Highly *n*-doped silicon: Deactivating defects of donors

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We report insight into the deactivation mechanisms of group V donors in heavily doped silicon. Based on our *ab initio* calculations, we suggest a three step model for the donor deactivation. In highly *n*-type Si grown at low temperatures, in the absence of excess native point defects, the intrinsic limit to n_e seems to rise in part by means of *donor deactivating distortions* of the silicon lattice in the proximity of two or more donor atoms that share close sites. Also, donor dimers play an important part in the deactivation at high doping concentrations. While the dimers constitute a stable or metastable inactive donor configuration, the lattice distortions lower the donor levels gradually below the impurity band in degenerate silicon. On the other hand, we find that, in general, none of the earlier proposed deactivating donor pair defects is stable at any position of the Fermi level. The lattice distortions may be viewed as a precursor to Frenkel pair generation and donor-vacancy clustering process (step 2) that account for deactivation at elevated temperature and longer annealing times. Ultimately, and most prominently in the case of the large Sb atoms, precipitation of the donor atoms may set in as the last step of the deactivation process chain.

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I. INTRODUCTION

Future generations of silicon-based integrated circuit technology require carrier concentrations in excess of the respective equilibrium dopant concentrations. In order to activate the highly doped samples after ion-implantation, laser annealing seems to be the means of choice.[1] However, such supersaturated samples with active doping concentrations well above the solid solubility limit deactivate upon subsequent thermal processing.[2–4] In the Si case with the group V donors P, As, and Sb, this deactivation has been ascribed mainly to the formation of large dopant precipitates (especially in the case of Sb), or small defect clusters comprising only a few dopants and native point defects.[5–12]

Experiments as well as theoretical studies have shown donor-vacancy (D_nV) clusters to be the most probable candidates for the deactivation of the group V donors.[13–17] At elevated temperatures ($\geqslant 600\ ^\circ C$), the high diffusivities of point defects and dopants in heavily doped silicon make this clustering process very fast, resulting in deactivation of a large dopant fraction within the initial seconds of high temperature annealing.[18–20]

Interestingly enough, there exists an intrinsic limit to the carrier concentration n_e even in samples prepared by low-temperature molecular beam epitaxy (LT-MBE), where the formation of clusters and precipitates is essentially ruled out because the diffusion of both dopants and native point defects is highly improbable.[21–23] Consequently, there must exist yet another mechanism in highly *n*-doped crystalline silicon that prevents the donors from contributing electrons to the conduction band, leading to a saturation of n_e above $n_e \approx 6\times 10^{20}$ cm^{-3}. High-resolution x-ray diffraction (HR-XRD) data[21] reveal that the inactive Sb dopants form structures that reside on substitutional sites during low-temperature anneals of samples with $n_d > 6\times 10^{20}$ cm^{-3}. Moreover, Voyles *et al.*, through annular dark-field scanning transmission electron microscopy (ADF-STEM), have found that the primary deactivating defects in highly Sb-doped Si grown at low temperatures contain only two Sb atoms.[10,23] They attributed the 30% inactive Sb in their 9.35×10^{20} cm^{-3} doped sample to a new class of donor-pair defects DP(2)V-I.

In this work, we studied various donor pair defects and donor-vacancy clusters in order to establish their respective importance in the deactivation mechanisms at low temperature and in the absence of excess vacancies. We will focus on Sb, although the same effects with very similar energetics have been evaluated for As and P. In the presence of two or more donor atoms, minimal distortions of adjacent Si atoms are likely to form. They can deactivate both dopants and have small formation energies (less than 0.3 eV), while contributing to a relatively large increase in vibrational entropy. In addition, at donor concentrations on the order of 10^{21} cm^{-3}, approximately 7% of randomly distributed donors form inactive donor pairs located on neighboring lattice sites (dimers). Both the donor deactivating distortions (δ^3 for short) and the dimers are therefore likely to become an important contribution to the deactivation mechanism in highly *n*-type Si samples with no excess point defects. Earlier proposed donor pair defects,[10,23] on the other hand, are found to have too high formation energies to be relevant at room temperature.

II. COMPUTATIONAL SETUP: SIMULATION OF A DEGENERATE SEMICONDUCTOR

Our simulations were performed with the DFT (density functional theory) code VASP (Vienna *ab initio* simulation package) (Refs. 24 and 25) with a supercell of 216 atoms. All calculations were carried out in the generalized gradient approximation (GGA) to the exchange-correlation energy functional and with projector augmented wave pseudopotentials.[26] A plane-wave-basis set with an energy cutoff of 18 Ry was used and a 2^3 Monkhorst[27] set was

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applied for the **k**-point sampling. The kinetic energy cutoff for the plane waves was 255 eV. The silicon lattice parameter which minimizes the total energy was determined to be 5.46 Å. Energy barriers for the Frenkel pair generation were calculated using the nudged elastic band method. In this setup, impurities and their mirror images in neighboring supercells are separated by 16 Å. Two dopant atoms per supercell correspond to a donor concentration of 4.6×10^{20} cm^{-3}, which means that the semiconductor is already degenerate. The impurity states of *shallow* donors, extending over approximately 20 Å, overlap with donor states of dopants in neighboring supercells. Accordingly, we obtain energy dispersions for the impurity level wave functions of approximately 0.2 eV or less, and the resulting impurity band overlaps with the conduction band for some **k** points. The energies of the two donor electrons in the supercell lie approximately 0.17 eV above the conduction band minimum, in fair agreement with the experimentally measured elevated Fermi level in samples of this donor concentration. In the supercell calculation, a donor level energy is determined by the energy difference of the supercell containing s and $s-1$ electrons, respectively. The resulting net charge of the supercell is then compensated by a constant background charge of opposite sign.[31]

Impurity states with energies deeper in the band gap have a correspondingly smaller extension and a defect potential with a large short range part, hence the overlap with mirror images is minimal. In the degenerate semiconductor, the Fermi level lies within the impurity-conduction band. For very heavy doping, the density of states at the band tail falls off almost exponentially in energy towards the band gap. In this case, a donor atom will be inactive if the distorted crystal structure in its proximity diminishes the diameter of the donor orbital and lowers the donor level below the impurity-conduction band edge. The perfect crystal symmetry and hence the sp^3 hybridization of the donor valence electron orbitals are disturbed, and the former donor electron occupies a localized state.

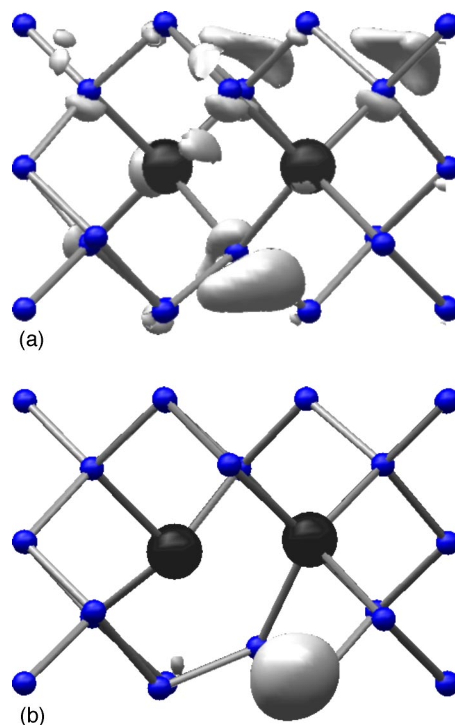

FIG. 1. (Color online) Localization of the two donor states of a second neighbor donor pair (NN^2) for (a) the active substitutional configuration and (b) for the δ^3 defect. The figure shows a small part of the supercell in the ⟨100⟩ direction. Large, black spheres represent the Sb atoms, small dark spheres are Si host atoms. The donor states are visualized by the isosurfaces of the charge density distribution function $\Delta\rho$ (white clouds). This distribution function $\Delta\rho$ is obtained by subtracting the charge density of the supercell lacking two electrons from the DFT-charge density of the neutral supercell.

III. DONOR DEACTIVATING CONFIGURATIONS

A. Dimers and the principle of δ^3 lattice defects

Donors in Si that share nearest neighbor sites (NN^1) form a dimer with split impurity levels. In the case of the As_2 dimer, the two donor levels lie at $E_{D1}-E_v=0.60$ eV and $E_{D2}-E_v=0.51$ eV above the valence band edge, respectively. Consequently, both donors in the dimer are inactive, and the complex remains neutral in the case of heavily n-doped silicon. The As_2 as well as the P_2 dimer in silicon are stable, exhibiting formation energies of –70 meV and –217 meV, respectively.[32] The Sb_2 dimer, due to the size mismatch of the large antimony atoms and the host Si atoms, is only metastable (a local energy minimum) with a formation energy of +117 meV.

If the two dopants occupy lattice sites further apart, both keep their sp^3 valence electron coordination. Such a configuration gives rise to shallow donor levels, and therefore the donors remain active. However, the silicon atoms in their close proximity may change this behavior considerably: The Si atoms can leave their respective lattice sites moving up to approximately 1 Å at comparatively low energy expense (<0.3 eV), to form a defect which deactivates both shallow donors. It is this change in the electronic structure of the donors that strongly favors such distortions energetically over any other in the doped crystal. However, our DFT calculations show that δ^3 defects *do not constitute a local energy minimum*, hence they are not metastable. Nevertheless, at finite temperatures, lattice vibrations will increase the time in which the crystal system adopts such deactivating configurations. For 300 K, due to the low energy configurations such distortions represent, this time fraction is already 4%.

For increasing distances Δ_{Si} of the involved Si atoms from their substitutional lattice sites, the donor levels of both dopants are gradually lowered below the impurity band edge. The reason for this behavior is illustrated by the examination of the charge densities calculated with DFT (Fig. 1): The slight displacement of a Si atom offers vacant space close to the donor atom. This geometry permits the formation of an s^2p^3-like orbital. The energy needed for this local distortion of the host crystal is largely dependent upon the number of donor atoms in the proximity and the distance between them. Generally, the donor atoms in a δ^3 defect remain essentially substitutional, while a vacant space in their close proximity is formed.

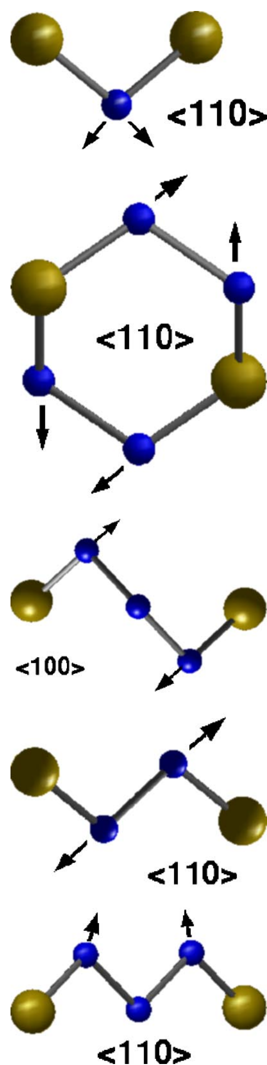

FIG. 2. (Color online) Donor pairs (large spheres) and possible δ^3 defects: Some of the energetically least expensive distortions of the corresponding silicon atoms (small spheres) are indicated by arrows. The indices denote the view axis. From top to bottom, NN^2 pair, NN^3 pair, NN^4 pair, NN^5 pair, NN^8 pair.

B. Donor concentration dependence of the δ^3 formation energies

An NN^2 donor pair (second nearest neighbors) lies in a $\{110\}$ plane and shares one central silicon atom (Fig. 2). If this Si atom is off-centered by $\Delta_{Si}=0.8$ Å along the $\langle -111 \rangle$ direction, both donor electron states are clearly localized. As Δ_{Si} grows, leaving more vacant space between the donor pair, the extension of the donor states decreases and the corresponding energy levels sink towards the valence band of Si, as depicted in Fig. 3. It is important to note that the formation energy of this displacement is *very sensitive to the total number of donors surrounding the moving Si atom*: Distortion energies or δ^3 formation energies are defined by the difference between the total energy of the neutral supercell containing *one* δ^3 defect and the total supercell energy of the neutral, relaxed system with all atoms on substitutional sites. We therefore denote them with the delta sign, $\Delta E_F = E_{\text{tot},\delta^3} - E_{\text{tot,subst}}$.

In the case of the NN^2 configuration with two neighboring donors, the distortion energy is only 0.23 eV for a displacement of the central silicon atom of 0.8 Å. This configuration, however, does *not* constitute a local minimum in the formation energy ΔE_F of the system (Fig. 4). Therefore, the total force $\mathbf{F}_{Si}$ acting on the central Si atom is not zero. However, $\mathbf{F}_{Si}$ undergoes a local minimum of 0.14 eV/Å for the δ^3 configuration with $\Delta_{Si}=0.8$ Å. The defect exhibits a first localized donor state with a level 87 meV below the conduction band edge E_c, the level of the second impurity state being at $E_c - E_{D2} = 290$ meV. Hence, in the degenerate semiconductor, these states are both filled with one electron, rendering the distorted state electrically neutral.

For comparison, in pure silicon the same displacement corresponds to an energy of 1.77 eV. In the case of *one* neighboring Sb atom, the energy required for the displacement is reduced to 0.93 eV (Fig. 4). Thus the distortion energy in the immediate neighborhood of the NN^2 donor pair is only 13% of the energy required in pure silicon and 25% of the energy required when only one donor is present. Next to four donor atoms, the δ^3 state even becomes a local energy minimum. Moreover, the energy needed for the central Si atom to diffuse to the closest hexagonal interstitial site is reduced considerably in the proximity of four donors: While in pure Si the Frenkel pair formation energy amounts to 7.0 eV,[28] in the Sb_4Si_1 and As_4Si_2 complex it is only 0.67 eV and 1.42 eV, respectively. This fact can account for the silicon interstitial injection observed experimentally in highly *n*-doped samples.[14,28,29] Consequently, both δ^3 formation and Frenkel pair generation are processes which depend, to a large extent, on doping concentration.

C. Other donor pairs

The strong effect of a low δ^3 formation energy can also be observed at a donor pair sharing third neighbor sites (NN^3). Here, the two dopants are located on a six-ring, separated by two host atoms in either direction. Out of all the possible distortion mechanisms, a migration of one single Si atom in the $\langle 111 \rangle$ direction is the most energetically favorable. The distortion energy for this configuration with one Si atom off-centered by $\Delta_{Si}=0.7$ Å is 0.29 eV. The donor levels of both Sb atoms now lie below the conduction band edge, the upper one at $E_c - E_{D2} = 140$ meV. An energetically more costly δ^3 pattern for the NN^3 pair configuration is a distortion involving all four Si atoms in the six-ring. In this case, an extra *p*-state splits off from the conduction band, such that the δ^3 defect can act as an electron acceptor (Fig. 5).

Donors forming an NN^4 pair are separated by one FCC lattice constant and are linked by a chain of three host atoms (Fig. 2). Since the coordination number z_4 in the diamond lattice is only six, such pairs are quite rare ($<7\%$ at $n_d = 10^{21}$ cm^{-3}). However, the δ^3 formation is enhanced in the NN^4 configuration, as a $\Delta_{Si}=0.7$ Å displacement of a Si atom next to one Sb ion deactivates both donors at a formation energy of 0.26 eV.

The NN^5 donor pair is separated by two center Si atoms in the $\{110\}$ plane. In this geometry, the energy cost for a $\Delta_{Si} = 0.7$ Å displacement of one Si atom is quite high (0.41 eV),

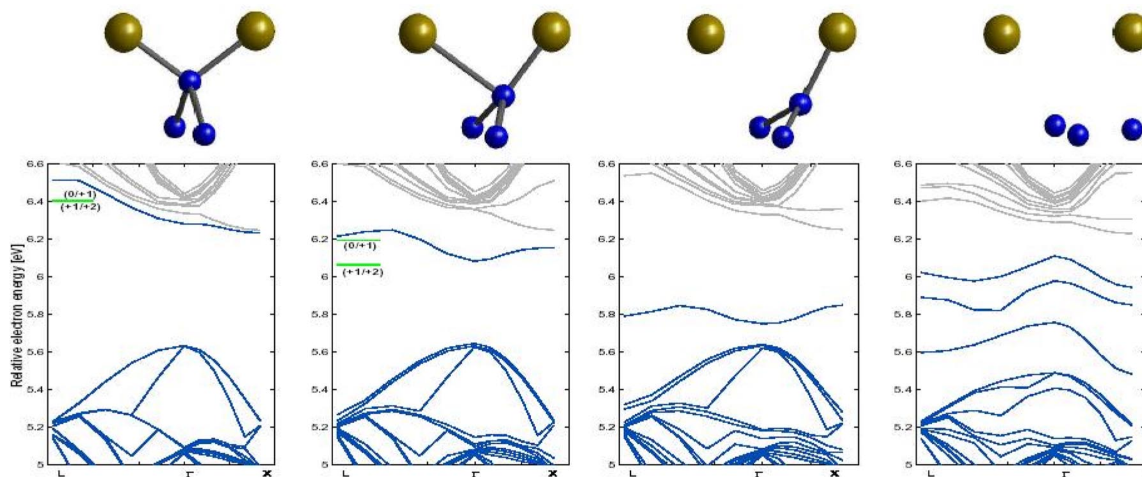

FIG. 3. (Color online) δ^3 formation band structures of a second neighbor donor pair with Sb for the above indicated configurations. The upper two large spheres in each configuration represent donor atoms, the lower three small spheres are Si atoms. From left to right, (a) substitutional (active) configuration. The donor levels of the active dopants are well above the conduction band minimum, indicating the high Fermi level of the system at a donor concentration of 4.6×10^{20} cm^{-3}. (b) δ^3 configuration with the central Si atom 0.8 Å off-centered. The two ionization levels are indicated on the left-hand side. (c) δ^3 configuration with the central Si atom 1.5 Å off-centered, (d) Frenkel pair configuration: the center Si atom has moved to the next hexagonal interstitial site. Occupied bands (at 0 K) are black, and empty bands are depicted in gray. The multitude of bands stems from foldover artifacts because the diameter of the Brillouin zone for the large supercell is only $2\pi/3a$.

and the enhancement of δ^3 formation upon the presence of the second donor is minimal.

In general, the effect of a low δ^3 formation energy at donor pairs decreases with increasing distance of the impurities. For NN^6 and NN^7 donor pairs, the effect is almost negligible according to our calculations. However, the NN^8 donor pair is an exception, exhibiting at least one prominent δ^3 configuration which involves two of the three host atoms that lie between the donors. (See Fig. 2.)

D. Statistical occurrence of donor pairs

Taking the distribution of donors in the crystal for a donor concentration n_d to be perfectly at random (which is a fair

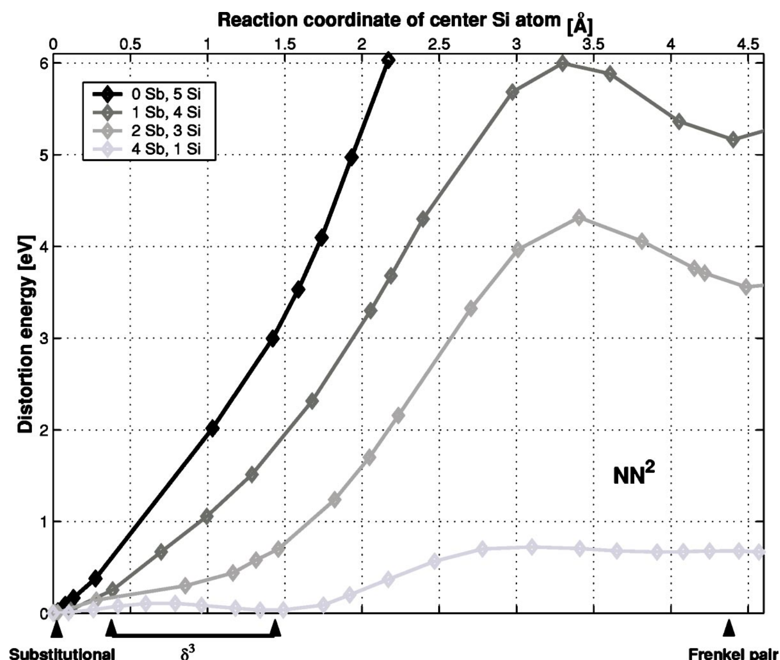

FIG. 4. Distortion energies for one moving central Si atom along the $\langle 111 \rangle$ direction as a function of distance from the substitutional lattice site. The lines correspond to distortion energies for configurations with different numbers of neighboring Sb atoms, as obtained with DFT in the nudged elastic band (NEB) method.

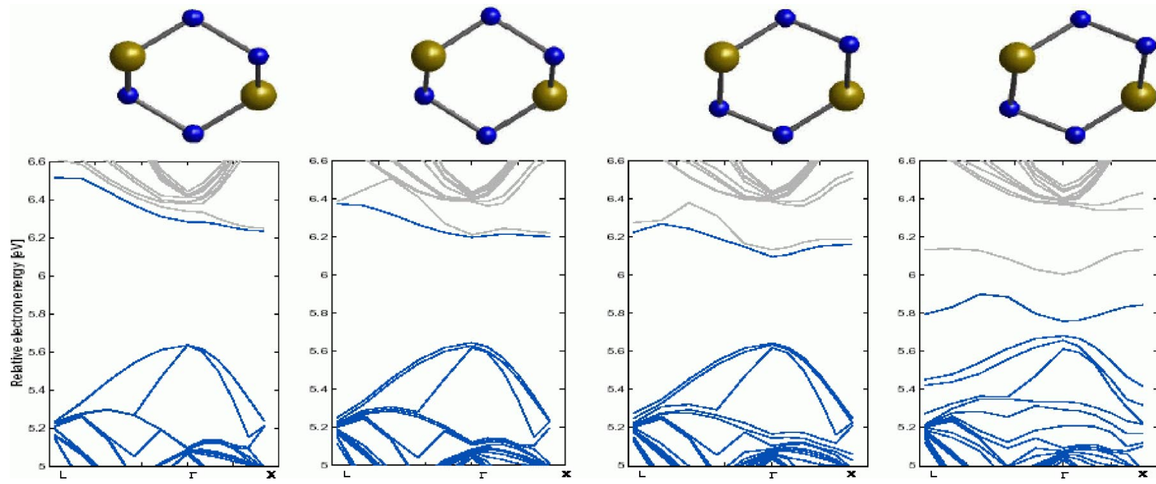

FIG. 5. (Color online) Band structures of a third neighbor (NN^3) Sb pair configuration. Displayed is the generation of deep impurity levels splitting off the conduction band when the atomic six-ring is distorted as depicted above. Large gray spheres represent the donor atoms. These distortions are not the energetically most favored for the NN^3 configuration, but they are effective at deactivating the donors, introducing an additional acceptor level.

assumption for low temperature MBE-grown samples), the *fraction of donors* participating in an NN^k donor pair configuration is given by[33]

$$c_k(n_d) = \frac{n_k}{n_d} = \chi^{S_{k-1}} - \chi^{S_k}, \quad S_k = \sum_{j=1}^{k} z_j \tag{1}$$

with $\chi = 1 - n_d/n_0$, n_0 being the concentration of crystal lattice sites. z_j represents the coordination number for jth neighbors in the silicon lattice. In Fig. 6, the c_k are plotted for $k=1, \ldots, 8$ in the high doping regime. For $n_d = 10^{20}$ cm^{-3}, roughly 18% of all donor atoms will be found in a donor pair configuration of the eighth neighbor or closer. At a doping concentration $n_d = 10^{21}$ cm^{-3}, this fraction is already 86%.

The expected average number of clusters with three or four donor atoms surrounding a single host atom, on the other hand, is extremely low even at very high doping on the order of 10^{21} cm^{-3}: For a random donor distribution the concentration of D_3Si_2 clusters is $n_3 \approx 10^{18}$ cm^{-3}. This in turn means that less than 0.5% of all donors will participate in such configurations, and only 0.003% in an even less probable D_4Si_1 cluster. So unless dopants and point defects rearrange within the crystal via diffusion, such configurations are negligible. This is in agreement with experimental findings of Voyles *et al.*[23] in LT-MBE samples. Under such conditions, the primary deactivating defect has been found to contain only two donor atoms.

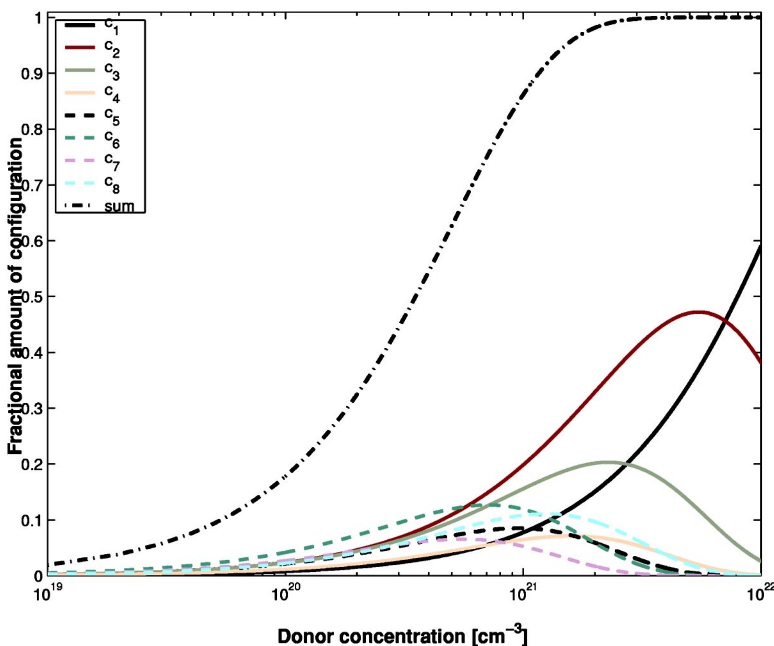

FIG. 6. (Color online) Fractional concentrations $c_k(n_d)$ of dopants participating in various donor-pair configurations according to Eq. (A3). At donor concentrations beyond $n_d = 10^{20}$ cm^{-3}, the fraction of donors forming close pairs and therefore the formation of dimers and δ^3 defects become predominant.

E. Thermodynamics of δ^3 defects

While the donor dimers represent local energy minima, the δ^3 lattice distortions do not. The average fraction t of time that the vibrating crystal system containing a donor pair finds itself in a δ^3 configuration depends both on the temperature and on the shape of the phase space in the proximity of these distortions. In order to estimate the fraction of inactive donors due to δ^3 defects, this average fraction t of time can in principle be evaluated by means of the corresponding canonical partition functions,

$$t_k(T) = \frac{Q_{\delta_k^3}(T)}{Q_{\text{tot}}(T)} = \frac{\int_{\mathbf{p}_1\ldots\mathbf{p}_N} d^{3N}p \int_{\mathbf{x}_1\ldots\mathbf{x}_N}^{\delta^3} d^{3N}x\, e^{-\beta E}}{\int_{\mathbf{p}_1\ldots\mathbf{p}_N} d^{3N}p \int_{\mathbf{x}_1\ldots\mathbf{x}_N} d^{3N}x\, e^{-\beta E}} \qquad (2)$$

with $\beta=1/kT$, where the spacial integral in the numerator is only over the δ^3 configurations. In the case of the vibrating Si atom between an NN^2 donor pair, for instance, there are four low-energy valleys pointing from the lattice site towards the four tetrahedral interstitial sites. The two valleys corresponding to the distortions indicated in Fig. 2 are energetically strongly favored due to the change in the electronic structure of the adjacent donors, as explained above. For the relatively small distortions, the expression in Eq. (2) can be evaluated to a good approximation by decoupling the moving atom from all others in the supercell,[34] and the expression (2) then becomes

$$t_{k=2}(T) \approx \frac{\int_{\mathbf{x}_1}^{\delta^3} d^3x\, e^{-\beta E(\mathbf{x}_1)}}{\int_{\mathbf{x}_1} d^3x\, e^{-\beta E(\mathbf{x}_1)}}, \qquad (3)$$

where the integrals over the three-dimensional subspace must be taken up to a reasonable energy cutoff which of course depends on the crystal temperature. The calculation yields that, at 300 K, on average a percentage of $t_{k=2}=5\%$ of the NN^2 donor pairs are inactive.[35] At 500 K, this fraction is already close to 11%. Again, since the defects exhibit a positive formation energy, the deactivation upon δ^3 can be minimized at low crystal temperatures, as they are stabilized exclusively by means of the term $T\Delta S_F$. This is in sharp contrast to the theory put forth by Chadi and Voyles *et al.* who evaluated negative formation energies for the similar so-called DP defects by subtracting an additional energy for the two localized donor electrons from the DFT total energies.[10,22] The formation energies ΔE_F of inactive configurations obtained by DFT total energy calculations already take into account all valence electron energies. Hence, adding this extra term to the ΔE_F amounts to a double counting.

F. Estimation of donor (de)activation

If the only compensating configurations were dimers and lattice distortions, the fraction of active donors should be estimated for a given donor concentration and temperature by

$$n_e(n_d,T) \approx n_d\left[1 - \sum_k c_k(n_d)\cdot t_k(T)\right], \qquad (4)$$

where the c_k and t_k are defined by Eqs. (1) and (2), respectively. For concentrations of $n_d=9.4\times10^{20}\ \text{cm}^{-3}$, Eq. (4) yields an active donor fraction of approximately 90% at 300 K (whereby dimers account for approximately 7% of the inactive donors and δ^3 defects for slightly more than 3%). This is considerably more than the experimentally measured activation of 70% in such samples.[22] In order to account for the 30% inactive donors, the donor pair defects should have formation energies of approximately 0.1 eV each. Distortions of this order may certainly deactivate one donor electron per pair, but possibly not both. Of course, there is in addition deactivation due to Sb_nV clusters in the LT-MBE samples that can explain to some extent the lower experimental degree of activation, though the contribution is rather small in the absence of excess vacancies.

G. Donor-vacancy complexes D_nV_m

Unlike LT-MBE, high-temperature sample preparation and dopant-ion implantation result in high vacancy (V) concentrations. Under such circumstances, both experiments and theoretical calculations suggest that the formation of D_nV_m clusters is the predominant deactivation mechanism for P and As, most probably also for Sb prior to precipitation.[14] Our calculations confirm that the strong binding energy of pentavalent donors with vacancies (1.26 eV for P-V, 1.40 eV for As-V, and 1.53 eV for Sb-V), as well as the lowered migration barriers for vacancies in a highly n-doped Si crystal promotes a rapid donor-vacancy clustering process. The larger Sb donors obviously gain in binding energy from stress relaxation. Consequently, the formation energies of D_nV_m clusters decrease with increasing donor radius, $E_f(P_2V)=1.19$ eV, $E_f(As_2V)=0.53$ eV, $E_f(Sb_2V)=0.41$ eV. So even though the Sb_2V formation is not exothermic,[36] according to these findings the Sb-V clustering prior to precipitation is in principle likely and quicker than that of As or P.

The deactivation process upon donor-vacancy clusters is more effective than the δ^3 formation because the vacancy introduces acceptor levels that can catch up to four electrons from the adjacent donors and from the conduction band.[17,30] The DFT band structure calculations reveal that, in addition to the localization of the fifth donor electron in a lone-pair orbital, D_1V complexes act as double electron acceptors and hence adopt a charge state −2 at high Fermi levels. Irrespective of the different binding energies, the position of these impurity levels is almost the same for P_1V, As_1V, and Sb_1V. On the other hand, while P_2V and As_2V agglomerates can only trap one extra electron from the Fermi sea (Fig. 7), Sb_2V exhibits its second acceptor level below the conduction band edge at $E_c-E_{A2}=78$ meV and can therefore be charged −2. D_3V clusters of all of the three donor species are single electron acceptors, and D_4V exhibit no acceptor or donor levels in the band gap or close to the valence or conduction band edge. Consequently, the latter remain neutral for virtually any position of the Fermi level. A more detailed discus-

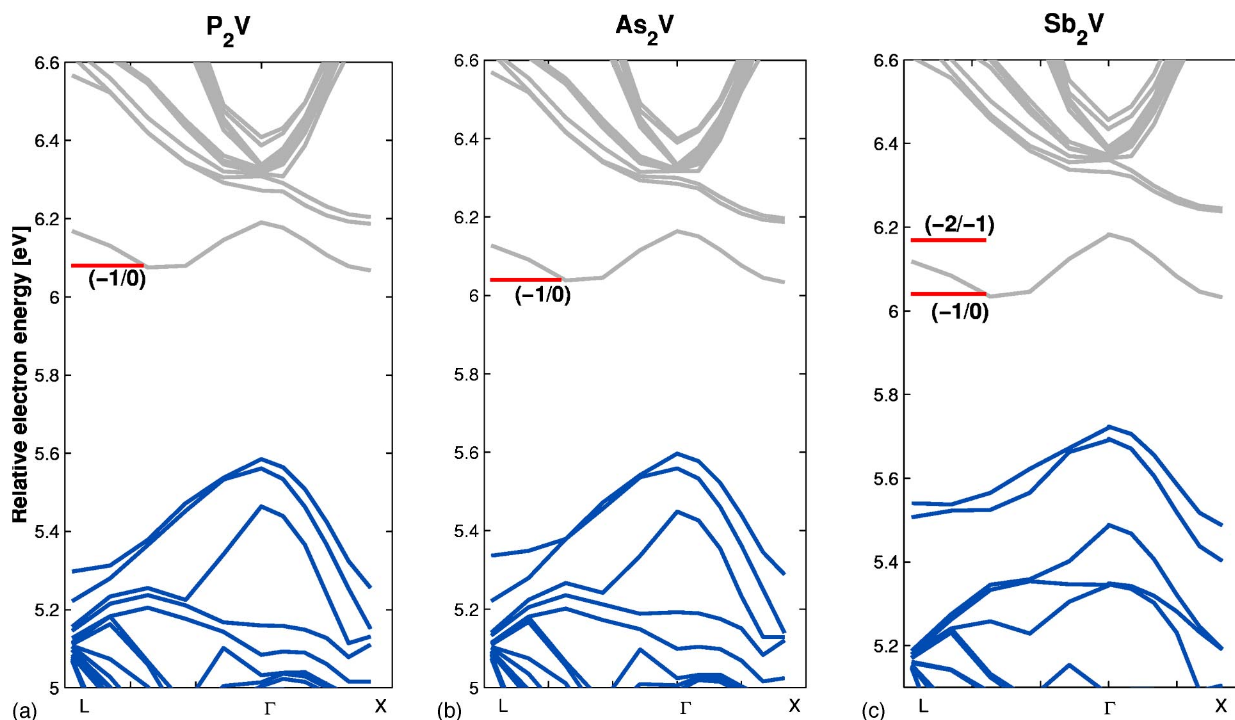

FIG. 7. (Color online) Band structures of the D_2V_1 complexes and ionization levels (depicted to the left of each band structure). From left to right, (a) P_2V, (b) As_2V, (c) Sb_2V. For all three donor species, the complexes act as electron acceptors, yet only in the case of Sb a second electron from the conduction band can be trapped.

sion and characterization of these clusters and their impurity states has been published elsewhere.[17]

IV. CONCLUSIONS

Donor dimers and (δ^3) defects which form in the proximity of two or more dopant atoms in silicon constitute an intrinsic limit on $n_e(n_d)$, as native point defects of the crystal are not involved in the deactivation process. They become therefore predominant in samples of high donor concentrations, and form even at low temperatures (<500 K) and in the absence of impurity diffusion. STEM and positron annihilation spectroscopy measurements have shown the inactive donors to be substitutional. This is perfectly in agreement with what must be expected at deactivation upon dimers and δ^3 defects.

Generally, the class of defects that do not involve vacancies or interstitials exhibit positive formation energies, though the latter depend to a large extent on the donor density itself. Therefore, only clusters with a large number of donors at nearest or next nearest lattice sites, such as the rare D_4Si_1, are an exception to this rule and exhibit negative formation energies. However, the low energy cost of Si distortions close to two or more donor atoms and the configurational as well as vibrational entropy they introduce enhances the formation of these defects at relatively low crystal temperatures.

However, the experimentally measured saturation of n_e at $n_e \approx 6\times 10^{20}$ cm^{-3} in LT-MBE samples as well as the inactive Sb fraction of 30% in samples with $n_d \approx 9.35 \times 10^{20}$ cm^{-3} at $T=300$ K can only be explained in parts with the presence of dimers and δ^3 defects. Further measurements on the fraction of active dopants as a function of the crystal temperature in highly *n*-type silicon must be performed in order to confirm the δ^3 theory. The compensation upon dimers, on the other hand, is a mere statistical fact in the absence of donor diffusion.

At such heavy impurity densities yet another deactivating effect might come into play, which could possibly explain the discrepancy of the estimated and measured active donor concentration. It remains to be examined to what extent the high impurity densities in silicon might raise the energy of extended electron wave functions as compared to localized electron orbitals. Theoretically, it is conceivable that the experimentally observed saturation of free carrier concentration n_e above $n_d = 10^{21}$ cm^{-3} is at least to some extent a manifestation of a Mott transition.

APPENDIX: STATISTICS OF THE DONOR DISTRIBUTION

In order to determine the fraction of inactive donors due to δ^3 formation, it is required to know the statistical distribution of donor pair configurations at a given donor concentration. If we assume the dopants to be randomly distributed in the crystal, then the probability for a lattice site *i* occupied by a donor atom to have *at least* one neighboring donor atom of order NN^k is

$$p_{\partial\Omega,k} = 1 - \left(1 - \frac{n_d}{n_0}\right)^{z_k}, \tag{A1}$$

where n_d and n_0 are the concentrations of donors and lattice sites, respectively. The term z_k represents the coordination

number for the kth neighbor in the silicon lattice, thus $z=\{4,12,12,6,12,24,\ldots\}$. The site i, however, only participates in an NN^k (or higher than k) donor pair configuration if there is no lattice site closer than NN^k occupied by another dopant. The probability for all closer sites to be occupied exclusively by host atoms is given by

$$p_{\Omega,k} = \left(1 - \frac{n_d}{n_0}\right)^{S_{k-1}} \left| \begin{array}{l} S_0 = 0, \\ S_{k-1} = \sum_{j=1}^{k-1} z_j \quad \text{if } k > 1 \end{array} \right. . \tag{A2}$$

Therefore, the probability for a dopant atom to be part of an NN^k donor pair (i.e., the *fraction of donors* in such pair configurations) is

$$c_k = \frac{n_k}{n_d} = p_{\partial\Omega,k} \cdot p_{\Omega,k} = \chi^{S_{k-1}} - \chi^{S_k} \tag{A3}$$

with $\chi = 1 - n_d/n_0$. Note that we have disregarded surface effects in this reasoning. The c_k in the above definition are hence the fractions of donors whose *nearest neighboring donor atom* is of order k, and obviously

$$\sum_{k=1}^{\infty} c_k = \chi^{S_0} - \chi^{S_\infty} = 1. \tag{A4}$$

The number $n_{\alpha=3,4}$ of D_3Si_2 and D_4Si_1 clusters as a function of donor concentration n_d is given by the binomial probability function

$$n_\alpha = \binom{z_1}{\alpha} (1-\chi)^\alpha \cdot \chi^{z_1-\alpha} \cdot (n_0 - n_d) \tag{A5}$$

with $\alpha = \{3,4\}$. Even for very heavy doping of $n_d = 10^{21}$ cm^{-3} there are not more than $n_3 \approx 10^{18}$ cm^{-3} D_3Si_2 clusters and even fewer D_4Si_1 clusters present. Hence we can, to a good approximation, take these complexes to be isolated from one another, and evaluate the fraction of donor atoms participating in such a configuration as follows:

$$C_\alpha \approx \frac{\alpha \cdot n_\alpha}{n_d} = \alpha \cdot \binom{z_1}{\alpha} (1-\chi)^{\alpha-1} \cdot \chi^{z_1-\alpha+1}. \tag{A6}$$

[1] P. M. Rousseau, P. B. Griffin, W. T. Fang, and J. D. Plummer, J. Appl. Phys. **84**, 3593 (1998).
[2] D. Nobili, S. Solmi, A. Parisini, M. Derdour, A. Armigliato, and L. Moro, Phys. Rev. B **49**, 2477 (1994).
[3] S. Solmi and D. Nobili, J. Appl. Phys. **83**, 2484 (1998).
[4] Y. Takamura, S. H. Jain, P. B. Griffin, and J. D. Plummer, J. Appl. Phys. **92**, 230 (2002).
[5] A. N. Larsen, F. T. Pedersen, and G. Weyer, J. Appl. Phys. **59**, 1908 (1985).
[6] K. C. Pandey, A. Erbil, G. S. Cargill, and R. F. Boehme, Phys. Rev. Lett. **61**, 1282 (1988).
[7] A. Parisini, A. Bourret, A. Armigliato, M. Servidori, S. Solmi, R. Fabbri, J. R. Regnard, and J. L. Allain, J. Appl. Phys. **67**, 2320 (1990).
[8] D. W. Lawther, U. Myler, and P. J. Simpson, Appl. Phys. Lett. **67**, 3575 (1995).
[9] M. Ramamoorthy and S. T. Pantelides, Phys. Rev. Lett. **76**, 4753 (1996).
[10] D. J. Chadi, P. H. Citrin, D. L. Adler, M. A. Marcus, and H. J. Gossmann, Phys. Rev. Lett. **79**, 4834 (1997).
[11] M. A. Berding, A. Sher, and M. van Schilfgaarde, Appl. Phys. Lett. **72**, 1492 (1998).
[12] Y. Takamura, P. B. Griffin, and J. D. Plummer, J. Appl. Phys. **92**, 235 (2002).
[13] K. Saarinen, J. Nissilä, H. Kauppinen, M. Hakala, M. J. Puska, P. Hautojärvi, and C. Corbel, Physica B **274**, 463 (1999).
[14] J. Fage-Pedersen, P. Gaiduk, J. L. Hansen, and A. N. Larsen, J. Appl. Phys. **88**, 3254 (2000).
[15] V. Ranki, J. Nissilä, and K. Saarinen, Phys. Rev. Lett. **88**, 105506 (2002).
[16] V. Ranki and K. Saarinen, Phys. Rev. B **67**, 041201(R) (2003).
[17] D. C. Mueller, E. Alonso, and W. Fichtner, Phys. Rev. B **68**, 045208 (2003).
[18] D. Mathiot and J. C. Pfister, J. Appl. Phys. **66**, 970 (1989).
[19] A. N. Larsen, K. K. Larsen, P. E. Andersen, and B . G. Svensson, J. Appl. Phys. **73**, 691 (1993).
[20] D. Nobili, S. Solmi, and J. Shao, J. Appl. Phys. **90**, 101 (2001).
[21] Y. Takamura, A. Vailionis, A. F. Marshall, P. B. Griffin, and J. D. Plummer, J. Appl. Phys. **92**, 5503 (2002).
[22] P. M. Voyles, D. A. Muller, J. L. Grazul, P. H. Citrin, and H.-J. L. Gossmann, Nature (London) **416**, 826 (2002).
[23] P. M. Voyles, D. J. Chadi, P. H. Citrin, D. A. Muller, J. L. Grazul, P. A. Northrup, and H.-J. L. Gossmann, Phys. Rev. Lett. **91**, 125505 (2003).
[24] G. Kresse, Phys. Rev. B **47**, 558 (1993).
[25] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
[26] G. Kresse and J. Joubert, Phys. Rev. B **59**, 1758 (1999).
[27] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[28] J. Xie and S. P. Chen, J. Appl. Phys. **87**, 4160 (2000).
[29] P. Gaiduk, J. Fage-Pedersen, J. L. Hansen, and A. N. Larsen, Phys. Rev. B **59**, 7278 (1999).
[30] S. Solmi, D. Nobili, and J. Shao, J. Appl. Phys. **87**, 658 (2000).

[31] The values given here are *not* corrected for the underestimated band gap in DFT. For a detailed description of the calculation of impurity levels see Ref. 17.
[32] The formation energies are given with respect to two substitutional donors infinitely apart (Ref. 17).
[33] See Appendix A for detailed calculations.
[34] This means that the positions of all other ions are kept fixed. Generally, the total energies of distorted configurations are slightly overestimated by such a procedure, such that the approximation yields an underestimation of t_k.
[35] The total energies were calculated by DFT with a reasonable subspace sampling, and the energies were interpolated.
[36] As was assumed in earlier work (Ref. 14).