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# *Theoretical Study of Photoluminescence Mechanisms in Semiconductor Materials*

**Mingrui Cao**

*Beijing National Day School, Beijing, China*
*18611570062@163.com*

***Abstract:*** With the advancement of digitalization, artificial intelligence, high-speed communications, vehicle electrification, and carbon neutrality, the demand for optoelectronics and power semiconductors is increasing. Device efficiency and stability depend on the luminescence behavior of semiconductor materials. This study constructs a theory-driven framework for interpreting photoluminescence (PL) by integrating band structure, exciton effects, defect state physics, and temperature-phonon interactions. Theoretical analysis reveals that near-band edge and exciton peaks indicate band gaps and binding energies, while broad low-energy bands indicate deep defects and stronger nonradiative losses. Power and temperature dependence help separate radiative pathways, and the full-width at half-maximum provides a practical indicator of crystal quality and disorder. This framework also clarifies why direct-bandgap materials exhibit efficient luminescence, while indirect-bandgap materials require phonon assistance and exhibit weak PL. However, this framework is limited to theoretical studies, and future research should combine it with quantitative studies for more in-depth analysis.

***Keywords:*** photoluminescence, band structure, defect states, excitons, temperature and phonon effects

## 1. Introduction

Global digitalization, artificial intelligence, 5G/optical communications, automotive electrification, and the goal of carbon neutrality are simultaneously driving growing demand for optoelectronics and power semiconductors. This is accompanied by higher demands for material energy efficiency, reliability, and manufacturability, as well as uncertainties arising from supply chain security and cost fluctuations. Semiconductor materials, due to their unique electronic band structures and excellent optoelectronic properties, are widely used in optoelectronics and microelectronics, particularly in devices such as light-emitting diodes (LEDs), semiconductor lasers, solar cells, and optical communication devices. The luminescence performance of semiconductor materials is directly related to the efficiency and stability of these devices. Photoluminescence (PL) is a noncontact spectroscopic technique that reveals a material's band structure, defect states, and carrier recombination dynamics [1]. Analyzing PL spectra clarifies carrier excitation, relaxation, and recombination and provides a solid basis for materials design and optimization. Theoretical research plays a key role in interpreting PL experimental results [1]. Band theory can describe the transition

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process of intrinsic carriers, while defect state theory demonstrates the important role of impurities and lattice defects in the recombination mechanism. Temperature and phonon effects also affect the luminescence peak position and intensity.

In recent years, significant progress has been made in photoluminescence research on typical semiconductor materials such as GaN, ZnO, and Si, providing a theoretical and experimental foundation for the development of high-efficiency blue LEDs, ultraviolet lasers, and silicon-based optoelectronic devices [2]. Therefore, this article will systematically study the photoluminescence mechanism of semiconductor materials through theoretical analysis, which has important scientific significance and provides a solid theoretical basis for improving the performance of optoelectronic devices and exploring new materials.

## 2. Theoretical framework

### 2.1. Semiconductor band structure

The photoluminescence mechanism of semiconductor materials must first be understood from the perspective of band theory. According to band theory, the energy of electrons in a crystal is distributed in a band-like pattern, mainly consisting of the valence band (VB) and the conduction band (CB), with an energy gap $E_g$ between the two.When the external photon energy is $hv \geq E_g$, the valence band electrons can be excited to the conduction band to form electron-hole pairs, thus opening up the possibility of radiative recombination [1].

In direct bandgap semiconductors (such as GaAs, GaN, and ZnO), the bottom of the conduction band and the top of the valence band are located in the same momentum space (spatial position) [1], and electrons and holes can directly release energy through radiative recombination as follows:

$$E_{photon} \approx E_g = E_c - E_v \tag{1}$$

Where $E_c$ is the energy at the bottom of the conduction band and $E_v$ is the energy at the top of the valence band. This type of recombination process does not require the participation of phonons, resulting in high photoluminescence intensity and sharp emission peaks, making it suitable for high-efficiency light-emitting devices.

Photoluminescence not only involves the direct recombination of free electrons and holes, but also involves the exciton effect. When electrons and holes form a bound state through Coulomb interaction, its energy is slightly lower than the band gap, and the emission peak position is:

$$E_{ex} = E_g - E_b \tag{2}$$

where $E_b$ is the exciton binding energy. The luminescence of free and bound excitons is particularly prominent in low-temperature PL spectra, revealing the intrinsic energy band characteristics of the material and the effects of localized defects.

### 2.2. Defect state theory

In actual semiconductor materials, various defect levels appear within energy bands due to the limitations of crystal growth conditions and the unavoidable presence of impurities. These defect states include point defects (such as vacancies and interstitial atoms), impurity levels (donor/acceptor impurities), and surface or interface states. The introduction of defect states alters

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the carrier capture and recombination processes, resulting in complex characteristics in the PL spectrum's energy and intensity.

According to the Shockley–Read–Hall (SRH) theory, the energy level positions of defect states within energy bands can be used to describe the nonequilibrium carrier capture and recombination dynamics [3]. The recombination rate can be expressed as:

$$R_{SRH}=\frac{np-n_i^2}{\tau_p(n+n_1)+\tau_n(p+p_1)} \quad (3)$$

Where $n$ and $p$ are the electron and hole concentrations, $n_i$ is the intrinsic carrier concentration, $\tau_n$ and $\tau_p$ are the characteristic electron and hole lifetimes associated with the defect (set by capture cross sections and defect density), and $n_1$ and $p_1$ are the effective carrier concentrations determined by the defect level. This model shows that defect states act as traps for electrons or holes and thereby influence the competition between radiative and non-radiative recombination.

## 3. Classification and analysis of photoluminescence mechanisms

### 3.1. Intrinsic band recombination luminescence

Intrinsic band recombination luminescence is the most fundamental and typical photoluminescence mechanism in semiconductor materials. It primarily involves interband recombination of free electrons and holes, and exciton-related luminescence. This type of luminescence generally occurs in the absence of significant defects in the material and truly reflects the intrinsic characteristics of the band structure [4]. Direct recombination of free electron-hole pairs is the most intuitive process. When an external light source excites an electron into the conduction band, the electron in the conduction band and the hole in the valence band recombine via radiation, emitting a photon with energy close to the band gap. In direct band gap semiconductors such as GaN, GaAs, and ZnO, this process does not require the participation of phonons, resulting in high luminescence efficiency, well-defined emission peak positions, and high intensity. This type of near-band edge luminescence is often the primary characteristic of the photoluminescence spectrum and is the foundation for the efficient emission of LEDs and semiconductor lasers.

Exciton luminescence is also important in many semiconductors. Excitons are bound states formed by Coulomb interactions between electrons and holes [5]. Their energy is less than the band gap energy. Exciton luminescence is more pronounced at low temperatures because thermal disturbances are small at these temperatures, allowing excitons to exist stably and resist dissociation. Exciton luminescence is generally narrower than the emission peak from free carrier recombination, indicating the material's high crystalline quality and low number of defects. Excitons can also be bound by impurities or defects, producing bound exciton luminescence. The emission energy of bound excitons is lower than that of free excitons, often resulting in a series of small, distinct emission peaks in the spectrum. Exciton luminescence is often used as a sensitive detector of material purity and defect levels. In experimental observations, intrinsic band recombination luminescence is usually located in the high-energy region of the spectrum, with the peak close to the band gap of the material, and the intensity rises rapidly with the increase of excitation power. The increase in temperature will cause the exciton dissociation, and the free carrier recombination will dominate. The peak position may be red-shifted due to the band contraction. These rules are of great reference value for analyzing the band properties of materials, judging whether the material has a

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direct band gap, and detecting the stability of excitons. Intrinsic band recombination luminescence is the core mechanism of semiconductor photoluminescence and an important means to study the intrinsic electronic structure and optical properties of materials. In device applications, maintaining the dominant position of intrinsic recombination and suppressing defect recombination are crucial to improving the performance of optoelectronic devices.

### 3.2. Defect-related luminescence

Lattice defects and impurities are unavoidable in practical semiconductor materials. They generate localized energy levels within the bandgap, leading to defect-related photoluminescence [6]. Compared to intrinsic band recombination, defect-related luminescence is more complex, with the spectral line position and morphology dependent not only on the defect type but also on temperature, excitation intensity, and material growth process. The most common type of luminescence is caused by impurity levels. Donor or acceptor impurities in semiconductors generate shallow energy levels within the bandgap. When electrons transition from the conduction band to acceptor levels, or when holes are trapped from the valence band to donor levels and then recombine with electrons, energy below the bandgap is released. This luminescence typically manifests as a narrowband peak in the spectrum, with its energy position proportional to the depth of the impurity level. In GaAs, Si impurities cause a specific near-infrared luminescence peak.

Luminescence associated with deep-level defects is often broadband. These defects are mostly caused by structural distortions such as vacancies, interstitial atoms, or dislocations. Because the energy levels are far from the band edge, the photons released when electrons and holes recombine at these defects are low in energy, resulting in a broad visible light emission band. A typical example is the green emission of ZnO, which is generally attributed to oxygen vacancies or zinc interstitial defects [7]. Unlike shallow energy levels, deep energy level recombination can compete with non-radiative processes, limiting luminescence. Defects can also form bound states with excitons. When excitons are localized near a defect, the luminescence peak is generally slightly lower than that of free excitons, exhibiting a series of differential peaks. This defect-assisted excitation is more pronounced at low temperatures and is often used to characterize crystal quality and defect density.

Experimentally, defect-related luminescence typically appears in the low- to mid-energy region of the spectrum, manifesting as broadband or secondary emission peaks. Its intensity is highly sensitive to temperature and excitation power. As temperature rises, deep energy level luminescence tends to become stronger, while increasing excitation power can saturate defect states, reducing their relative contribution.

### 3.3. Multi-phonon effects and temperature effects

Phonons participate in momentum conservation in PL and also alter the spectral shape through electron/exciton-phonon coupling [8]. Recombination in indirect bandgap materials (such as Si and Ge) requires the assistance of phonons, resulting in lower efficiency. In direct bandgap materials, multi-phonon processes generate phonon replica peaks/side bands, whose spacing is typically close to the material's characteristic LO phonon energy. This allows for an estimate of the phonon energy and characterizes the coupling strength using the Huang-Ries factor. Side band intensity varies with temperature and excitation power, allowing for the distinction between band-to-band, free/bound exciton, and phonon-assisted channels. Temperature affects PL in three ways: peak position redshifts with decreasing bandgap (often fitted using the Varshni or O'Donnell-Chen relations); linewidth broadens due to phonon scattering, with acoustic phonons dominating at low temperatures (roughly

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proportional to T) and polarons dominating at high temperatures; in terms of intensity, thermal excitation leads to exciton dissociation, enhancing nonradiative channels and weakening near-band-edge emission, while some deep-level centers may be thermally activated and enhanced [8]. Therefore, temperature-dependent PL measurements can identify different defect energy levels and estimate their thermal activation energies, providing an experimental basis for exploring the physical origins of defects.

## 4. Experimental phenomena and theoretical explanations

### 4.1. Typical PL spectral analysis

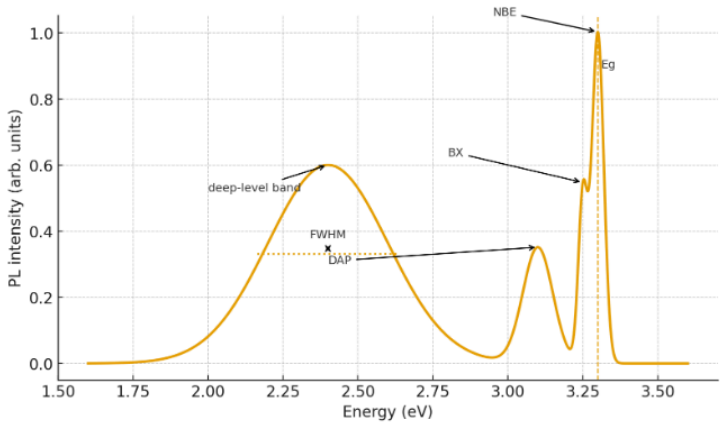


Figure 1: Schematic Diagram of a Typical Semiconductor

A typical semiconductor photoluminescence (PL) spectrum often contains multiple emission peaks [1]. The position, intensity, and full width at half maximum (FWHM) of these peaks can provide a wealth of physical information. In the high-energy region, emission peaks close to the material band gap are generally attributed to near-band-edge emission (NBE), which is primarily caused by interband recombination or free exciton emission. The energy position of these emission peaks is closely correlated with the height of the material band gap and is therefore often used as a key measure of the semiconductor band gap [1]. Emission peaks associated with bound exciton emission or shallow impurities typically appear slightly below the band gap energy, reflecting the localization of carriers by impurities or defects within the material. Broadband emission often occurs in the low- to mid-energy region. This type of emission is mostly caused by deep-level defects, such as vacancies, interstitial atoms, or compound defects. Its spectral characteristics are characterized by wide peaks, generally covering the visible light range. For example, ZnO's typical green emission is generally believed to be associated with oxygen vacancies or zinc interstitial defects [7], while GaN's yellow emission is associated with nitrogen vacancies or impurity levels such as carbon and oxygen. Figure 1. Illustrative PL spectrum showing NBE, BX, DAP, and a broad deep-level band. The dashed line marks $E_g$ ; FWHM indicates crystalline quality and disorder. Schematic, not measured data.

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In addition to peak position, the full width at half maximum (FWHM) of the PL spectrum is also crucial. A narrow FWHM indicates good crystalline quality and a low number of impurities and defects. Conversely, a broad peak indicates strong electron-phonon coupling or energy release. The intensity variation pattern is also an important indicator. For example, with increasing excitation energy, the NBE peak intensity often shows a roughly linear increase, while defect-related luminescence may gradually decrease due to saturation of the density of states. Temperature-dependent experiments also demonstrate excitability and the activation of defect states by heating. Therefore, PL spectroscopy is not only a useful tool for studying band gaps and defects, but also a visual method for assessing material quality and controlling defects.

### 4.2. Comparison of experiments and theory

The interpretation of photoluminescence requires the combined assistance of band theory and defect state models. For direct-bandgap materials such as GaN and ZnO, near-band-edge emission is consistent with the theoretical band gap. Multiple exciton emission lines are common at low temperatures. As temperature increases, band gap contraction and exciton thermal dissociation weaken these emission lines, leading to a gradual dominance of free-carrier recombination. Regarding defect-related luminescence, first-principles results support that the green emission of ZnO is associated with oxygen vacancies or zinc interstitials, while the yellow emission of GaN is consistent with carbon-related impurity energy levels. Comparison of experiments with theory also reveals the influence of process technology on luminescence. Reducing defect density through doping and epitaxial optimization weakens defect emission and enhances near-band-edge emission, consistent with the competitive relationship between radiative and non-radiative channels within the SRH framework. .

## 5. Conclusion

In conclusion, this study links key PL features to simple mechanisms. Near-band-edge and exciton peaks track the band gap and binding energy; broad low-energy bands indicate deep defects and stronger nonradiative losses. Power and temperature trends help distinguish radiative pathways and, using the full width at half maximum (FWHM) as a simple metric, provide practical clues about crystal quality. This framework also explains why direct-bandgap materials emit efficiently, while indirect-bandgap materials require phonons and exhibit weak PL.

However, this analysis is theoretical and relies on schematic spectroscopy rather than calibrated measurements. Because parameter extraction was not performed, quantities such as absolute quantum yield, lifetime, capture cross section, and Huang-Ries factor remain unverified. Several simplifications were employed, including a single dominant defect level, parabolic bands, and the absence of strain, alloy disorder, and many-body effects. Without time- or spatially resolved data, pathway assignments may not be unique. Future studies should employ Arrhenius and Varshni fits for temperature- and power-dependent PL, time-resolved PL to separate radiative and SRH lifetimes, and spatial mapping to correlate defects with morphology.

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