Fermi-Level-Pinning Defects in Highly *n*-Doped Silicon

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Based on first-principles calculations and analysis of x-ray absorption measurements, an unconventional mechanism is proposed for the saturation of carriers in highly *n*-doped Si. The mechanism is Fermi-level pinning from a new class of defect centers containing two separated but interacting dopant atoms with no associated Si vacancies. The number of such centers increases sharply at high doping levels. A simple model provides very good agreement with the maximum carrier concentrations observed in Si. [S0031-9007(97)04827-8]

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A fundamental factor in the evolution of increasingly small Si-based components is the maximum achievable free-carrier concentration [1]. Electron carrier densities in *n*-type Si, doped either by implantation [2] or molecular beam epitaxy [3,4], are typically found to saturate at $\lesssim 5 \times 10^{20}$ cm^{-3}. The observed saturation arises not from the dopant (d) atom's solubility limit in Si, which is generally well below the concentration of the nonequilibrium-deposited dopants [5,6], but rather from the formation of inactive clusters or deactivating defects that trap free carriers. While there is presently no consensus on the detailed nature of these dopant complexes, all of those considered thus far fall into one of two categories: precipitates, d_m [2,5,7,8], or defects containing one or more Si vacancies (V), $d_m V_n$ [2,9–12]. Direct evidence for electrically inactive precipitates has been found, e.g., in highly Sb-doped Si samples ($>5 \times 10^{20}$ cm^{-3}) that have been annealed at elevated temperatures (>800 °C) [4,8]. Dopant-vacancy defects are more difficult to identify unambiguously, but their presence in highly As- and Sb-doped Si has been inferred in interpreting a variety of Mössbauer [2,13], positron annihilation [14,15], and extended x-ray fine structure (EXAFS) [10,16,17] measurements, which suggest either a lowered coordination of Si atoms with, or an increased volume around, these dopant donors.

The inference that $d_m V_n$ defects are important deactivating centers in these systems seems well motivated. A donor-vacancy complex provides a natural mechanism for trapping carriers in Si, because it allows a group V donor atom in a fourfold-coordinated substitutional site to revert to its natural threefold-coordinated *neutral* state. Furthermore, theoretical studies [10,12] show that such donor-vacancy defects become more favorable as the number of dopants in the complex increase. For example, formation energies for V, AsV, As$_2V$, As$_3V$, and As$_4V$ are, respectively, 3.8, 2.5, 0.8, -0.5, and -2.4 eV [12]. Finally, such defects offer a ready explanation for the enhanced impurity diffusion observed in Si at high doping levels [18].

Why, then, should the general importance of dopant-vacancy complexes be questioned? Formation energetics alone [12] cannot explain carrier saturation: Since deactivating d_3V and d_4V defects are thermodynamically favored over electrically active complexes containing no vacancies, the most energetically stable samples would therefore be fully *deactivated* at very *low* doping levels, in clear contradiction with persistently active samples that have been annealed for long time periods at elevated temperatures [5]. To reconcile these inconsistencies, kinetic processes are generally invoked [12], but this too leads to difficulties: Since complexes with 1 or 2 dopants are endothermic while those with 3 or 4 are exothermic, the formation of the latter should be sensitive to initial dopant concentrations and to sample annealing times, *neither* of which are experimentally observed [6,19]. Moreover, as shown below, a detailed analysis of EXAFS data from highly Sb-doped Si shows that Sb$_4V$ is, in fact, clearly *not* the dominant defect responsible for the observed electrical deactivation.

In this Letter, we propose an alternative explanation for carrier saturation in highly *n*-doped Si, which involves a class of defects containing *pairs* of separated dopant atoms *without* vacancies. The new defects exist in either a stable electrically active 2+ charge state that donates electrons to the conduction band or a metastable neutral charge state that captures two electrons from the Fermi sea. In the neutral trap state, each dopant atom is threefold coordinated and the relaxation of the neighboring Si atoms creates an increased volume, consistent with experimental observations [2,10,13–17]. As the energy of the electrons at the Fermi level increases with doping, it becomes energetically favorable to deform the lattice and create localized states instead of continuing to add electrons at the Fermi level.

The suggestion of defects that pin the Fermi level in Si is quite surprising. The conduction band minimum (CBM) near the X point of the Brillouin zone in Si has a sixfold degeneracy and a relatively large effective density-of-states mass [20], two factors which tend to suppress the rise in Fermi level with doping. Near the maximum free-electron density of $\lesssim 5 \times 10^{20}$ cm^{-3}, the Fermi level lies only about 0.2 eV above the energy of the Si CBM, so

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the formation energy of a compensating center must be small, i.e., $\lesssim 0.2$ eV. For comparison, the Fermi level in GaAs lies about 0.3 eV above the CBM at a much lower free-electron density of 2×10^{19} cm^{-3}. Since the Si-Si bond energy of 2.35 eV is significantly larger than the 1.7 eV value in GaAs, with correspondingly larger shear elastic coefficients, it would appear that forming defects with large lattice relaxations is more energetically costly and unlikely in Si. Indeed, *DX*-like centers (similar to those in GaAs) containing a single dopant atom are found to be unstable in Si, but deactivating centers can still be formed with low energy once the interaction between two nearby donor atoms is considered.

The electronic properties of group V dopants in Si were examined with *ab initio* pseudopotential calculations in the local density approximation [21]. Brillouin-zone sampling of three-dimensionally periodic unit cells containing 64 atoms was done by averaging zone center and zone boundary results [22]. Kleinman-Bylander-type separable potentials [23] and Troullier-Martins pseudopotentials [24] were used along with a 12-16 Ry energy cutoff for the plane wave expansions. Calculations with this approach for unit cells containing one substitutional dopant atom per cell gave Sb- and As-Si bond lengths in excellent agreement with present and previous [8,10] EXAFS results from correspondingly low-doped Si samples.

The identity of the most important deactivating center(s) in Si doped with P, As, and Sb was initially explored through calculations of defect structures containing isolated or clustered dopant atoms in substitutional or interstitial sites and coordinated to 0, 1, or 2 neighboring vacancies. Consistent with previous work on these structures [12], precipitates d_m and complexes $d_m V$ with $m \geq 3$ were found to have exothermic formation energies (we found $d_m V_2$, with $m \geq 4$, to be exothermic, too). The difficulties encountered with considering only these types of complexes, as discussed above, motivated exploration of other, more unconventional structures along the lines of recent studies involving defects with significant lattice relaxations [25]. Our search also included structures with 2 dopants per 64-atom cell (corresponding to an equivalent bulk concentration of $\sim 1.6 \times 10^{21}$ cm^{-3}) because the saturation of carriers in Si occurs at relatively high doping levels.

In the absence of precipitates or vacancies, the defect structures found to have the lowest formation energies in Si are schematically illustrated in Fig. 1 for the case of Sb dopants. They belong to a general class of donor-pair (DP) defects in which two nearby donor-atom–Si bonds are broken and a new Si-Si bond is formed [26]. The DP(4) and DP(2) defects in Figs. 1(a) and 1(b), denoting fourth- and second-neighbor separations between two donors as seen along the Si⟨110⟩ direction, have different structures with similar features and properties. Both involve large lattice relaxation, forming five- and seven-membered Si rings in DP(2) and three-membered rings in DP(4). Each

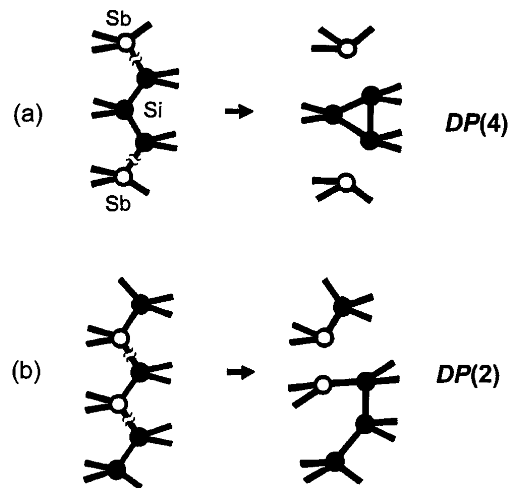

FIG. 1. Schematic picture of two types of donor-pair (DP) defect structures in Si (right), shown here forming from Sb dopants separated at (a) fourth-neighbor distances, and (b) second-neighbor distances, as measured along the ⟨110⟩ direction in ideal Si (left). The two Sb atoms in DP(2) are above and below the (110) plane.

of the two *d* atoms in both defect structures are threefold coordinated and thus are neutral.

Before discussing the energetics and other features of these defects, it is important first to determine whether such unusual structures are even compatible with experiment. Figure 2 displays the Fourier transforms (FT) of Sb L_3-edge EXAFS data from representative Si samples

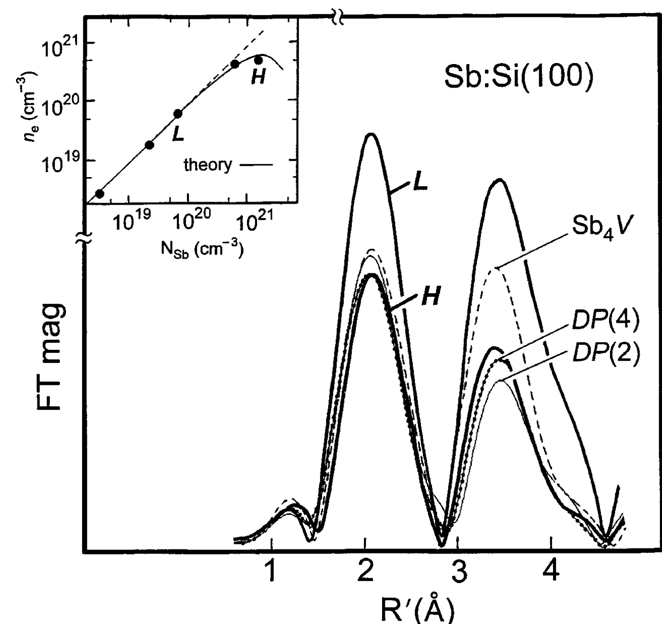

FIG. 2. Fourier transformed Sb L_3-edge EXAFS data (uncorrected for phase shifts) from Si doped with two different concentrations of Sb, and simulated data containing three different types of defects (see text). Inset: Electrical activity of Sb-doped Si as a function of Sb concentration (points). Solid curve labeled “theory” is from Eq. (1).

doped with "low" and "high" concentrations of Sb, labeled L and H. The data, measured at ~50 K to minimize effects of thermal disorder [27], were obtained with fluorescence-yield detection using the Bell Laboratories X15B beam line [28] at the NSLS. The samples were grown by low-temperature molecular beam epitaxy (LT-MBE) [3] with Sb concentrations, N_{Sb}, of 7×10^{19} and 1.5×10^{21} cm^{-3}, and had corresponding electrical activities (i.e., carrier concentration, n_e, divided by N_{Sb}) of approximately 1.0 and 0.35 (see inset).

Analysis of data from sample L using AlSb as a model compound [27,29] indicates substitutional occupancy of Sb with first-, second-, and third-neighbor Sb-Si distances of 2.58(2), 3.86(4), and 4.50(4) Å [30], in agreement with previous work [8]. The FT data from both samples exhibit no signs of a peak corresponding to a Sb-Sb first-neighbor distance of ~2.9 Å. This is consistent with transmission-electron microscopy studies of these and similarly prepared [4] samples, which show no evidence for Sb precipitates in as-grown LT-MBE Si, even at doping levels of ~3×10^{21} cm^{-3}.

The large decrease in EXAFS amplitudes with increasing Sb concentration is reflected in the FT peak intensities, and has been observed in a variety of differently prepared Sb- and As-doped Si samples [7,8,10,16,17]. The reduced EXAFS amplitudes can arise from a reduced coordination of Si atoms and/or different, destructively interfering Sb-Si (and other Sb-Sb) distances in defects which coexist with the substitutional Sb configuration. Previous analyses of EXAFS data considered d_2V [7], d_4V [10], or dV_2 [17] structures with the relative concentrations of the components, their coordinations, and their Debye-Waller-like (DW) factors left as variable parameters and with their atomic positions in assumed configurations. However, even knowing the equilibrium (i.e., relaxed) geometries of the defect structures, it is still difficult to determine unambiguous structural information from such data because the parameter correlations are so strong. Our approach, therefore, is simply to test for consistency between the experimental data from sample H and sets of simulated data using the known calculated structures for the lowest-energy deactivating defects.

The simulated H data are constructed as follows. Sample L, which shows complete electrical activation, is taken as a model for pure (donor) substitutional occupation. Electrically neutral defects such as Sb_4V and DP contribute to deactivation by effectively decreasing the number of available donor Sb atoms. Data from sample L is thus combined with that from a given calculated defect in a ratio that conserves both the measured total Sb and measured total free-carrier concentrations [31]. For simplicity, the DW factor for each defect structure is kept the same as in sample L, so the simulations have no adjustable parameters.

In Fig. 2, the experimental H data are compared with three sets of simulated data corresponding to deactivation from the most energetically stable vacancy-dopant complex, Sb_4V, and the two lowest energy donor-pair defects, DP(4) and DP(2). These three complexes each reduce the magnitude of the first-neighbor Sb-Si FT peak by comparable amounts, but show clear differences in their effect on the overlapping second- and third-shell peaks. This result, which is relatively insensitive to physically plausible variations in the DW factor for these higher-neighbor shells, demonstrates that the observed electrical deactivation in the highly Sb doped Si sample cannot arise primarily from Sb_4V defects. It also shows that the DP(4) and DP(2) defects, despite their unusual structure, are indeed compatible with the data (if we include contributions from small amounts of Sb_4V, which is certainly possible, the agreement would be improved).

Electrical deactivation at a DP site can be represented by $2d^+ + 2e^- \rightarrow \mathrm{DP}^0$, where d^+ is a donor atom in a fourfold-coordinated, electrically active state. Singly or doubly positive charged DP(4) and DP(2) states are found to be energetically unstable, and they relax back to their d^+ configurations. At high doping levels, the two-donor, two-electron DP state effectively acts as a negative-U defect with the structural appearance of two coupled, interacting DX centers. At low doping levels, when the Fermi energy is near the CBM, the formation of the DP(4) and DP(2) states for Sb is endothermic by 0.10(3) and 0.13(3) eV per donor electron, respectively. For P and As, the corresponding energies are 0.17(3) and 0.06(3) eV. Two factors contribute to the relatively low energy of these DP states: (1) the formation of a new Si-Si bond as two Si–donor-atom bonds are broken [analogous to the energy lowering of the Si(100) surface by forming a Si-Si dimer bond in the 2×1 reconstruction [32]], and (2) the natural tendency of group V dopants to be threefold coordinated. In a related but different manner, the strain energy of the three-membered ring in the DP(4) center is offset by the dativelike bonding between the lone-pair orbital of each donor atom and the antibonding orbital of a Si-ring atom. The already low formation energies of both DP states become lower still as the Fermi level rises and the energy of the free electrons increases. At high doping levels, carrier saturation occurs when electrons at the Fermi level become energetically degenerate with the DP state(s). The rise in Fermi level and the increased probability for finding donor-atom pairs at distances needed to create DP states each contributes to the electrical deactivation process at high doping concentrations.

It is possible to obtain reasonable estimates of the maximum free-carrier density and other doping characteristics in Si from the above picture of DP defects. A substitutional dopant atom in Si has 24 possible locations for a second dopant to form either a DP(4) or DP(2) defect. There are also four first-neighbor sites that lead to electrically inactive dimers, giving a total of 28 sites that must not be occupied by a second dopant atom in order for both to remain electrically active. The probability for dopant atoms of concentration N_d to occupy any of the N_0 lattice sites in Si (with density 5.0×10^{22} cm^{-3}) is N_d/N_0. If the

donor dopants are distributed *randomly* and the formation energies of the DP states are less than or equal to the ideal (fully activated) Fermi level, then the free-electron density would be given by

$$n_e = N_d(1 - N_d/N_0)^{28}. \quad (1)$$

Maximizing n_e with respect to N_d gives $[n_e]_{\max}$ when $[N_d]_{\max} = N_0/29 \approx 1.7 \times 10^{21}$ cm^{-3}, or $[n_e]_{\max} \approx (0.013)N_0 \approx 6.5 \times 10^{20}$ cm^{-3}. This is very close to the value of $\sim 5.5 \times 10^{20}$ cm^{-3} observed in sample H. Equation (1) applies when electrons at E_F are degenerate with the formation energies of the DP(4) and DP(2) states; in Sb-doped Si, these energies ($\sim$0.10–0.13 eV) correspond to free-electron densities (or, equivalently, Sb concentrations) greater than $(\sim 1-3) \times 10^{20}$ cm^{-3}. As shown in the Fig. 2 inset, the doping behavior calculated with Eq. (1) agrees very well with experiment [33].

The proposed DP structures and carrier-saturation mechanism in Si find additional support in other types of experimental data as well. Reports of at least two defects in highly As-doped Si with very different barriers for electron capture, one being 1.6–2 eV [5,6], are consistent with calculated capture barriers in As-doped Si of 0.6(2) eV for the DP(4) state and 1.6(3) eV for the DP(2) state (both values are lowered by $2E_F$). Thermodynamic data from As-doped Si, which show that the dominant deactivating complexes contain between 1.7 and 2.8 dopant atoms [5], are also compatible with the composition of these DP states. Finally, the open volume associated with the structure of defects in highly Sb-doped Si, which had been attributed to vacancies in the interpretation of Mössbauer [2,13] and positron annihilation [14,15] data, can instead be explained by the open volume created from the sizable lattice relaxation in the DP(4) and DP(2) structures.

On the basis of the above results, we conclude that DP defects represent an inherent limitation to the electrical activity of Si doped with group V donors. That is, while additionally deactivating vacancy-dopant complexes and/or inactive precipitates may also be formed in amounts that depend on sample preparation conditions (e.g., annealing temperatures and rates), deactivating DP defects in such highly n-doped Si will always be created—even under the best of circumstances—because these centers result only from the mutual interaction between nearby dopants occupying substitutional sites. It remains to be shown whether analogous defects involving other types of donor, or even acceptor, atoms are as important as the group V dopants in Si.

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