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Silicon-Modified Rare-Earth Transitions - a New Route to Near- and Mid-IR Photonics

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Silicon underpins microelectronics, but lacks the photonic capability needed for next generation systems and currently relies on a highly undesirable hybridization of separate discrete devices using direct band gap semiconductors. Rare-earth implantation is a promising approach to bestow photonic capability to silicon, but is limited to internal rare-earth transition wavelengths. Reported here is the first observation of direct optical transitions from the silicon band-edge to internal f -levels of implanted rare-earths (Ce, Eu and Yb); this overturns previously held assumptions about the alignment of rare-earth levels to the silicon band gap. The photoluminescence lines are massively red-shifted to several technologically useful wavelengths and modeling of their splitting indicates that they must originate from the rare-earths. Eu implanted silicon devices display a greatly enhanced electroluminescence efficiency of 8%. Also observed is the first crystal field splitting

in Ce luminescence. Mid-IR silicon photodetectors with specific detectivities comparable to existing state-of-the-art mid-IR detectors are demonstrated.

1. Introduction

Silicon underpins the whole of microelectronics and the digital world as we know it. Despite being the “champion” electronic semiconductor it lacks key photonic capability needed for next generation systems and currently relies on separate discrete devices using alternative direct band gap semiconductors. This hybridization is highly undesirable, seriously violating the paramount technological and cost advantages inherent in silicon integration that has driven its exponential growth. The ultimate vision of silicon integration is a totally single silicon solution incorporating both electronic and photonic functions. Here we report a novel phenomenon – silicon-modified rare-earth (RE) transitions – and demonstrate light emitting diodes (LEDs) and mid-IR photodetectors. Universally, luminescence from RE doped semiconductors has shown only the expected characteristic intrinsic transitions; consequently emission from REs with transitions greater than the semiconductor band gap energy should not occur. Europium, ytterbium and cerium have their lowest energy transitions well above the band gap energy of silicon. Remarkably, we see photoluminescence (PL) and electroluminescence (EL) due to Eu, Yb and Ce in silicon but dramatically red-shifted in wavelength and strikingly enhanced in intensity by up to 900 times compared with conventional RE doped silicon LEDs. These results refute previous thinking on the interaction of REs with semiconductors and offer a promising route to efficient, fully-silicon-based, optoelectronic devices across the near- and mid-IR.

Silicon photonics has seen rapid advances^[1-12] and the technology is seen not just as required for next generation computers but also as a vehicle for a wide range of other high value and important, societal, environmental, security and health applications, such as green house gas and explosive residue sensing, and fast medical diagnostics.^[13] REs elements in silicon have long been considered promising for optical sources, and more recently for quantum technologies.^[14] The partially filled inner $4f$ shell gives sharp internal transitions highly insensitive to crystal host and temperature and many of the transitions have intrinsic gain and support lasing. However, because the transitions are internal to the RE they have not been seen so far as a particularly promising route to photodetectors.

Light emission at $1.54\ \mu\text{m}$ due to Er ions in III-V and Si has been extensively investigated and light emitting devices successfully demonstrated although with limited efficiency.^[15-21] PL and EL from silicon and III-V semiconductors incorporating the RE thulium have also been achieved - transitions between the Tm^{3+} lowest excited states and the ground state lead to emissions around 0.8 , 1.2 and $2\ \mu\text{m}$.^[22-24] Both Er and Tm in silicon, and indeed all others RE reported in silicon and other standard semiconductors behave “conventionally” – emitting at their well-known characteristic internal transition wavelengths.^[25-27]

Here we investigate the incorporation of the RE elements Eu, Yb and Ce in silicon – REs that have their lowest energy internal transitions above the band gap energy of silicon ($1.1\ \text{eV}$). The lowest energy internal transitions of the Eu^{3+} are in the red at $\sim 2\ \text{eV}$; in Yb they are in the near-IR at $\sim 1.3\ \text{eV}$ and in Ce in the UV/blue ($3-4\ \text{eV}$). All these transitions are at energies greater than the silicon band gap and conventional wisdom holds that emission due to these REs could not occur in silicon. Light emission in several larger band gap semiconductors and other hosts

incorporating Eu^{3+} , Yb^{3+} and Ce^{3+} has been previously reported.^[28-33] PL at low temperatures was the main technique used to optically characterize these materials. Luminescence due to their well-known RE internal transitions is observed at around 615 nm for Eu, 980 nm for Yb and in the UV/blue (300-400 nm) for Ce. For Eu these are the lowest energy transitions from the $^5\text{D}_0$ excited state to the $^7\text{F}_J$ states ($J = 0$ to 6); for Yb, PL emission is due to the $^2\text{F}_{5/2}$ - $^2\text{F}_{7/2}$ internal transitions and for Ce these are from the lowest lying $5d^1$ level to the lowest excited $4f$ manifold ($^2\text{F}_{7/2}$) and to the ground state manifold ($^2\text{F}_{5/2}$) - both Ce bands are broad due to the unshielded starting $5d^1$ state. We report here on PL and EL from LEDs made by ion implantation of Eu, Yb and Ce into standard silicon substrates. Remarkably, emission due to Eu, Yb and Ce states is observed but in all these cases has been dramatically red-shifted. For the Eu doped silicon, from the visible to the IR around 1.4 to 1.5 μm . For Yb doped silicon, from 980 nm to around 1.3 μm . For Ce the shifts are from two bands in the UV/blue spectral regions to the 1.4 μm and 1.9 μm IR regions. We attribute these red-shifts, for Eu, to transitions from carriers in silicon to the $^7\text{F}_J$ states ($J = 0$ to 3); for Yb to transitions from the silicon to the $^2\text{F}_{7/2}$ ground state manifold and for Ce from the silicon to the $^2\text{F}_{5/2}$ ground state and the $^2\text{F}_{7/2}$ manifolds respectively. Crystal field analysis shows that the observed PL lines must originate from the implanted REs.

Previous observations have shown that universally, when luminescence is observed from REs in conventional semiconductors only the characteristic transitions between the internal levels are seen. These transitions are excited by indirect energy transfer from recombining electrons and holes. The direct interaction shown here between bulk silicon states of the host and individual intrinsic RE levels is, we believe, unique in conventional semiconductor systems. This could be highly significant for their application in semiconductor optoelectronic devices particularly, as

demonstrated here, in the technologically and commercially most significant semiconductor – silicon. Significantly, the new Eu 1.4 to 1.5 μm , the Yb 1.3 μm and the Ce 1.4 and 1.9 μm emissions are the wavelengths of most importance in optical communications systems.

2. Results

2.1. Silicon Band-Edge-Modified Rare-Earth Luminescence

In **Figure 1** we show the PL measured at 20 K from (a) Eu, (b) Yb and (c) Ce doped silicon p-n junctions. The EL spectra measured at 80 K are shown in Figure 1d. For comparison we also show in Figure 1a the spectra for silicon control samples which were implanted with boron only and with europium only and processed under otherwise identical conditions - for the control samples only the band-edge silicon emission is observed and there is no radiative defect emission caused by the implants. This is also the case for the Yb and Ce controls (not shown). The importance of the boron in enabling the RE emission in silicon is clear. The mechanism for boron enabling and enhancing luminescence has been previously extensively reported for both bulk and RE doped silicon.^[1,20,23,24,26,27] For Eu, Yb and Ce distinct main lines can be seen on all the spectra with additional fine structure. These spectra do not correspond to any known implant damage induced spectra in the literature^[34] and not to spectra associated with the well known silicon D-line defects^[35] or, as far as we are aware, any previously reported spectra in silicon. In addition, the spectra for Eu, Yb and Ce are quite different from each other, despite having similar atomic masses, and quite distinct from PL and EL spectra of all other RE we have previously studied^[27] when all implanted at the same doses and with the same thermal processing. These

include Sm and Gd, which bracket Eu, and Tm and Pr, which are adjacent to Yb and Ce respectively in the lanthanide series. We have also measured EL from the Eu, Yb and Ce LEDs under conventional forward bias from 80 K to room temperature. The EL measurements show the same spectral characteristics as the PL at the corresponding measurement temperatures. The EL quenches as the temperature is raised but can still be clearly seen up to 240 K. We believe that further optimisation of the annealing conditions could lead to room and high temperature emission as observed previously in undoped silicon LEDs.^[1]

The Eu, Yb and Ce spectra are immediately suggestive of RE transitions but are unexpectedly in the wrong energy range, far too low, for the lowest allowed internal transitions which are all much greater than the silicon band gap energy. Further, the peak positions of the lines broaden and move with measurement temperature, closely following the silicon band edge temperature dependence, unlike internal RE transitions which are temperature invariant. Note this temperature dependence implies the absolute energies of the silicon RE “manifolds” are temperature independent as expected for REs. **Figure 2** shows a comparison of the PL spectrum of Eu in silicon with a Eu spectrum from a zinc oxide host.^[30] The upper plot shows PL data in the 5500-8000 cm^{-1} range measured at 20 K and at 80 K from silicon samples co-implanted with B and Eu (Si:B&Eu). The lower plot shows the usual Eu^{3+} PL spectrum in the visible (14700-17200 cm^{-1}), in this case in a ZnO host abstracted from Ref. [30], taken at 10 K. The energy scales for the upper and lower plots are the same but have been displaced in energy to aid direct comparison of the relative peak positions. The spectra have been matched at the F_0 terminal state, which required a blue shift of our data by 9200 wavenumbers (1.14 eV). The ZnO spectral features labelled in Figure 2, as in Ref. [30], correspond to the usual 5D_0 to 7F_J ($J = 0$

to 3) multiplets observed in Eu^{3+} . The corresponding transitions observed in the Si:B&Eu p-n junctions are attributed to silicon transitions to the same ${}^7\text{F}_j$ multiplets. The close coincidence in the energy spacing of the spectral features in the two materials is striking, particularly given the different hosts, and well within the spread expected between different hosts. Because of totally different selection rules and hosts, we would not expect any exact correspondence of the peak intensities. The better resolved features in our Si:B&Eu spectra are attributed to the much higher crystal quality compared to the ZnO nanocrystals. Our Si:B&Eu results show a clear correspondence with the published data from many hosts, once blue shifted.

We have previously carried out a detailed crystal field analysis in silicon of two “classical” REs, *i. e* REs that show only the expected internal transitions, Dy and Tm, and used a point charge model to determine that the REs sit in a substitutional, rather than an interstitial Si site.^[14] Here, in addition to Eu, Yb and Ce, a crystal field analysis of Ho was also performed for completeness. Crystal field parameters (CFPs) are structural factors which represent the symmetry of the RE’s environment.^[36] Local symmetry was determined by fitting sets of CFPs corresponding to commonly occurring symmetries to the experimental ground state splittings determined from PL measurements (see Experimental Section). The results are listed in **Table 1** which shows that the best fit occurs for tetragonal symmetry for all the REs. For cubic symmetry the constraints: $B_4^4 = 5B_0^4$ and $B_4^6 = -21B_0^6$ applies.^[37]

Figure 3a shows a comparison of the experimental splittings from our Eu data and the fits obtained from the crystal field analysis as well as the calculated energy levels for the Eu^{3+} free ions. The CFP values obtained and the spin-orbit coupling coefficients used for Ce, Eu, Yb, Dy, Ho and Tm are listed in **Table 2** and plotted as a function of the number of f electrons in **Figure 3b**. It can be seen that the calculated

CFPs for both the classic and modified REs show a clear trend across the lanthanide series. The theoretical fits to the energy levels and the peaks selected from the experimental data for the crystal field analysis for Si:B&Yb and Si:B&Ce are shown in **Figure 4** and **Figure 5** respectively.

If the fitted PL peaks originate from transitions to RE f -shells energy levels we would expect, firstly, that these peaks are reasonably close to those observed.

Secondly, that the same sets of CFPs (corresponding to the same symmetry) are the best fit for all the REs. Thirdly, and most importantly, that there is a trend in the CFPs across the lanthanide series, as this would be the most improbable observation if the peaks do not originate from REs. All of these expectations are met in our fitting, confirming that the observed PL lines that we fitted originate from REs. Figure 3b shows that there is a linear change in all the CFPs across the lanthanide series apart from the B_0^2 and B_4^4 parameters at Ce. The change in CFPs caused by the varying nuclear charge of the REs across the lanthanide series should be greatest early in the series because the ionic radii exhibit their greatest relative decrease. It is therefore not unexpected to find a discontinuity in CFPs at Ce. From Eu to Yb the B_0^2 parameter displays a linear decrease down to around zero at Yb. The B_0^2 parameter represents the degree of axial asymmetry experienced by the RE.^[38] This indicates that the arrangement of Si atoms around the RE is “stretching” in one axis and the amount of stretching decreases as the ionic radii of the REs decrease across the lanthanide series, as may be expected. The B_0^4 and B_4^4 parameters are dominated by the covalency of the RE to Si bonds,^[39] both these parameters generally decrease linearly across the lanthanide series.

In Figure 4a we plot as a function of energy the PL spectrum of the 20 K Si:B&Yb sample and a 20 K PL spectrum from Yb doped YAG.^[40] The experimental

and calculated energy splittings for the Yb^{3+} in the Si:B&Yb are shown in Figure 4b. Again, a highly compelling correspondence of the spectral features and the theoretical fit is observed. Figure 4b also shows the Yb^{3+} energy splittings in three other hosts (YAG,^[40] CsCdBr_3 ^[41] and $\text{Sr}_5(\text{PO}_4)_3\text{F}$ ^[41]). The wide spread in the Yb^{3+} splittings in different hosts is not atypical and is due to the particular sensitivity of the Yb^{3+} to the crystal field interaction.^[41] For example, the ${}^2\text{F}_{7/2}$ manifold overall splitting in CsCdBr_3 is only 421 cm^{-1} but is very large (1190 cm^{-1}) in $\text{Sr}_5(\text{PO}_4)_3\text{F}$.

Figure 5a and 5b show PL spectra of Si:B&Ce sample in the $6500\text{-}7350\text{ cm}^{-1}$ range and in the $4600\text{-}5350\text{ cm}^{-1}$ range respectively. Additional weaker sidebands of the main peaks are attributed to local vibronic modes. We note that due to the elimination of the unshielded $5d^1$ starting state, this is the first PL associated with Ce in any material that reveals the inherent crystal field splitting of the ${}^2\text{F}_{5/2}$ and ${}^2\text{F}_{7/2}$ manifolds previously only observed in mid-IR absorption.^[42] Figure 5c shows a comparison of Si:B&Ce experimental and theoretical splittings from the lowest ${}^2\text{F}_{5/2}$ ground state level to the ${}^2\text{F}_{7/2}$ manifold calculated using the data shown in Figure 5a and 5b with Ce^{3+} transitions from the lowest ${}^2\text{F}_{5/2}$ level to the ${}^2\text{F}_{7/2}$ manifold in LaF_3 and in CeF_3 measured by mid-IR absorbance^[43] and with the f - f splitting of the Ce^{3+} free ion.^[43] Again, a strong correspondence of the spectral features in Si:B&Ce and in other hosts is observed.

We conclude that for Eu, Yb and Ce the silicon band edge has in effect substituted the respective usual starting excited states. Previous observations in the literature, also involving Eu, show significant red shifts of the emission to the 3+ terminal states can occur. In Refs. [44, 45] in the hosts europium gallium garnet doped with chromium and boron nitride co-doped with Eu and Cr, Eu–Cr pair emission is observed corresponding to a red shift of the ${}^5\text{D}_0\text{-}{}^7\text{F}_J$ Eu^{3+} transitions by an

amount equal to the energy difference in the Eu^{3+} and Cr^{3+} excited states, showing that the Cr^{3+} ground state has been substituted by the Eu^{3+} ground state. This is attributed to a direct exchange interaction between the ions. Further, in Ref. [46] the authors studied a magnetic semiconductor, $\text{Pb}_{1-x}\text{Eu}_x\text{Te}$, a solid solution where Eu is an element of the alloy rather than a dopant as in our case. They observe in addition to the main inter-band transitions additional lines attributed to transitions from the hybridized conduction band to discrete Stark split Eu^{3+} levels.

The REs can exist in solid hosts in the divalent $2+$,^[47] trivalent $3+$ ^[47] and more rarely in the tetravalent $4+$ state^[48] or indeed in more than one valence state in the same host.^[49] The highly structured spectra and the fits to the splittings clearly indicate the involvement of the $3+$ valence state on a silicon substitutional site as the final terminal state for the optical transitions. Possible excitation mechanisms could be direct charge transfer of an excited electron thermalized at the silicon conduction band edge to the $3+$ state followed by a subsequent valence switch of the RE to the $2+$ state followed by relaxation back to the $3+$ state by electron emission to the valence band. Alternatively we are simultaneously capturing an electron hole pair or silicon exciton, in both of these cases maintaining the $3+$ state.

In the isolated RE ions it is known that the lower $3+$ RE levels are far from the vacuum level which has led to a presumption that in narrow band gap semiconductors with low electron affinities these levels would lie deep in the valence band.^[50-53] There is however no clear theoretical or experimental data confirming this, in particular in silicon. This presumption **is effectively implying** that the vacuum levels remain aligned even though the vacuum level has no meaning in the bulk. This concern about the different alignment from the surface or an interface and the bulk has been raised previously for extrapolation of the relative RE energy levels and

silicon valence/conduction bands in photoemission experiments.^[54] The alignment experimentally observed here suggests that when the REs are incorporated within the bulk of the silicon host the energy difference is in effect taken up by offsetting the “vacuum level”, analogous to that seen in the well-established semiconductor heterojunction systems. **Figure 6** shows the energy levels of Eu^{3+} , Yb^{3+} and Ce^{3+} and the proposed effective alignment with the silicon energy band.

An expected consequence of transitions from or fed by a continuum of band states to a RE level, rather than just a single starting state, would be a significant enhancement in the emission intensity. The Eu EL reported here shows an enhancement by a factor of 25 over our best previous “classical” RE device (doped with Tm^[27]) and an enhancement of 900 times over our previous best “classical” RE devices in the 1.3 to 1.5 μm range (doped with either Tm^[23] or Er^[20]).

The light output against operating current density for the Si:B&Eu diode is shown in **Figure 7**. The sub linear behaviour at the higher current densities is the result of sample heating that quenches the EL. We have calculated the internal quantum efficiency (QE_{int}) using the method described in detail in the Experimental Section. We obtain a value in the linear regime, at a current density of 2 A cm^{-2} , of 8% for the QE_{int} . The QE_{int} is the product of the radiative efficiency and the carrier injection efficiency implying a lower limit for the most critical parameter, the radiative efficiency of 8%, assuming 100% injection efficiency. In practice the injection efficiency, which we have not so far attempted to optimise, is likely to be much lower than unity and so the radiative efficiency will be correspondingly higher.

2.2. Silicon Mid-IR Photodetectors

Intrinsic RE transitions are internal to the RE and do not contribute directly to carrier conduction in the bands of the host. Consequently, this makes them of limited use as a basis for optical detectors. The band edge modified RE levels exemplified here interact directly with the silicon bands and so offer the possibility of extrinsic photovoltaic or photoconductive detectors. The wavelengths that could be detected using Eu, Yb and Ce cover wavelengths from the near-IR at 1.1 μm , the band gap of silicon, out to the mid-IR for the lowest energy valence band to RE transitions. We have observed photoresponse from our diodes. An example of our Si:B&Eu diode being used as a silicon mid-IR photodetector (SMIRP) is shown in **Figure 8** where we plot the specific detectivity D^* from 1 to 6 μm (the current limit of our measurement system). For comparison we also plot the detectivity of a control silicon diode without the Eu doping but otherwise identically processed and of existing state-of-the-art commercially available detectors.^[55] Our recent SMIRPs, designed as photodiodes by placing the Eu in the depletion region, have shown much improved detectivities as seen in Figure 8. It can be seen that our latest detectors at 4 μm already have specific detectivity as good as state-of-the-art Mercury Cadmium Telluride (MCT) detectors and are close to the best available detectors in this spectral region. In Figure 8b and 8c we show transmission spectra measured with our original detector showing the important water vapour and CO_2 absorption lines present at ambient levels in the air.

3. Conclusion

In summary, we report the first and surprising observation of red shifted Eu, Yb and Ce emission in silicon and demonstrate IR LEDs operating under conventional forward bias. All emissions are massively red shifted in wavelength from those expected. This has been attributed to the direct intercession of the silicon providing a

primary state replacing the usual intrinsic excited Eu^{3+} , Yb^{3+} and Ce^{3+} states, $^5\text{D}_0$, $^7\text{F}_{5/2}$, and the $5d^1$ levels respectively. The direct involvement of the bulk band state continua rather than a single excited starting state and the absence of the usually required “third party” energy transfer mechanisms are highly significant as both changes leads to much greater effective optical emission, as evidenced here by up to a 900 fold enhancement of EL intensity at the key 1.3 to 1.5 μm optical communication wavelength compared to classical RE devices. These observations suggest that current presumptions of the alignment of RE levels when incorporated in the bulk of semiconductors should be revisited.

In addition we have demonstrated the first silicon mid-IR photodetector with specific detectivities – the key figure of merit – comparable to current state-of-the-art mid-IR detectors. We note that strained silicon and SiGe alloys, both of which vary the band gap energy, are now used in state-of-the-art CMOS technology and could be used to provide additional tuning of the modified RE transitions.

The exemplars, Si:B&Eu, Si:B&Yb and Si:B&Ce, demonstrated here, by themselves, offer access to emitters and detectors across a wide range of wavelengths opening up new discrete and integrated photonics technologies scanning much of the near- and mid-IR.

4. Experimental Section

Crystal Field Analysis: Crystal field analysis was carried out using both our method described in Ref. [14] and the program SPECTRA developed at Argonne National Laboratory and available to download at <http://chmwls.chm.anl.gov/downloads/index.html>. SPECTRA had an advantage over our previous methodology in that it is able to fit multiple f -shell manifolds

simultaneously and it uses a differential evolution algorithm to determine a global minimum which gave a significant reduction in computation time. Our method and SPECTRA gave very similar results. Only the four PL lines expected from the $^2F_{7/2}$ manifold were observed and five lines are needed to obtain the five CFPs. Therefore the lower level of the $^2F_{5/2}$ manifold in Yb:YAG from Ref. [41] was used to enable a valid fit and confirm the Yb tetragonal symmetry. The largely host independent free ion parameters were taken from fitted absorption spectra of REs in LaF₃ [56]. However, for Si:B&Ce and Si:B&Eu we found that fitting the spin orbit coupling parameter (ζ) gave a more satisfactory fit, but did not vary significantly from previously published values.^[56,57] ζ is given in Table 2.

Device Fabrication: Si:B&RE (RE = Ce, Eu, Ho and Yb) structures were fabricated by B implantation (10^{15} B cm⁻² at 30 keV) into n-type Si [100] substrates. Some substrates were annealed after B implantation at 950 °C for times ranging from 30 seconds to 20 minutes. Subsequently 400 keV RE ions were implanted (10^{13} – 10^{14} ions cm⁻² range) and annealed either at 800 °C or 850 °C for times up to 5 minutes.

The optimum processing conditions to achieve the brightest RE luminescence in silicon is similar for most of the REs and has been discussed in detail elsewhere.^[27]

The implant energy chosen placed the REs on the *p*-side of the junction outside the depletion region. A second generation of Si:B&Eu devices were specifically engineered as photodectors, which required Eu implantation at multiple energies chosen to ensure that the Eu was uniformly distributed across the depletion region at zero bias. The depletion width at zero bias is ~ 2 μm . The diffusion length of the REs for the maximum anneal temperature and time used here (850 °C / 5 minutes) is ~ 0.02 μm ^[58], which is much less than the depletion width.

Device Characterisation: EL and PL were measured between 20 K and room temperature from 1000 to 2200 nm using an InGaAs detector. The EL was performed under forward bias and the light was extracted through a window in the back electrode.^[20] Current-voltage measurements were made and diode characteristics were observed with typical turn-on voltages of ~ 0.5 V. For the PL experiments, the samples were excited by a 532 nm diode pumped laser line at a power density of ~ 3 kW m⁻².

Quantum efficiency measurements were made by first obtaining the external power efficiency, optical power out over electrical power in, by absolute measurements of the electrical power (drive current \times operating voltage) in to the LED and optical power out. The optical power out was measured with a calibrated large area broad band power meter placed after the collecting optics. The power meter was an Ophir Laser Star fitted with a PD300 IR head. The total optical power out of the device can then be calculated taking in to account the efficiency of the collecting optics. The external power efficiency can then be calculated. The external quantum efficiency is then given by the power efficiency times the drive voltage divided by the energy per photon. The internal quantum efficiency can then be calculated by multiplying the external quantum efficiency by the device optical extraction efficiency which is the product of the absorption, Fresnel and internal reflection losses. The Fresnel and internal reflection losses can be obtained directly from the known refractive indices of silicon, and air. As the emission is well below the silicon band gap the absorption losses are taken to be zero.

The initial photodetection measurements were made at 80 K on the same LEDs but in unbiased photovoltaic mode. The diodes were illuminated through the window in the back of the sample and the photovoltage was measured using a lock-in

amplifier. The specific detectivity D^* ($\text{cm Hz}^{1/2} \text{W}^{-1}$) was calculated using the usual formula for an unbiased detector in photovoltaic mode,^[59] $D^* = R_i \times (R_0 A / 4kT)^{1/2}$, where R_i is the responsivity (A W^{-1}), A is the area of detector (cm^2), k is Boltzmann's constant, T the absolute temperature (K) and R_0 is the dynamic resistance (Ω). The spectral responsivity measurements between 1.2 and 6 μm were obtained by illuminating the detector through a SPEX 1680 (0.22 m) double monochromator fitted with 4 μm gratings and order sorting filters (1.05, 1.65, 2.4 and 3.6 μm). The IR source was a Newport 6363 IR emitter operated at 90 W with a colour temperature of 1050 K. Power measurements as a function of wavelength were made using a calibrated Newport optical power meter 1916-C. The dynamic resistance was obtained from current voltage measurements at 80 K using an Agilent B1505 parameter analyser. This methodology was validated by applying it over the same spectral range to a calibrated Hamamatsu CMT detector (Type P9697-02) of known spectral responsivity, dynamic impedance, specific detectivity and detector size.

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Figure Captions

Figure 1. Luminescence spectra of Eu, Yb and Ce doped silicon p-n junctions. a) PL at 20 K of silicon co-implanted with B and Eu, of a control sample implanted with B only and of a control sample implanted with Eu only. All samples have otherwise been identically processed. The spectra have been displaced for clarity. b) PL at 20 K of silicon co-implanted with B and Yb. c) PL at 20 K of silicon co-implanted with B and Ce. d) EL at 80 K from Ce, Eu and Yb LEDs measured at a forward bias of 1 V and a forward current density of 3.1 A cm^{-2} .

Figure 2. Comparison of the PL spectrum of Eu in Si:B&Eu with a Eu spectrum from a ZnO host.^[30] The upper graph shows the PL data from a Si:B&Eu p-n junction measured at 20 K (green line) and data from a second Si:B&Eu p-n junction measured at 80 K (black line). The lower plot shows the usual Eu^{3+} PL spectrum in the visible, in this case in a ZnO host taken at 10 K. The energy scales for upper and lower spectra are the same (identical energy increments) but have been displaced to aid direct comparison of the relative peak positions. Spectra have been matched to the F_0 terminal state. The vertical red lines on the Si:B&Eu plot are theoretical fits obtained from the crystal field analysis. The solid black arrows indicate the peaks selected from the Si:B&Eu spectra for the crystal field analysis – their corresponding energies in the displaced Zn:O spectrum are also shown.

Figure 3. a) Comparison of experimental splittings from Si:B&Eu p-n junctions data and the theoretical fits obtained from the crystal field analysis. The energy splittings in the free Eu^{3+} are also shown. b) CFP values obtained and the spin-orbit coupling

coefficients (ζ) used for Ce, Eu, Yb, Dy, Ho and Tm plotted as a function of the number of f electrons.

Figure 4. Comparison of Yb emission in Si:B&Yb with an Yb emission in YAG:Yb. a) PL spectra of a Si:B&Yb (20 K) and of a YAG:Yb^[40] (20 K) as a function of energy. The energy scales for both plots are the same but have been displaced to aid direct comparison of the relative peak positions. Spectra have been matched to the lowest terminal state. The vertical red lines on the Si:B&Yb plot are the theoretical fits obtained from the crystal field analysis; the vertical black arrows indicate the peaks selected for the crystal field analysis. The vertical arrows in the YAG:Yb plot indicate the peak centres in the YAG:Yb spectrum. b) Comparison of experimental splittings from our Si:B&Yb p-n junctions data and the theoretical fit obtained from the crystal field analysis. The energy splittings for the Yb³⁺ in three other hosts (YAG^[40], CsCdBr₃^[41] and Sr₅(PO₄)₃F^[41]) are also shown.

Figure 5. Spectra of Ce emission in Si:B&Ce and a comparison with mid-IR absorbance spectra from Ce in other hosts showing the Ce f - f transitions. a) Si:B&Ce higher energy range PL spectrum. b) Si:B&Ce lower energy range PL spectrum expanded by a factor of ten. In (a) and (b) the fits for Si:B&Ce are shown as vertical red lines; the solid black arrows indicate the peaks selected for analysis. The dotted arrows indicate additional weaker sidebands of the main peaks attributed to local vibronic modes. c) Comparison of experimental splittings from the lowest ²F_{5/2} ground state to the ²F_{7/2} manifold obtained from the data shown in (a) and (b) with the fit obtained from the crystal field analysis, and with Ce³⁺ transitions from the lowest ²F_{5/2} level to the ²F_{7/2} manifold in LaF₃ and in CeF₃ measured by mid-IR absorbance.^[42] The energy splittings in the free Ce³⁺^[43] are also shown.

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Table 1. Goodness of fit (σ) of various symmetries for the REs. $\sigma = \sqrt{\sum(\Delta_i)^2 / (L_{obs} - p)}$, $\Delta_i = E_{exp} - E_{fit}$, L_{obs} is the number of lines, p is the number of CFPs, E_{exp} are the experimentally determined energy levels and E_{fit} are those determined by fitting sets of CFPs.

Symmetry (CFPs)	Trigonal ($B_0^2 B_0^4 B_3^4 B_0^6 B_3^6 B_6^6$)	Tetragonal ($B_0^2 B_0^4 B_4^4 B_0^6 B_4^6$)	Hexagonal ($B_0^2 B_0^4 B_0^6 B_6^6$)	Cubic ($B_0^4 B_0^6$)
RE				
Ce	209	24	604	2216
Eu	194	31	73	91
Dy	75	12	62	210
Ho	1164	52	124	96
Tm	61	13	97	106
Yb	31	9	27	37

Table 2. Fitted crystal field parameters ($B_0^2 B_0^4 B_4^4 B_0^6 B_4^6$) representing tetragonal symmetry for various REs implanted Si and the spin orbit coupling parameter (ζ), taken from Ref. [56] apart from Ce and Eu where ζ was fitted along with CFPs. Units are cm^{-1} .

RE	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6	ζ
Ce	929	310	-17	-18	-20	580
Eu	1095	-182	2034	296	644	1358
Dy	386	-555	1510	201	863	1913
Ho	200	-668	1216	180	949	2145
Tm	100	-796	1098	201	1077	2636
Yb	-3	-885	938	193	1326	2936

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Strong red shifting of Eu electronic transitions to the IR is achieved by the direct involvement of silicon band edges. This leads to super enhanced electroluminescence and the extension of silicon detectors from the near-IR to the important mid-IR region with detectivities comparable to current state of the art. This pushes silicon's reach into significant high value societal, environmental, security and health applications.

Keyword

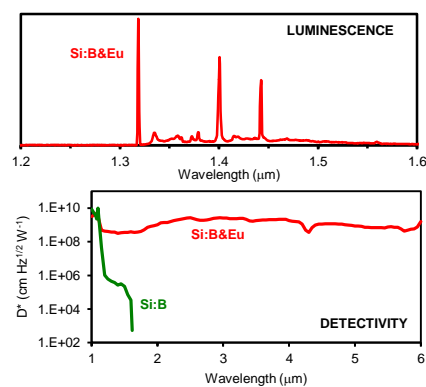
electro-optical materials, electronic structures/processes/mechanisms, photovoltaic devices, luminescence, photonics

Manon A. Lourenço^{*}, Mark A. Hughes, Khue T. Lai, Imran M. Sofi, Willy Ludurczak, Lewis Wong, Russell M. Gwilliam, and Kevin P. Homewood

Title

Silicon-Modified Rare-Earth Transitions - a New Route to Near- and Mid-IR Photonics

ToC figure (55 mm broad × 50 mm high)



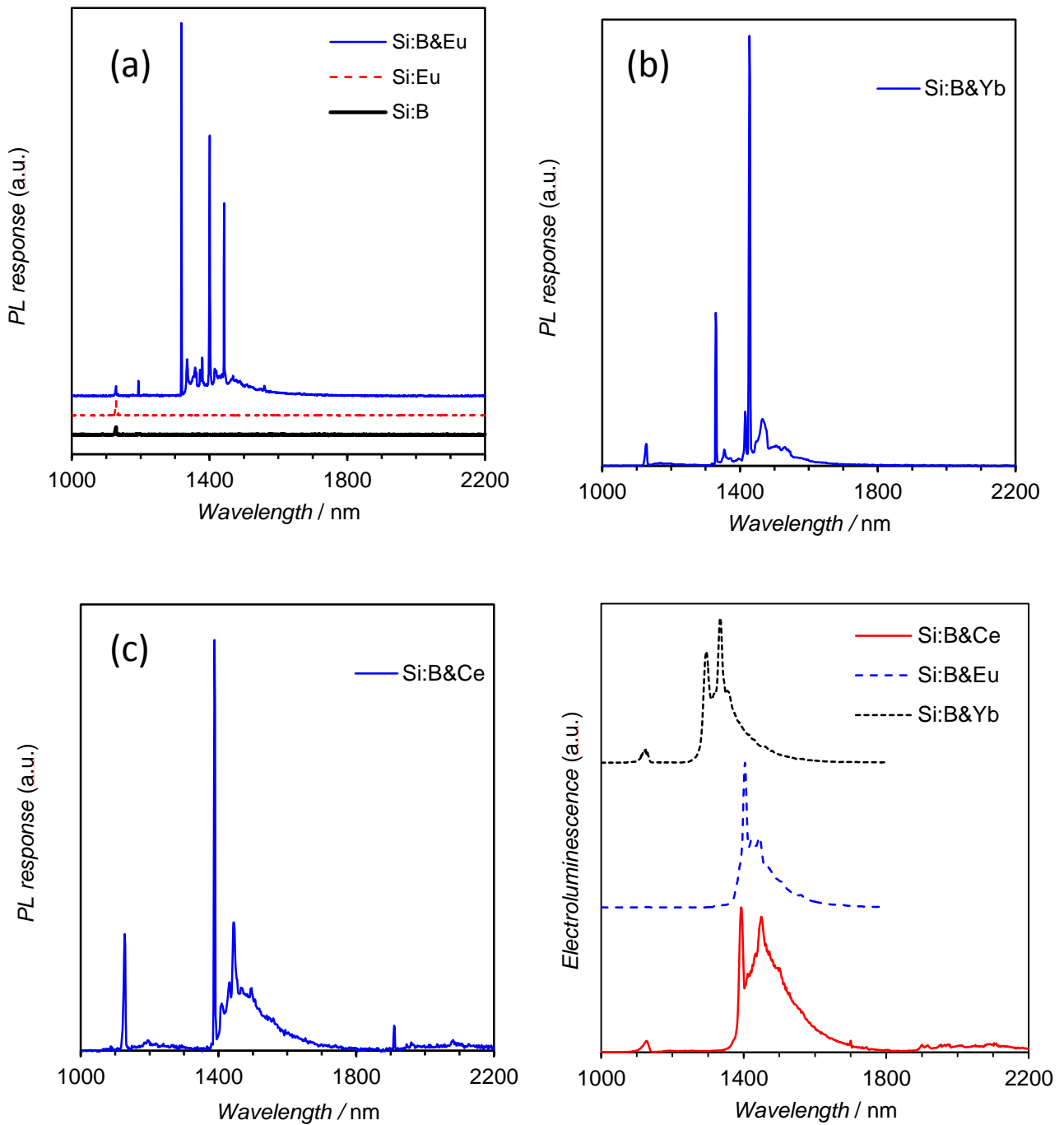


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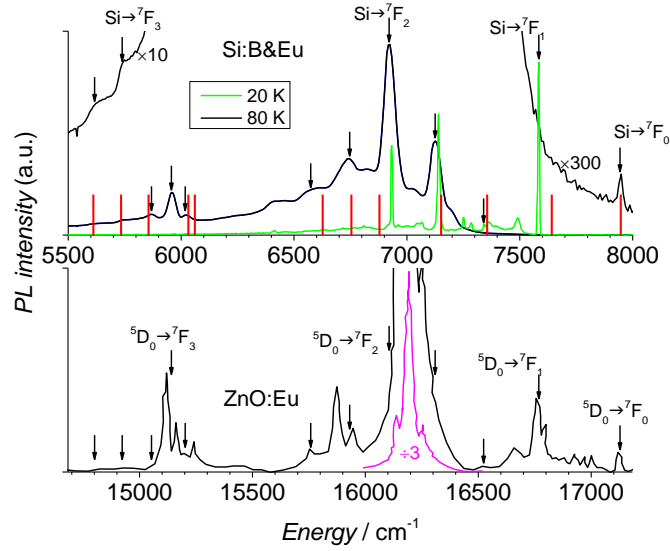


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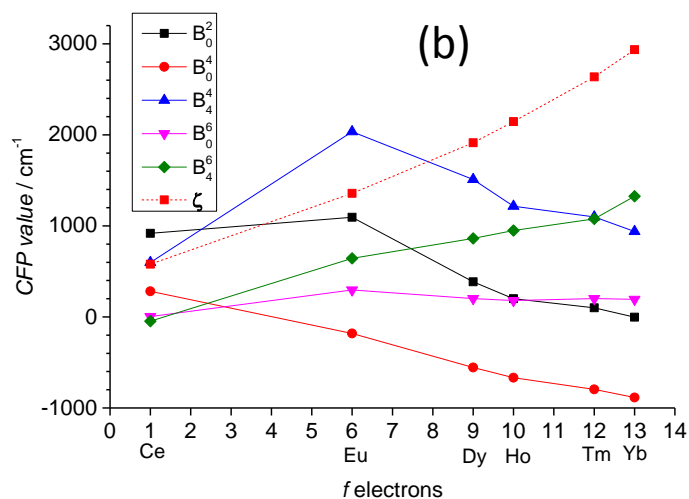
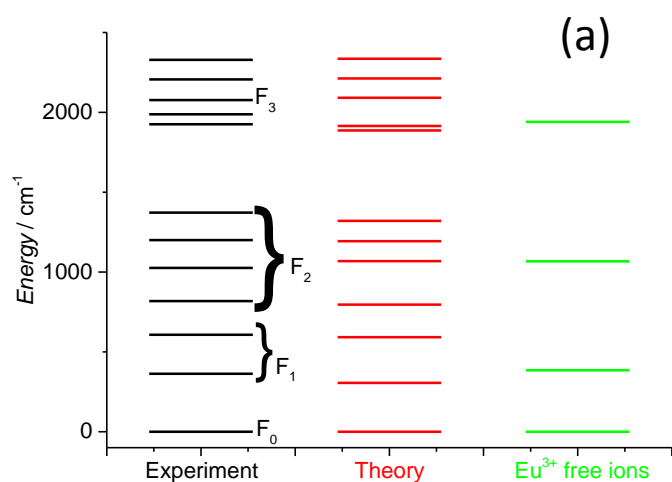


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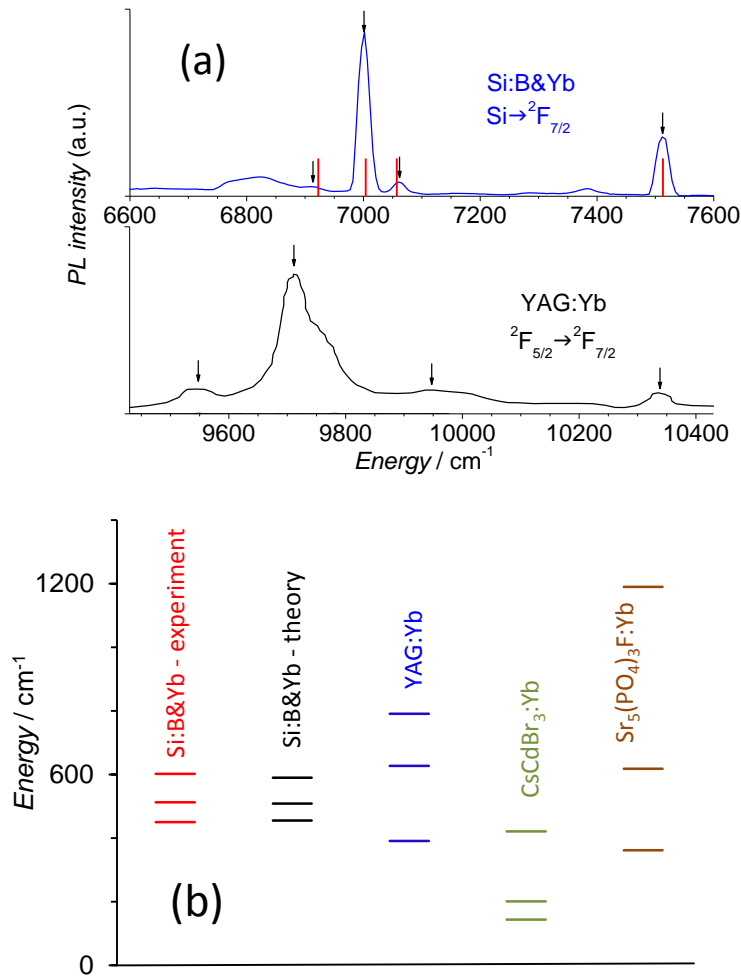


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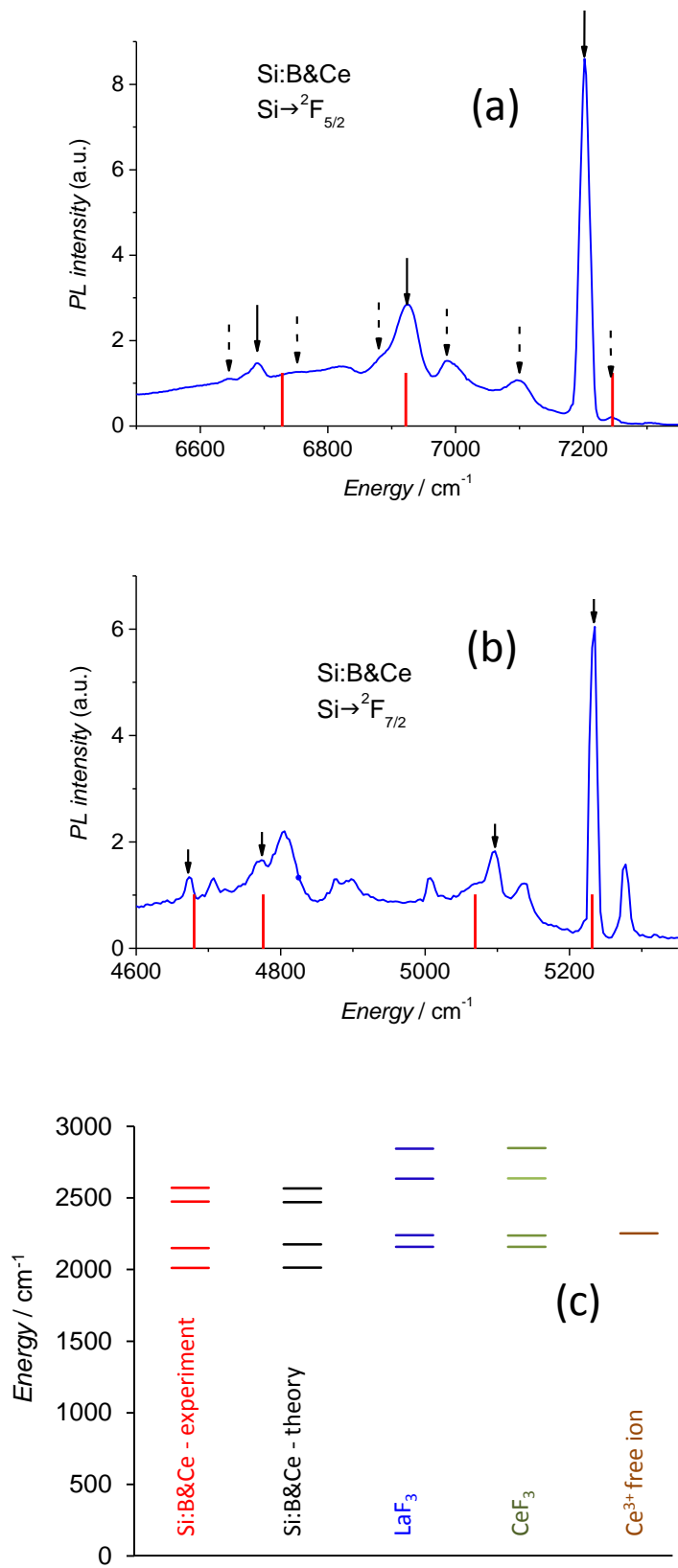
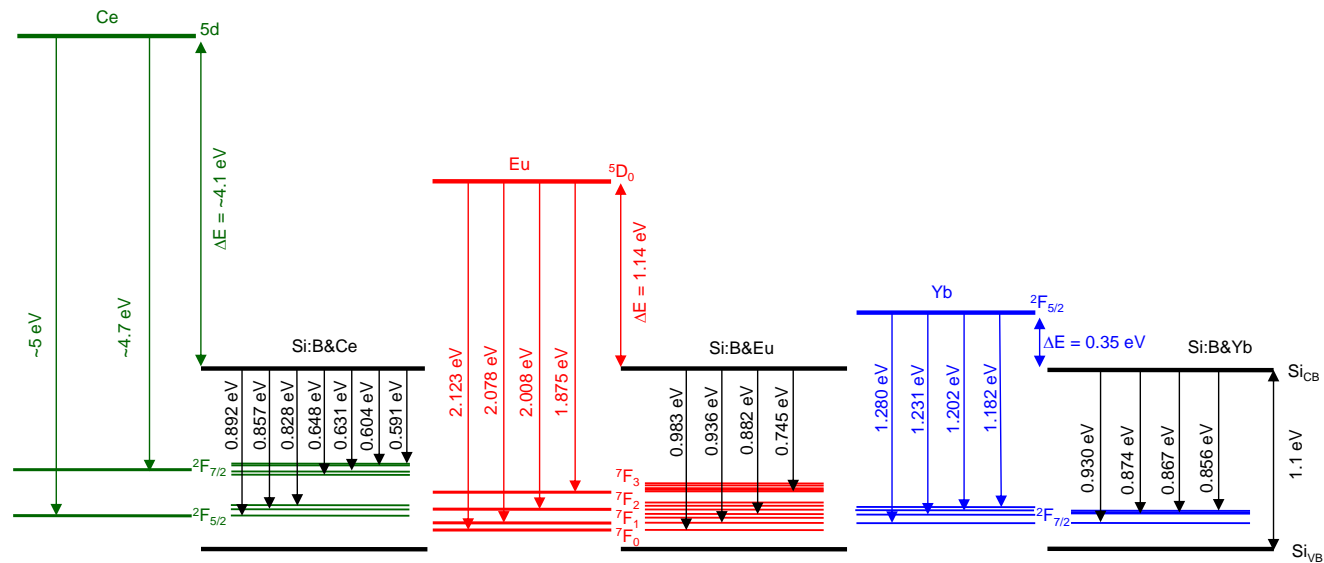


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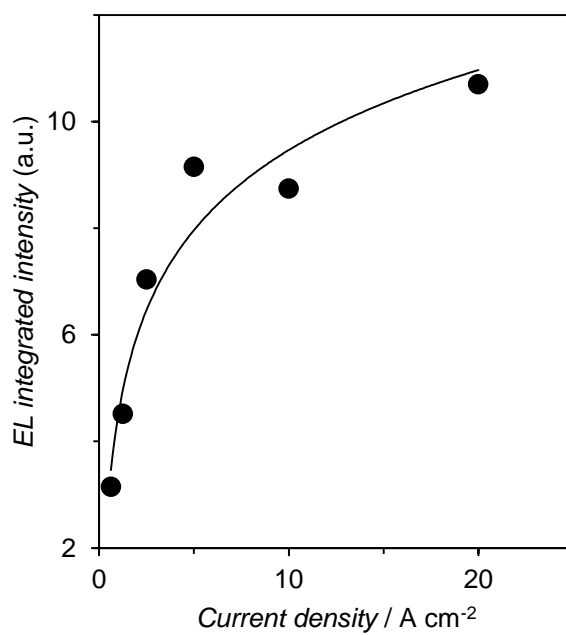


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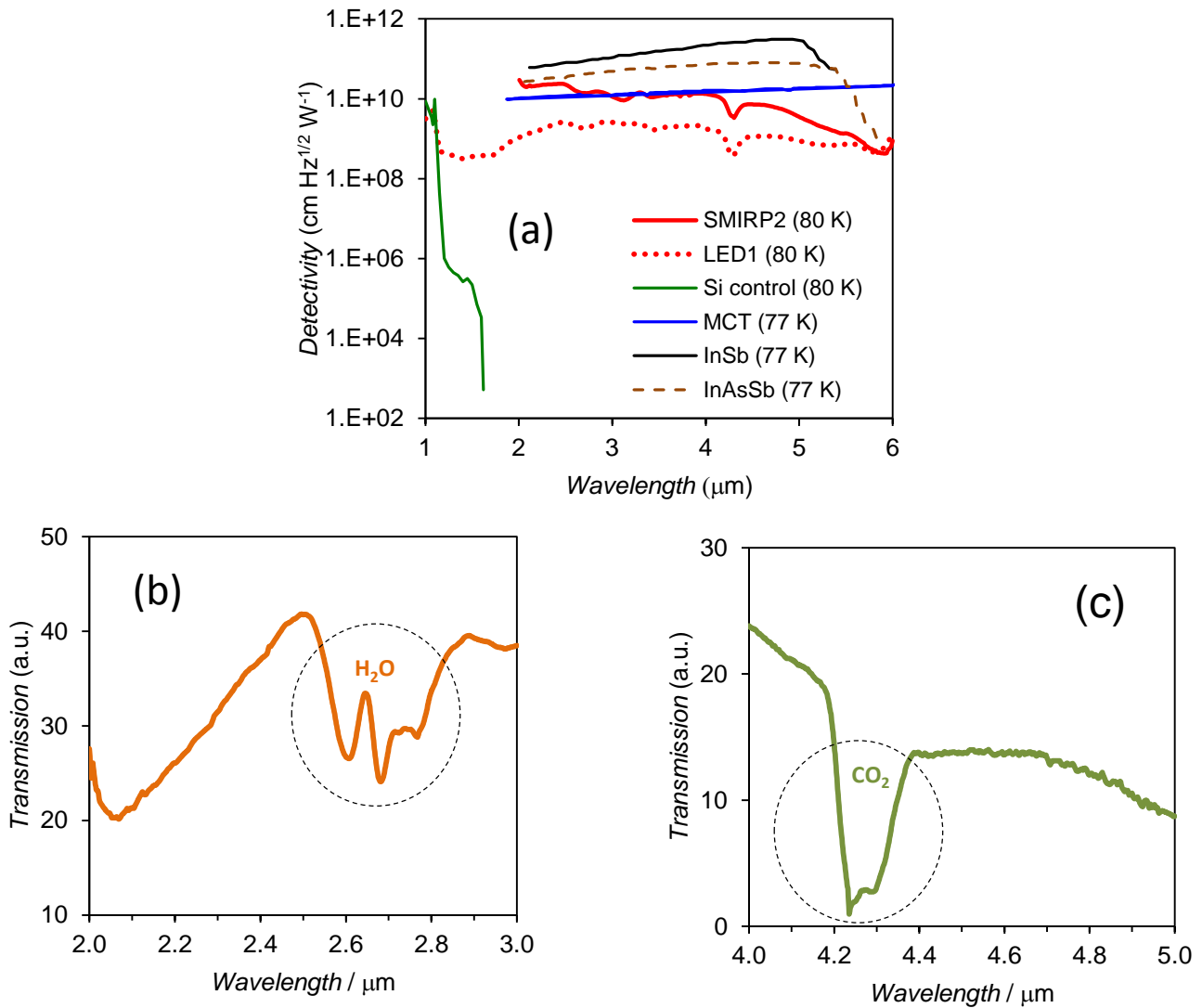


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