# New Class of Related Optical Defects in Silicon Implanted with the Noble Gases He, Ne, Ar, Kr, and Xe

N. Bürger, K. Thonke, and R. Sauer
*Physikalisches Institut, Universität Stuttgart, D-7000 Stuttgart 80, Federal Republic of Germany*

and

G. Pensl
*Institut für Angewandte Physik, Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany*
(Received 28 December 1983)

A unique class of electronic-vibronic photoluminescence spectra in silicon is observed exclusively after noble-gas ion implantation and partial annealing. Characteristic features are mass-dependent systematic line shifts, systematic behavior in the defect formation and annealing, and the common trigonal defect symmetry. The spectra are closely related with the previously studied $I_1$ (1.018-eV) spectrum emitted by an intrinsic lattice defect. It is concluded that the noble gases are incorporated into the intrinsic defect in an analogous way, constituting a class of related deep optical defects.

PACS numbers: 78.55.Ds, 71.35.+z, 71.55.Fr

A large variety of photoluminescence (PL) spectra in Si due to deep defects created by electron, neutron, or ion irradiation have been discovered and tentatively identified since about 1960.[1] Recent progress (such as the observation of isotopic line shifts) in a few cases have even allowed the development of specific microscopic defect models.[2-6] Referring to the present knowledge, all optical defects heretofore studied seem to be *entirely different*, having no common structural features.

In this Letter we present evidence for a class of similarly structured optically active defects in Si forming from an intrinsic lattice defect upon incorporation of the noble-gas atoms He, Ne, Ar, Kr, or Xe. The basic lattice defect, in turn, is a very common defect which has been observed in all sorts of silicon and after very different sample treatments although its true nature has not yet been positively identified. The possibility of systematically modifying the optical properties of this universal defect by known impurities is not only a new phenomenon but could also help to clarify the identity of the intrinsic defect.

The PL spectra in Fig. 1 were obtained—independent of the doping—from doped or undoped, *n*- or *p*-type silicon samples which were bombarded at room temperature with 350-keV noble-gas ions at doses of $10^{16}$ cm$^{-2}$. The spectra were recorded in annealing stages corresponding to the individual maxima of the intensities. They exhibit sharp no-phonon (NP) transitions ($He_0$, $Ne_0$,...), and many relatively sharp low-energy satellites (labels 1, 2,...) due to the coupling of localized defect vibrations. The sharp line structure is superimposed on two strong broad bands (displacement from NP lines at maximum intensities $\approx 18$ or $\approx 36$ meV) which we attribute to electronic-vibronic transitions involving one or two acoustic lattice phonons near the maximum of the phonon density of states. All vibronic lines (1–8) correspond to in-band quasilocal modes and possess about 3 times larger halfwidths than the local-mode line (9) corresponding to defect vibrations above the Raman frequency. The rich vibronic spectra are an unusual feature since deep irradiation-induced defects often couple strongly to only one or two distinct vibration modes in the optical spectra. (This is so, for instance, for the compact defects studied by Davies and do Carmo[3] or Thonke and co-workers.[4-6])

The ample vibronic structure of our spectra is an important issue as it is virtually identical with that of the long-known $I_1$ (or *W*, 1.0181-eV) luminescence spectrum (Fig. 1). This spectrum was previously investigated in several independent works[7-10]; it was found that the spectrum depended neither on the donor or acceptor doping of the starting material nor on the persistent impurities carbon or oxygen, and it was observed after high-energy neutron irradiation of Si,[7] after ion implantation (irrespective of the ion species) and thermal[8,10] or laser annealing,[11] or in neutron-transmutation–doped (NTD) unannealed Si regardless of the neutron dose and energy.[12] The underlying defect is obviously intrinsic and was tentatively identified[8,9] with the EPR Si-*P*1 center (a nonplanar five-vacancy cluster of $C_{1h}$ symmetry[13,14]) or recently, on the basis of a trigonal symmetry classification,[15] with the EPR Si-*A*3 center (a trigonal tetravacancy clus-

 

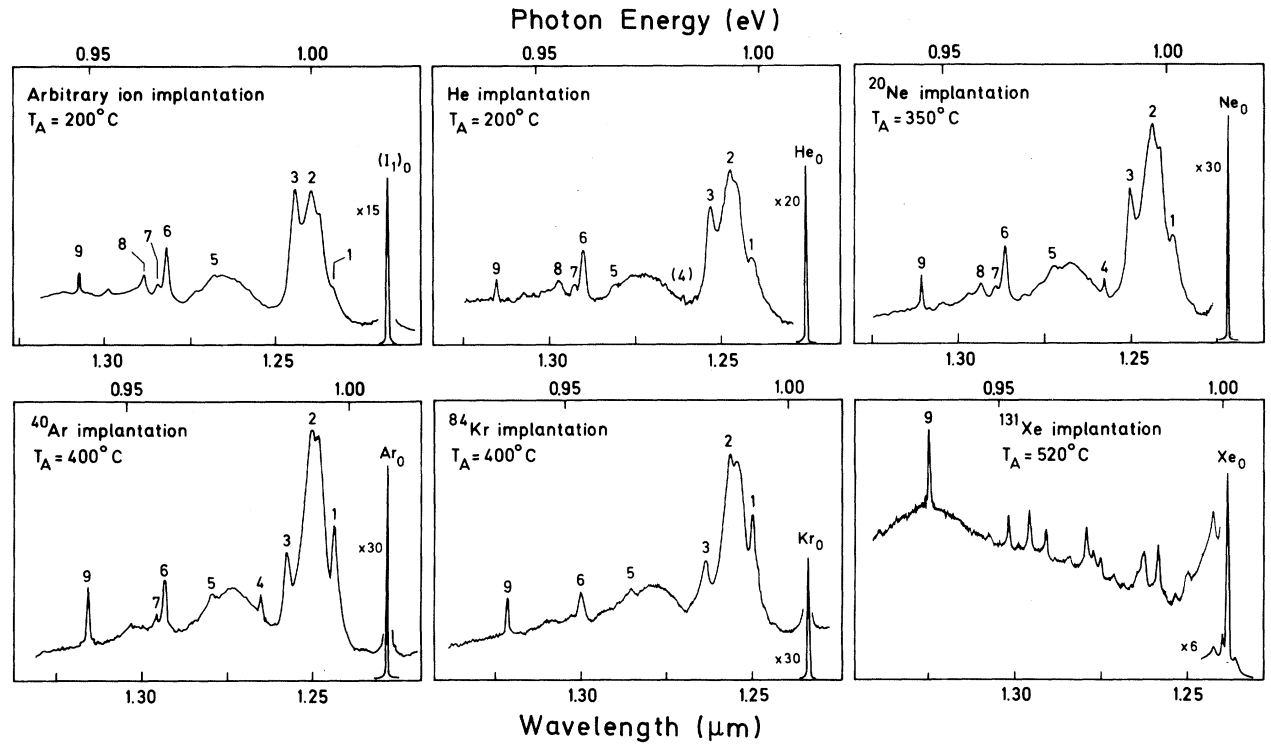


FIG. 1. PL spectra of the intrinsic lattice defect ($I_1$) and of the noble-gas defects. $He_0$, $Ne_0$,... are NP transitions; lines 1 through 9 are due to (quasi)localized defect vibrations. Upper scales denote photon energies (in electronvolts), and lower scales, wave-lengths (in micrometers). Resolution is $\Delta\lambda = 0.4$ nm.

ter[14]) or a ⟨111⟩ Si split interstitial.

We confirmed in our experiments the previously established impurity independence of the $I_1$ spectrum which we observed, e.g., in boron-implanted or unannealed NTD silicon. In contrast, the novel spectra need the implantation of the noble-gas ions to appear.[16] Once a noble gas is implanted, on annealing the samples we observe the $I_1$ line due to the ion-unspecific damage event. Dependent on the noble-gas species, the novel spectra emerge at similar temperatures (He, Ne) at the cost of $I_1$ or at higher anneal temperatures (Ar, Kr, see Fig. 2). The He spectrum virtually grows in with $I_1$ and is unstable beyond 300 °C; the Ne spectrum has a similar formation temperature and anneals out at 350 °C. The Ar and Kr defect formation is practically identical (allowing for experimental errors); and finally, the Xe spectrum grows in above 400 °C. Although there is no direct proof of the incorporation of the noble gases into the optical centers we made certain that we are not simply concerned with mass-dependent damage effects: Upon $^{28}$Si, $^{30}$Si, or $^{69}$Ga implantation we always observed the $I_1$ spectrum but never the novel spectra.

The spectral positions of the PL lines also exhibit systematic trends (Table I). The NP lines have lower energies for larger gas masses (provided the He and Ne cases are interchanged), the difference amounting to 18 meV from the "no-mass" $I_1$ spectrum to the Xe spectrum. In the same order of

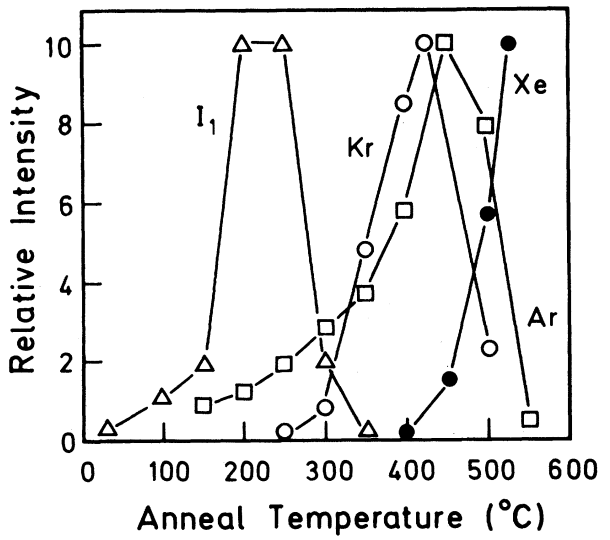


FIG. 2. Isochronal (1 h) annealing curves for $I_1$, Ar, Kr, and Xe defect spectra.

TABLE I. Spectroscopic data of $I_1$ and of noble-gas–induced defects. $E_{th}$ is the thermal deactivation energy of the NP line intensity. All values in millielectronvolts.

| | NP transition[a] | Half-width | Local mode energies[b] $E_{th}$ | Line 3 | Line 9 |
|---|---|---|---|---|---|
| $I_1$ | 1018.19 | 0.09 | 37 | 21.9 | 70.0 |
| He | 1011.76 | 0.15 | · · · | 22.4 | 69.4 |
| Ne | 1014.40 | 0.12 | · · · | 23.2 | 69.0 |
| Ar | 1009.32 | 0.12 | 21 | 23.7 | 67.2 |
| Kr | 1004.53 | 0.15 | 18 | 23.9 | 66.5 |
| Xe | 1000.78 | 0.24 | · · · | · · · | 66.0 |

[a] ±0.02 meV. [b] ±0.2 meV.

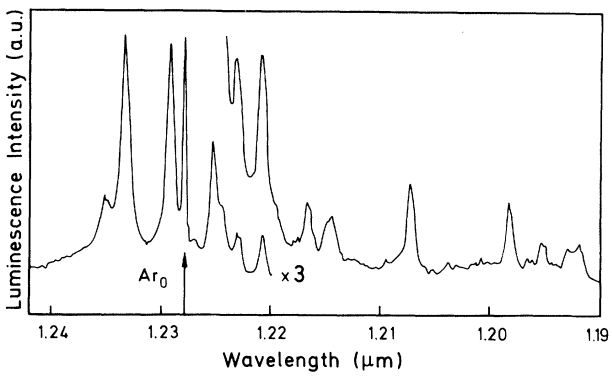


FIG. 3. "Out-anneal" spectrum of the Ar defect. All lines emerge *after* annealing at $T_A = 550\,^{\circ}C$. The arrow indicates the remainder of the original Ar no-phonon line.

atomic masses, the displacement energies from the corresponding NP transitions increase for the vibronic line 3 whereas they decrease for the vibronic line 9. The relative shifts of these lines are very much smaller than expected for a square-root mass dependence of a harmonic oscillator model. All other vibronic lines have identical mass-independent relative shifts within their experimental uncertainties ( ±0.2 MeV): line 1, 13.1 meV; line 2, 18.2 meV; line 5, 40.5 meV; line 6, 51.1 meV; line 7, 53.0 meV, and line 8, 56.2 meV. An exception are the lines 4 at about 29 meV shift which are not invariant and where Ne possibly exhibits an isotopic shift between $^{20}$Ne and $^{22}$Ne. Also, Xe exhibits a different general spectral structure but shares the systematics with respect to the NP line and line 9. Several other weak vibronic lines were observed in the present work but are not listed here. Line 9 shows no isotopic shift in the $I_1$ spectrum from selectively $^{13}$C-enriched material, demonstrating that it is not related to carbon which is known to be mainly responsible for vibronic line shifts of 71.9 meV ($^{12}$C) or 69.85 meV ($^{13}$C) in the $G$ (0.97-eV) defect spectrum.[3,4]

Applying uniaxial stress, Minaev, Mudryi, and Tkachev[15] have recently shown that the $I_1$ defect has trigonal symmetry and that the NP transition corresponds to a $\pi$ oscillator with the piezospectroscopic tensor element $A_1 = -0.04$ meV/GPa and $A_2 = 0.22$ meV/GPa. Our stress experiments (up to 0.5 GPa) are consistent with these data for $I_1$, and exhibit similar splittings of the Ar and Kr NP lines into one, two, or two components under ⟨100⟩, ⟨111⟩, or ⟨110⟩ stress, respectively. The splitting rates are nonlinear for stress $\gtrsim 0.2$ GPa. The analysis in the linear low-stress regime after Kaplyanskii[17] shows that we are in both cases concerned with $\pi$ oscillators ($A \rightarrow A$ transitions) in trigonal symmetry with the parameters $A_1 \approx 0$, $A_2 = 1.48$ (Ar) and $A_1 = -0.30$, $A_2 = 0.90$ (Kr) in units of millielectronvolts per gigapascal. For Ne, only the ⟨111⟩ direction was studied, where the line splits twofold and a trigonal symmetry classification yields $A_1 = 0.9$ meV/GPa and $A_2 = 1.35$ meV/GPa. Apart from the same trigonal symmetry of the $I_1$, Ar, and Kr (and probably Ne) defects, these stress parameters are similar in that $A_1$ is always much lower than $A_2$. We note that Zeeman measurements were also performed on all NP lines except for Xe and no splitting or line broadening was exhibited up to field strengths of 5.3 T.

Finally, we have observed that many new lines emerge in the same spectral range when the noble-gas spectra are annealed out. Part of the "out-anneal" spectrum associated with Ar is shown in Fig. 3. All new lines are considerably broader than the original NP transition. Some of the lines are *independent* of the implanted gas species since they appear likewise in the "out-anneal" spectra of Kr, Ar, or Ne.

The photoluminescence data presented give evidence that the noble gases form defects which are very similar to each other and are, in turn, similar to the basic intrinsic $I_1$ lattice defect. They modify the electronic properties of this defect slightly and do not alter its symmetry. This suggests that the observed spectral variations are mostly due to mass and size effects of the noble gases and that their binding to the intrinsic defect is related to their closed-shell electron configuration. The intrinsic defect has been ascribed to the extended pentavacancy or tetravacancy clusters.[8,9,15] Indications exist in our PL spectra that all present defects are larger aggregations. First, the rich vibronic side-

band structure could be the consequence of the unusual complexity of the defects and could explain that some of the modes reveal mass-dependent shifts whereas others have constant energies. Second, the "out-anneal" spectra indicate that fractional defects begin to luminesce when the original centers are broken up and that part of them can form from *any* of the noble-gas precursors. If a multivacancy model applies for $I_1$ one could imagine that the noble-gas atoms simply occupy those vacancy sites which leave the symmetry invariant; however, such speculations need further experimental substantiation.

We are indebted to Professor G. Watkins (Lehigh University, Bethlehem, Pa.) for the gift of a $^{13}C$-enriched silicon crystal and for helpful discussions. The financial support of the Deutsche Forschungsgemeinschaft under Contract No. Sa 311/2 is gratefully acknowledged.

[1]See, e.g., the survey by R. Sauer and J. Weber, Physica (Utrecht) **116B**, 195 (1983).

[2]L. Canham, G. Davies, E. C. Lightowlers, and G. W. Blakemore, Physica (Utrecht) **117&118B**, 119 (1983).

[3]G. Davies and M. C. do Carmo, J. Phys. C **14**, L687 (1981).

[4]K. Thonke, H. Klemisch, J. Weber, and R. Sauer, Phys. Rev. B **24**, 5874 (1981).

[5]K. P. O'Donnell, K. M. Lee, and G. D. Watkins, Physica (Utrecht) **116B**, 258 (1983).

[6]K. Thonke, J. Weber, J. Wagner, and R. Sauer, Physica (Utrecht) **116B**, 252 (1983).

[7]A. V. Mudryi and A. V. Yukhnevich, Fiz. Tekh. Poluprovodn. **8**, 1351 (1974) [Sov. Phys. Semicond. **8**, 875 (1975)].

[8]C. G. Kirkpatrick, J. R. Noonan, and B. G. Streetman, Radiat. Eff. **30**, 97 (1976), and earlier references therein.

[9]V. D. Tkachev and A. V. Mudryi, in *Radiation Effects in Semiconductors 1976,* edited by N. B. Urli and J. W. Corbett, IOP Conference Proceedings No. 31 (Institute of Physics, London, 1977), p. 231.

[10]V. D. Tkachev, C. Schrodel, and A. V. Mudryi, Radiat. Eff. **49**, 133 (1980).

[11]M. S. Skolnick, A. G. Cullis, and H. C. Webber, J. Lumin. **24/25**, 39 (1981), and further references therein.

[12]M. Tajima, in *Neutron Transmutation Doped Silicon,* edited J. Guldberg (Plenum, New York, 1981).

[13]Y. H. Lee and J. W. Corbett, Phys. Rev. B **8**, 2810 (1973).

[14]Y. H. Lee and J. W. Corbett, Phys. Rev. B **9**, 4351 (1974).

[15]N. S. Minaev, A. V. Mudryi, and V. D. Tkachev, Phys. Status. Solidi (b) **108**, K89 (1981).

[16]A spectrum with NP transition at 1.010 eV which appears after Ar implantation and anneals out near 500 °C was briefly mentioned in Ref. 8.

[17]A. A. Kaplyanskii, Opt. Spectrosc. **16**, 329 (1964).