**Literature review of Er:Si**

Outline:

Review of past research (PL, EPR, EXAFS)

Review of recent research (spectroscopy, optical lifetime, coherence measurements)

mention T center in Si, Er in molecules, CaWO4/GaN

Aspects: centers, symmetry, energy level structure, electronic states

**Motivation**

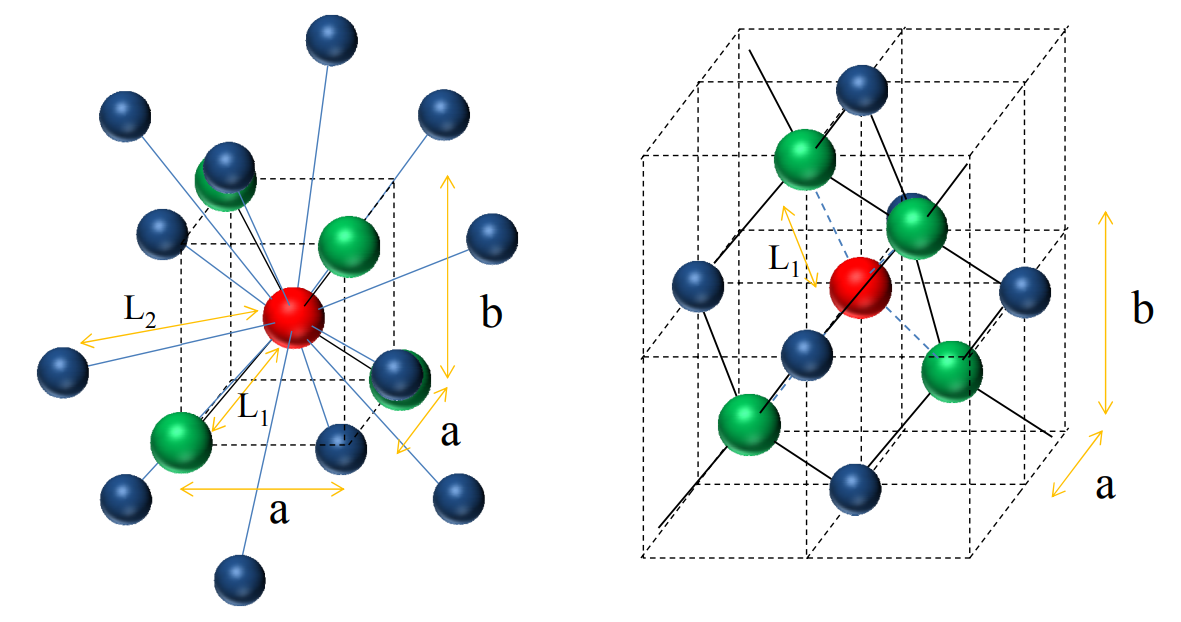
Erbium in silicon was explored extensively in the beginning of twentieth century, with the interest of building a silicon-based on-chip optical source. As a poor photonic material, silicon suffers from fast non-radiative decay dominating over slower radiative routes, and indirect bandgap (band edge luminescence at 1.1 μm). It was hoped that implanting optical active centers into this material will allow photoluminescence at specific wavelengths determined by the rare-earth optical transitions. Er3+ was chosen for its direct 4I13/2 → 4I15/2 transition at 1532 nm falling in the telecom band, which is convenient for optical fiber links in modern communication.

There have been considerable experimental researches towards this platform. To begin with, a major problem facing researchers was the relatively low solubility of erbium in crystalline silicon. This problem was solved by enhancing the equilibrium concentration by co-doping with impurities such as oxygen, carbon, nitrogen and fluorine. In experiments, co-implanting Er with O significantly increases the photoluminescence and leads to sharp lines in EPR spectroscopy. In later parts of this review, I will mainly discuss erbium and oxygen co-doped silicon.

**Electronic structure of Er and O co-doped silicon**

However, ion implantation also suffers from the disadvantage of introducing significant damage to the matrix. High temperature annealing can recover the majority of this damage and initiate the formation of Er–O clusters, but at the cost of producing aggregates of rare-earth ions or forming optically inactive silicides.

In practice, incorporating erbium into an interstitial site is more strongly preferred than a substitutional site, as the interstitial sites are predicted to be more stable from the estimations of the bonding mismatch between the rare earth ion and the covalent semiconductor.



substitutional site and interstitial site

There have been contradictory experimental findings on the local electronic structure of Er in Si, indicating that processing and annealing conditions have a strong influence in the local environment of Er implanted into Si.

Studies further demonstrate that neither of the simple erbium point defects, substitutional or interstitial, can be optically active, as both have electronic states too deep in the silicon band gap to produce 4f emission. The optically active center must be associated with erbium–impurity complexes like Er–O.

There are three generic models for the Er–O species: tetrahedral interstitial (Ti-O), tetrahedral substitutional (Ts-O), and hexagonal interstitial (Hi-O).

**Spectroscopic studies**

PL studies [1]: Er3+ ion in a semiconductor matrix tends to form a variety of centers, resulting in multiplicity of photoluminescence (PL) spectra and, consequently, inhomogeneous broadening of emission lines.

From analysis of the Zeeman effect we conclude that all the major lines of the observed PL spectrum originate from the same center, the Er-1.

Because of the low number of optically active ions in implanted samples compared to bulk doped samples, measuring the crystal field splitting from absorption measurements in implanted samples is extremely difficult. PL spectra can often be detected, but are inherently weak because above band gap excitation is required, and this only penetrates the first few hundred nm from the sample’s surface. Above-bandgap excitation has the advantage of exciting many ions at the same time to provide a strong signal, it comes at the price of limiting the sensitivity to the small fraction of implanted dopants that is coupled to the conduction band. The spectrum includes decay from the lowest 4I13/2 to the multiple 4I15/2 levels following the excitation of the Si host, where the intensity depends on the excitation transfer efficiency from the Si. Therefore, various peaks in the crystal field split spectra can be undetected or unresolved.

Some information on microscopic structure of centers responsible for Er-related 1.5 um emission in Si was revealed by a high-resolution PL study which identified more than 100 emission lines. These were assigned to several, simultaneously present Er-related centers.

OMMR [2]: Under 1.5-μm illumination an EPR resonance from a PL-active Er center with orthorhombic symmetry in Er-implanted Si can be observed, which has an intensity 3 orders of magnitude higher than that of unilluminated EPR resonances. This implies the presence of an Er-O defect state below 4I13/2 Er3+ excited state to enable spin selective non-radiative decay to the Zeeman ground state. This mechanism is analogous to the optical spin polarization mechanism of NV centers in diamond, and if correct could mean high temperature operation of Er qubits in Er implanted Si is possible.

Fitting the temperature quenching of PL indicated that the 4I15/2 Er3+ ground state was buried in the valence band, this was also indicated by OMMR measurements.

EPR studies: Measure magnitude and the average of the observed g-values, point symmetry around the Er3+ ion by means of EPR, in the quest to understand the mechanism associated with the diffusion of O in Si. Make use of Er3+ implanted into Si to probe the EPR complexes.

Not only are the g-values of the center OEr-1 (and OEr-3) similar to those found for Er-doped Y2O3, but also gav for OEr-1 is almost identical.

The attainment of well-defined impurity-related luminescent Er centers is responsible for both the luminescence enhancement at low temperatures and for the reduction of the temperature quenching of the luminescence.

The principal g values and symmetries of several erbium complexes have been determined and we have shown that the formation of these centers depends on the concentration of the coimplanted species and on the anneal process.

The EPR active and PL active centers have been shown to be different and we believe that the principal function of the impurity atoms is to prevent precipitation by forming Er-O or Er-F complexes, which leads to an increase in the effective solid solubility of Er in crystalline Si.

**Unsolved puzzles**

Only a small number of sites have been positively identified. Site properties undetermined.

(2004) Unfortunately, neither channeling experiments nor total energy calculations have shown whether the identified high-symmetry Er centers are responsible for the emission observed in PL measurements. Also, EPR has not been successful in the case of the optically active Er-related centers in crystalline silicon.

Structural information on optically active centers could be provided by magneto-optical studies. Unfortunately, in spite of numerous attempts, no successful observation of Zeeman effect in PL has been reported for Si: Er. Due to the aforementioned inhomogeneous character of the linewidth, application of magnetic field results in broadening and subsequent vanishing of emission lines.

**Recent Quantum researches**

Quantum coherence is of key importance in the context of modern researches. The coherence time of individual dopants is paramount, specifically, the forbidden 4f-4f intra-shell transitions of erbium become weakly allowed in the presence of crystal field, which result in sharp optical transitions with high quantum efficiency falling in telecom C-band. This provides great convenience for optical fiber links between distant quantum nodes, since telecom photons travel in fibers without significant loss of their coherence.

Additionally, the confinement of the inner 4f electrons near the erbium nucleus and the shielding of the crystal field by the outer 5s and 5p electrons protects the electronic state from decoherence via phonons, and also hinders phonon-sideband emission that reduces the radiative efficiency of other defects. Silicon is a predominantly spin-free material. Combining the shielding of RE f-electrons with the low nuclear spin and processing pedigree of silicon offers a novel system in which to implement quantum technologies. Further isotopic purification eliminates the coupling of dopants to nuclear spins and facilitates ultra-narrow optical linewidths and significantly improved coherence time.

**Recent spectroscopic studies**

A novel in-situ PLE method [3]: The crystal field levels in the excited 4I15/2 state are inaccessible in PL, but obtainable in PLE when using a narrow band laser to resonantly excite the population into multiple 4I13/2 levels and collect the photoluminescence. Less free carriers are generated that can affect the spectrum and lifetime. Achieved a highly efficient detection of 70 excitation frequencies, of which 63 resonances have not been observed in literature. Observed inhomogeneous broadening of less than 400 MHz and an upper bound on the homogeneous linewidth of 1.4 MHz and 0.75 MHz for two separate resonances, which is a reduction of more than an order of magnitude observed to date. These narrow optical transition properties show that Er in Si is an excellent candidate for future quantum information and communication applications.

A hybrid electro-optical detection method [4]: The first measurements of individual interacting Er ion pairs. Two examples of Er3+ pairs were identified in the optical spectrum by their characteristic energy level splitting patterns, and linear Zeeman spectra were used to characterize the sites. The identical pair displayed Ising-like g-tensors and a very strong, 200 GHz, Ising spin interaction in addition to a 1.5 GHz optical interaction between the ions of the pair.

Integrating erbium dopants into nanophotonic wire waveguides [5]: Perform pulsed resonant fluorescence spectroscopy in weakly doped samples. resonant fluorescence technique, sensitive to all dopants that decay radiatively. observe erbium incorporation at well-defined lattice sites with a thousandfold reduced inhomogeneous broadening of about 1 GHz and a spectral diffusion linewidth down to 45 MHz.

Spin echo from erbium implanted silicon [6]: Origin of the echo is an Er center surrounded by six O atoms with monoclinic C1h site symmetry. T2 and T1 were measured to be 7.5 us and 1 ms respectively at 5 K. The spin echo decay profile had superimposed modulations due to strong superhyperfine coupling with a spin bath of 29Si nuclei.

Coupling erbium dopants to superconducting resonators [7]: Address the difficulty in characterizing, identifying, and controlling the large number of generated EPR- and PL-active centers by coupling the Er spin ensemble to a superconducting resonator, which provides sensitivity enhancements over traditional EPR techniques. Low doped sample (1017 cm−3). Observe coupling between a SC resonator and Er implanted Si with gcol = 1 MHz and gi > 6 Hz. Of six known Er-related EPR centers, only one trigonal center couples to the SC resonator at 20 mK.

The large magnetic moment of Er in the ab plane - up to 4 times larger than a free electron - makes it particularly interesting for coupling to superconducting circuits.

Electrical charge sensing in combination with optically resonant excitation [8]: Detect single Er3+ ions in silicon. Provide high spectral resolution for probing the local environment of single Er3+ ions and for investigating different Er3+ sites in silicon.

Time-resolved measurement: investigate the resonant excitation and relaxation of a single Er3+ ion in a silicon nano transistor.

Dilution temperature photoluminescence spectroscopy [9]: Study Er3+-dopants in silicon-on-insulator as a telecom-coupled spin qubit. narrow inhomogeneous linewidths of Γinh ~2GHz. Photoluminescence was measured at ~100mK in a dilution refrigerator using a double pass optical setup. The sample was illuminated with 1ms pulses and the photoluminescence was detected using superconducting nanowire single photon detectors. The photon counts were recorded as the laser wavelength was swept over 1530nm to 1542nm.

The long lifetime of erbium in silicon can slow readout and manipulation of erbium qubits. Therefore, the ion’s emission rate needs to be increased by coupling to an optical cavity via the Purcell effect. We fabricated Si cavities with quality factors up to 6,000, and a mode volume of 0.042 um3. a Purcell factor F~800 near the center of the implanted distribution.

Will use these cavities to measure the optical homogeneous linewidth and optical dipole moment of the erbium ions. We will perform two-pulse photon echo experiments to obtain the optical T2.

§ enhance photoluminescence § collection efficiency § address individual spin qubits

20um tapered waveguide ~52,000 optically active Er ions ~4K in dilution refrigerator lensed fiber coupling

§ RT resonance: 1550.1nm § developed tapered fiber coupling η~72%

§ Purcell enhanced photoluminescence § T1 shortens to ~15 μs § Purcell enhancement ~87

**Other platforms**

Radiation damage centers in Si [10]: Assess the centers for its potential as a silicon telecom photon-spin interface. Most radiation damage centers have ZPL transitions that are unsplit by magnetic fields, with no unpaired electron spins in their unexcited states, limiting their usefulness as photon-spin interfaces.

These individual emitters provide a wide diversity of bright, linearly polarized single-photon emissions in the near-infrared range. Some single defects exhibit additional appealing properties, such as a small spread of the ZPL energies or a strong PL intensity well above the liquid nitrogen temperature.

Er3+: CaWO4 [11]: Erbium ions doped into crystals have unique properties for quantum information processing, because of their optical transition at 1.5 um and of the large magnetic moment of their effective spin-1/2 electronic ground state. By selecting a host matrix with a low nuclear-spin density (CaWO4) and by quenching the spectral diffusion due to residual paramagnetic impurities at millikelvin temperatures, we obtain an Er3+ electron spin coherence time of 23 ms, without having to resort to ZEFOZ transitions nor isotopic purification.

Er3+ electron spin transition can exhibit first order magnetic sensitivity greater than 200 GHz/T and has thus demonstrated electron spin coherence no greater than 10 us in Y based materials.

Er in GaN [12]: A fundamental understanding of the interaction between RE dopants and the semiconductor host is key to realizing the material’s full potential. GaN has also been identified as a promising host material for defect-based qubits, mainly due to its wide band gap and weak spin-orbit coupling. Defects suitable for quantum applications are not limited to native point defects and non-RE impurities but can also be RE impurities which, in addition to the sharp optical transitions, have excellent spin coherence properties.

Defect association can significantly modify the electronic behavior of a defect and may thus offer interesting physics useful for electrical and optical control.

Eu3+: Y2SiO5 [13]: Nuclear spin states of Eu3+: Y2SiO5 are particularly attractive for quantum protocols using spin-wave storage and manipulation due to their extremely long observed lifetime of 23 days and their optical accessibility. By employing dynamic decoupling, a ground-state hyperfine coherence time of 370±60 minutes was achieved at 2 Kelvin.

167Er3+: Y2SiO5 [14]: Describe the spin dynamics of 167Er3+: Y2SiO5 in a high magnetic field and demonstrate that this material has the characteristics for a practical quantum memory in the 1550 nm communication band. Observe a hyperfine coherence time of 1.3 seconds. Demonstrate efficient optical pumping of the entire ensemble into a single hyperfine state.

**Proposals for Er:Si**

**Points to mention:**

REI as qubits: long coherence times, rich selection of spin levels, optical addressability

REI as spin ensemble: large g factors, as the orbital angular momentum is not quenched, advantageous for strong coupling.

exhibit large static inhomogeneous broadening of the optical transitions, which can be tailored and used as a resource for various storage protocols, e.g., enabling temporally and spectrally multiplexed quantum memories.

given the large inhomogeneous broadening of optical zero-phonon lines, up to 100-gigahertz (GHz), rare-earth-ion-doped crystals in principle offer storage of photons with less than 100-picosecond duration when being used in conjunction with a suitable quantum memory protocol.

Rare-earth-doped crystals possess optical transitions with homogeneous linewidths close to the lifetime limit, high optical depths, long-lived hyperfine states accessible via optical excitation and no spatial diffusion.

Matter-photon interface: Long-distance entanglement distribution is a vital capability for quantum technologies. An outstanding practical milestone towards this aim is the identification of a suitable matter-photon interface that possesses, simultaneously, long coherence lifetimes and efficient telecommunication-band optical access.

In order to isolate matter qubits that feature an optical interface enabling the long-distance exchange of quantum information while benefiting from well-advanced silicon integrated photonics, one strategy is to investigate defects in silicon that are optically active in the near-infrared telecom bands.

Combining optical and microwave magnetic excitations could enable the investigation of the spin properties attached to these unidentified single-photon emitters in view of isolating individual spin-photon interfaces in silicon operating at telecom wavelengths.

Quantum memories: operate by reversibly mapping the quantum state of light onto the quantum transitions of a material system. quantum interfaces between flying and stationary qubits. quantum repeater relies on an efficient, long-lived quantum memory.

Importance of identifying the sites/symmetry: Implanted Er3+ in Si has shown comparable spin coherence times in low magnetic fields to Er substitutional dopants, but it can occupy a large variety of possible sites in silicon, and the properties of these sites, even for ensembles, are not well known. Sites have been studied with PL, PLE and EPR. However, only a small number of sites have been positively identified.

Knowledge of rare-earth ion symmetry is important in maximizing the number of optically active centers and for quantum technology applications where local symmetry can be used to control decoherence.

Need of PhC: strongly enhanced light-matter interaction via collective effects in nanophotonic waveguides, and via optical resonators. Increase optical depth by using longer crystals or optical cavities. Enhance storage efficiency. Great Purcell-enhancement with ultra-high Q photonic crystal cavities. bring the system into the strong-coupling regime of cavity QED, shorten the radiative decay time. overcome the small dipolar transition strength of erbium.

Host material: Dilute paramagnetic impurities in a crystal lose phase coherence by interacting with the surrounding fluctuating magnetic moments of other paramagnetic species and nuclear spins of the host matrix. To obtain long coherence times, it is thus beneficial to use crystals that have minimal concentrations of paramagnetic impurities and a low nuclear-spin density. a convenient and attractive host for a photon-spin interface, the most established integrated electronics and integrated photonics platforms. isotopically purified 28Si be a host to many atomically reproducible defects with exceptional spin and/or optical properties.

Er: Si: an optical interface of single spin qubits, operating in the telecom C-band. offers unique promise for cavity-based quantum networks and distributed quantum information processors based on a scalable platform. spatially multiplexed, on-chip quantum memories.

Measure coherence: For networks, the quantum coherence times of the transitions must be long compared to the network transmission times, approximately 100 ms for a global communication network.

long ground-state hyperfine lifetimes: efficient optical spin pumping. long hyperfine coherence times. These properties are key to the successful operation of efficient, long lived quantum memories.

Spin-wave storage: a method for achieving on-demand re-emission, additional benefit of allowing longer storage times owing to the more robust spin coherence. photons are mapped onto collective atomic excitations. Λ-type transitions enabling spin-wave storage. efficient optical pumping of the entire ensemble into a single hyperfine state, a requirement for broadband spin-wave storage.

On-demand read-out can be achieved by actively controlling the optical collective excitations, with a storage time limited by the coherence of excited states. Another solution is to transfer the optical excitations to long-lived collective spin excitations (or spin waves), using strong control pulses. This gives access to much longer storage times.

Telecom memory, host material: Due to a lack of a suitable storage material, a quantum memory that operates in the 1550 nm optical fiber communication band with a storage time greater than 1 us has not been demonstrated.

candidate for an efficient broadband quantum memory at telecommunication wavelengths

host matrices for REIs are often based on yttrium, such as Y2SiO5 and YVO4, and tend to have high residual REI paramagnetic impurities due to the chemical similarity amongst rare-earth elements. Moreover, Y has only one natural isotope with nuclear-spin I = 1/2 in 100% abundance, so it cannot be isotopically enriched to suppress nuclear magnetic noise. Therefore, it has been difficult to achieve long coherence times with magnetically-sensitive electron-spin transitions in these materials.

Compatibility with the telecom bands is offered by Kramers ions, with an odd number of electrons (like Er). However, it is much more difficult to make quantum memories with Kramers ions, and not a single Kramers system has demonstrated an on-demand quantum memory. The root of the difficulty is that, unlike for non-Kramers ions, the electronic magnetic moment of Kramers ions cannot be quenched by a crystal field as they possess a half-integer spin. For these ions there is a rapid electronic spin relaxation which shortens the hyperfine state lifetimes. This is similar to the electron spin lifetime and only an order of magnitude longer than the optical excited state lifetime, making efficient optical spin pumping very difficult. Once the electron spin is frozen in the lower ground state, the hyperfine levels associated with this state can have extremely long lifetimes and coherence times.

As a Kramers ion, however, the electronic magnetic moment of Er cannot be quenched by crystal field and has a shortened hyperfine lifetime, making telecom memory difficult to achieve.

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