Review

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Temporally modulated energy shuffling in highly interconnected nanosystems

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Abstract: Advances in lighting and quantum computing will require new degrees of control over the emission of photons, where localized defects and the quantum confinement of carriers can be utilized. In this contribution, recent developments in the controlled redistribution of energy in rare earth (RE)-doped nanosystems, such as quantum dots or within bulk insulating and semi-conducting hosts, will be reviewed. In their trivalent form, RE ions are particularly useful dopants because they retain much of their atomic nature regardless of their environment; however, in systems such as GaN and Si, the electronic states of the RE ions couple strongly to those of the host material by forming nanocomplexes. This coupling facilitates fast energy transfer (ET) (<100 ps) and a carrier-mediate energy exchange between the host and the various states of the RE ions, which is mediated by the presence of carriers. A model has been developed using a set of rate equations, which takes into consideration the various ET pathways and the lifetimes of each state within the nanocomplex, which can be used to predict the nature of the emitted photons given an excitation condition. This model will be used to elucidate recent experimental observations in Eu-doped GaN.

Keywords: cavity confinement; color tuning; microdisplays; quantum computing; rare earths.

1 Introduction

The development of a “smart society” will require advancements in display and quantum computation technologies. These advancements will likely come in the form of color-tunable pixels that can be fabricated on the micrometer scale and the fabrication of systems whose quantum states can be isolated and precisely controlled, both of which can be addressed by “trapping” rare earth (RE) ions in a semi-conducting host. RE metals are the set of elements belonging to the lanthanide series, which have found practical use in solid state lasers and phosphors [1–7], telecommunications [8], magnetism [9–12], and quantum information processing [13, 14]. One of the most enticing properties of these elements is that in their trivalent form, the optically active 4*f*-shell is strongly shielded from its environment due to fully filled *outer* shells. This means that RE ions can be placed into almost any host environment and retain most of their original atomic properties. RE ions doped into a semiconducting host are predicted to be electrically inert and addressing them electrically with low applied voltages and injection currents seemed to be impractical just two decades ago [15–17]. However, light-emitting devices based on Eu-doped GaN have been fabricated with output powers and maximum external quantum efficiencies exceeding 1.25 mW and 9%, respectively, making them viable for commercial use [18, 19]. In addition, it was shown that the spin from a trapped carrier could couple to the spin of the Eu³⁺ electron configuration, strongly shifting the Eu emission wavelength and altering its magneto-optical properties [20]. Lastly, it was recently demonstrated that one could manipulate the atomic level that a Eu³⁺ ion will emit from through the precise modification of pulsed injection current or laser stimulation [21, 22]. This latter property is due to a strong coupling that exists between electrically active localized defects and the inert RE ions and the energy transfer (ET) mechanism between them [21–26]. In general, RE ions in GaN exhibit a unique combination of sharp optical transitions and long lifetimes (allowing for high-fidelity quantum control), integrated into a mature semiconductor platform that enables efficient, fast energy/information transfer (~100 ps).

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The energy-saving benefits of solid-state artificial lighting applications are known; however, the negative the impacts on human sleeping habits and circadian rhythms are also becoming more widely recognized. This issue stems from the high-intensity blue InGaN/GaN LEDs that are used to produce white light via secondary excitation of a phosphor mixture since the circadian system is sensitive to blue light [27–31]. Similar concerns arise for displays, such as computer and smartphone screens, which utilize white LEDs as a backlight. This has led some manufacturers to allow for the adjustment of color by combining LEDs with different colors (RGBY) in a hybrid package, allowing for significantly improved control of the emitted color spectrum. In the future, all consumers may expect this functionality in their homes. In this context, producing red color efficiently is of particular importance in order to realize warmer colors without an overabundance of blue light. For a similar reason, a new family of violet-based white LEDs is being explored to produce white light without the circadian-sensitive blue wavelengths ~ 450 nm [32, 33]. Moreover, it is becoming more apparent that sensitivity to blue and violet light changes as humans age, which is prompting researchers and industry to revisit our chromaticity standards [34–36]. At this critical juncture in the way that artificial lighting is produced, it is necessary to explore new options for creating color-tunable light sources that do not have unwanted negative effects on human health. Color-tunable LEDs that can produce all three primary colors within a single element reduce the size and complexity of pixels within displays [15, 37–45] and would be most beneficial for micro-LED displays [39]. There have been some reports of proof-of-concept color tunable LEDs [37–40]; however, so far, these devices lack the efficiency to be commercially viable. Inorganic halide perovskites have also shown promise for color-tuning, however, while their tunable emission wavelength has facilitated LEDs of external quantum efficiency (EQE) $>20\%$ for green, red and near-IR light, the output powers and efficiencies are still far below those of nitride-based devices [46–49].

Another area of interest that can be addressed with RE-doped GaN is quantum information technology [50–55]. RE-doped crystals have a long history in quantum science, especially in ensemble photon memories [56]. More recently, there has been growing interest in realizing quantum devices based on individual RE-ion qubits [57]. Quantum technologies require material systems that both facilitate controllable quantum coherence and provide suitable interactions to produce entanglement. Single-dopant atoms or dopant-related defect centers “trapped” in a solid-state matrix are strong candidates as physical systems proposed to meet these requirements [58, 59].

Currently, some of the best available systems (in terms of quantum coherence times) require ultralow temperature and very high vacuum. While this may not be a practicality barrier for special purpose machines such as supercomputers, for other applications, such as quantum communication nodes that need to interface with fiber-optic networks, compact devices that can operate close to room temperature will need to be developed.

Recently, there have been several reports of room temperature single-photon emitters that could be used for these applications based on quantum dots (QDs) in GaN and defects in hexagonal boron nitride (h-BN) [60–63]. However, there is still a need for a new family of material systems that can be utilized at room temperature, and that can be electrically, as opposed to optically, excited, as well as have the ability to prepare and readout spin states. RE ions are the closest analogs to trapped ions and provide a unique physical system due to shielding of the $4f$ -electron shell from the host environment, which results in very narrow emission lines and hyperfine states with exceptionally long coherence times [58, 64, 65]. These properties should enable the generation of a large number of qubits with strong dipolar interactions between them, which could also facilitate the creation of fast quantum gates. The emission of RE ions also spans the visible range and into telecom wavelengths, which will allow quantum processors to be connected within a quantum network [64, 65]. Moreover, unlike the commonly used insulating complex oxide hosts where electronics is out of reach, GaN is already a technologically mature platform for optoelectronics. Long optical storage times with good spin coherence at the single-photon level have been reported in Eu-doped complex oxide hosts such as Y_2SiO_5 and YAlO_3 [66–70]. If similar characteristics can be obtained in Eu-doped GaN, quantum memory devices with well-preserved quantum states can be realized.

In this review, we will provide an overview of common ET mechanisms including resonance ET, upconversion, downconversion and quantum cutting, as well as the current models for ET between semiconducting hosts and RE ions. The various schemes for controlled energy shuffling between various emitting centers will then be discussed with a focus on excitation schemes that facilitate temporal control of the energy redistribution, allowing for color-tunability and modification of the photon emission properties. We will introduce a generalized model for energy shuffling in highly coupled nanosystems, where the lifetimes of the constituent emitters differ by a few orders of magnitude, and end with an outlook on this phenomenon for future applications in lighting, display and quantum information technologies.

2 General energy transfer processes

2.1 Overview

Upon the absorption of energy in complex material systems, energy dissipation can occur via several pathways, both radiative (photon emission) and nonradiative (phonon generation and heat). However, as the energy is lost, it can be spatially relocated. This spatial relocation may take place between molecules (chromophores) or between defects or dopants that are spatially separated in solids. There are two categories of internal ET processes between two or more constituents that are pertinent for this review, which is either through resonance energy transfer (RET) or the Auger effect. Note: both of these processes can occur within the same material system, and it is important to distinguish their properties [71]. Several reviews on these ET processes have been written over the years; here, we summarize the most salient points for our purposes and direct the reader to these reviews for a more in-depth look [72–84].

Although there has been substantial advancement in the theoretical understanding of nonradiative resonance ET over the last ~75 years, the primary aspects of this process were first captured in the works of Förster (Coulombic dipole-dipole mechanism) and Dexter (multipole interactions and electron-exchange transfer) [85–87]. In the case of Förster-type ET, it is assumed that the two constituents of the ET, referred to as the donor and acceptor (D-A), can be approximated as dipoles, where the donor absorbs the initial energy and transfers it to the acceptor. The efficiency and rate of this ET depend on three main properties: (1) the proximity of the D-A, (2) the spectral overlap of the D-A absorption and emission bands and (3) the relative orientation of the dipole moments. The proximity dependence of RET is usually broken down into two regions, the near-field region and the far-field region. The near-field region is characterized by the well-known R^{-6} dependence and is mediated by virtual photons [82, 86], whereas the far-field region, which has an R^{-2} dependence, is mediated by real photons [86]. It should be noted that as the D-A become close in proximity (the distance is much shorter than the wavelength of the absorption), higher order terms begin to dominate, and the R^{-6} dependence is no longer observed [82, 86]. Dexter-type ET is quite different in its mechanism as it is based on the instantaneous exchange of electrons, where an excited electron of the acceptor goes to the donor, and the ground-state electron of the donor goes to the acceptor [86]. Dexter

Figure 1: Illustration of Förster and Dexter energy transfer processes between a donor and an acceptor.

processes require overlap of the wavefunctions between the donor and acceptor in order to facilitate this exchange of electrons. Figure 1 shows a schematic of the Förster and Dexter ET processes.

Strict resonance between the D-A is not required for ET to take place. For small energy differences, the energy difference between the two can be bridged with phonons, where the rate goes down proportional to the number of phonons needed to bridge the gap [88–91]. In addition, if three centers exist where one of the centers has twice the energy of the other two, then a three-body ET known as “double ET” can take place. Double ET can also occur if two of the centers have half the energy of the third center [92–95]. These processes are referred to as (cooperative) upconversion or downconversion for the cases of $E + E \rightarrow 2E$ and $2E \rightarrow E + E$, respectively, and both of these processes require close proximity for effective ET to take place [95].

In semiconducting and insulating systems, the absorption of energy can also lead to generation of carriers (electrons and holes) within the material. Depending on the energy used, the carriers generated may be coupled (excitons) or exist with excess kinetic energy (e.g. “hot” electrons). This energy is lost through the recombination of carriers either through excitonic recombination, defect-level assisted (Shockley-Read-Hall) recombination [96, 97] or can take place with energy being transferred to a third “entity,” usually an electron, via the Auger effect [23, 72, 98–105]. Since the Auger effect is a three-particle interaction, it is typically only significant in nonequilibrium conditions, where the carrier density is very high. These different processes are illustrated in Figure 2.

It is important to first note that all of these mechanisms are defined in terms of rates. In principle, if no phonon-assisted processes are considered, all mechanisms are intrinsically 100% (or 200%) efficient; there is no energy

Figure 2: Different carrier recombination mechanisms in semiconductors, including monomolecular recombination such as excitonic recombination (radiative) and Auger (trimolecular) recombination (nonradiative). Trap-assisted recombination (e.g. Shockley-Read-Hall) can result in both radiative and nonradiative recombination.

lost in the processes themselves. Only if there are competing processes does the total (external) efficiency lower. It is not that the process becomes less efficient, just that other processes will remove energy from the system. For example, one way to estimate the efficiency for F-D processes is using a formula that contains the ratio of the lifetime of the donor when an acceptor is present to the donor lifetime with no acceptor. These processes can be very efficient, but they lose efficiency with distance. Moreover, these lifetimes are calculated per material, which will factor in competing processes within the sample. Second, it is important to distinguish between internal and EQE. The ET for a process would be most associated with the internal quantum efficiency (IQE) or quantum yield (QY), while EQE is determined from the IQE and is

based on absorption properties. While Auger processes can be less efficient in some materials and are especially low in bulk wide-band gap semiconductors, they become dominant in nanocrystals (NCs) where, in some cases, it can lead to IQEs and QYs of 200%. The same is true for F-D processes, for example, highly efficient downconversion. In any case, this depends on the system of study. In the following sections, several systems and their ET mechanisms will be reviewed.

2.2 Sensitized energy transfer in RE-doped systems

There are several mechanisms by which RE ions can be excited in a host, the most straightforward of which is to address the RE ion directly by using a light source tuned to precisely match the energy difference between the ground state and one of the excited states of the RE ion [88, 100, 106–108]. The absorption cross section for these transitions will be comparatively small as transitions within the $4f$ -electron states are parity forbidden [88, 100, 106, 109, 110]. As a result, ET to REs is typically facilitated by using the host material as a “sensitizer”, which is normally achieved through one of two processes. One is by matching the bandgap of the material to a desired energy separation by alloying the material or tailoring the bandgap through quantum confinement, such as the formation of nanoparticles with varying radii (Figure 3(A)). For example, SiO_2 films containing Er^{3+} ions and Si nanoparticles with different size showed resonant ET from excitonic recombination in the nanoparticles to the discrete states of the Er^{3+} ions [111–115]. Additionally, CdSe and CdS QDs have been doped with several RE ions, and it has been shown

Figure 3: (A) Quantum dot (QD) sensitized rare earth (RE) excitation. (B) Upconversion scheme for Yb^{3+} sensitized Er^{3+} emission.

that the efficiency of the ET from the excitonic levels formed in the QD to the RE ions depends on the radii of QD and the energy separation of the desired transition within the RE [92, 112–117]. The other method to enhance ET from the host material, particularly in bulk systems, is to use another RE with a complementary energy spectrum (meaning that the RE ions have nearly identical energy separations between certain levels) that can be more easily accessed within the host material, where energy can be transferred to the other RE by upconversion or downconversion [92, 116, 117]. For example, Yb^{3+} ions have a significantly higher absorption cross section than any of the other REs [116, 118, 119], and the energy spectrum of Yb^{3+} has only two $4f$ -energy states whose energy separation closely matches the transitions between the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ states of Er^{3+} and the $^3\text{H}_4 \rightarrow ^1\text{G}_4$ states of Pr^{3+} . Moreover, Yb^{3+} has also been shown to effectively sensitize other REs such as Tm^{3+} and Ho^{3+} [120–123]. In the case of Yb^{3+} sensitized Er^{3+} -doped materials, the Yb^{3+} ions can efficiently absorb light at ~ 980 nm and transfer it to the Er^{3+} ions, which will subsequently emit at 1.54 μm (Figure 3(B)), which is used in many telecommunication applications [8, 124].

The two sensitization methods mentioned above have led to interesting observations, such as the ability to control the emission ratio between a RE-sensitizer and RE-“emitter.” Several REs can be doped into NCs with a core-shell architecture, where different REs can be separated within the different materials of the core and shells. Using this design, ET can be manipulated by changing the thickness of the shell layers facilitating either partial or complete ET from one RE to another. This has been successfully demonstrated for different sets of REs in a variety of host materials including LaF_3 , YPO_4 and NaYF_4 [123, 125–129]. Aside from sensitizing the 1.54 μm emission from Er^{3+} , Yb^{3+} can also be used for cooperative upconversion. The separation between the $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$ and $^4\text{I}_{11/2} \rightarrow ^4\text{F}_{7/2}$ states are roughly the same, and so the Er^{3+} ion can be excited by two Yb^{3+} ions (~ 980 nm) and emit ~ 525 nm (Figure 3(B)). For all RE-RE-based ET, proximity is critical, and so high concentrations are usually required for efficient ET in practical applications. Additionally, the energy may “hop” between sensitizer atoms (e.g. Yb^{3+}) before encountering the emitter (e.g. Er^{3+}) [82]. Note: QDs are usually considered nanoparticles which are not necessarily crystalline and have diameters < 20 nm. In addition, QDs are quasi 0-dimensional, which strongly affects their properties. NCs, which will also be discussed, refer to samples with a crystalline structure and a size < 100 nm (although in some literature a sample with a diameter < 1 μm can be considered a NC). The term NC will be used for the remainder of this review since this definition is broader in its scope.

2.3 Quantum cutting with NCs

While for downconversion between RE ions, it is essential for the ions to have nearly identical energy separations between certain levels, this requirement is not strictly necessary for a system where the sensitizer is a NC. As mentioned above, in a system where Er^{3+} ions and Si NCs are doped into a SiO_2 matrix, the NCs can resonantly transfer energy to Er^{3+} ions after optical excitation. However, when the photon energy of the excitation is increased above the threshold of the bandgap energy plus the energy of the first excited state of the Er^{3+} ion, a new ET path opens up. This process is indicated in Figure 4A; the excess energy of the “hot” carrier in the NC allows for an Auger-type intraband relaxation with simultaneous excitation of an Er^{3+} ion. Subsequently, the cooled down exciton can still excite another Er^{3+} ion by the conventional process. This so-called “space-separated” quantum process becomes more efficient for larger photon energies and is observed in the photoluminescence (PL) dynamics as an increasingly large fast component [130], as well as an increasing QY of the Er-related emission [131]. More recently, the doping of REs in perovskite NCs has also shown to be very efficient to sensitize emission from REs [132, 133]. In Yb^{3+} -doped $\text{CsPb}(\text{Cl}_{1-x}\text{Br}_x)$, the bandgap can be tuned by varying the composition. Interestingly, it was shown that for bandgap energies larger than the quantum cutting threshold, the PL QY of Yb-related emission reaches nearly 200% [134].

Figure 4: (A) Quantum cutting process for Er-doped Si nanocrystals (NCs). If the excitation energy is equal to the bandgap plus the energy separation of $\text{Er}-\text{Er}^*$, the excess energy, in the form of a hot electron can be transferred to a neighboring Er-doped NC through an Auger energy transfer (ET). The Er^{3+} ion in the originally excited NC will also be excited yield two emitted photons for one excitation photon [131]. (B) This quantum cutting process does not requires a rare earth (RE) ion, quantum cutting can occur between neighboring Si NCs via a similar Auger ET process [136].

This is another demonstration that resonance is not a requirement for quantum cutting processes in which NCs are involved. In fact, quantum cutting with Si NCs does not even require REs. For high concentrations of Si NCs in SiO_2 , it was shown that not only does resonant ET occur between them [135] but also that space-separated quantum cutting occurs at large enough excitation photon energies. In this case, another Si NC is now functioning as the acceptor in place of Er^{3+} , and absorption of a single photon leads to the excitation of two Si NCs (see Figure 4(B)) [136]. It is important to note that in the mentioned Si NCs systems both with and without RE's, the proximity of D-A is important for quantum cutting to occur, and it was estimated that >50% has a neighbor within 1 nm distance making it a highly interconnected nanosystem [131].

2.4 Carrier localized energy transfer

In the previous sections, ET to RE ions within a host material was achieved through resonance with the excitonic levels of NCs or via RE-RE RET. However, efficient ET between bulk semiconductors hosts such as Si, GaN, InN and GaAs and single RE^{3+} dopants has also been demonstrated, and whereas the aforementioned systems could only be optically addressed, electrical excitation of REs doped into semiconductors via current injection has been demonstrated by several groups [15–19, 21, 22, 137–146]. While the exact nature of this ET is different from those mentioned above, the underlying principles of resonance and proximity still play a critical role. Before this is discussed, it is important to review the principles of carrier recombination and the importance of carrier localization and wavefunction overlap for efficient recombination in semiconductor-based devices.

As mentioned in Section 2.1, when free carriers are generated within a semiconductor, energy is lost due to recombination of electrons and holes. For this recombination to occur, the wavefunctions of the electrons and holes must have sufficient spatial overlap. For example, with blue LEDs based on InGaN, quantum confinement was used in the form of a multiple quantum well (MQW) structure to enhance this overlap within the quantum wells [147–155]. Additionally, the immiscibility of In atoms within GaN caused In segregation, leading to localized areas of higher In-content, which also helped to localize carriers since there was a localized energy minimum in these regions. The carrier localization due to In segregation combined with the quantum confinement effect is one of the main reasons for the high efficiency of blue LEDs [156–158]. The same carrier localization effects are also essential for effective ET to REs in semiconducting hosts.

The nature of ET between semiconductors and RE ions in dilutely doped systems lies somewhere between the mechanisms mentioned above. Effective ET has been observed between GaN and various RE ions doped @ <1% [1, 11, 12, 15–19, 137–146, 159–170], and several models for this ET have been proposed over the years; however, a common thread among these models is that the carriers must be highly localized at the RE ions for efficient ET to take place [21–24, 98–102, 171–177]. In the case of wide-bandgap semiconductors such as GaN and GaAs, the relevant RE levels lie within the bandgap of the host, and in order to localize free carriers to the RE ions and facilitate efficient ET, it is critical that defects themselves are located in close proximity to the RE ions [19, 98–102, 177–180]. These defects can be intrinsic defects such as vacancies or foreign atoms introduced during the growth, but it is critical that these defects induce states within the bandgap that are resonant with the desired transition within the $4f$ -manifold of the RE ion [19, 21–24, 98–102, 108, 180–184]. Once the carriers have been localized to the defect level, their proximity to the RE can facilitate ET through an Auger-type recombination [19, 23, 98–101, 164, 177]. Once excited, the RE can lose energy either through an Auger-type back-transfer to the host or through a combination of radiative and nonradiative relaxation within the $4f$ -manifold of the RE. In these processes, the Auger-mechanism, which is a three-body interaction, is assumed to occur between an electron-hole pair (or an exciton) and RE ion's $4f$ -electron configuration. It is important to note that in the ET between the defects and the REs described above, there is no transfer of carriers to the RE^{3+} ion (i.e., the RE does not change its valence state), and so this is not, in most cases [185], a Dexter-type process.

While defect-mediated ET to RE ions due to localization of carriers has been observed in several RE-doped semiconductor systems, the exact nature of the carrier localization depends on the material system and the excitation mechanism [99–101, 177]. For the case of the laser excitation, two general situations exist: (1) where the laser excitation leads to the creation of excitons (coupled electron and hole), and the exciton gets localized at the RE and recombines or (2) an electron or hole is first localized, and then the second carrier gets subsequently localized leading to recombination and ET [171–174, 177]. Excitons can be formed using excitation energies above and just below the bandgap, while the subsequent localization of carriers is generally believed to occur during current injection where carriers are not generated at the same location, as is the case during laser excitation [177]. Recently, it was shown that the excitation cross section for Eu^{3+} -doped atoms in GaN was significantly different under current injection as compared to photoexcitation, increasing for certain defect environments and

decreasing for others, demonstrating the difference between the two methods of introducing carriers and the importance of the location of the local defect levels relative to the RE levels [25]. Figure 5 illustrates the commonly used model for defect-mediated excitation of REs under (A) photoexcitation and (B) current injection [23, 98, 100, 101, 164, 177].

If the desired transition does not occur, it may be necessary to modify the bandgap of the materials through alloying. For example, in Tm-doped GaN, the 1G_4 and 1D_2 levels of Tm^{3+} are needed for blue luminescence, but these levels lie high within the bandgap of GaN and typically only weak blue luminescence is observed in samples grown by molecular beam epitaxy through impact excitation [186–188], and has not been observed in samples grown by organometallic vapor phase epitaxy (OMVPE) [190]. However, after alloying GaN with ~20% Al to form AlGaN, strong blue emission has been observed both under photoexcitation and current injection [189–191]. This is very likely because the intrinsic defects in GaN required for ET are not resonant with the 1G_4 and 1D_2 states [178, 179]. However, Tm^{3+} has been shown to produce bright near-infrared (NIR) luminescence in GaN due to transitions originating from the lower lying 3H_4 and 3H_5 states, without the need for Al alloying [192]. In addition, external dopants have been found to enhance the ET by forming new localized defect complexes. This was observed for the case of O-doping into GaAs, where a new Er-2O complex formed with a higher ET efficiency [193]. In

addition, Mg-codoping of Eu-doped GaN was found to substantially increase the Eu emission under photoexcitation [181–183, 194] and under current injection [146]. It is notable that RE ions are notorious for long radiative lifetimes (~0.1–1 ms) owing the parity forbidden nature of the $4f-4f$ transitions; however, their emission dominates over the bandgap emission, as well as other defect-related emission within the host, which typically occur on the order of μs – ns [176]. Several authors have reported that ET from a semiconducting host to the RE ions can take place in less than 100 ps [22–24, 26, 162]. In the case of Er-doped GaAs, ET to the Er^{3+} ions was found to take place on a scale of ~30 ps [162], and for Eu^{3+} ions doped into GaN, the ET was shown to be ~85 ps [22–24, 26, 177]. Interestingly, the exciton lifetime is drastically reduced by the incorporation of RE ions. In Eu-doped GaN, the exciton lifetime changed from a single exponential decay with a time constant of 220 ps to a biexponential decay with time constants of 2.2 and 88 ps, once Eu was incorporated into the material, even at a concentration of <0.1% [23, 26]. Thus, the incorporation of REs has a clear impact on the ET channels within the host, leading to the case where ET to the RE overcomes the other decay channels within the bulk of host. A benefit of the shorter carrier lifetimes and mobility due to RE doping is that the resulting shorter carrier diffusion length can strongly limit sidewall related nonradiative processes, which is useful for micro-LED applications [195].

Figure 5: Model for defect-trap-mediated energy transfer (ET) in rare earth (RE) systems.

(A) Under photoexcitation, (1) the incoming photons generate a localized electron and hole within the host, (2) the carriers then localize at the local defect levels of the RE nanocomplex. (3) Energy is transferred to the RE or from the RE back to the defect via an Auger process. (4) The excited RE ion emits a photon. (B) Under current injection, (1) carriers injected from different sides of the device must be localized to the defect. (2) Energy is then transferred to the RE or back to the defect. (3) The RE ion emits a photon.

3 Energy shuffling in RE-doped systems

As mentioned in Section 2.3, energy can be back-transferred from a RE ion to the host via a carrier-mediated Auger process. This was directly verified in Er-doped Si and Yb-doped InP by observing a decrease in emission under simultaneous irradiation with a free-electron laser tuned to the ionization energy of the local trap level [99, 101]. It was also observed in a similar two-laser experiment on Er-doped GaN [164]. In essence, this back-transfer de-excites the RE ion into its ground state, where the lost energy is stored at the defect or within the host. Depending on the strength of the coupling between the host and the RE, this energy may be transferred back to the RE, re-exciting it. This is one example of “energy-shuffling”, where energy is transferred between multiple entities in a multiple step or cyclical manner.

All the aforementioned cases of energy shuffling require resonance between two or more states within the

nanosystem. This means a matching of the hot-carrier energy with the optical-gap for quantum cutting, host sensitization or a matching of the energy states between RE ions for upconversion and downconversion, and the engineering of defect states that are resonant with energy levels of RE ions that are doped into the host matrix. A common requirement for energy shuffling within these systems is that the energy must be stored in a state or center, where it can then be transferred to another state or center. For computing and display applications, precise temporal triggering of this energy shuffling from the storage state to another state is critical. In this section, we discuss two prominent schemes for temporally modulated energy shuffling, which could have unique applications in color-rendering and quantum computing. In this section, some of the common energy shuffling schemes that have been developed and had significant advancements in the last decade are discussed with a focus on those that can be temporally triggered.

3.1 Controlled upconversion through energy migration in RE core-shell NCs

Section 2.2 introduced the idea of a core-shell architecture, which allowed for control of the relative emission between

two different RE ions such as Eu^{3+} and Tm^{3+} [126–128]. This can be expanded by implementing a multiple RE system in connection with the core-shell architecture. Wang et al. demonstrated a four RE ion scheme where light is absorbed in the core of the NC by Yb^{3+} ions and through successive upconversion between adjacent RE ions that are placed radially away from the core, the energy will migrate to a Gd^{3+} ion that stores the higher energy. This energy can then be transferred to a variety of desired RE^{3+} ions, such as Eu^{3+} , Sm^{3+} , Tb^{3+} and Dy^{3+} , that are placed in the outer shell. The lateral placement of the REs along with the core-shell structure inhibited cross-relaxation and facilitated this controlled energy migration [196].

This method can be taken one step further by using multiple shells with a different RE ion compositions. Using this structure, Deng et al. [197] demonstrated that the energy shuffling between the RE ions could be temporally modulated by adjusting the duration of a 980 nm excitation laser pulse. In this case, the length of the pulse duration determined the level from which a Ho^{3+} ion emitted. Shorter pulses favored green emission (541 nm) resulting from the $^5\text{F}_4 \rightarrow ^5\text{I}_8$ transition, while longer pulses favored red emission (646 nm) resulting from the $^5\text{F}_5 \rightarrow ^5\text{I}_8$ transition (Figure 6(A)). The relative ratio of the emission lines could be controlled by modulating the pulse width continuously from short (0.2 ms) to long (6 ms) durations (Figure 6(B)). In

Figure 6: (A) Schematic and Transmission Electron Microscope (TEM) image of a NaYF_4 -based core-shell nanocrystal (NC) capable of emitting different colors based on the excitation laser properties. Photoluminescence (PL) emission spectra of the NCs under excitation with a 980 nm pulsed laser with pulse durations of 6 ms or 200 μs at 100 Hz, as well as with an 808 nm c.w. laser. (B) PL emission spectra of the NCs for different pulse durations, which demonstrates the red/green temporal tuning capability of the NCs. (C) Schematic of the experimental set-up for a volumetric 3-D full-color display. The array of colors is generated by modulating the availability of the c.w. 800 nm laser and pulse width of the 980 nm laser. Color images generated by these NCs demonstrate the capability of additive color mixing within the NC template, which exhibits a wide color gamut. [Reprinted (adapted) with permission from a study by Deng et al. 197, Copyright 2015, Springer Nature].

addition, using an 800 nm continuous wave (c.w.) laser, blue emission from additionally doped Tm^{3+} ions could also be achieved, without interfering with the Ho^{3+} excitation pathway (Figure 6(A)). By combining precisely tuned 980-nm laser pulse trains with the 800 nm c.w. laser excitation using a 3-D laser scanner, a full-gamut of colors was achieved (Figure 6(C)) [197]. This impressive proof-of-principle demonstrates the potential of temporally modulated energy shuffling in RE systems, which can yield full-color tunability within a single nano-system via variation of the excitation parameters. One weakness of this approach for consumer display technology is the necessity for multiple laser excitation, and the requirement that the REs must be addressed directly. These challenges can be overcome by doping RE ions into an electrically addressable semiconducting host such as GaN and utilizing a different energy shuffling mechanism [82, 196–198].

3.2 Carrier-mediated re-excitation of Eu^{3+} ions in GaN

Europium is well known for its red emission at ~ 620 nm due the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (Figure 7(A)). The lifetime of the $^5\text{D}_0$ state for Eu^{3+} ions in GaN is typically on the order of ~ 250 μs [22–24, 199–201], which means that a Eu^{3+} ion that has been

excited into the $^5\text{D}_0$ state will remain excited for a significant period of time. Zhu et al. demonstrated that if sufficient carriers are present, Eu^{3+} ions in GaN that are already excited can be “re-excited” leading to green emission at ~ 545 nm due to transitions originating at the higher lying $^5\text{D}_1$ state. This was demonstrated under both c.w. laser excitation and current injection [21, 22]. In the case of current injection, the color of the device visibly changed from red to yellow, which was consistent with the mixing of red ($^5\text{D}_0$) and green ($^5\text{D}_1$) emission observed in the emission spectrum. To gain insight on the nature of this behavior, pulsed laser excitation consisting of short (~ 200 fs) pulses was used, and it was found that the time interval between pulses had to be shorter than the lifetime of the $^5\text{D}_0$ state before the emission from $^5\text{D}_1$ states was observed (Figure 7(B)) [21].

To understand this phenomenon, it is important to first go over the different pathways of ET in the Eu-doped GaN system. Eu atoms are known to incorporate into GaN in a variety of defect environments. At least 10 different defect environments have been identified in Eu-doped GaN grown by OMVPE [12, 19, 199, 202–204]. Each combination of a Eu^{3+} ion and local defect can be considered a different nanocomplex, which has absorption and emission properties that are unique from those of the host itself. Two of these Eu complexes have been shown to play the largest

Figure 7: (A) Photoluminescence (PL) decay measurements of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_1 \rightarrow ^7\text{F}_1$ transitions. The insets show zoomed-in images, where the slow and fast rise contributions can be observed for the $^5\text{D}_0$ state emission. Roughly half of the intensity comes shorter than the temporal resolution of the setup and the other half takes ~ 2 μs to occur. The lifetime of the $^5\text{D}_0$ state was determined to be ~ 260 μs from fitting the exponential decay. For the $^5\text{D}_1 \rightarrow ^7\text{F}_1$ transition, only a fast rise can be observed, and the lifetime of the $^5\text{D}_1$ state was determined to be ~ 2.4 μs from fitting the exponential decay [22]. (B) Normalized PL emission spectra at a high pulse energy and pulse interval of 250 and 5 μs . When the pulse interval comparable to the lifetime of the $^5\text{D}_0$ state, no emission from the $^5\text{D}_1$ state is observed; however, the emission becomes significant for pulse intervals much shorter than the lifetime of the $^5\text{D}_0$ state. [Reprinted (adapted) with permission from a study by Zhu et al. [21] and Mitchell et al. [22], Copyright, 2018–2019 American Chemical Society].

role in device applications and have been labeled OMVPE4 and OMVPE7 [12, 19, 99, 166, 184, 204]. It has been proposed that these complexes consist of a Eu atom with a shallow donor or deep acceptor within a first/second nearest neighbor position for OMVPE4 and OMVPE7, respectively [19, 184]. The respective location of the defect levels relative to the energy levels of the Eu^{3+} has a significant impact of the ET pathway [19, 23–25, 108, 177]. For the case of OMVPE7, it was shown that the Eu^{3+} ion was excited directly into the $^5\text{D}_0$ state [24]. However, for OMVPE4, it is found that the Eu^{3+} ion is either excited directly into the $^5\text{D}_0$ state or initially into the $^5\text{D}_2$ state with a cascading non-radiative relaxation following the path $^5\text{D}_2 \rightarrow ^5\text{D}_1 \rightarrow ^5\text{D}_0$ before a radiative relaxation from the $^5\text{D}_0$ state into one of the $^7\text{F}_j$ states. The two competing excitation pathways of OMVPE4 have been confirmed with time-correlated single photon counting (TCSPC) measurements using excitation above the bandgap, which show that the excitation curve of the $^5\text{D}_0$ state has two components: a fast component (confirmed to be <100 ps using a streak camera [23, 24, 26]) and a slow rise component with a lifetime of ~ 2 μs , which matches the decay lifetime of the $^5\text{D}_1$ state (Figure 7(A)) [22–24]. The insets of Figure 7(A) show a zoomed in view, and it can be seen that about half of the $^5\text{D}_0$ emission comes within the resolution of the measurement (~ 500 ns), while the other half comes after the ~ 2 μs component. For the $^5\text{D}_1$ emission, all of the emission comes within the resolution of the detection system. Furthermore,

TCSPC measurements performed at excitation energies within the bandgap and around that of the $^5\text{D}_2$ state indicated that absorption directly into the $^5\text{D}_1$ state is not strong [22, 24]. The re-excitation relies on the cascade from the $^5\text{D}_2$ to the $^5\text{D}_0$ state, and therefore, OMVPE7 is not believed to produce green emission via re-excitation.

The relative timescales of the $^5\text{D}_0$ and $^5\text{D}_1$ states are a critical component of the carrier-mediated re-excitation process. For the case of pulsed laser excitation, during a first pulse, nearly all Eu^{3+} ions that are excited eventually end up in the $^5\text{D}_0$ state, regardless of the path taken. If a subsequent laser pulse arrives later than the $^5\text{D}_0$ state lifetime, the Eu^{3+} ion will have decayed radiatively at primary 620 nm, ending in the ground state before the subsequent pulse arrives (Figure 8(A)). If the second pulse arrives within the $^5\text{D}_0$ lifetime, the Eu^{3+} can be de-excited through the Auger back-transfer process leaving the Eu^{3+} ion in the ground state, where the energy is potentially stored at the local defect or within the host (Figure 8(B)). The Eu^{3+} ion can then be excited again with a nonradiative relaxation into the $^5\text{D}_1$ state, where there is again a probability of further relaxation into the $^5\text{D}_0$ state or radiative relaxation to a $^7\text{F}_j$ state. Overall, the temporal availability of carriers was determined to be the primary catalyst for the re-excitation, as no significant $^5\text{D}_1$ emission was observed even when the individual pulse energy was increased by an order of magnitude [21, 24]. Thus, for the case of c.w. laser excitation or constant current injection, if sufficient

Figure 8: The basic principle of the re-excitation of Eu^{3+} : (A) carriers are trapped at a localized defect (1), energy is transferred to the Eu^{3+} leaving it in the $^5\text{D}_2$ state (2) followed by a nonradiative decay to the $^5\text{D}_1$ state (3), from the $^5\text{D}_1$ state there is a small probability of radiative decay, but almost all Eu^{3+} ions will end up in the $^5\text{D}_0$ state through non-radiative decay. (B) If the next excitation comes after the lifetime of the $^5\text{D}_0$ state, most of the Eu ions will have radiatively relaxed to the ground state and this next excitation will simply cause the same excitation leading primarily to emission from the $^5\text{D}_0$ state (4). However, if the next excitation comes within the lifetime of the $^5\text{D}_0$, there is a significant chance that the Eu will back transfer its energy into the local defect (5) and end up in the ground state, the energy can then be transferred back to the Eu^{3+} ion (6), however, this next time, the Eu^{3+} ion may radiatively decay from the $^5\text{D}_1$ state (7). However, if the Eu^{3+} ion ends up in the $^5\text{D}_0$ state again, it will lose its energy via back transfer upon the next excitation.

carriers are present, there is significant chance that a carrier will pass near an already excited Eu^{3+} ion and cause a back-transfer, initiating the re-excitation process.

For sufficiently short laser pulses, the degree of re-excitation (measured by the amount of $^5\text{D}_1$ emission relative to $^5\text{D}_0$ emission) depended on two main things: (1) pulse energy and (2) sample structure. While the pulse energy had a negligible effect on re-excitation for long pulses, once the pulses were sufficiently short, re-excitation could be observed even for low pulse energies [21]. When the pulse energy was increased, the $^5\text{D}_1$ emission increased linearly suggesting, for example, that if twice as many carriers were generated, twice as many re-excitations occurred per second, yielding twice the probability of a Eu^{3+} ion radiatively emitting from the $^5\text{D}_1$ state [24]. In regards to sample structure, while re-excitation has been observed under laser excitation for all Eu-doped GaN samples grown by OMVPE that have been explored, the amount of $^5\text{D}_1$ emission at a particular pulse energy was closely tied to the design of the active layer. Three active layer structures have been prominent in the literature: continuous layers of Eu-doped GaN [137–141, 199–203], samples with alternating Eu-doped GaN/GaN layers [18, 19, 142, 143], and MQW structures with alternating Eu-doped GaN/AlGaIn layers [21, 22], each with increasing degrees of carrier confinement within the Eu-doped GaN regions. The MQW samples exhibited the most $^5\text{D}_1$ emission at each pulse energy, and LEDs made with this structure had the largest degree of color tunability [22]. This is likely due a result of high spatial overlap between the carriers and the Eu^{3+} ions, resulting in efficient carrier capture and thus, efficient re-excitation.

In general, this re-excitation process relies on relative decay rates and statistics; the more excitations that occur

per second, the higher the odds that the Eu^{3+} ion will decay radiatively from the $^5\text{D}_1$ state and the lower the odds that it will emit from the $^5\text{D}_0$ state, leading to a shift in the relative intensities from each state and a change in the perceived color of the emission. The emission spectrum and perceived color are found to be stable over time since an equilibrium ratio between the $^5\text{D}_0$ and $^5\text{D}_1$ state emission is reached after several re-excitation cycles. This equilibrium can be captured within the integration time of a detector (emission spectra) or a camera exposure (picture), which is shown in Figure 9(A). While this approach yielded the ability to color tune a device between red and yellow with increasing current, blue could not be achieved using Eu^{3+} emission alone at room temperature [22]. It would be advantageous to introduce a new emitting center with an emission wavelength around 430 nm (which is ideal for color mixing) that can interact with the Eu-complex, and with a transition rate that is at least an order of magnitude lower than that of the $^5\text{D}_1$ state. Fortunately, an emitting defect center with these properties is well known in GaN and is introduced by the codoping of Si and Mg [205–207]. A Eu-doped GaN LED codoped with Mg/Si was fabricated, and the emission spectrum and photos of the emission are shown in Figure 9(B).

The combination of emission from the $^5\text{D}_0$ and $^5\text{D}_1$ states can be translated into a color coordinate via one of the standard chromaticity conventions. In this way, each repetition rate can be assigned a “color”. This is analogous to the technique used by Deng et al. with NCs [82, 197], however, the Eu-doped GaN system has the added benefit that it can be electrically addressed. Under current injection, color tuning can be achieved by generating arbitrary current pulse waveforms, where the duty cycles, frequencies and amplitudes are varied. The result is shown in

Figure 9: (A) Normalized electroluminescence (EL) spectra from a Eu-doped GaN LED. At low currents, the emission from the $^5\text{D}_1$ state is negligible and the emission is dominated by the emission from the $^5\text{D}_0$ state. The inset shows an image of the LED under different injection currents. (B) EL spectra from a Eu-doped GaN LED that was codoped with Si and Mg. The emission from this LED is primarily a mixture of red and blue emission, where the blue and red emission is due to Si/Mg related levels and the $^5\text{D}_0$ state of the Eu^{3+} ions, respectively. [Reprinted (adapted) with permission from a study by Mitchell et al. [22]. Copyright 2019, American Chemical Society].

Figure 10: As the duty cycle of a pulsed current with a frequency of 10 kHz and a constant peak current is decreased, the emission color changes from yellow to red or from pink to red for the Eu-doped GaN samples with and without Mg-Si codoping, respectively [Reprinted (adapted) with permission from a study by Mitchell et al. [22], Copyright 2019, American Chemical Society].

Figure 10(left circles) for a current of 200 mA and a frequency of 10 kHz at duty cycles of 99.9, 50 and 5%. This was also observed for the Eu-doped GaN LED codoped with Si and Mg (Figure 10 (right circles)).

Overall, the temporally modulated energy shuffling processes discussed above are similar in that energy is stored in a state until it can be transferred to another state. The subsequent ET transfer process facilitated by this stored energy is then inhibited or promoted by the availability and duration of laser pulses or injected carriers, which leads to a controlled continuous modulation of the emitted photons. In the next section, the re-excitation process will be modeled, and simulations will be

performed to gain insight on the potential extent to which re-excitation can be enhanced in Eu-doped GaN, as well as translated to other systems.

4 Modeling and simulation of carrier induced RE-excitation

4.1 Current injection model for Eu-doped GaN devices

To better understand the current injection properties of Eu-doped GaN LEDs based on the alternating Eu-GaN/GaN and QW active layer structures and further improve their performance, a detailed device model was proposed by Fragkos et al. This model takes into consideration both the excitation properties of RE ions in the presence of charged carriers, as well as the processes that are present in devices such as current injection efficiency (CIE) and carrier transport within the active layer [208]. To address these issues, a comprehensive device model was developed, and the key ingredients of this model are illustrated in Figure 11 [209, 210]. In this model, the excitation path is dissected into four main stages (blue boxes). The first two stages are related to the device structure, while the other two are related to the processes that are going on within the active layer and involve the abovementioned donor and/or

Figure 11: Excitation path in Eu-doped GaN-based LED devices. Black arrows indicate the transition of electron-hole pairs into the next level and red arrows represent the energy recycling mechanisms. [Reprinted (adapted) with permission from a study by Fragkos et al. [210], Copyright 2017, Springer Nature].

Table 1: Parameters used for the numerical calculations described in a study by Fragkos et al. [210]. The parameter A is the Shockley-Read-Hall coefficient. All other parameters are defined in the model in Figure 11.

Parameters	Study I	Study II	Study III	Study IV	Study V	Study VI
A (10^8 s^{-1})	0.001–1	0.1	0.1	0.1	0.1	0.1
τ_{cap} (10^{-8} s)	100	100	1–1000	100	100	100
τ_{tr} (10^{-7} s)	360	360	360	0.36–3600	360	360
τ_{diss} (10^{-6} s)	1000	1000	1000	1000	1000	1000
τ_{bt} (10^{-6} s)	200	200	200	200	200	200
$\tau_{\text{ex_heat}}$ (10^{-3} s)	1	1	1	1	1	1
$\tau_{\text{Eu_heat}}$ (10^{-3} s)	1	1	1	1	1	1
$\tau_{\text{Eu_rad}}$ (10^{-6} s)	400	400	400	400	10–600	400
$L_{\text{GaN}}, L_{\text{Eu-GaN}}$ (nm)	5, 2.5	2.5–6.5, 2.5–6.5	5, 2.5	5, 2.5	5, 2.5	QW region

acceptor defects. An additional box is added (yellow) when the barrier layers are AlGaIn as opposed to GaN resulting in a higher degree of quantum confinement. Within these defect complexes, carriers are captured and facilitate recombination within the vicinity of the Eu^{3+} ion. For the Eu^{3+} ions themselves, radiative and nonradiative de-excitation are considered. Moreover, the forward and backward transfer of energy and carriers are considered, as indicated by the black and red arrows.

This model was used to develop expressions for the internal and external quantum efficiencies under optical and electrical excitation [209, 210]. The parameters in the model were varied to gain insight on the impact of each parameter on the EQE and to compare the optical and electrical injection cases. Six simulated studies were performed where the IQE was calculated for different photon fluxes and current injection conditions, where one parameter in the model was varied with the other parameters held fixed. The parameters ranges used in these studies are summarized in Table 1 [210].

The experimental results from various reports could be modeled quite accurately, and insight on how improvement of certain parameters would impact device performance was gained. It is important to note that the simulated IQE values under optical excitation were almost an order of magnitude lower than those found under current injection for all cases [209]. These results are consistent with the experimentally determined excitation cross sections reported later by Timmerman et al. [25]. This model also identifies a distinct limitation to bright red emission from Eu-doped LEDs, which is the long lifetime of the $^5\text{D}_0$ state. For example, a 50% decrease in the $^5\text{D}_0$ state lifetime was found to lead to a 144% enhancement in the simulated EQE [209]. However, for the re-excitation process

and to produce LEDs of sufficient brightness for display applications, this is not a significant concern.

4.2 Model for re-excitation in Eu^{3+} -doped GaN-based LEDs

The re-excitation process itself can be modeled by using a series of rate equations and assuming that the current injection and ET efficiency is sufficiently high for the Eu complexes of concern. However, first, several parameters of the ET must be established. Based on TCSPC results, the decay rates (k) of the $^5\text{D}_0$ and $^5\text{D}_1$ states are taken to be $\sim 4 \times 10^3$ and $\sim 4 \times 10^5 \text{ s}^{-1}$, respectively. While no emission from the $^5\text{D}_2$ state was directly observed at room temperature, the rise of the $^5\text{D}_1$ state could not be resolved within 500 ns (Figure 7(a)), suggesting that the decay rate of the $^5\text{D}_2$ state is at least one order of magnitude longer or $\sim 4 \times 10^6 \text{ s}^{-1}$ [22]. The initial ET to the Eu^{3+} ion was found to be $< 85 \text{ ps}$, as was the recovery after re-excitation [24, 25], thus, it can be assumed that all ET takes place on a time-scale that is negligible compared to the decay rates of the Eu^{3+} ions. With these parameters in mind, a simplified model for re-excitation can be developed (Figure 12(A)) [22]. In this model, focus is placed on the $^5\text{D}_2$, $^5\text{D}_1$, $^5\text{D}_0$ and $^7\text{F}_{(0-6)}$ states, and where all of the ^7F states are taken together. It is assumed that non-radiative decay dominates the transitions from the $^5\text{D}_2 \rightarrow ^5\text{D}_1$ and $^5\text{D}_1 \rightarrow ^5\text{D}_0$ levels while the $^5\text{D}_0 \rightarrow ^7\text{F}$ transition is dominated by radiative decay. The current (I) dictates the total number of available carriers per unit time, which governs the excitation into the $^5\text{D}_1$ states, in addition to the back-transfer. Only excitation into the $^5\text{D}_0$ and $^5\text{D}_2$ states are considered significant, and the branching ratio (B) between excitation into the $^5\text{D}_0$ and $^5\text{D}_2$

Figure 12: (A) (Left) relevant energy levels and transitions of a Eu^{3+} ion. Blue arrows indicate the excitation pathways, black arrows the carrier-induced de-excitation, and red arrows the radiative and nonradiative transitions. (Right) simulations of the level occupancy as a function of injection current for a value of the branching parameter $B = 0.5$. (B) Extension of the Eu complex model, which includes the local defect in the excitation scheme. [Reprinted (adapted) with permission from a study by Mitchell et al. [22], Copyright 2019, American Chemical Society].

state is taken as 50%. With these considerations, the set of rate equations describing this model take the form:

$$\begin{aligned} \frac{dn_{\text{D}_2}}{dt} &= B \frac{I}{N_{\text{Eu}}} - n_{\text{D}_2} k_{21} - n_{\text{D}_2} \frac{I}{N_{\text{Eu}}} \\ \frac{dn_{\text{D}_1}}{dt} &= n_{\text{D}_2} k_{21} - n_{\text{D}_1} k_{10} - n_{\text{D}_1} \frac{I}{N_{\text{Eu}}} \\ \frac{dn_{\text{D}_0}}{dt} &= (1-B) \frac{I}{N_{\text{Eu}}} + n_{\text{D}_1} k_{10} - n_{\text{D}_0} k_0 - n_{\text{D}_0} \frac{I}{N_{\text{Eu}}} \\ \frac{dn_{\text{F}}}{dt} &= n_{\text{D}_0} k_0 - n_{\text{F}} \frac{I}{N_{\text{Eu}}} \end{aligned}$$

where n_x indicates the fractional population of the four levels involved, k_{21} , k_{10} and k_0 are the transition rates from $^5\text{D}_2 \rightarrow ^5\text{D}_1$, $^5\text{D}_1 \rightarrow ^5\text{D}_0$ and $^5\text{D}_0 \rightarrow ^7\text{F}$, respectively, and N_{Eu} is the total number of Eu^{3+} ions available. The populations of each state at a particular current was calculated by temporal integration of the rate equations with a step size of 100 ns and running the calculation until a steady-state population had been reached after 1 ms. Under the assumption that the radiative rates of the $^5\text{D}_1$ state and the $^5\text{D}_0$ state are equal [22, 24, 25, 91], the occupancy of both levels directly reflects the emission intensity. Figure 12(A) shows the results of these simulations compared to the integrated emission intensity from the LED in Figure 9(A) at various injection currents.

When a pulsed laser excitation is used, the model above must be modified. Wei et al. [24] developed a model (Figure 13(A)) and a set of rate equations to simulate the temporal evolution of the various Eu^{3+} states under excitation from a ~ 200 fs laser pulse with a repetition rate of 200 kHz. In this model, the pulse intensity (P) governs the excitation processes, and the coefficients b , c and d are branching ratio parameters for the different excitation and decay processes involved. Power-dependent PL results on the $^5\text{D}_1$ state emission revealed a linear relationship between PL emission intensity and pulse interval for all pulse energies, which indicates that the branching ratios are

Figure 13: (A) The Eu^{3+} energy levels and transitions used in the simulation. The light arrows indicate back-transfer; the blue arrows indicate excitation, and the red arrows represent the radiative and nonradiative transitions. (B) Simulation of the $^5\text{D}_0$, $^5\text{D}_1$ and $^5\text{D}_2$ state time evolution under high pulse intensity and high repetition rate.

constant within the excitation parameters of these experiments [24]. In this model, the radiative emission from the $^5\text{D}_1$ state was considered, and the relative decay is determined by a different branching ratio parameter, b . Lastly, the back transfer out of the $^5\text{D}_1$ and $^5\text{D}_0$ was assigned a branching ratio parameter, d . For excitation under a pulsed laser, T represents the pulse period and t_0 is used for the “pulse on” time. Since the duration of the pulse is short, only the excitation process as it occurs after the pulse was considered, relaxation that occurs while pulse is on was ignored. With these assumptions, the set of rate equations describing the model under pulsed laser excitation takes the form:

$$0 \leq t \leq t_0, \begin{cases} \frac{\partial n_{\text{D}_2}}{\partial t} = cPn_{\text{F}} - dPn_{\text{D}_2} \\ \frac{\partial n_{\text{D}_1}}{\partial t} = -dPn_{\text{D}_1} \\ \frac{\partial n_{\text{D}_0}}{\partial t} = (1-c)Pn_{\text{F}} - dPn_{\text{D}_0} \\ \frac{\partial n_{\text{F}}}{\partial t} = -Pn_{\text{F}} + dP(n_{\text{D}_0} + n_{\text{D}_1} + n_{\text{D}_2}), \end{cases}$$

$$t_0 \leq t \leq T, \begin{cases} \frac{\partial n_{D_2}}{\partial t} = -k_2 n_{D_2} \\ \frac{\partial n_{D_1}}{\partial t} = k_2 n_{D_2} - k_1 n_{D_1} \\ \frac{\partial n_{D_0}}{\partial t} = (1-b)k_1 n_{D_1} - k_0 n_{D_0} \\ \frac{\partial n_F}{\partial t} = (b)k_1 n_{D_1} + k_0 n_{D_0} \end{cases}$$

where n_x indicates the fractional population of the four levels involved, and k_2 , k_1 and k_0 are the decay rates of the 5D_2 , 5D_1 and 5D_0 states, respectively. The branching ratio c is estimated from the rise for the profile of the 5D_0 state emission to be 0.5 and ratio d is estimated 0.7 from the TR-PL spectrum of the 5D_0 state under the experimental conditions [24]. The branching ratio b is estimated to be 0.1 since the 5D_1 intensity from PL measurements under low excitation densities is usually one order smaller than 5D_0 . The time evolution of the relative population of the 5D_0 , 5D_1 and 5D_2 states is shown in Figure 13(B). After five periods ($\sim 25 \mu s$), the evolution results are consistent with experimental results, where the 5D_0 state is depopulated after each pulse, and then subsequently repopulated both directly and via relaxation from the 5D_1 state [24]. In addition, the 5D_2 state lifetime is sufficiently short such that no rise is observed in the 5D_1 state related emission.

4.3 Inclusion of the local defect and generalization of re-excitation model

While the simplified models in the previous section demonstrated that the re-excitation phenomena can be understood and predictions can be made using rate equations, these models do not consider the influence of the localized defect, where the energy is stored during the re-excitation. Moreover, they do not allow us to track the population of the localized defect, which would be necessary to model the three-color situation observed in the Mg/Si codoped system. To expand these models, a two-level localized defect, which could transfer energy either to the 5D_0 and 5D_2 state (Figure 12(B)), can be included.

For pulse intervals less than $2 \mu s$, the 5D_2 state can effectively be neglected, and for simplicity, it is assumed that any excitation into the 5D_2 will end up in the 5D_1 state within a negligible time frame. In this model, the localized defect is excited by the carriers into the excited state (m_l). It then excites the Eu^{3+} ion into either the 5D_0 or 5D_1 state at a rate of x and y , respectively. Back-transfer can occur from

either the 5D_1 or 5D_0 state, repopulating m_l , with a subsequent repopulation of the Eu^{3+} with the same ratios as the initial excitation. With these considerations, this model can be expressed with the following set of rate equations:

$$\begin{aligned} \frac{dm_l}{dt} &= \frac{I}{N_{Eu}} m_0 - m_l (x + y) \underbrace{(n_{F_0} + n_{D_0} + n_{D_1})}_{N_{Eu}} \\ \frac{dn_{D_1}}{dt} &= m_l (y) (n_{F_0} + n_{D_0}) - m_l (x) n_{D_1} - n_{D_1} k_1 \\ \frac{dn_{D_0}}{dt} &= m_l (x) (n_{F_0} + n_{D_1}) - m_l (y) n_{D_0} - n_{D_0} k_0 + n_{D_1} k_1 \\ \frac{dn_{F_0}}{dt} &= -m_l (n_{F_0}) (x + y) + n_{D_0} k_0 \end{aligned}$$

As before, the *radiative* rates of the 5D_0 and 5D_1 are assumed to be identical; thus, their relative populations can be translated into relative emission intensity. In this case, if the localized defect has an appreciable radiative decay probability, the population of m_l can give insight onto the potential relative emission; however, the radiative rate for, e.g., the Si/Mg defect in GaN is on the order of 10–100 ns [176, 211, 212], and thus the populations would have to be scaled appropriately to gauge the relative emission intensity. Once this is done, however, simulations can be performed using pulsed current trains to predict the color gamut that can be achieved with the three color centers of the nanocomplex, in this case: (1) 5D_1 , (2) 5D_0 and (3) Si/Mg defect. An additional benefit of this model is that it allows for more predictive power for arbitrary defects that may be introduced into the material in the future. This model will also give insight on the practicality of applications using certain defects since the required carrier densities for particular occupancy ratios can be estimated. Moreover, while the intrinsic radiative rates are determined for the emitting centers, this model can also predict the influence of external modification of the radiative rates, which can be achieved using cavity confinement and will be discussed in the next section.

5 Cavity confinement

5.1 Planar Fabry-Perot cavity

The re-excitation mechanism strongly depends on the decay rates of the emitting centers, particularly the radiative decay rate. While these are intrinsically determined for each transition of the REs once they are doped into the host [91], it is possible to manipulate the radiative decay rates externally

Figure 14: (A) Schematic of a resonant cavity enhanced Eu-doped GaN LED and electroluminescence (EL) spectra comparing the EL emission intensity for an LED with and without the cavity. [Reprinted (adapted) with permission from a study by Inaba et al. [221], Copyright 2020, American Chemical Society]. (B) The photoluminescence (PL) emission from Eu-doped GaN active layers with and without cavities, which demonstrates the ability of the cavity to enhance or inhibit certain emission peaks.

via coupling to the modes of a resonance cavity through the Purcell effect, which has been demonstrated in several systems [200, 213–221]. According to Fermi's Golden Rule, an increase of the radiative rates of RE³⁺ ions can be achieved by increasing the photonic density of states at the frequency of spontaneous emission [214]. This effect was already demonstrated in Eu-doped GaN using a planar Fabry-Perot cavity [200]. In this case, a Eu-doped layer was embedded into a microcavity consisting of an AlGaIn/GaN distributed Bragg reflector (DBR) and a top layer of Ag, which resulted in a ~20% increase in the radiative rate under optical pumping at room temperature [200]. Furthermore, by replacing the Ag top reflector with another DBR reflector, this time consisting of alternating ZrO₂/SiO₂ layers, a proof-of-concept LED was fabricated, which exhibited a 10-fold enhancement of Eu³⁺ emission (Figure 14(A)) [221]. This increase was due to a ~12% increase in the radiative rate and increased extraction efficiency.

In addition, by changing the thickness of the Eu-doped layer and modifying the reflectivity of the top reflector, it was shown that the PL emission spectrum from the Eu-doped layer could be significantly modified. Figure 14(B) shows the PL spectra for three samples, one without a top reflector and two with different cavity thicknesses and top DBR reflector properties. Under re-excitation conditions (high laser pulse rate), one DBR cavity is capable of removing all emission lines except the line at 622 nm, leading to a very “clean” red emission, while the other DBR cavity was able to remove nearly all of the emission except the green emission at 545 nm. It should be noted that the thickness of the samples in Figure 14(B) was not uniform, and variations in the degree of emission inhibition was observed; however, these results demonstrate that more precise control of this process could result in high purity red and green emission from Eu³⁺ ions, where the relative intensities can be controlled using a combination of cavity manipulation and current injection conditions.

5.2 Microdisk resonator

While Fabry-Perot cavities exhibited a reasonable influence on the radiative rate from the Eu³⁺ ions, Timmerman et al. [222] demonstrated that microdisk resonators were more effective at increasing the radiative rate of the ⁵D₀ state due to coupling with whispering gallery modes. The microdisks were fabricated by growing the Eu-doped layer on top of a AlInGaIn sacrificial layer, which is independently etched, leading to the structure shown in the inset of Figure 15. TCSPC and PL measurements confirmed that the Eu³⁺ ions had coupled to the cavity modes, resulting in a strong increase in the spontaneous radiative rate and a significantly sharper and brighter emission peak at ~622 nm (Figure 15) [222]. The microdisks exhibited a biexponential decay behavior, which is due to the fact that only Eu³⁺ ions that were located near the outer edge of the microdisks coupled to the cavity modes. It is possible to remove this “undesired” uncoupled emission by using a ring-resonator design, which has been realized on other GaN systems [223, 224]. While coupling RE ion emission to whispering gallery modes has been demonstrated in insulating hosts direct optical pumping of the RE ions was required [225, 226]. The coupling of Eu³⁺ emission reported by Timmerman et al. represented the first report of clear coupling to cavity modes and enhancement of emission due to an increasing the spontaneous radiative rate of the Eu³⁺ ions [222, 227, 228].

6 Outlook and conclusions

Using a combination of re-excitation and external cavity confinement, it may be possible to cover a large portion of the color space used in display technology with a single material, potentially a single diode, under current

Figure 15: (Left) Photoluminescence (PL) decay spectra for Eu-doped GaN samples with different microdisk structures. The nonresonant microdisk exhibited a single exponential fit with a lifetime consistent with that of a bulk Eu-doped GaN samples (239.8 μ s). The resonant microdisk exhibited a biexponential decay with a fast component of ~ 63 μ s and a slow component of 239.8 μ s, indicating that the 5D_0 state decay rate of Eu^{3+} ions that had coupled to the cavity modes increased by a factor of four. The inset shows a scanning electron microscope image of an Eu-doped GaN microdisk. (Right) PL emission from the resonant and nonresonant microdisks.

injection. Figure 16 shows the degree of the CIELUV color space that can be covered by the 5D_1 and 5D_0 states of Eu^{3+} ions along with the Si/Mg-related emission, which has already been demonstrated in GaN [22]. The star represents the maximum achievable green coordinate due to the 545 nm 5D_1 state emission, which can be facilitated using an external cavity. It may also be possible to expand this color gamut by codoping multiple RE ions such as Tm, Ho,

Figure 16: CIELUV plot containing various images of color-tunable Eu-doped GaN LEDs under different excitation and filtering conditions. The star indicates the maximum achievable pure green emission from the 5D_1 state. The triangle containing the emission from the 5D_0 state, the star and the Mg-Si defect indicates the gamut of colors that can be achieved by additively mixing the emission from these levels. [Reprinted (adapted) with permission from a study by Mitchell et al. [22], Copyright 2019, American Chemical Society].

or Er. For example, Steckl et al. [17, 229] demonstrated that the ratio between Eu^{3+} and Er^{3+} emission could be controlled by changing the magnitude or polarity of the applied voltage in Eu,Er codoped GaN LEDs. However, this required high applied voltages exceeding ± 50 V and was based on impact excitation rather than the ET mechanisms discussed in this review. Still, these observations demonstrate the ability to generate a large array of colors from a single material by manipulating the different absorption properties of various color centers. It is also important to note that the most effective structure for re-excitation was the MQW structure; however, the Si-Mg-codoped, Fabry-Perot cavity and microdisk samples were all grown using a continuous Eu-doped GaN layer. The combination of confinement cavities and codoping with the MQW structure has not yet been achieved. If achieved, it could facilitate a new degree of control over this process.

In the case of the Fabry-Perot cavity device, the higher extracting efficiency was largely due to a narrower and more directed spatial emission profile, which could find potential use in single photon application, as it would optimize collection efficiency. In addition, typical Eu-doped samples show several emission peaks between 600 and 640 nm. However, in Figure 14(B), the cavity resulted in a narrow 622 nm emission, where other emission wavelengths were nearly completely inhibited. This includes side peaks around 622 nm from other Eu complexes. Such an ability to enhanced single center emission would be useful for quantum emitting applications. It should be noted that Sekiguchi et al. [230] demonstrated that when the concentration of Eu atoms in thin epilayers of Mg codoped Eu-doped GaN is lowered to $\sim 3 \times 10^{18} \text{ cm}^{-3}$, only a single Eu center forms, which could also be beneficial for quantum computing technologies.

Several schemes have been proposed to exploit RE ions for quantum manipulation [53, 64, 67, 231], which so far involve addressing the RE ions optically and coupling through dipole-dipole interactions between ions that are situated close to each other. Due to the small optical transition probabilities of RE ions, the coupling of distant single atoms through light is challenging. Still, single photon characteristics have been demonstrated using two-photon excitation schemes in Pr^{3+} [50], selected Pr^{3+} or Ce^{3+} transitions with high transition probabilities [54, 61], or by exploiting cavity structures to enhance the $4f \rightarrow 4f$ transition probabilities [55]. A nice example of how advanced semiconductor device technology can be exploited is the electrical detection of single Er^{3+} ion spin states in a silicon device [52].

The two-cavity confinement structures discussed above have different benefits and shortcomings. The Q-factor of planar Fabry-Perot cavities at a particular wavelength is determined by the reflectance of the mirrors. The light is emitted from the top reflector, where the reflectivity is reduced to allow sufficiently light to escape. As with all cavities, the more light that escapes, the lower the Q-factor. Since these Fabry-Perot cavities are grown using OMVPE, the thickness can be small enough to contain only once cavity mode, the fundamental mode. In addition, the thickness of the cavity can be easily controlled and varied if different Eu wavelength enhancements are desired. However, electrical devices based on this structure require electrical current to go through both reflectors to produce the emission, which can inhibit the electrical properties due to scattering and overall device thickness, and device fabrication is relatively elaborate. For the Eu-doped GaN microdisks, the diameters were $\sim 2 \mu\text{m}$, and so several cavity modes exist around the outside. Thus, while light at 620 nm from the Eu is enhanced, and there are also other resonance peaks in the spectrum. The light in microdisk structures escapes due to imperfections around the radius but can also be easily outcoupled using a waveguide which is useful for light delivery. The structure of the microdisks more easily facilitates device fabrication, which is useful for microdisplay applications. However, microdisks that are on-resonance are more difficult to produce, although their resonance wavelengths can be thermally tuned. Overall, it is important to explore both of these cavity structures in addition to others, such as photonic crystals [232], in order to advance the application of these materials.

The coupling between the Eu^{3+} ions and a local defect has another benefit, which may be useful for quantum computing applications as well. It was recently reported that the OMVPE7 center could capture a free carrier at elevated temperatures, which shifted its emission from 622 to 618 nm but more importantly increased the effective

g-factor of the center by a factor of two [20, 233, 234]. Density functional theory results suggest that a coupling between the magnetic moment of a local charged V_{Ga} and the Eu^{3+} is responsible for this enhanced g-factor [20]. Thus, it may be possible for spin information to be prepared and transferred from a charged defect in GaN to a Eu^{3+} ion. A foundational understanding of the physics behind this process would open a wide range of new possibilities for initializing and reading out RE ion qubits, which could enable design of compact, efficient quantum devices. Moreover, Kachkanov et al. [235] reported that a magnetic moment could be optically induced for the $^7\text{F}_2$ state of Eu^{3+} ions doped into GaN. This magnetic moment can be induced by “forcing” the Eu^{3+} ion to emit a photon, and it can be switched off by shining light that is resonant with the Eu nanocomplex but transparent to GaN.

The use of RE ions such as Eu for quantum computing applications has several advantages and disadvantages compared to other common defect centers. For example, one of the most studied single photon sources for quantum computing applications is the NV center in diamond, which consists of a carbon vacancy and a substitutional nitrogen, where spins localized at this defect can be easily manipulated with external magnetic and electric fields [236–238]. While NV centers have broad absorption and emission spectra at room temperature, at low temperatures, the red zero-phonon line at 637 nm is very narrow [237, 238]. This emission line is the most useful for quantum computing applications, but it would be necessary to suppress the phonon sidebands at ambient temperatures since they act as alternative energy pathways [237, 238]. In addition, the high refractive index of diamond is a limiting factor on the extraction efficiency of the single photons [239]. A benefit of RE ions such as Eu^{3+} , is that the emission remains sharp, without phonon sidebands at room temperature, although transitions to other Eu states could be considered an analogous concern. Both systems have long coherence times; however, NV centers have significantly faster radiative lifetimes (~ 10 ns) compared to the $4f$ -states of Eu^{3+} ions ($\sim 100 \mu\text{s}$), which is an obstacle for quantum applications [23, 24, 236, 239]. As discussed in this review, the use of optical cavities for both systems can assist with narrowing the emission, shortening the lifetime and enhancing extraction efficiency [200, 221, 239, 240].

In conclusion, the systems described above address a major challenge for encoding, manipulating and controlling the photons emitted from a material. For future applications in quantum information and graphics imaging, it will be critical to have versatile materials whose emission can be temporally manipulated externally using current

injection, light, and temperature, as well as through the application of electric or magnetic fields. The recent results for Eu-doped GaN demonstrate that the coupling between RE ions and semiconducting hosts facilitates many of these properties, including effective transfer of energy and potentially spin information, along with color tunability from a single RE ion. In combination with recent developments such as Tm-doped NIR LEDs and Er-doped GaN-based lasing mediums, these phenomena wait to be fully exploited within a variety of RE-doped systems leading to significantly enhanced control over the nature of photon emission.

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