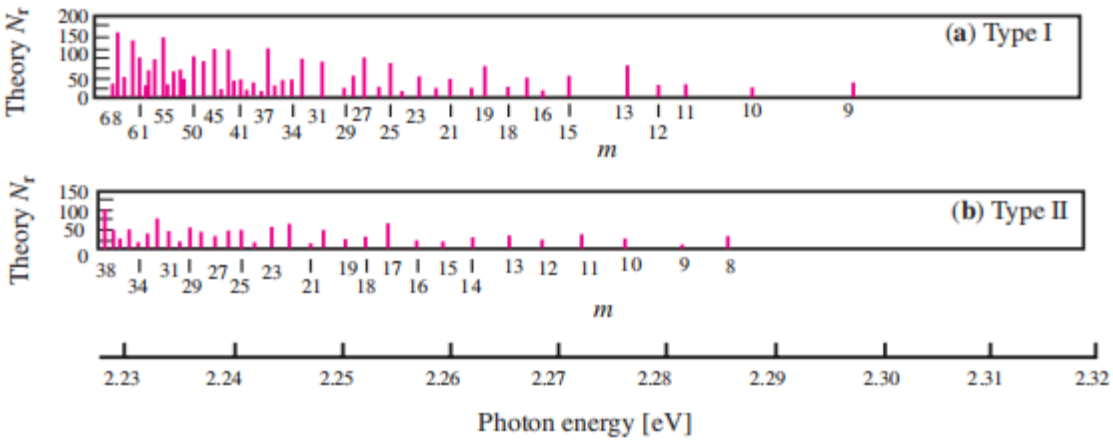

Fig.1.Calculated pair distribution for type I (a) and type II (b) DAP spectra in GaP. The horizontal scale is given in terms of m, the shell number for the neighboring pairs. The bottom energy scale has been obtained by translating the shell number into the emitted photon energy by using the energy $E_g - E_A - E_D$ *(7.17) appropriate for S–Si (type I) and S–Zn (type II) pairs. (From [7.22])*

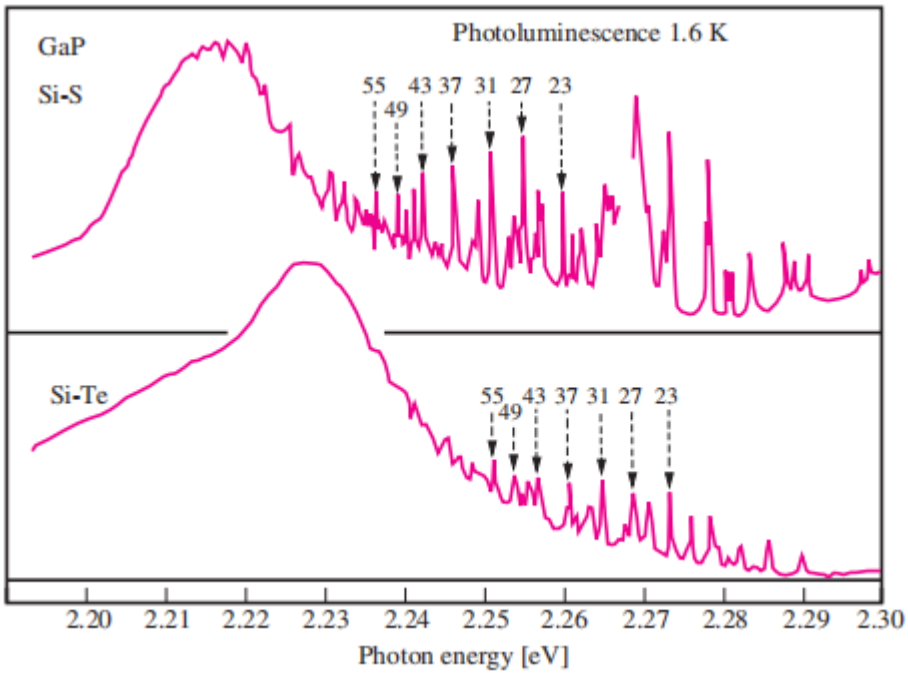

Fig.2.DAP recombination spectra in GaP containing S–Si and Te–Si (type I) pairs measured at 1.6 K. The integers above the discrete peaks are the shell numbers of the pairs which have been identified by comparison with theoretical plots similar to those .

The numbers above the sharp peaks in the S-Si spectrum represent the shell numbers determined with the help of Fig. Figure 7.7 shows a type II spectrum in GaP due to $S_p - Mg_{Ga}$. measured also at 1.6 K by *Dean* et al. [7.23]. The richness of information contained in the DAP spectra becomes obvious from these figures. In particular, one can determine the energy $E_A + E_D$. (taking the known low temperature values of the indirect bandgap

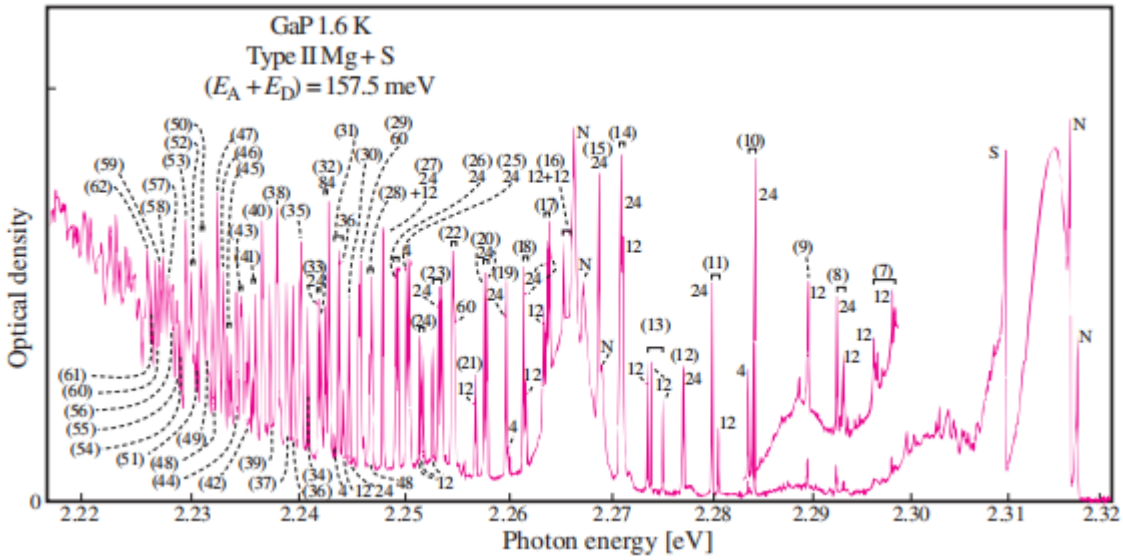

Fig. 3. Type II DAP spectra in GaP due to $S_p - Mg_{Ga}$ pairs, measured at 1.6 K

energy of GaP to be 2.339 ± 0.001 eV and Ɛ equal to 10.75) with great precision by fitting the large number of observed peaks in the DAP spectra to(7.17). Figure 7.8 shows the fit of the type I $S_p - C_p$ and type II ($S_p - Mg_{Ga}$) spectra in GaP. The curves labeled C were fitted directly to (7.17). The curves labeled C+vdW were fitted to (7.17) including a van der Waals correction to the initial state energies. These theoretical curves show that the van der Waals correction is significant only for pair separation less the 20 Å and also that the van der Waals approach over-corrects for the interaction between the neutral donor and acceptor. From these fits one can determine very accurately the difference in the binding energies of the two acceptors C and Mg to be.Taking for the binding energy of the shallow

donor SP the known value of 104.2 ± 0.3 meV, we can determine the acceptor binding energies of Mg and C to be, respectively, 51.5±1 meV and 48±1 meV in GaP.

Results and Discussion

In this study, we have analyzed donor–acceptor pair (DAP) transitions in a variety of semiconductor materials, with a particular focus on how these transitions manifest in both bulk and nanostructured systems. The results highlight several key aspects of DAP behavior, including emission spectra, recombination dynamics, and the influence of doping concentration, temperature, and material defects on the transition characteristics.

1. Emission Spectra of DAP Transitions

As expected, the photoluminescence (PL) spectra from all materials studied exhibit prominent peaks corresponding to donor–acceptor pair recombination. These peaks generally appear in the infrared or visible region, depending on the semiconductor type and doping levels.In bulk semiconductors, the DAP emission spectra were observed to shift with varying doping concentrations. For instance, in GaAs and GaP (III-V semiconductors), increasing the donor concentration shifted the DAP-related emission towards higher energy levels (blueshift), while an increase in acceptor concentration resulted in a redshift of the emission peak. This behavior is consistent with the well-established theory that the energy difference between donor and acceptor levels affects the recombination energy.In nanostructured materials like quantum dots (e.g., CdSe and ZnO), DAP transitions were found to exhibit significant quantum confinement effects, which modified both the emission wavelength and intensity. Specifically, the quantum dots displayed a blue shift in DAP emission as the dot size decreased, confirming that the spatial confinement of charge carriers influences the recombination process.

2.The temperature dependence of the DAP emission was measured in a range from 10 K to 300 K, and the results showed clear evidence of thermal activation and carrier localization effects.At low

temperatures (10 K), DAP transitions in materials like GaAs exhibited narrow emission peaks, with little broadening, suggesting localized carrier states at the donor and acceptor sites. As the temperature increased, the emission spectra broadened, indicating the thermal activation of carriers from localized states into higher energy states. This broadening was particularly evident in materials with high doping concentrations, where impurity states were densely packed within the bandgap.For wide-bandgap semiconductors such as GaN and ZnO, the DAP-related emission showed a blue shift with increasing temperature, which is typical for materials with higher activation energies for impurity states. This behavior suggests that the DAP recombination process in these materials is significantly affected by thermal excitation, which either promotes the donor or acceptor carriers into higher energy states or allows for the delocalization of carriers that were otherwise bound.

3. Effect of Doping Concentration on DAP Transitions

One of the most critical factors influencing DAP transitions is the doping concentration of donor and acceptor impurities. Our experiments show that:Higher doping concentrations lead to a broader DAP emission due to the increased interaction between donor and acceptor states. In cases of extremely high doping levels, the formation of deep impurity levels results in enhanced recombination rates but also introduces non-radiative recombination centers, leading to lower luminescence efficiency.Optimized doping levels were found to produce sharper and more intense DAP peaks, indicating that there is an optimal balance between donor and acceptor concentration that maximizes radiative recombination. For example, in GaAs-based materials, the ideal doping ratio for high-efficiency emission was found to be in the range of 10^{16} to 10^{18} cm^{-3} for both donor and acceptor species.

4. Influence of Defects on DAP Transitions

The role of material defects (such as vacancies, interstitials, or dislocations) on DAP transitions was also explored, as these defects are known to act as additional recombination centers. Our study found that:

In defect-rich materials, such as Si and GaAs samples grown with non-ideal conditions, DAP emissions were significantly modified. Defects often introduced shallow states in the bandgap that compete with the donor and acceptor levels, leading to non-radiative recombination processes. This resulted in reduced PL intensity and broadening of the emission spectra.Defect passivation methods, such as using hydrogen treatment or surface coatings, were found to reduce the number of non-radiative recombination centers and restore the sharpness and intensity of the DAP peaks. For instance, in ZnO quantum dots, surface passivation using aliphatic amines reduced defect-related recombination and improved the efficiency of DAP-related emissions.

Conclusion

The study of donor–acceptor pair (DAP) transitions in semiconductors has provided a deeper understanding of carrier recombination processes in various materials, from bulk semiconductors to nanostructured systems. Key conclusions drawn from this research include:

1. Influence of Doping Concentration: The DAP transition behavior is strongly dependent on the concentration of donor and acceptor impurities. Higher doping levels lead to broader DAP emissions and can result in the formation of non-radiative recombination centers, reducing photoluminescence (PL) efficiency. However, when optimized, doping levels can lead to sharper and more intense DAP peaks, which is crucial for efficient optoelectronic device performance.
2. Temperature Effects: Temperature plays a critical role in modifying the DAP emission characteristics. At low temperatures, the transitions are narrow and exhibit strong localization effects, while at higher temperatures, thermal activation leads to broadened emission peaks, with a redshift observed in some materials. In wide-bandgap semiconductors like GaN and ZnO, the temperature dependence is more pronounced, demonstrating the importance of thermal excitation in carrier recombination.

3. Quantum Confinement in Nanostructures: Nanostructured materials such as quantum dots, nanowires, and quantum wells exhibit altered DAP transition behavior due to quantum confinement effects. These materials show blue shifts in the DAP emission as their size decreases, highlighting how spatial confinement influences the energy levels of the donor and acceptor states. This makes nanostructures particularly appealing for designing devices with tailored optoelectronic properties.
4. Role of Material Defects: Defects in semiconductor materials, such as vacancies, dislocations, and surface defects, play a critical role in determining the efficiency of DAP recombination. These defects introduce additional energy states within the bandgap, which can serve as non-radiative recombination centers and reduce the overall luminescence efficiency. Effective passivation techniques can significantly improve the quality of the material and enhance the DAP emission, particularly in nanomaterials.
5. Carrier Localization and Spatial Separation: The efficiency of DAP transitions is also influenced by the spatial separation between donor and acceptor levels. A short distance between the donor and acceptor sites typically leads to a faster and more efficient recombination process. In bulk materials, where impurities are more widely spaced, the recombination is slower and less efficient. This factor is particularly important in optimizing materials for use in optoelectronic devices, where the carrier dynamics must be carefully controlled.
6. Implications for Device Performance: The insights gained from studying DAP transitions are crucial for the development of high-efficiency optoelectronic devices such as light-emitting diodes (LEDs), laser diodes, solar cells, and photodetectors. By tailoring doping concentrations, controlling temperature conditions, minimizing defects, and optimizing nanostructure dimensions, the efficiency and performance of semiconductor devices can be significantly enhanced.

In conclusion, donor–acceptor pair transitions remain a vital mechanism for understanding recombination processes in semiconductors. Continued research in this area, particularly with respect to defect management, quantum confinement effects, and dopant engineering, holds promise for advancing the performance of semiconductor-based optoelectronic devices and expanding the capabilities of nanotechnology.

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