Reduction of the Linewidths of Deep Luminescence Centers in ^{28}Si Reveals Fingerprints of the Isotope Constituents

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Dramatic reductions of the linewidths of well-known deep centers in ^{28}Si reveal "isotopic fingerprints" of the constituents. The ~1014 meV Cu center, thought to be either a Cu pair or an isolated Cu, is shown to contain four Cu atoms, and the ~780 meV Ag center is shown to contain four Ag. The ~944 meV *Cu center, thought to be a different configuration of a Cu pair, in fact contains three Cu and one Ag, and a new two-Cu two-Ag center is found. The ~735 meV center, previously assigned to Fe, actually contains Au and three Cu. This suggests a family of four-atom (Cu, Ag, Au) centers.

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Many deep defects in Si, including those associated with deleterious, rapidly diffusing contaminants such as Fe, Cu, Ag and Au, have been associated with photoluminescence (PL) centers [1–26]. The involvement of a given element in an optically active deep center can often be demonstrated by observing an isotope shift of the transition energy, but these shifts are normally small compared to the linewidths, and hence reveal nothing further [27]. The elimination of the inhomogeneous isotope broadening inherent in natural Si (^{nat}Si) by using highly enriched ^{28}Si has been shown to result in dramatic improvement in the linewidths of shallow bound exciton PL transitions [28–30] and impurity absorption transitions [30–32]. Here we show that the PL transitions associated with some well-known deep centers are also remarkably sharper in ^{28}Si than in ^{nat}Si, revealing well-resolved components for different combinations of impurity isotopes. These isotopic fingerprints yield surprising results regarding the defect constituents.

Heine and Henry [27] explained the isotope shifts of the energies of no-phonon (NP) optical transitions in terms of the mass dependence of the zero-point vibrational energies of the binding center constituents, together with the change in these energies resulting from the change in electronic charge density between the initial and final states. These shifts are very small, and while the shifts of replicas due to local vibrational modes (LVM) (used loosely here, regardless of the mode energy) are larger, in both cases the shifts are typically less than the observed linewidths. One exception was the NP transition of a center involving Li and a Si vacancy (V_{Si}), which due to the large relative mass difference between ^{6}Li and ^{7}Li showed resolved components for centers having different numbers of the two isotopes [33]. This resolved isotopic fingerprint allowed for the conclusive identification of this center as a Li$_4$ complex.

All of the results presented here use the same highly enriched (99.991%) ^{28}Si which has produced the narrowest linewidths in our previous studies [29,32,34,35]. Diffusions were carried out in quartz ampoules, sealed after evacuation and backfilling with Ar, using diffusion temperatures and times typical of those reported previously. Diffusants were either evaporated onto the sample or a small quantity was sealed in the ampoule with the sample. The diffusants were ^{nat}Cu (69.2% ^{63}Cu + 30.8% ^{65}Cu), 99.8% ^{63}Cu, 99.6% ^{65}Cu, ^{nat}Ag (51.8% ^{107}Ag + 48.2% ^{109}Ag), 99% ^{107}Ag, 99% ^{109}Ag, and ^{nat}Au (100% ^{197}Au). It should be noted that Cu was always detected due to the difficulty in eliminating trace Cu contamination. While this unintentional Cu accurately reflected the ^{nat}Cu abundances before enriched Cu diffusions were performed, it later showed slightly different ratios due to contamination of the furnace and quartzware.

The sealed ampoules were quenched into methanol, and the samples were then cleaned and etched in HF/HNO$_3$. In some cases the samples were later requenched directly into methanol after a quick heating to ~700 °C. A Bomem DA8 Fourier transform spectrometer was used to obtain the PL spectra with instrumental resolutions of up to 0.6 μeV. The samples were loosely held in superfluid helium at a temperature of 1.5 K. The PL spectra were collected using bulk excitation at 1047 nm and a liquid nitrogen cooled Ge photodetector. It should be noted that for all of the previously known centers studied here, the characteristic LVM structure was observed. The NP transition energies differ slightly from those in ^{nat}Si, which can be related to the difference in band gap energy [30].

We begin with the ubiquitous [1–3] Cu-related center, whose lowest energy NP line at $\sim$1014 meV was labeled Cu_0^0 by Weber *et al.* [2] in a comprehensive earlier study, which also introduced the idea that the center was a Cu pair. The pair model was bolstered by *ab initio* calculations of Cu_s-Cu_i pair properties [4], and the center is now often (but incorrectly) referred to as the "Cu pair center" [5,6], notwithstanding continuing arguments [7,8] that it is due to a single Cu. We have shown conclusively in a preliminary report [34] that the center in fact contains four Cu atoms (ignoring for simplicity the possibility of additional Cu which does not contribute to the isotope shift). We reproduce some of these results for the Cu_4 (Cu_0^0) center in Fig. 1, since all of the centers to be discussed later have strong similarities. Also, since this PL system is seen in all of the samples, it provides a convenient means of measuring the actual Cu isotope ratio in a given sample. The relative intensities of the $N = 0$ through 4 components (N is the number of ^{65}Cu) of both the ground state Γ_4 and the excited state Γ_3 transitions in this particular sample are very accurately predicted by the $^{\text{nat}}\text{Cu}$ isotopic ratio [34], since it was produced before any enriched Cu diffusions.

A related Cu-containing center with a NP line at $\sim$944 meV, labeled $^*\text{Cu}$, has been previously studied in $^{\text{nat}}\text{Si}$ [9,10], and was later argued to result from a different configuration of a Cu pair [11]. Our preliminary study of this center in ^{28}Si as a function of Cu isotopic composition found that it contains three Cu atoms, and revealed a further, unexplained $\sim$3.2 μeV doublet splitting of each component into two almost-equal subcomponents [35]. Ag is, like Cu, a rapid interstitial diffuser in the positive charge state, comes from the same column of the periodic table, and has almost equal natural abundances of its two isotopes, which suggested to us that the $^*\text{Cu}$ center might also contain Ag. We have now verified this by studying the center as a function of Ag isotopic composition, as shown on the right-hand side of Fig. 2. $^*\text{Cu}$ is thus convincingly shown to be a Cu_3Ag_1 center by its isotopic fingerprint versus Cu and Ag in ^{28}Si. The Cu isotopic composition for these samples, as determined from the Cu_4 PL, is $\sim$55% ^{63}Cu for the $^{\text{nat}}\text{Ag}$ sample and $\sim$62% ^{63}Cu for the two enriched Ag samples, which agrees well with the observed relative intensities of the $N = 0$ through 3 components of Cu_3Ag_1. The relative intensities of the "*a*" and "*b*" components in the $^{\text{nat}}\text{Ag}$ spectrum accurately reflects the natural abundance.

This immediately suggests that other centers of the form $\text{Cu}_x\text{Ag}_{4-x}$ might exist, and we have indeed found a new center in the same samples at $\sim$867 meV, shown on the left-hand side of Fig. 2. The triplet structure with respect to both the Cu and Ag isotopes reveals it to be a Cu_2Ag_2 center. The relative intensities of the $N = 0$ through 2 components (the number of ^{65}Cu) is in good agreement with the known Cu composition and the relative intensities of the "*a, b, c*" components (0, 1, and 2 ^{109}Ag, respectively) are accurately predicted from the Ag isotopic composition. The Cu_2Ag_2 PL was always weaker than the Cu_3Ag_1 PL, which in samples containing Ag could be comparable to the Cu_4 PL intensity. No Cu_1Ag_3 center was found in these samples.

The remaining possibility is an Ag_4 center, and Si diffused with Ag and quenched to room temperature is known

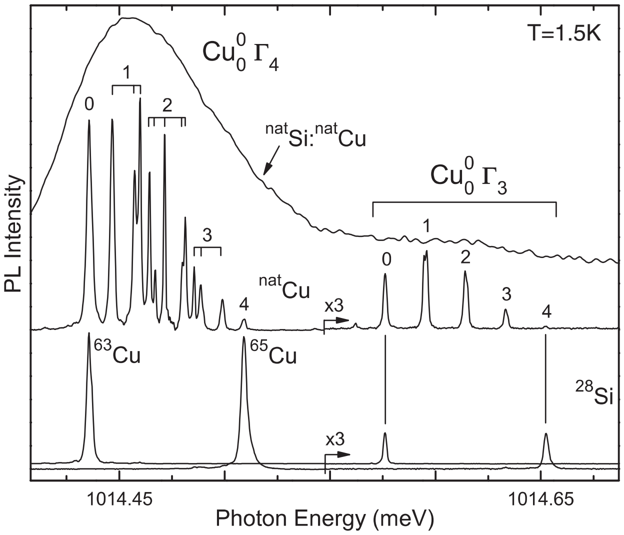

FIG. 1. The Cu_0^0 NP lines ($\sim$ 1014 meV) in $^{\text{nat}}\text{Si}$ diffused with $^{\text{nat}}\text{Cu}$ (top, down-shifted by 62 μeV for clarity) are compared with those in ^{28}Si samples diffused with either $^{\text{nat}}\text{Cu}$ (middle) or enriched ^{63}Cu or ^{65}Cu (bottom). $N = 0, \ldots, 4$ denotes the number of ^{65}Cu in the Cu_4 complex. Γ_4 is the ground state transition and Γ_3 is a low lying electronic excited state [2].

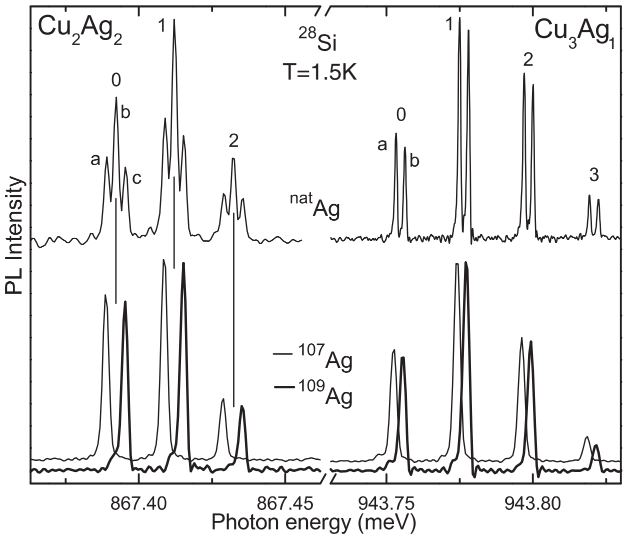

FIG. 2. NP lines of two centers in ^{28}Si containing Cu and either $^{\text{nat}}\text{Ag}$, ^{107}Ag, or ^{109}Ag. The higher energy center, previously labeled $^*\text{Cu}$ [9], is here labeled Cu_3Ag_1 since it is seen to contain one Ag atom and three Cu atoms. The lower energy Cu_2Ag_2 center is seen to contain two Ag and two Cu atoms. Labels $N = 0, \ldots, 3$ specify the number of ^{65}Cu in a given center, while "*a, b, c*" specify the number of ^{109}Ag, 0, 1, and 2, respectively.

to have a dominant PL center with NP lines at ~780 meV [12–15], which Son *et al.* [13] pointed out were also observed as the lowest-energy components of a deep donorlike spectrum seen in an earlier absorption study [16]. While there have been no definitive claims regarding the structure of this center, a single Ag$_s$ has been suggested [13,16], based on its expected properties [16], and the observed energy of the LVM has also been given as evidence for a single Ag [15]. We observe this same center as the most intense line in Ag-diffused ^{28}Si after quenching in the closed ampoule. As shown in Fig. 3, in ^{28}Si diffused with $^{\mathrm{nat}}$Ag, both the F_0 ground state and A excited state, as labeled by Davies *et al.* [15], split into five components, labeled "*a*" through "*e*," denoting from 0 to 4 ^{109}Ag in an Ag$_4$ center. The relative intensities of the "*a*" through "*e*" components are accurately predicted by the $^{\mathrm{nat}}$Ag isotopic abundance for the top spectrum, while the spectra for the enriched ^{107}Ag and ^{109}Ag samples are dominated by the "*a*" and "*e*" components, respectively, as expected. Thus the 780 meV Ag center [12–16] is conclusively shown to be an Ag$_4$ complex, very similar to the Cu$_4$ (Cu$^0_0$) center.

The Cu-Ag chemical trend leads us to Au, perhaps the most thoroughly studied deep metallic defect in Si. Au is known to have a PL system with NP lines at ~793 meV, which was suggested [18] to be associated with the deep Au donor studied in absorption [16,19]. The similarities between the 793 meV Au system and the 780 meV Ag system have been previously noted by Olajos *et al.* [16]. In addition to this deep donor system, Au is also associated with a deep acceptor, and Watkins *et al.* [19] have presented strong evidence that both systems arise from the same defect, and further argued that this defect was the isolated Au$_s$, based on its expected properties [17]. The similarities between the 780 meV Ag center and the 793 meV Au center, together with our discovery that the Ag center in fact contains four Ag atoms, suggests that the 793 meV Au center might be a Au$_4$ complex. Unfortunately, Au has only one stable isotope, ^{197}Au, and in addition we have been unable to make a sample with strong 793 meV PL, although we have seen the system in absorption. It may be that it is necessary to rigorously exclude other contaminants such as Cu in order to see a strong 793 meV PL system in Au-diffused Si.

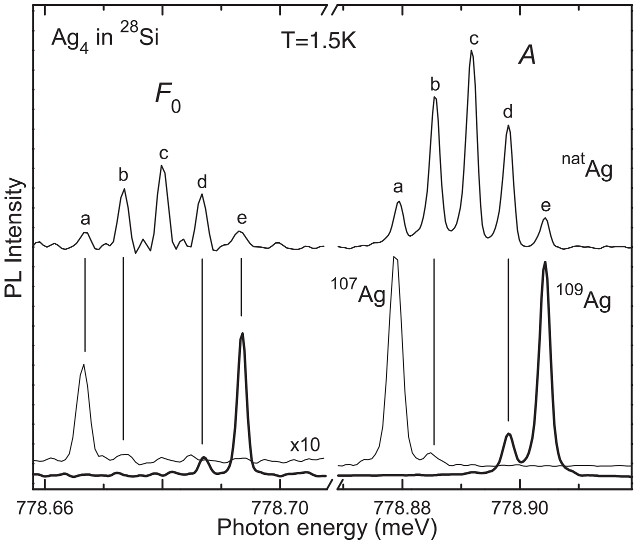

FIG. 3. NP lines of the ~780 meV Ag center in ^{28}Si. The electronic states are labeled F_0 and A as in previous $^{\mathrm{nat}}$Si results [15]. Labels "*a*" through "*e*" denote the number of ^{109}Ag, from 0 to 4, respectively, in the Ag$_4$ complex.

Our Au-diffused ^{28}Si samples had a dominant PL system with NP lines at ~735 meV, together with characteristic LVM replicas, which has been previously observed in $^{\mathrm{nat}}$Si but originally attributed to Fe [20–23]. The attribution to Fe was brought into some doubt by the absence of any observable Fe-isotope shift [24], and Au was later demonstrated to be a component of the 735 meV system by monitoring the intensity of the PL as unstable implanted ^{195}Au decayed into Pt [25,26]. As shown in Fig. 4, in ^{28}Si the isotopic fingerprint of the 735 meV system reveals that it contains three Cu atoms. While we have no direct evidence as to the number of Au atoms, the similarity to the Cu, Ag, and Cu + Ag centers strongly argues that the 735 meV center is in fact Cu$_3$Au$_1$. We were unable to observe Cu$_2$Au$_2$ or Cu$_1$Au$_3$ centers in our samples, but it is possible that the unintentional Cu contamination was simply too high.

The evidence to this point strongly suggests a family of four-atom centers where the constituents are chosen from Cu, Ag, and Au. It should be noted that all of the known members of this family (Cu$_4$, Cu$_3$Ag$_1$, Ag$_4$, Cu$_3$Ag$_1$, and

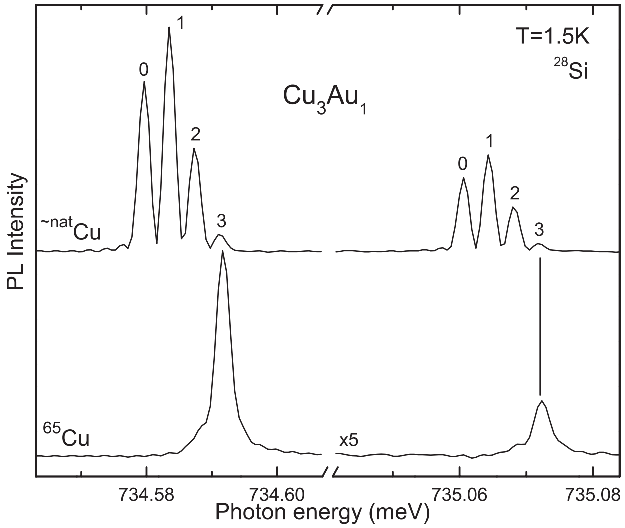

FIG. 4. NP lines of the ~735 meV Cu$_3$Au$_1$ complex, previously thought to be related to isolated Fe [20–23], are compared in ^{28}Si diffused with Au and Cu of either almost natural composition (top) or enriched ^{65}Cu (bottom). $N = 0, \ldots, 3$ specifies the number of ^{65}Cu atoms in the center. The left-hand and right-hand features come from the ground state and an electronic excited state [21].

possibly Au) have many similarities, including strong low energy LVM replicas, low symmetry (typically trigonal) with an ability to reorient at low temperature, and an electronic structure typical of that of a deep donor, or the closely related pseudodonor isoelectronic bound exciton. Much work needs to be done in understanding the properties of these four-atom complexes, and how they come to be ubiquitous in rapidly quenched Si containing a supersaturation of the constituent atoms. It should also be noted that, except for the low energy LVM replicas, many of these properties are shared by the previously investigated $V_{\mathrm{Si}} + \mathrm{Li}_4$ center [33] and that Li is also a rapid interstitial diffuser in a positive charge state. Possible structures for the $V_{\mathrm{Si}} + \mathrm{Li}_4$ center have already been investigated [36,37].

In understanding the properties of these centers, the values of the NP isotope shifts may be useful. Expressed in terms of a 1 amu change in the total mass of a given constituent, the Cu isotope shifts are (in μeV per amu) 9.3 for Cu_4, 11.0 for $\mathrm{Cu}_3\mathrm{Ag}_1$, 10.1 for $\mathrm{Cu}_2\mathrm{Ag}_2$, and 1.9 for $\mathrm{Cu}_3\mathrm{Au}_1$. The Ag isotope shifts are 1.5 for $\mathrm{Cu}_3\mathrm{Ag}_1$, 1.6 for $\mathrm{Cu}_2\mathrm{Ag}_2$, and 3.2 for Ag_4. The details of the characteristic LVM replicas of the different centers, and their isotope shifts, may also be helpful in understanding the defect structures. The Cu_4 (Ag_4) center has a single, dominant low energy LVM with energy of $\sim$7.0 meV ($\sim$ 5.8 meV), which shows almost the full isotope shift expected for motion of only the Cu (Ag). The 735 meV $\mathrm{Cu}_3\mathrm{Au}_1$ center, on the other hand, has two strong low energy LVM replicas [20–23], and we find that the higher energy LVM ($\sim$ 9.3 meV) has essentially the full expected Cu isotope shift, while the lower energy LVM ($\sim$ 7.3 meV) has essentially zero Cu isotope shift. Thus the former may involve predominantly motion of the three Cu atoms, while the latter involves Au.

In conclusion, isotopic fingerprints of supposedly well understood PL centers in highly enriched ^{28}Si have produced surprising results. Of the four known centers studied here, none is what it was earlier thought to be. These four centers, and the previously unknown $\mathrm{Cu}_2\mathrm{Ag}_2$ center, suggest a remarkably stable family of four-atom centers where the constituents are chosen from Cu, Ag, and Au. The nature of the 793 meV Au center remains an open question: isolated Au_s or the Au_4 member of this family? An isotopic fingerprint of the center might be obtained by combining stable ^{197}Au with implanted ^{195}Au, which has a sufficiently long half-life ($\sim$ 186 days) [25,26]. It would also be interesting to look for further members of the family of the form $\mathrm{Ag}_x\mathrm{Au}_{4-x}$, where the Ag isotope structure could be observed. These results suggest a number of future research directions, both experimental and theoretical, and may require a thorough reevaluation of our understanding of many deep centers in Si.

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