

Complex Dynamical Phenomena in Heavily Arsenic Doped Silicon

Madhavan Ramamoorthy and Sokrates T. Pantelides

Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37209

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Several complex dynamical phenomena have been observed in heavily doped Si, but a comprehensive account of the underlying atomic-scale processes is lacking. We report a wide array of first-principles calculations in terms of which we give such a comprehensive account. In particular, we find that vacancies (V), AsV pairs, As_2V complexes, and higher-order As_nV_m complexes play distinct roles in the observed dopant deactivation, reactivation, and anomalous diffusion. The latter is mediated by mobile As_2V complexes that form in “prepercolation” patches of a very high dopant concentrations and gives rise to fast As clustering at moderate temperatures. Our results are quantitative and in agreement with experimental numbers where available. [S0031-9007(96)00428-0]

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For some time now it has been possible to prepare Si specimens with very high concentrations of dopants such as As (as high as 10^{21} cm^{-3} ; i.e., roughly one As atom per 50 host atoms) with a corresponding high conductivity. Such specimens exhibit a wide array of complex dynamical phenomena that have been investigated extensively over the last 25 years. These investigations fall into two distinct categories.

(i) Beginning in the 1970s, a number of investigators [1–4] found that annealing of heavily doped samples at moderate temperatures (400–500 °C) results in a dramatic drop in conductivity. The phenomenon has been universally attributed to the formation of electrically inactive As complexes. This deactivation of dopants is partially reversible by heating to higher temperatures (800–1000 °C). The major focus of most investigations has been the identification of the dominant electrically inactive complex. There is extensive experimental evidence that the dominant defect is an As_nV complex, where V stands for a vacancy, but there is no consensus on the value of n [5–11]. The most perplexing feature of the observations is that at 400–500 °C, in lightly doped Si, As diffusion is negligible. Yet, somehow, at these temperatures, in heavily doped specimens, the As atoms are rapidly rearranged [1–3] from isolated substitutional sites to form As_nV clusters [9–11] and precipitates [12], generating silicon self-interstitials [11]. No atomistic mechanism for the deactivation and subsequent reactivation has been proposed so far.

(ii) A different set of investigators studied As diffusion in heavily doped samples at temperatures in the range of 1000–1100 °C. Early investigations [5] showed that the As diffusion constant increased linearly with dopant concentration n for $n < 3 \times 10^{20} \text{ cm}^{-3}$. For $n > 3 \times 10^{20} \text{ cm}^{-3}$ the diffusion constant *decreased*. This was ascribed to clustering [5]. However, later rapid thermal annealing (RTA) experiments [13,14] revealed *increased* As diffusivity for $n > 3 \times 10^{20} \text{ cm}^{-3}$. Other RTA studies [15] of the diffusion of small concentrations of As in heavily P-doped Si also showed a dramatic increase in As dif-

fusivity for donor concentrations above $\sim 2 \times 10^{20} \text{ cm}^{-3}$. The most intriguing suggestion to account for the observed enhanced dopant diffusion above a critical doping threshold is the formation of a percolation network of dopant atoms [15,16]. However, other theories [17] account for the enhanced diffusion without invoking percolation. No attempt has been made thus far to give a unifying interpretation of the diffusion data *and* the deactivation or reactivation data.

In this Letter, we report a comprehensive set of first-principles calculations in terms of which we obtain a detailed description of the dynamical atomic-scale processes that occur in heavily As-doped Si. These results allow us to give a systematic account of both the deactivation-reativation observations and the anomalous diffusion data. In particular, we find that vacancies, AsV pairs, As_2V complexes, and higher-order As_nV_m complexes play distinct roles in the observed deactivation, reactivation, and anomalous diffusion phenomena. A percolation network, which in principle may exist in heavily doped specimens prior to any thermal treatments, would in fact quickly break up due to the formation of As_nV_m complexes and thus would not sustain long-term As diffusion and clustering. We find that fast As diffusion at high doping levels is mediated by mobile As_2V complexes that form in “prepercolation” patches of very high dopant concentrations and give rise to rapid As clustering at moderate temperatures. Our predictions are quantitative and in agreement with experimental numbers, where available.

The calculations were based on the density functional method, using the local density approximation. Pseudopotentials [18] were used for Si and As. Electronic wave functions were expanded in a plane wave basis, with a 15 Ry cutoff. Tests for bulk Si gave a lattice parameter of 5.42 Å and a bulk modulus of 0.99 Mbar. Defect configurations were simulated using the supercell method. The formation energies of individual defects changed by only 0.25 eV on going from 16 to 32 site supercells, indicating that the results from 32 site supercells were well

converged. Two special k points were used [19]. Migration energies of the As-vacancy complexes were calculated using 64 site supercells. Calculated forces on atoms were used to relax each structure to equilibrium.

First, we report our calculations of the formation energies of defect clusters containing As atoms and native point defects in Table I. Our results show that As atoms have negligible affinity for each other but bind strongly to vacancies and interstitials. The binding energy per As atom in a cluster containing a vacancy is appreciably larger than that containing an interstitial, reflecting the preference of As for threefold coordination. In fact, each time an As atom is taken from an isolated substitutional fourfold-coordinated site and placed next to a vacancy, there is an energy gain of about 1.5 eV. All As_nV_m complexes with $n > 2m$ have negative formation energies, including the As_4V complex, where our result is in agreement with the calculation reported by Pandey *et al.* [9]. These authors studied only the As_4V complex and asserted that, because of its negative formation energy, it is the dominant defect in deactivated samples. However, as we see, this complex is only one among a hierarchy of such complexes. In these results, we observe a clear trend: *At any doping level, compared with isolated fourfold-coordinated configurations, thermodynamics would favor the agglomeration of As atoms with vacancies in the form of As_nV_m complexes or the attachment of As atoms to microvoid surfaces.* In other words, As-doped Si is metastable at any doping level and the preparation of electrically active samples is possible only because of *kinetic limitations*.

The results presented above allow us to conclude that the defects that underlie deactivation and reactivation of heavily doped Si are As_nV_m complexes. This conclusion is fully consistent with earlier analysis of experimental data [6,8–11]. It is clear, however, that formation energies

TABLE I. The formation energies, in eV, of the complexes of As atoms with a vacancy.

Defect complex	Formation energy	Binding energy per As atom
As_2	0.10	0.05
As_4	-0.10	-0.03
V (vacancy)	3.78	
AsV	2.47	1.31
As_2V	0.82	1.48
As_3V	-0.53	1.44
As_4V	-2.39	1.54
V_2 (divacancy)	6.07	
As_2V_2	2.70	1.69
As_4V_2	-0.54	1.65
As_6V_2	-3.23	1.57
I (interstitial)	4.14	
As_2I	3.76	0.19
As_4I	2.19	0.49

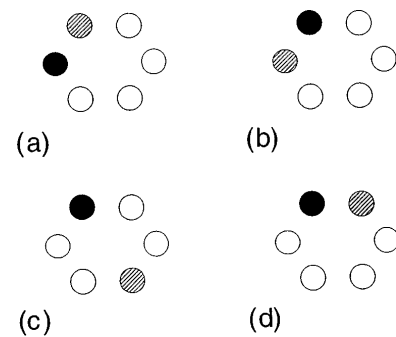


FIG. 1. Migration of AsV. Si: white circle, As: dark circle, V: shaded circle. (a) Initial configuration; (b) As and V have exchanged positions; (c) saddle configuration: V is third neighbor of As; (d) final configuration; one diffusion step is complete.

alone (thermodynamics) do not tell us what role each As_nV_m complex plays, which one is dominant if any, what are the mechanisms that allow them to form only in heavily doped materials, and how diffusion is enhanced. We must, therefore, investigate the *dynamical processes* (kinetics) that are possible only in heavily doped materials.

It is helpful to start with the process that underlies As diffusion in lightly doped Si. It is well known that diffusion proceeds primarily by the formation and migration of AsV pairs [20]. The migration of AsV is illustrated in Fig. 1: The vacancy loops around the As atom for the pair to make one step. The diffusion activation energy of the AsV complex is the sum of its formation energy and migration energy. From Table I, the formation energy of the AsV complex is 2.5 eV. The migration energy is made up of two contributions: the change in energy when the vacancy goes from the nearest neighbor to the third neighbor position of the As atom and the energy of vacancy migration, which we calculate to be 0.9 and 0.5 eV, respectively. This gives a net activation energy for AsV diffusion of 3.9 eV, in good agreement with experiment [20]. With such a large activation energy, negligible As migration occurs at moderate temperatures.

In the heavily doped limit, Mathiot and Pfister (MP) [16] have suggested that enhanced diffusion comes about as follows: AsV pairs during their migration are not isolated. Specifically, MP considered the case there two As atoms are fifth neighbors. If one of these As atoms is connected to a vacancy, then, during the migration of the AsV pair, when the V is a third neighbor of one As atom, it would be a second neighbor of the other. The net effect is a lowering of the migration energy. For a uniform As distribution, such a cluster would not occur even at an As concentration as high as 10^{21} cm^{-3} , for As atoms would be eighth neighbors, on average. MP proposed a resolution to this quandary by invoking percolation theory. They found that when the As concentration exceeds $\sim 3 \times 10^{20} \text{ cm}^{-3}$, fluctuations in the As distribution would result in the presence of an infinite network of As atoms in the sample, in which any two As atoms are fifth neighbors of each

other (or closer). They described a scenario for enhanced As diffusion above this critical doping threshold, due to accelerated diffusion of vacancies through this “infinite percolation network.” We have performed the relevant calculations in this limit using supercells and found that both the formation and migration energy of an AsV pair are lowered, leading to a decrease in the diffusion activation energy of about 1 eV. This is consistent with the number obtained by MP [16] from simulations. A simple calculation, assuming no significant change in the pre-exponential factor in the expression for the diffusion coefficient [$D = D_0 \exp(-Q/k_bT)$], indicates that *the rate of As diffusion in a heavily doped specimen at $\sim 450^\circ\text{C}$ is comparable to that in a lightly doped specimen at $\sim 900^\circ\text{C}$.* This can explain how fast As migration can occur at moderate temperatures.

However, there is a problem with the above scenario. The percolation model yields a quantitative account of enhanced diffusion for As concentrations above $\sim 3 \times 10^{20} \text{ cm}^{-3}$, but it is not consistent with the fact that enhanced diffusion causes As clustering with vacancies. Such clustering would break up the percolation network into high concentration patches and halt enhanced diffusion and further clustering after a few seconds of annealing. This would be in contradiction with deactivation observations [1,2] that indicate continued As clustering over many hours at moderate temperatures.

We note that other workers have claimed to account for enhanced diffusion [17] in heavily doped specimens without invoking percolation. Here, we propose an atomistic mechanism that does not require a fully connected percolation cluster and yet explains the diffusion data [5,14], namely, *a mobile As_2V complex*. The formation energy of

As_2V , from Table I, is 0.8 eV. Its migration is illustrated schematically in Fig. 2. Two basic steps are depicted: the sequence (abcd) and the sequence (abef), with comparable migration energies. The net diffusion activation energy is 2.7 eV for the As_2V complex, which is 1.2 eV lower than that of the AsV pair. This is virtually identical to the result we obtained for AsV migration in the percolation network. Thus, based on activation energies alone, one cannot distinguish between the percolation model and the migration of As_2V . While earlier investigators [5,7,10] had proposed that As_2V complexes [21] are present in deactivated specimens, they were not considered mobile. In modeling diffusion of Sb in P-doped Si, Larsen and Weyer [22] had considered diffusion mediated by SbPV complexes, but in later work [15] abandoned this mechanism in favor of the percolation model. *We believe, however, that As_2V plays a key role in enhanced diffusion in heavily doped Si as it does not need a continuous percolation network, something that would not be sustained when As agglomeration into As_nV_m complexes occurs.* We propose that enhanced As diffusion starts below the percolation threshold, calculated by MP [16] to be $3 \times 10^{20} \text{ cm}^{-3}$. High-concentration “prepercolation patches” in which two As atoms are fifth neighbors or closer enable the formation of large numbers of As_2V complexes. These As_2V complexes can migrate fast through the sample, even at moderate temperatures. During their motion, they react with other defects to form larger, immobile complexes. Modeling diffusion data on the basis of these reactions is beyond the scope of this Letter.

We now summarize the main experimental observations and how the theory described above accounts for them.

(1) *Diffusion data.*—Early observations [5] showed that the diffusion constant of As decreased for dopant concentrations greater than $3 \times 10^{20} \text{ cm}^{-3}$. However, later RTA experiments [14] on As-implanted Si found fast As redistribution (within 20 s) which reduced the peak As concentration to $(2.5\text{--}3) \times 10^{20} \text{ cm}^{-3}$, if the as-implanted peak As concentration exceeded this value. Otherwise, negligible As migration was observed. RTA experiments [15] on small concentrations of As in heavily P-doped Si found enhanced diffusion for donor concentrations greater than $\sim 2.0 \times 10^{20} \text{ cm}^{-3}$. The early diffusion studies were carried out over several hours. The decreased As diffusivity at high doping levels was correctly attributed to As clustering [5]. The fast As migration observed in RTA experiments is due to As_2V migration over a very short time scale (6–60 s), during which extensive clustering does not occur. The investigations of As diffusion in heavily P-doped Si establish that the onset of enhanced dopant diffusion is indeed below the percolation threshold. The enhanced As diffusion observed in these latter experiments is mediated by AsPV complexes. The extracted activation energy [15] of 2.7 eV is identical to that of the As_2V complex.

(2) *Deactivation data.*—During deactivation at moderate temperatures (400–600 °C), the rate of deactivation is

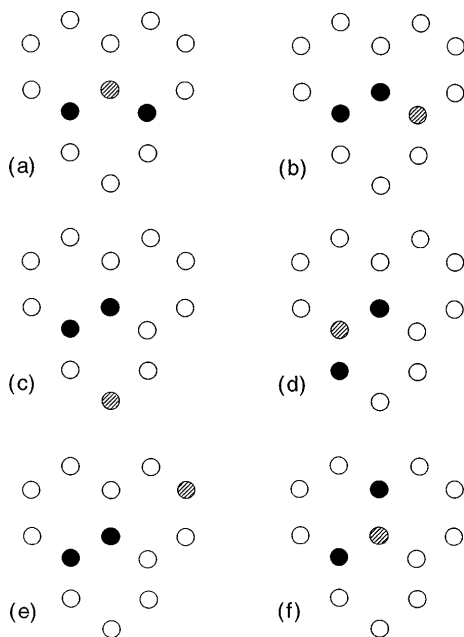


FIG. 2. Migration of As_2V . (a) Initial configuration; (b) one As and V have exchanged positions; (c),(d) translation; (e),(f) reorientation starting with configuration (b).

highest initially and then continues at a slower rate [1,2,4]. Initially As atoms are close to each other in prepercolation patches. Migrating As_2V complexes have a high cross section for reaction inside such patches, giving rise to larger immobile complexes. Thus, the initial deactivation rate is high. Once a degree of clustering takes place, As atoms are further from each other, on average, and As_2V complexes have to travel greater distances to cause further deactivation. At some point, deactivation becomes extremely slow and effectively stops. The distribution of complexes is determined by kinetics, for the system does not reach thermodynamic equilibrium at these temperatures.

(3) *Reactivation data.*—Annealing of deactivated specimens at elevated temperatures (800–1000 °C) is found to reactivate carriers. Schwenker, Pan, and Lever [1], assuming that one complex is predominant in deactivated specimens, obtained the activation energy for the reactivation to be 1.6 eV and the number of As atoms in the complex to be between 1.7 and 2.8 As atoms. For concentrations of order $2 \times 10^{20} \text{ cm}^{-3}$, most of the initial As concentration is reactivated. Reactivation is a result of the breakdown of complexes formed at lower temperatures, releasing As atoms, and requires the removal of an AsV pair or an As_2V complex, for these are the mobile species. From Table I, we find that the energy required to break up AsV ($AsV \rightarrow As + As$), As_2V ($As_2V \rightarrow AsV + As$), and As_3V ($As_3V \rightarrow As_2V + As$), are all about 1.5 eV, in excellent agreement with the data. Larger complexes do not decompose into $As + X$, as X is not mobile. They would have to break up into larger fragments and that requires more energy. Therefore, we conclude that AsV , As_2V , and As_3V may be present in deactivated specimens. AsV is ruled out by experiments [9,11] which find that most As atoms in deactivated specimens have another As atom as a second neighbor. The fact that most of the As atoms were reactivated at a doping level of $2 \times 10^{20} \text{ cm}^{-3}$ indicates that As_2V and As_3V are the dominant complexes in deactivated specimens, near the enhanced-diffusion threshold.

(4) *The saturation of the carrier concentration.*—The carrier concentration in heavily doped Si does not exceed $\sim 3 \times 10^{20} \text{ cm}^{-3}$ at elevated temperatures (1000 °C) [3], even if the total As concentration exceeds this value. This concentration, as MP [16] showed, marks the threshold above which an infinite percolation network of As atoms is present initially in the sample. If the initial As concentration exceeded this value, then, in the very early stages of annealing, a very high flux of vacancies would flood the sample along the percolation network. Thus, the As concentration in excess of the critical value would become bound very rapidly in As_nV_m complexes with $n > 2m$ (like As_4V). Such complexes would not decompose even at 1000 °C.

In conclusion, we reported extensive calculations of formation energies, migration energies, and defect reaction

energies in terms of which we have been able to give a systematic account of the major observations of both deactivation or reactivation and enhanced diffusion in heavily doped Si.

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- [1] R. O. Schwenker, E. S. Pan, and R. F. Lever, *J. Appl. Phys.* **42**, 3195 (1971).
 - [2] W. K. Chu, *Appl. Phys. Lett.* **36**, 273 (1980).
 - [3] A. Lietoila, J. F. Gibbons, and T. W. Sigmon, *Appl. Phys. Lett.* **36**, 765 (1980).
 - [4] K. Itoh *et al.*, *Jpn. J. Appl. Phys.* **21**, L245 (1982).
 - [5] R. B. Fair and G. R. Weber, *J. Appl. Phys.* **44**, 273 (1973).
 - [6] S. M. Hu, in *Atomic Diffusion in Semiconductors*, edited by D. Shaw (Plenum, New York, 1973), p. 306.
 - [7] W. K. Chu and B. J. Masters, in *Laser-Solid Interactions and Laser Processing*, edited by S. Ferris, H. J. Leamy, and J. M. Poate, AIP Conf. Proc. No. 50 (AIP, New York, 1979), p. 305.
 - [8] M. Y. Tsai, F. F. Morehead, J. E. E. Baglin, and A. E. Michel, *J. Appl. Phys.* **51**, 3230 (1980).
 - [9] K. C. Pandey *et al.*, *Phys. Rev. Lett.* **61**, 1282 (1988).
 - [10] Th. Wichert and M. L. Swanson, *J. Appl. Phys.* **66**, 3027 (1989).
 - [11] D. W. Lawther *et al.*, *Appl. Phys. Lett.* **67**, 3575 (1995).
 - [12] A. Lietoila *et al.*, *Appl. Phys. Lett.* **35**, 532 (1979).
 - [13] J. L. Hoyt and J. F. Gibbons, *Mater. Res. Soc. Symp. Proc.* **52**, 15 (1986).
 - [14] A. N. Larsen, S. Yu. Shiryayev, E. S. Sorensen, and P. Tidemand-Peterson, *Appl. Phys. Lett.* **48**, 1805 (1986).
 - [15] A. N. Larsen, K. K. Larsen, P. E. Andersen, and B. G. Svensson, *J. Appl. Phys.* **73**, 691 (1993). The study of small concentrations of As in heavily P-doped Si was motivated by the high solubility of P in Si, which at 1000 °C is $\sim 4 \times 10^{20} \text{ cm}^{-3}$. Thus, enhanced dopant diffusion can be studied at high donor concentrations, without clustering. See R. B. Fair, *Inst. Phys. Conf. Ser.* **46**, 559 (1979); D. Nobili, A. Armigliato, M. Finetti, and S. Solmi, *J. Appl. Phys.* **53**, 1484 (1982).
 - [16] D. Mathiot and J. C. Pfister, *J. Phys. (Paris), Lett.* **43**, L-453 (1982); *Appl. Phys. Lett.* **42**, 1043 (1983); *J. Appl. Phys.* **66**, 970 (1989).
 - [17] E. Antoncik, *Appl. Phys. A* **56**, 291 (1993); S. T. Dunham and C. D. Wu, *J. Appl. Phys.* **78**, 2362 (1995).
 - [18] D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
 - [19] D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
 - [20] P. M. Fahey, P. B. Griffith, and J. D. Plummer, *Rev. Mod. Phys.* **61**, 289 (1989).
 - [21] Fair and Weber [5] considered V^0 combining with two neutral As atoms whereas Chu and Masters [7] considered V^{--} combining with two As^+ atoms to form As_2V . As a thermodynamic quantity, the formation energy of As_2V is independent of the charge states of the constituent defects.
 - [22] A. N. Larsen and G. Weyer, *Mater. Sci. Forum* **83–87**, 273 (1992).