Chapter 2
History of the Observed Centres in Silicon

Many of the IBE centres studied in this thesis have been discussed in the past. While none of those prior publications could ultimately determine the actual constituents of these complexes, a number of important properties have been determined, over the years, through various different experiments. Many of these characteristics are introduced in this chapter for the “Cu-pair” (Cu₄), the “*Cu-pair” (Cu₃Ag), the “single Ag” (Ag₄), the “Au-Fe pair” (Cu₃Au), the “Fe-B pair” (Cu₄Au), and the Cu₄Pt and Cu₃Pt complexes. The related Sₐ and Sₐ centres as well as the Li₄-vacancy centres, are introduced as well.

2.1 The 1014 meV “Cu-pair”: The Cu₄ Centre

Among all TM-containing IBE centres, the ∼1014 meV Cu₄ complex, the NP transition of which is often labelled Cu⁰, has been studied the most in recent literature, both experimentally and theoretically, and the complex can be considered the prototype of the entire family of centres. In fact, it is difficult not to observe this PL centre after rapidly quenching Si from above 700 °C to room temperature. This is due to the high diffusivity and solubility of Cu at elevated temperature, together with the difficulty of eliminating Cu as a contaminant in all but the most rigorously clean environments. The centre was first observed by Minaev et al. [1] at 1015 meV (various authors refer to the centre as the 1014, 1015 meV, or more accurately, the 1014.7 meV centre) in heat treated and subsequently quenched n-type Si. In view of the technique used to create this centre, the authors called it a “thermal defect”. The low temperature, low resolution spectra clearly show the intense NP line, together with up to 10 lower energy pLVM replicas. At a temperature above 10 K, higher energy components were observed. Using uniaxial stress spectroscopy, pLVM replicas and the NP transition split in the same way, indicating totally symmetric vibrations. Minaev et al. concluded that this luminescence is due to the recombination of an exciton bound to a trigonal, neutral centre (an IBE), with ⟨111⟩ axial symmetry. It was also
found that this defect anneals out at less than 300 °C, with an activation energy of 0.6 eV and has an estimated formation energy of 2.6 eV. It was concluded that the defect is likely due to the presence of TM impurities in the Si sample, with Fe and Cr as possible candidates. The centre was then briefly mentioned by Weber et al. [2] as a PL centre at ∼1016 meV, which was found to be especially strong in Cu-doped samples.

Shortly after these initial reports, Weber et al. [3] published a comprehensive study of the ∼1014 meV Cu PL centre. The authors systematically assigned labels to NP, Stokes and anti-Stokes vibrational replicas, as well as to electronically excited states of the NP transition detected at higher temperatures. The characteristic pLVM structure formed by the Stokes vibrational replicas was described in detail in this study. The investigated samples were prepared by intentionally evaporating Cu onto them, before subjecting them to diffusion steps in a furnace. No increase in PL intensity was observed after more than 5 min of diffusion time for a sample thickness of ∼1 mm. A high cooling rate was necessary for strong PL emission, as already noted by Minaev et al. [1]. PL was observed for samples diffused above 700 °C with an increasing intensity up to 1100 °C. No difference in the experimental results was found with different n or p-type doping levels of P, B, or Al in the starting Si material for concentrations of either of the dopants in the range between 10^{12} and 10^{17} cm^{-3}. The intensity of the Cu spectrum decreased for concentrations above 10^{17} cm^{-3}, but no details were given [3]. It was also confirmed that the centre anneals out at temperatures above 150 °C. For the first time, isotopic Cu was used to show clearly the role that Cu plays in the 1014 meV PL line. A total isotope shift of 0.06 meV was observed for the NP line, which compares very well to the experimental result obtained in this work (a total shift of 0.06 meV corresponds to 7.5 µeV per amu as shown in Table 4.2), and proved that Cu is indeed part of this PL centre [3]. An isotope shift was also observed in the first order pLVM replica. With a ratio of 1.010 of the lighter over the heavier mode energy, this value is comparable to the shift determined in this work (see Table 4.3). In an attempt to determine the number of Cu atoms needed to form the 1014 meV PL centre, experiments were done to find a relationship between the PL intensity I and the Cu concentration N_{Cu} in the sample. To determine the Cu concentration, the relationship between diffusion temperature and Cu concentration as determined by Struthers [4] was used (see Sect. 1.6.3). These experiments were conducted at the high temperature Cu solubility limit. After a quadratic dependence was found (I ∝ N_{Cu}^{2}), conclusions were made based on the law of mass action that the centre was composed of two Cu atoms [3]. Thus the complex was often referred to as the “Cu-pair” centre until it was demonstrated to be a Cu_4 complex by isotopic fingerprint measurements in ^{28}Si (see below).

Weber et al. [3] also observed the weak Γ_3 excited state, as a shoulder ∼0.15 meV above the main Γ_4 peak. The higher energy NP lines (Γ_3 and Γ_5 at 1016 meV) were identified as thermally populated split ground states of the trap. The localization energy of the BE of Cu_4 was found to be 140.3 meV with respect to the free exciton (FE) or 155 meV with respect to the band gap energy (the FE binding energy is 14.7 meV). As determined in a thermalization experiment, the donor electron is bound by 32 meV, whereas the hole is bound by 123 meV in the short range potential of the
isoelectronic trap. This finding agrees reasonably with a hole trap at $E_V + 0.1$ eV, which was found in a deep-level transient spectroscopy (DLTS) experiment involving Cu-doped Si [5] at about the same time. The authors concluded that the centre is a donor-like IBE. This argument is further supported by the observed high quantum efficiency of the centre. Through uniaxial stress and Zeeman spectroscopy experiments, and assuming a Cu-pair, the authors verified that the IBE centre is in a $\langle 111 \rangle$ trigonal configuration with at least one Cu on an interstitial site ($\text{Cu}_i\text{Cu}_j$). The centre reorients itself along the $\langle 111 \rangle$ axis under stress, which again suggests the involvement of a highly mobile $\text{Cu}_i$.

Almost simultaneously, Watkins et al. [6] found that the 1014 meV PL centre is present at low Cu concentration, but has a high PL efficiency. The authors focused on the details of the pLVM replicas, and on the temperature dependence of the PL lifetime. In addition to the $\sim 7$ meV mode, and the various overtone and combination modes, distinct pLVM were observed with energies of 16.4 and 25.1 meV. The measured long PL decay times of the centre were consistent with an IBE model. Decay times of up to 480 $\mu$s were measured at 1.3 K and up to 670 $\mu$s at 4.2 K. The measured temperature dependence of the lifetime was later explained by Sauer et al. [7] to fit the level scheme for the split ground state suggested in reference [3], where the excited $\Gamma_3$ state has a very long lifetime, which explains the longer measured lifetimes at higher temperature.

Davies [8] reviewed a number of PL centres in Si, among them the 1014 meV PL complex. This publication noted that the structure of the centre was not known, even though it was thought to be a “Cu-pair” [3]. It was unclear though, whether all of the Cu dissolved in the Si sample actually forms the 1014 meV PL centre, and, thus, a connection between Cu concentration and PL intensity could not be made [8].

The connection between this PL centre and the $E_V + 0.1$ eV hole trap observed by DLTS was further supported by Brotherton et al. [9], and firmly established by Erzgräber et al. [10], who found a linear relationship between the PL saturation intensity of the 1014 meV centre and the concentration of the $E_V + 0.1$ eV DLTS centre. The 1014 meV centre is one of the few examples of a firm connection between a deep defect seen in PL and one seen in a DLTS experiment.

Nazaré et al. [11] have investigated the excited states of the 1014 meV centre at 16 K under uniaxial stress and confirmed that the centre is an IBE with trigonal $C_3v$ symmetry. In a different interpretation of the system than the one given by Weber et al. [3], it was found that a built-in axial strain splits the ground state of the centre into the $\Gamma_5$ (1014 meV, $\Gamma_5 = \Gamma_1 + \Gamma_3$) state together with higher lying $\Gamma_1$ (1016 meV) and $\Gamma_3$ (1024 meV) states. Both interpretations are consistent with a donor-like IBE model.

By this time, many authors were referring to the 1014 meV centre as the Cu-pair centre [12–17]. Istratov et al. [12] found the binding energy of the 1014 meV Cu PL centre was 1.02 eV in a DLTS experiment. With the assumptions that interstitial $\text{Cu}_i$ is singly positively charged and substitutional $\text{Cu}_s$ is doubly negatively charged (fitting the measured binding energy), the only solution that fits a donor-acceptor pair model for the Cu-pair is that the centre is a single acceptor ($\text{Cu}_2^–\text{Cu}_i^+$), contradicting the commonly accepted model of the centre being donor-like. The authors also found
that the pair formation is limited by the availability of Cu\textsubscript{s}. Shortly thereafter, Istratov et al. [13] revised these results, as they found that the two Cu atoms in the Cu-pair were not exclusively bound Coulombically, thus invalidating the previous assumption of a donor-acceptor pair model. This new result is based on the fact that in a purely ionic model, the binding energy between Cu\textsuperscript{−} and Cu\textsuperscript{+} is only 0.52 eV, half of the experimentally determined value of 1.02 eV [12, 13]. In a double deep-level transient spectroscopy (DDLTS) experiment, the possibility of the Cu-pair being an acceptor was now excluded, therefore the centre has to be a donor-like IBE [3]. However, the only possibility to have a dissociation energy of 1.02 eV for an ionic Cu pair is if it was an acceptor [13]. Thus the centre was argued to have a strong covalent contribution to its binding energy.

In contrast to the Cu-pair model, Nakamura et al. [18] started arguing for a single Cu model. Their initial argument was based on the measured relationship between the PL intensity of the centre and the Cu concentration (which was kept below the solubility limit) in the crystal. The Cu concentration in the crystal was determined through a measurement of the surface concentration together with a constant-concentration depth profile at the used diffusion temperature. The linear relationship that was determined contradicts the results of Weber et al. [3], which were obtained at much higher concentrations. No difference was found for n or p-type samples for B and P doping concentrations between $5 \times 10^{14}$ and $2 \times 10^{15}$ [18]. Nakamura et al. suggested a bond-centred (BC) model for a single Cu atom, which satisfies the trigonal symmetry requirement, but the authors realized possible interference with the rapid rearrangement under stress, which had been suggested before [3]. In a following publication [19], this problem was clarified by measuring a small dissociation energy for the centre that the authors thought would allow for the reorientation. In a later publication, Nakamura et al. [20] suggest that a DLTS centre at $E_C - 0.15$ eV is a precursor to the 1014 meV Cu PL centre (which corresponds to the $E_V + 0.1$ eV DLTS centre). The authors also found that the dissociation energy of the 1014 meV centre was only 0.63 eV in a PL experiment, as compared to the value of 1.02 eV determined by Istratov et al. [13] in a DLTS experiment. The smaller value was thought to be erroneous [15, 17], as it was measured by PL, and the long exciton diffusion length would contribute a signal from deeper regions of the bulk; whereas Istratov et al. measured the dissociation energy with DLTS, where only a near-surface region is probed, thereby increasing the likelihood that only material is probed in which the Cu\textsubscript{i} had a high chance to out-diffuse. The out-diffusion process is likely slower in the deeper bulk probed by PL, and thus PL would only measure the effective dissociation. Nakamura et al. [21] confirmed this suggestion, and explained the discrepancy between the different values of the measured dissociation energy in a depth-dependent DLTS experiment. The formation energy of the Cu\textsubscript{4} centre of 0.57 eV, as determined by Nakamura et al. [20] via DLTS, was found to be slightly less than the measured DLTS dissociation energy, indicating that the formation process is different than the dissociation process.

Knack et al. [15] then undertook a number of experiments to achieve a better understanding of the formation mechanism of the 1014 meV Cu PL centre. A sample with Cu\textsubscript{s} incorporated during the floating-zone growth process was used. After
initially observing the $E_v + 0.1\,\text{eV}$ DLTS peak, only a DLTS signal due to Cu$_s$ and Cu-H complexes was observed after a 30 min annealing process at 250°C. Cu$_s$ has no corresponding luminescence signal. A Cu-containing etch solution restored the $E_v + 0.1\,\text{eV}$ DLTS peak. The authors concluded that Cu$_i$ diffuses out of the sample during the annealing step, whereas it diffuses back into the sample during the room temperature etch process and then binds to the still available substitutional Cu$_s$, which forms only at higher temperatures (>700°C). Thus, the concentration of the complex is $[\text{Cu}_s\text{Cu}_i] = [\text{Cu}_s] = k[\text{Cu}_{\text{tot}}]$, where the solubility of the substitutional Cu$_s$ determines the saturation of the pair formation, not the much higher total solubility, which is dominated by interstitial Cu$_i$. The authors [15] argued that this model can comply with the linear relationship between PL intensity and Cu concentration for a Cu content in the sample below the solubility limit, as observed by Nakamura et al. [18]. Regarding the quadratic dependence of the PL signal at higher concentrations at the Cu solubility limit determined by Weber et al. [3], Knack et al. [15] show that literature values for [Cu$_i$], as well as the Si vacancy concentration and the formation enthalpy of Cu$_s$, lead to a near quadratic dependence of the PL intensity on the Cu concentration, which is controlled by the Cu$_s$ concentration, not the total Cu concentration.

The similarity between the 1014 and the 944 meV Cu related PL centres (see Sect. 2.2) was noted by Estreicher et al. [22], and their formation and vibrational properties were discussed. For the 1014 meV centre, the authors ruled out Cu-pairs of either two interstitial or two Cu$_s$, and also determined that a BC site, as was suggested by Nakamura et al. [18], is not energetically favorable for Cu in Si. It was found from ab-initio calculations, that the energy gained by a Cu atom taking the place of a vacancy in Si is between 2.71 and 2.78 eV. On this substitutional site, the Cu-Si bond length to the four Si neighbours was determined to be 2.236 Å, within ~0.1 Å of Si-Si bonds. Trapping of a Cu$_i$ by a Cu$_s$ would then result in an additional gain of 0.75 eV. Potentially, this Cu$_s$Cu$_i$ pair can react with another vacancy and form a Cu$_i$Cu$_s$ pair, possibly with a Si in between (Cu$_s$-Si-Cu$_s$), resulting in a further energy gain of more than 2 eV. The authors calculated the energy of a vibrational mode for these models, where both Cu atoms are moving together along the trigonal axis, preserving their bond length. The result is close to the experimentally measured pLVM energies of the 1014 and the 944 meV Cu centres. These results strongly suggest that the 1014 meV is a Cu$_s$Cu$_i$ pair (whereas the 944 meV centre was thought to be a Cu$_s$Cu$_s$ pair, see Sect. 2.2).

The association of the 1014 meV PL centre with a Cu$_s$Cu$_i$ pair was supported later by Estreicher et al. [23] with ab initio calculations involving the centre’s vibrational modes. One pLVM mode was found for a Cu$_s$Cu$_i$ that has appropriate symmetry to couple to the electronic transition and has a frequency close to the experimentally observed vibrational replica of the 1014 meV centre. The analysis also showed that neither Cu$_i$Cu$_s$, nor Cu$_s$-Si-Cu$_s$, nor Cu$_i$ alone could produce the observed vibrational mode structure. These findings were confirmed in further reviews [17, 24].

Nakamura et al. [25] claimed that the substitutional model was unlikely due to the high concentration of Cu centres detected in DLTS and the small number of available Cu$_s$ in Si at the diffusion temperatures typically used to produce the 1014 meV
PL centre. An experiment compared the Cu PL intensities in Si samples with, and without, vacancies, and found them to be very similar. Thus it was concluded that the presence of vacancies does not increase the formation of the Cu PL centre, even though it should facilitate the formation of substitutional centres, hence making Cu$_s$ an unlikely part of the Cu PL centre. As a consequence, Nakamura et al. [26] kept arguing in favour of a single bond-centred Cu$_{BC}$ model. Their argument continued to be based on the linear relationship of the Cu PL intensity and the DLTS concentration, where the maximum concentration of the centre was thought to be larger than the Cu$_s$ solubility. They concluded that a single Cu$_{BC}$ is more appropriate than the proposed pair models [24], in contrast to calculations that show Cu$_{BC}$ to be unstable [22, 23].

Thewalt et al. [27] then discovered that the 1014 meV Cu centre consists not only of one or two Cu atoms, but a cluster of four Cu atoms. The experimental evidence for this surprising discovery was found through high resolution PL spectroscopy of isotopically enriched $^{28}$Si, which had been shown before to exhibit drastically reduced PL linewidths of shallow impurities due to the removal of inhomogeneous isotope broadening [28–32]. With the increased spectroscopic resolution it was now possible to observe the PL lines that originate from different combinations of the stable Cu isotopes in the impurity cluster [27]. Five PL lines could be observed for the $\Gamma_3$ representation, leading to the conclusion that they are due to the five possible arrangements of four Cu atoms of the naturally occurring isotopes $^{63}$Cu and $^{65}$Cu. This conclusion was tested by diffusing monoisotopic Cu and non-natural isotopic mixtures as well as by comparing the relative areas of the peaks in the natCu spectrum to the natural abundances of the Cu isotopes. The controversy about the 1014 meV Cu centre was settled by these unambiguous experimental results, which are discussed in detail in Sect. 4.1.1.

Nevertheless, in a further publication, Nakamura et al. [33] assume a BC model of a single Cu atom forming the 1014 meV centre. Contrary to Weber et al. [3], the authors found that the concentration of PL centres is not a simple increasing function of diffusion temperature in Cu saturated samples. A sharp drop-off in concentration at higher temperatures was explained as a result of increased precipitation and out-diffusion. Again, the authors measured a higher concentration of PL centres than what was thought to be the saturation concentration of Cu$_s$, making a single Cu$_{BC}$ atom their favoured configuration [33]. In light of the $^{28}$Si high resolution spectroscopy results [27], this model was revised finally and Nakamura et al. [34] suggested a model for the Cu$_4$ centre, in which one BC Cu is surrounded by three equatorially bound Cu$_i$. The authors concede that this model is in contradiction to calculations regarding the stability of the BC site by Estreicher et al. [23]. In a further publication [35], the authors argue again in favour of Cu$_{BC}$Cu$_{3i}$ model, based on the argument that the BC site would be stable at higher temperatures and “freeze in” at lower temperature. They argue that centres involving Cu$_s$ are not a realistic model for the 1014 meV line, as there would not be a sufficient number of vacancies available to form Cu$_s$ at the observed concentrations, and there would be a large discrepancy between the Cu$_s$Cu$_{3i}$ binding energy [36] and Nakamura’s observed dissociation energy [20]. The BC model was reiterated in a further publication [21], although none of these papers
contain any detailed calculations supporting the stability or formation mechanism of the proposed centre.

After it was found that the 1014 meV PL centre is a Cu$_4$ centre, another model for the structure of the centre was proposed. Shirai et al. [36, 37] suggested a model where three Cu$_i$ are grouped around a Cu$_s$ in $C_{3v}$ symmetry. This arrangement has the strongest binding energy of a number of calculated combinations, but its formation energy has not been determined, therefore different configurations cannot be excluded. The authors also attempt to explain the observed splitting in the $\Gamma_4$ representation, by taking vibronic coupling to non-totally symmetric vibrations into account, but a complete explanation of these splittings could not be given. Possible pLVM of the Cu$_s$Cu$_{3i}$ complex have also been studied [37]. Very recently Estreicher et al. [38] and Carvalho et al. [39] explained the formation pathway of the Cu$_4$ defect, in terms of the capture of the positively charged Cu$_i$ by Cu$_s$, Cu$_s$Cu$_i$, and Cu$_s$Cu$_{2i}$ which were all found to be negatively charged, if the Fermi-level was near mid-gap. The Cu$_s$Cu$_{3i}$ centre, on the other hand, has its acceptor level almost resonant with the conduction band, and would be uncharged in intrinsic Si. The model thus explains why no Cu$_s$Cu$_i$, Cu$_s$Cu$_{2i}$ or Cu$_s$Cu$_{4i}$ centres are observed. In this regard it is important to observe that the samples used here, and to the best of our knowledge in all previous studies, were lightly doped, with Fermi-levels near mid-gap, with the single exception of the brief comment by Weber et al. [3], that the intensity of the PL of the 1014 meV centre decreases in intensity for doping levels above $10^{17}$ cm$^{-3}$.

2.2 The 944 meV “Perturbed Cu-pair”: The Cu$_3$Ag Centre

The $\sim$944 meV Cu$_3$Ag complex, formerly labelled $^\star$Cu$_i$, was long thought to be a Cu-pair similar to the Cu$_0^0$ centre. This centre was likely first observed by Minaev et al. [1], who reported PL lines at 950 and 875 meV in thermally quenched Si, in their paper which first reported the very similar 1014 meV Cu$_4$ centre. These energies are very close to those of Cu$_3$Ag and Cu$_2$Ag$_2$ (see Sect. 4.1.3), therefore, it is assumed that they are the same centres. The 944 meV centre was described in detail by McGuigan et al. [40] in Si lightly doped with Cu, and found to have a pLVM structure very similar to that observed for the 1014 meV Cu$_4$ centre. Extensive experiments made the authors believe that this IBE PL line could only be observed in Si that was lightly doped with Cu. Due to the similarity of the two centres, it was thought that this centre is a precursor to Cu$_4$ at lower Cu concentrations, before a high enough Cu concentration is present in the sample to form Cu$_4$. It was also found that the centre anneals out at temperatures lower than those necessary for the Cu$_4$ centre. The involvement of elements other than Cu was not ruled out.

In a later report, McGuigan et al. [41] investigated the defect in uniaxial stress and Zeeman experiments. The authors found that their uniaxial stress and preliminary Zeeman data was consistent with a high symmetry $T_d$ defect centre. Because they could observe the centre only at low Cu concentrations, they suggested that the $\sim$944 meV PL centre was a singly positively charged Cu$_i$, at a tetrahedral interstitial
site with $T_d$ symmetry. In this state, Cu has a full 3$d$ shell and creates a single level. However, it was concluded that more data was needed to fully identify this centre. The proposed interstitial Cu$_i$ character of the centre has later been the subject of controversy [17, 23, 42]. As Cu$_i$ is not stable at room temperature, it would instead diffuse out to the surface of the Si sample. In a later publication [43], members of the group of reference [41] put the measured $T_d$ symmetry in doubt as well, because the results were obtained only for low uniaxial stresses.

Later, Knack et al. [15] suggested a connection between the 944 meV *Cu PL centre and a DLTS centre at $E_v + 0.185$ eV. While going through different treatment and annealing steps, these two centres had always been observed simultaneously in their samples. The authors drew no conclusion about the microscopic origin of the centre.

On the basis of formation dynamics, energetics, symmetry, and low frequency pLVM, Estreicher et al. [22] initially suggested that *Cu is a Cu$_s$Cu$_i$ pair (see Sect. 2.1), which was later ruled out [23] because it was not possible to find matching pLVM modes for the Cu$_s$Cu$_i$ pair that would couple to PL and thus be visible in experiments to generate the characteristic pLVM replica spectrum [23, 24]. In his review, Knack [17] noted that the proposed substitutional pair would have trigonal $C_{3v}$ symmetry, as opposed to the observed tetrahedral $T_d$ symmetry [41], as $T_d$ only allows for a single Cu$_i$ or Cu$_s$, both of which can be ruled out for several reasons [42].

The most recent modeling by Estreicher et al. [42] revised the previous findings and identified *Cu as a Cu$_s$Cu$_i$ centre in a different configuration than that of the 1014 meV Cu$_4$ centre. This new configuration is Cu$_s$-Si-Cu$_i$ as opposed to Si-Cu$_s$-Cu$_i$, which was suggested for the 1014 meV centre [23, 24]. Both configurations have $C_{3v}$ symmetry. A pLVM that couples to PL was found close to the measured energy for this new configuration. In this mode, as is the case for the 1014 meV mode, three atoms (Si + 2 Cu) move along the trigonal axis, which explains the strong similarity in the optical spectra of *Cu and Cu$_4$. It was suggested that further experiments be undertaken to examine the centre’s symmetry and formation conditions.

A lot of the efforts to explain *Cu have been hampered by what were thought to be the conditions needed to produce strong PL from the centre. There were uncertainties in the necessary Cu concentration to produce the centre, its appearance in conjunction with dislocations, special annealing and quenching procedures, or the assumption that *Cu would be a precursor to the 1014 meV PL centre. These speculations were put to an end when the inconsistent formation conditions of the *Cu centre were shown to be connected to the presence of Ag in the centre [44, 45] as detailed in Sect. 4.1.2. Hence, in the past, *Cu was always observed under conditions with sufficient accidental Ag contamination. Through the isotopic fingerprint characterisation method in $^{28}$Si, Yang et al. [44] unambiguously identified the 944 meV PL centre as Cu$_3$Ag.

The photoionization of the $\sim$944 meV centre was studied using time-resolved free-electron laser spectroscopy by Vinh et al. [43], in samples where the $\sim$944 meV centre PL signal was much stronger than the normally dominant $\sim$1014 meV centre. It is interesting to note that the authors also observed the 778 meV Ag-related PL system in this sample, and had been preparing Ag-doped samples for similar studies [46]. Given that the isotopic fingerprint result proves that the $\sim$944 meV *Cu centre is,
in fact, a Cu$_3$Ag complex, the surprising strength of the $\sim$944 meV system in the sample studied by Vinh et al. [43] is readily understood. This centre also provides a good example of the difficulty in avoiding cross-contamination when preparing TM-doped samples.

2.3 The 778 meV “Single Ag”: The Ag$_4$ Centre

Ag is an extensively studied contaminant in Si as it is electrically active. The $\sim$778 meV Ag PL system was first observed by Olajos et al. [47] in absorption experiments. The centre was linked to Ag, and the authors suggested that the symmetry of the centre is $C_{2v}$ or lower. The authors also suggested that the centre is an isolated, single substitutional Ag donor-like IBE centre and hence a link to the DLTS Ag donor level $E_v + 0.34\text{ eV}$ [48] was established.

Nazaré et al. [49] reported on IBE centres in PL spectra of Si samples diffused and implanted with Ag at 778.9 and 777.3 meV, and found that both lines are thermalizing excited defect states, decaying to the same ground state. Upon closer examination, the reported PL spectrum bears some similarity to Pt related spectra [50], especially when considering the reported PLVM energy of 9.5 meV and, hence, an accidental Pt contamination of the samples used in reference [49] cannot be excluded.

Some of the earlier results were confirmed by Son et al. [51] in PL and absorption experiments. The authors proposed a donor-like IBE model, and also studied the PLVM replica spectrum in which the lowest energy mode was found at 6 meV. Three NP lines originating from the Ag-centre ground state manifold, labelled A, B, and C were observed, and a table listing PLVM and EMA excited state energies was published. These results are also summarized in reference [52]. Son et al. [53, 54] stated that even though Ag-related centres were identified in electron paramagnetic resonance (EPR), no correlation between magnetic resonance and optical spectra could be established.

At about the same time, Iqbal et al. [55], in a study of the IBE ground state splittings, showed the first evidence of the 778.7 meV $F_0$ forbidden transition $\sim$0.2 meV below the $A$ transition at low temperature. With temperature-dependent intensity measurements, it was shown that the $F_0$, $A$, $B$, $C$ PL lines thermalize and originate from one split ground state of the IBE, and that the dominant PLVM replicas originate from the newly discovered $F_0$ level. A trigonal symmetry of the defect centre was suggested on the basis of uniaxial stress experiments.

In an experiment where different Ag isotopes were used for the first time to form the 778 meV centre, Vinh et al. [56] reported an Ag-isotope shift for the $A$, $B$, $C$ components. A total isotope shift of 0.034 meV was observed between $^{107}$Ag and $^{109}$Ag, corresponding reasonably well to a new result of 0.025 meV obtained in $^{28}$Si ([45] and Sect. 4.1.4). The authors also concluded, on the basis of lifetime measurements that the centre is an IBE centre. A lifetime of up to 250 $\mu$s was determined at low temperature, which is long when compared to the lifetimes of regular donor or acceptor BE in Si that typically range on the ns scale. At higher temperature (25 K), additional
PL bands $D$ and $E$ were identified. For this analysis, it was assumed that the centre contained a single Ag atom.

Davies et al. [57] studied the Ag centre in detail. Zeeman spectra were observed to be near isotropic, thus no information could be extracted about the point group of the centre. This result is expected for a tightly bound hole in $C_{3v}$ symmetry, because its orbital angular momentum is quenched and the remaining spin angular momentum responds isotropically to the magnetic field [58]. Uniaxial stress experiments confirmed the EMA character of the electron and the centre was characterised as a donor-like IBE with trigonal $C_{3v}$ symmetry. Temperature-dependent intensity measurements associated the pLVM replicas with the forbidden $F_0$ state just below the $A$ line, redefining the phonon energy slightly. Due to the energetic closeness of $A$ and $F_0$, their pLVM replicas could overlap, but it was found that the pLVM replica luminescence is dominated by the $F_0$ state. The measured isotope shifts of the pLVM and calculations of the effective mass of the centre responsible for the observed pLVM isotope shifts made the authors conclude that the centre consisted of a single Ag atom.

Only experiments with isotopically enriched $^{28}$Si could finally show the nature of the 778 meV PL centre [45]. It was found to consist of four Ag atoms and a detailed analysis is presented in Sect. 4.1.4.

2.4 The 735 meV “Fe, or Au-Fe pair”: The Cu$_3$Au Centre

In 1973, Otha [59] published extensive results on infrared absorption spectroscopy of Au in Si, suggesting the occurrence of single Au centres causing broad absorption bands and Au pair centres causing sharper absorption lines. It was proposed that the Au pair would likely occupy second nearest neighbour sites in the Si lattice.

After these first spectroscopic experiments involving Au defect centres in Si, the $\sim$735 meV centre (now known to be Cu$_3$Au) was discussed thoroughly in the literature. The first occurrence appeared in a publication on Fe in Si [2], as the centre was believed to be due to Fe, and the Au and Cu content in the sample was likely due to contamination. The 735 meV PL line’s characteristic pLVM replicas were observed. Two thermalizing NP lines were detected and a BE model was proposed. The symmetry was determined to be trigonal using Zeeman spectroscopy.

The participation of Fe in the 735 meV centre was put in doubt by Schlesinger et al. [60], because no Fe isotope shift could be observed in their experiments using $^{54}$Fe and $^{56}$Fe diffused Si samples.

Do Carmo et al. [61] found the 735 meV PL centre was trigonal on the basis of uniaxial stress tests. The centre was interpreted as an IBE centre with a tightly bound hole and a shallow electron, making it a donor-like IBE. Similar to Ag$_4$ [58], the hole angular momentum is quenched in the low symmetry environment of the optical centre and, as a result of the axial strain, thereby leading to singlet-triplet splitting of the bound exciton. Thermalization of the resulting three electronic states was observed. No attempts to identify the constituents were undertaken.
Singh et al. [52] claimed that the occurrence of the 735 meV PL peak in their Au doped samples was a result of the Fe contamination of even the purest Au source and that the centre is unlikely to contain Au, which had been shown in Fe diffused samples before. Earlier results were interpreted [61] and explained with additional data. Besides the already observed three electronic states that were attributed to the $1s(A_1)$ split states, the authors found two higher excited states and predicted the presence of a third. With this information, the hole binding energy was estimated and found to be close to the level observed for Fe$_i$ donors in Si. Therefore the authors suggested that the defect contains an interstitial Fe atom and possibly other unknown constituents, with an overall trigonal symmetry. The electronic structure would be dominated by Fe and the centre would fit into the donor-like IBE model.

In the first publication where the decay of ion-implanted, radioactive Au isotopes in Si was studied, Henry et al. [62] found that the 735 meV centre decays according to the half life time of the implanted radioisotope $^{195}$Au. It was concluded, therefore, that Au was involved in the formation of this centre and it was relabeled the Au-Fe centre [50, 63].

PL spectroscopy of Cu and Au-diffused $^{28}$Si samples revealed the presence of Au and 3 Cu atoms in this centre, while no fingerprint of Fe was found [45]. Detailed experimental results for this Cu$_3$Au centre are presented in Sect. 4.2.1.

2.5 The 1066 meV “FeB pair”: The Cu$_4$Au Centre

Initially, the $\sim$1066 meV Cu$_4$Au centre was thought to be an FeB pair centre [2], based on observing it in Fe diffused $p$-type samples. Sauer et al. [64] observed two thermalizing lines, which were both split into a thermalizing triplet under a magnetic field. The two components were interpreted as one forbidden and one allowed transition from an IBE state to the ground state. The centre was found to have trigonal symmetry and pLVM replicas were detected for both PL lines. The authors also confirmed earlier results that linked this 1066 meV PL centre to a DLTS centre at $E_v + 100$ meV, which was ascribed to FeB pairs [65, 66].

Schlesinger et al. [67] have done experiments to determine a possible Fe isotope shift of the 1066 meV PL line and its phonon vibrational modes. Samples diffused with $^{54}$Fe and $^{56}$Fe did not show any detectable isotope shift in NP and pLVM replica PL lines. This result was not expected for an Fe containing defect, especially for its pLVM, which were described as due to Fe motion [64].

Mohring et al. [68] did extensive research on the 1066 meV PL centre. Three electronic states and their pLVM replicas were observed. Zeeman spectra showed no significant anisotropy, limiting the possible symmetries to cubic $T_d$, as all lower symmetries would show some anisotropy. It was found that the centre decays at annealing temperatures of more than 80 °C and the centre was not observed in samples with low B concentration, while its intensity was found to be enhanced with higher B doping levels. Hence, Mohring et al. [68] assumed that B is part of the centre. Diffusion experiments also suggested the participation of Fe in the formation of the centre. The
determined dissociation energy of 0.9 eV was close to values previously determined for FeB pairs in other experiments. The produced PL samples were also used for DLTS studies, and only a limited correlation was found with the $E_v + 100 \text{ meV}$ centre. Mohring et al. [68] also pointed out points of conflict with a possible FeB assignment of the 1066 meV PL centre. For one, Fe diffuses interstitially, so a pair would likely be B$_s$-Fe$_i$ and thus aligned along a $\langle 111 \rangle$ axis with axial symmetry, which would show some anisotropy in Zeeman spectra, which was not observed. The PL intensity was relatively low for the expected overall number of centres, taking into account the amount of available B in the sample into account. The authors concluded that the composition of the centre could not be identified, but their experimental data was inconsistent with an FeB assignment.

After experiments with B and Fe doped Si, Conzelmann et al. [69] concluded that it seems necessary to have Fe in the sample to produce the 1066 meV PL centre (“FeB”), but admitted that his results were “controversial” in light of some previous publications.

Kluge et al. [70] found no correlation between the intensities of the 1066 meV PL signal and that of FeB pairs in EPR experiments after annealing the samples, and suggested that the PL centre is not due to B$_s$-Fe$_i$. No conclusion on the structure of the centre was reached, but a different configuration or the participation of other ions in the formation of the 1066 meV PL centre was suggested.

Davies et al. [71] explained the unusual pLVM structure of the 1066 meV centre, where the pLVM replicas at low temperature are stronger than the NP PL lines. The centre was reviewed by Istratov et al. [72], suggesting that EPR FeB centres might not have corresponding PL centres. It was suggested that sample contamination possibly led to incorrect conclusions in the past.

The 1066 meV PL centre was then observed in Au implanted Si [62], but only later was the involvement of Au confirmed by Henry et al. [50, 73] by observing the decay of the PL line with the decay of the $^{193}$Au radioisotope. Although this method could not exclude any of the previously discussed constituents, evidence certainly increased against the necessity of Fe for the formation of this centre.

With the availability of isotopically purified $^{28}$Si, it was then shown that the 1066 meV PL centre actually is Cu$_4$Au [45], whereas no Fe isotope shift could be observed. These experimental results are presented in detail in Sect. 4.2.3.

2.6 The 777 meV Cu$_4$Pt and the 884 meV Cu$_3$Pt Centres

Originally the 777 meV Cu$_4$Pt and the 884 meV Cu$_3$Pt centres were thought to be Fe related [2]. The 777 meV centre was described to have near isotropic and linear Zeeman splitting, which was attributed to cubic symmetry. However, later studies involving the $^{195}$Au/$^{195}$Pt radioisotope decay pair found evidence that Pt played a major role in these centres [62]. At first, Henry et al. [62] ascribed the 777 meV line to the already documented 778 meV Ag system. After observing the rapid decay of this line in a sample implanted with $^{191}$Pt and an increase in intensity in samples implanted
with $^{195}$Au decaying to $^{195}$Pt, it was concluded that Pt and not Ag was responsible for this PL centre, overseeing the possibility of a potential overlap in energy in between two different centres. This overlap issue was resolved recently [45, 74]. In a later publication, Henry et al. [50, 73] confirmed the involvement of Pt in the 777 and 884 meV PL centres. The 777 meV centre was assigned to Pt-Fe initially and a decay of both PL lines was detected with the expected half-life time of the Pt radioisotope.

Alves et al. [75] have observed the 777 and 884 meV PL lines in samples implanted with natural Pt. Through preliminary uniaxial stress studies, it was concluded that the centres are axial in nature. A parallel was drawn between the 735 and 777 meV centres, as they were shown before to decay or increase in similar ratios in appropriate Au-Pt decay experiments [62]. Leitão et al. [76] have studied the 777 meV centre under uniaxial stress and determined it was an axial defect with $C_{2v}$ symmetry. The centre was described as a donor-like IBE centre.

Only later has the involvement of 4, respectively 3 Cu atoms in the 777 and 884 meV centres in addition to Pt been shown [77] in high resolution PL in $^{28}$Si. The presence of only a single Pt atom in these centres was confirmed in a further publication [74] and these results are explained in detail in Sect. 4.3. The centres were, therefore, labeled Cu$_4$Pt and Cu$_3$Pt respectively. The assumed connection between Cu$_4$Pt and Cu$_3$Au [75] could not be confirmed.

A 1026 meV PL centre that was mentioned on several occasions in literature [50, 73, 75], together with two previously discussed Pt defect centres, is generally too weak in our spectra to study its isotopic fingerprints. Alves et al. [75] claimed to observe a Si isotope effect and an intensity enhancement through Li, and concluded that the centre was likely large and involved a few atoms.

### 2.7 The 968 meV $S_A$ and 812 meV $S_B$ Centres

PL from S-doped Si was first reported in 1986 by Brown et al. [78]. Two PL systems were observed and labelled $S_B$ and $S_A$, with NP lines at ~812 and ~968 meV respectively [79]. A configurational metastability between $S_B$ and $S_A$ was observed and was the subject of several detailed studies [79–82]. A zero field ODMR study revealed a triplet splitting of both NP transitions [81, 83]. The detected nuclear hyperfine splitting due to a $I = 3/2$ spin suggested a single Cu at the core of both centres [81, 83]. Later, a model consisting of substitutional S and Cu$_i$ was proposed [82]. Both centres were found to have triclinic $C_1$ symmetry [82]. Bradfield et al. [84] reported a similar PL system in Si doped with Se, and suggested the involvement of O. It has recently been shown that the $S_B$ centre contains at least three Cu atoms in addition to S by analyzing the centre’s isotopic fingerprint in $^{28}$Si [44].
2.8 The 1044 meV “Q Line”: The Li$_4$ V$_{Si}$ Centre

A discussion of this centre is included, even though it contains no TM, for two reasons. First, the properties of this centre have much in common with those of the previously discussed TM-containing IBE centres. Second, we believe that the structure, stability, and formation mechanisms of this centre are related to those of the TM centres, which are not yet fully understood. As shown later, Li can be a constituent in the TM-containing centres, which is perhaps not surprising given that both Li and TM are rapid interstitial diffusers in Si, and, being interstitials, are in a positive charge state. We speculate that the Li$_4$ V$_{Si}$ centre can be thought of as a member of the same family, where the V$_{Si}$ takes the place of a substitutional TM.

The 1044 meV PL centre was reported by Johnson et al. [85] and further investigated by Canham et al. [86, 87], who both concluded on the basis of temperature dependent, stress and isotope measurements that the “Q” lines at 1044, 1045, and 1048 meV thermalize with each other and are the electronic states of a centre with 4 Li atoms at a Si vacancy, with overall symmetry $C_{3v}$. In a subsequent study, DeLeo et al. [88] concluded that the Li atoms are likely situated in interstitial regions surrounding the vacancy, rather than placed in the vacancy itself. Lightowlers et al. [89] and Davies et al. [90] then confirmed previous experimental results, and found that decay time and Zeeman measurements indicate that the centre was a donor-like IBE. The properties of the Li$_4$ V$_{Si}$ centre were reviewed by Davies [8]. Later Tarnow [91] undertook ab initio calculations, and found that similar to earlier studies [88], the lowest energy ground state would have $T_d$ tetrahedral symmetry with the Li atoms sitting interstitially outside of the Si vacancy, while not excluding an axial $C_{3v}$ symmetry for the IBE state as observed in experiments.

It is interesting to note that although this centre contains Li, no high energy LVM replicas were observed, even though we will see that these do exist for Li-containing TM centres (see Sect. 4.3.4). The Li$_4$ V$_{Si}$ centre also has none of the very low energy pLVM replicas typical of the TM-containing IBE, which is perhaps easier to understand. The system does have some intermediate energy pLVM replicas, labelled $A$, $B$, and $C$ [92], whose energies remain unexplained.

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Transition-Metal Defects in Silicon
New Insights from Photoluminescence Studies of Highly
Enriched 28Si
Steger, M.
2013, XII, 97 p. 35 illus., 18 illus. in color., Hardcover
ISBN: 978-3-642-35078-8