

Evidence for a New Class of Defects in Highly *n*-doped Si: Donor-pair-vacancy-interstitials

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 Beamline(s): X15B

Significant progress has been made towards understanding the fundamental barriers to creating the highest possible free-carrier concentrations in *n*-type Si. Earlier x-ray absorption and theoretical work [1] had proposed donor-pair (DP) defects over previously accepted Sb_3V or Sb_4V defects containing 3 or 4 Sb atoms with a vacancy [2]. Recent scanning transmission electron microscopy (STEM) measurements from individual Sb dopant atoms and clusters in Si [3] confirmed that work, finding that the dominant electrically deactivating defects do contain *two* Sb atoms. The STEM measurements lacked sufficient resolution, however, to rule out the possibility of Sb_2V complexes, so different STEM experiments were performed to make defect identification more clear-cut.

By detecting channeled electrons at low and high collection angles simultaneously, the new data were able to show that the Sb atoms associated with deactivating defects are *incompatible* with *either* Sb_2V or DP(2) configurations (see figure). More extensive calculations were performed to explore other configurations, and a new class of defects was uncovered. We call them *donor-pair-vacancy-interstitials* to suggest a hybrid of DP and Frenkel-pair (i.e., vacancy-interstitial) defects, but there are important differences from each type. Unlike the Frenkel pairs generally found in ionic crystals, these are formed in doped semiconductors with the interstitial Si atoms remaining localized near their own vacancy. The DP(2)V-I complex, like the DP(2) and Sb_2V defect, is overall neutral and contains 2 Sb atoms that capture 2 free electrons, but now only one of the Sb atoms is itself neutral and 3-fold coordinated; the other is formally ionized (+1) and coordinated to a negatively charged Si interstitial. Most significantly, the DP(2)V-I formation energy is ~35% and ~50% lower than that for DP(2) and Sb_2V . Other defects in this class with comparably low formation energies are DP(4)V-I and DP(3)V-I (each has 2 Sb atoms but in different Si sites). That these formation energies are so low implies that *Fermi-level pinning from DP(*n*)V-I defects represents the dominant electrical saturation mechanism* as the free-carrier concentration (and thus E_F) increases. Similar conclusions apply to the other Group V dopants, P and As. The new defects not only account for the recent STEM results from Si:Sb, but they explain a number of other measurements from highly *n*-doped Si that had indicated the presence of vacancy-related defects yet were unable to reconcile the prohibitive energies needed to form them. Importantly, the x-ray absorption data used initially to rule out Sb_3V/Sb_4V clusters and point out the need for different structures are found to be consistent with DP(*n*)V-I defects.

[1] D. J. Chadi, P. H. Citrin, D. L. Adler, M. A. Marcus, and H.-J. Gossmann, "Fermi-Level-Pinning Defects in Highly *n*-doped Silicon", *Phys. Rev. Lett.* **79**, 4834 (1997).

[2] K. C. Pandey, A. Erbil, G. S. Cargill, III, R. F. Boehme, and D. Vanderbilt, "Annealing of Heavily Arsenic-Doped Silicon: Electrical Deactivation and a New Defect Complex", *Phys. Rev. Lett.* **61**, 1282 (1988).

[3] P. M. Voyles, D.A. Muller, J. L. Grazul, P. H. Citrin, and H.-J. Gossmann, "Atomic-Scale Imaging of Individual Dopant Atoms and Clusters in Highly *n*-type Bulk Si", *Nature* **416**, 826 (2002).

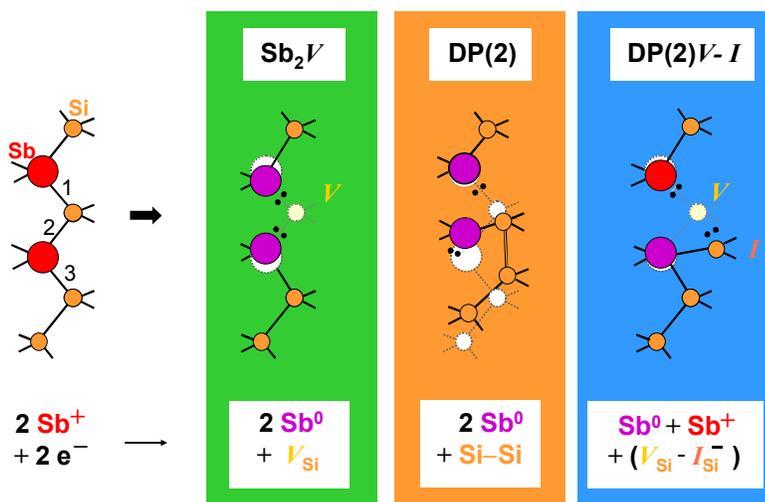


Fig. 1. Three Types of Sb-pair Defects in Si. A pair of dopant donor Sb atoms (left) reconfigure their structure and recapture 2 free electrons from the conduction band by either (a) breaking bonds 1 and 2 and forming a Si vacancy complex, Sb_2V , (b) breaking bonds 1 and 3 and forming a new Si-Si bond in a donor-pair complex, DP(2), or (c) breaking bond 1 and forming a donor-pair-vacancy-interstitial, DP(2)V-I.