Violation of selection rules for parity-forbidden optical intracenter transitions in crystalline silicon: substitutional versus interstitial defects

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Binding energy of excited even-parity states of hydrogen-like impurities in silicon (Si) are of critical importance for understanding of the state coherency and the rates of electronic nonradiative decay. Infrared absorption spectroscopy, the main analytical technique for determination of impurity content in doped semiconductors, returns data on binding energy of odd-parity excited impurity states (p-, f-, h- types) due to dipole-allowed intracenter transitions of electrons bound to the 1s ground state, conventionally observed at low lattice temperatures, while optical transitions into the even-parity excited states (s-, d-, g- types) (Fig. 1) have vanishing strengths due parity selection rules.

Different defects in crystals cause lattice distortion that may violate selection rules and affect the probability of particular intracenter optical transitions of conventional substitutional donors. Perturbations due to large concentration of donors enhance, in principle, all parity-forbidden atomic transitions, which becomes significant, however, only at the densities approaching the Mott transition value, and by this - exhibits too large line' broadening which prohibits spectral resolution of optical transitions at close photon energies.

Substitutional residual carbon in silicon at similar concentrations induces weaker broadening of donor lines at moderate densities and enables resolution of several parity-forbidden intracenter transitions, namely into 1s (Fig. 1), 2s, 3s, $3d_0$, $3d_\pm$ states using conventional, low-temperature infrared absorption spectroscopy of bulk Si crystals doped by substitutional, hydrogen-like group-V and also by interstitial group-Ia donor centers. The results show unambiguous correlation of the enhancement of detected parity-forbidden transitions with substitutional carbon. In contrast, no such enhancement has been observed due to interstitial oxygen, up to 7×10^{17} cm^{-3}. The best trade-off concentrations of defects providing the largest transition' intensity contrast together with the necessary spectral resolution of impurity lines is $(3\text{-}7)\times10^{15}$ cm^{-3} for a dominant donor and $(1\text{-}3)\times10^{16}$ cm^{-3} for carbon [1, 2].

The experimental binding energy of excited s-, d- states made corrections to the most of known energies of even-parity excited states, which were derived by other analytical techniques (photoluminescence, Raman spectroscopy) or from absorption spectroscopy of heavily-doped *n*-Si [3]. Several excited even-parity states were resolved for the first time. The derived values for 1s, 2s, $3d_0$ states fit well to theoretical predictions on a base of the effective-mass approximation [4] while those for $3d_\pm$ states are in a close vicinity to the theory with prolate ellipsoid conduction band valleys [5].

Other lattice defects, such as in polycrystalline Cz-Si and in neutron transmutation doped FZ-Si, also exhibit enhancement of intracenter transitions into the excited s-states, but it is less useful for determination of their binding energies because of inherent, strong line broadening.

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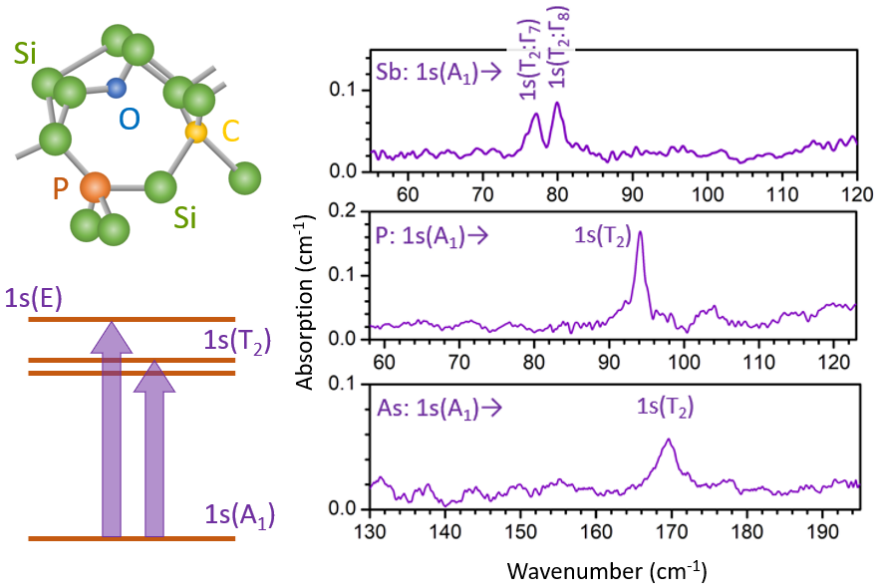

Fig. 1. Parity-forbidden 1s→1s intracenter optical transitions (e.g. as schematically shown on the left panel) becomes detectable in the low-temperature infrared absorption spectra (right panel) of moderately doped *n*-Si with concentrations of substitutional carbon about 10^{16} cm^{-3}.