

Electronic quasichemical formalism: Application to arsenic deactivation in silicon

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A statistical mechanical formalism is developed to simultaneously treat chemical and electronic disorder. The method is based on a quasichemical approximation with an arbitrary number of chemical components and defects, and an arbitrary cluster size. The chemical potentials of the atomic constituents are explicitly included so that both open and closed systems can be treated. For the electronic subsystem, bandlike excitations can be treated separately, and Fermi-Dirac statistics are employed. The formalism is applied to the problem of electrical deactivation in heavily arsenic-doped silicon, using *ab initio* total energies. Our results are in good agreement with the observed experimental behavior. The deactivation can be explained by equilibrium densities of arsenic clustering about a single vacancy. Clusters containing more than one vacancy and second-neighbor arsenic pairs relaxed to threefold coordination but not accompanied by a vacancy are present, but in equilibrium do not dominate the deactivation. Because of the rarity of four arsenic atoms surrounding a single silicon atom in randomly solidified material, for which the deactivating clusters can form in one step, vacancy clusters containing only two or three arsenic atoms and pairs of threefold-coordinated arsenic atoms not accompanied by vacancies may dominate the initial deactivation, prior to the rearrangement of atoms needed to achieve full equilibrium. At low arsenic concentrations, activated arsenic represents the equilibrium state for temperatures at which equilibrium can occur. An explanation of the experimentally observed transient reactivation is proposed. [S0163-1829(98)03531-0]

I. INTRODUCTION

There are numerous problems in which the equilibrium or quasiequilibrium state of a crystalline system is sought, but the precise solution of the statistics for the general case is difficult, even for simple Hamiltonians. Some of these problems can be formulated, at least in part, in terms of short-range interactions of the solid, and many of these problems can further be modeled by an ensemble of statistically independent clusters, where the cluster size is less than a correlation volume; examples include the short-range order state of alloys and the populations of point defects and defect complexes in semiconductors.

The quasichemical approximation (QCA) is a cluster approximation in which the cluster populations are determined by the cluster free energies, but which ignores statistical correlations among clusters. The cluster variation method (CVM),¹ which includes some correlations between clusters, represents an improvement over QCA, but is considerably more difficult to solve. Because of its relative simplicity, the QCA is to be preferred over the CVM in cases in which their differences vanish, as in the case of pair clusters, or when long-range order is not important and the material is spatially homogeneous.

Sher *et al.*² developed a generalized quasichemical formalism (GQCA) for pseudobinary alloys that is applicable to arbitrary-size, nonoverlapping clusters. In this paper, the GQCA theory is extended to include an arbitrary number of components and overlapping clusters, and to include the electronic subsystem so that electronic excitations can be treated on the same footing as the configurational disorder. In this electronic quasichemical (EQC) formalism, the free energy is divided into three parts: (1) a free energy, which can be assigned to a specific class of distinguishable cluster;

(2) a configurational free energy related to the number of ways of arranging the atoms and clusters on the available sites; and (3) the free energy of electrons and holes in the conduction and valence bands, and which are treated as bandlike excitations of the extended crystal. The theory is formulated to provide an explicit connection with an external system, so that equilibration with other phases can be explicitly included. A relatively general cluster is considered, which includes an arbitrary number of distinguishable and indistinguishable sites, and either nonoverlapping or overlapping clusters. The cluster free energy can include zero-temperature electronic energies, temperature-dependent vibrational terms, and relatively localized electronic excitations.

As an example of an application of the EQC formalism, the problem of arsenic deactivation in silicon is examined. Some of our results have been published elsewhere.^{3,4} Because of its high solubility and slow diffusion rate, arsenic is the most widely used *n*-type dopant for silicon ultra-large-scale integration (ULSI) applications. Although the temperature-dependent solubility limit at which arsenic ceases to be electrically active has been well described,⁵⁻⁷ this equilibrium is not reached for many ULSI processes. Furthermore, metastable electrically active concentrations of arsenic are easily obtained by various methods.⁸⁻¹¹ Understanding the process and kinetics of arsenic deactivation is of great interest for both technological and scientific reasons; this includes an understanding of deactivated arsenic structures and how those structures form.

The process of arsenic deactivation has been the subject of extensive and ongoing research. Many models of the deactivation have been proposed¹¹⁻¹³ with good fits to selected sets of experimental data. Much experimental evidence is available that indicates the generation of vacancies during

deactivation. Recently, Nobili *et al.*⁷ have shown that, although precipitation occurs at higher arsenic concentration, clusters are responsible for the electrical deactivation below the solid solubility limit. Investigations using x-ray standing wave¹⁴ and backscattering¹⁵ spectroscopies find that arsenic remains on the lattice sites after deactivation, thus ruling out interstitial arsenic or noncoherent precipitates as the inactive species in some regimes. Structural measurements also show arsenic remains coherent with the lattice during deactivation,¹⁶ suggesting clusters instead of incoherent precipitates. Extended x-ray absorption fine structure measurements show arsenic nearest neighbors going from 4 to 3 during deactivation,^{17,18} an indication of a nearest-neighbor vacancy to the arsenic. Rousseau, Griffin, and Plummer¹⁹ observed strong diffusion enhancements in boron layers buried beneath a highly arsenic-doped surface layer during deactivation and concluded that the deactivation mechanism releases large numbers of silicon interstitials, indicative of vacancies forming in the arsenic-doped layer. The presence of vacancies in the deactivated material was further supported by recent work using a positron-beam technique,²⁰ which indicates between two and four arsenic atoms as nearest neighbors to these vacancies.²¹ An alternative explanation for some of these data has been recently proposed,²² based on deactivation of arsenic atom pairs, but not accompanied by vacancy generation; this alternative interpretation will be discussed further below.

Theoretically, Pandey *et al.*¹⁷ have shown a neutral complex, consisting of a lattice vacancy surrounded by four arsenic atoms VAs_4 , is an energetically favorable structure and proposed it as the deactivating complex. However, entropy disfavors the formation of such a large defect complex, and a complete free-energy calculation is therefore needed to determine the role of VAs_4 in deactivation. Because ionized arsenic atoms repel one another in the absence of a vacancy, there are also fundamental questions regarding the pathway and time constant for the formation of such a large defect complex, since the number of $SiAs_4$ clusters out of which VAs_4 complexes can form in one step is quite low. Ramamoorthy and Pantelides²³ examined other defect clusters involving arsenic, including the vacancy coordinated by fewer than four arsenic atoms, but did not consider the ionized states or the entropy which, as shown in this paper, are important and lead to conclusions in disagreement with theirs. Although they, too, find the VAs_4 cluster to be low energy, Chadi *et al.*²² dismissed this class of clusters and proposed a model for deactivation based on defects with no vacancies. Although their model is consistent with some of the experimental data suggesting threefold-coordinated arsenic and large voids near to arsenic atoms in deactivated material, it does not explain the generation of interstitials during the deactivation process,¹⁹ nor does it explain why the lower-energy vacancy complexes do not form.

The second part of this paper presents results on the equilibrium behavior of heavily arsenic-doped silicon using the EQC formalism. No fitting to deactivation data was done, and the only experimental data used in these calculations relate to the temperature-dependent band structure, which was deduced from totally separate experiments. The energies for various defect complexes were taken from *ab initio* calculations. Unlike previous calculations, the full free energy

to determine the deactivation mechanism is included, including the temperature-dependent electronic excitations and the entropy. Preliminary results can be found in Refs. 3 and 4. Here, details of the calculation and a sensitivity analysis, as well as some more physical insight into the statistical theory, are provided. In addition, the DP(2) defect proposed by Chadi *et al.*²² and the V_2As_6 cluster discussed by Ramamoorthy and Pantelides²³ are included and shown not to be important deactivation complexes in equilibrium.

II. EQC FORMALISM IN THE ABSENCE OF ELECTRONIC EXCITATIONS

In this section a statistical theory for neutral systems is developed. The method has grown out of the QCA, in which the crystal lattice is divided into an ensemble of clusters, each of which is taken to be statistically and energetically independent of its surroundings. The present theory is developed for an arbitrary number of atomic species and unique site occupation. An arbitrary cluster is also assumed, although it must be described by numerable sites for counting purposes. The sites can include both lattice sites typically thought of as occupied by the atomic constituents and various types of numerable interstitial positions. Although the method can be applied to various levels of cluster overlap, here our derivation is restricted to nonoverlapping clusters and clusters in which only sites, but not bonds, are shared. Discussion of electronic excitations is deferred until Sec. III.

Begin by considering a system containing N sites, with I distinguishable species that can occupy these sites, and with N_i sites occupied by the i th distinguishable species. The sites are grouped into K distinguishable classes, with N^k sites belonging to the k th class. The number of sites of class k occupied by species i is given by N_i^k , such that

$$\sum_{k=1}^K \sum_{i=1}^I N_i^k = \sum_{i=1}^I N_i = \sum_{k=1}^K N^k = N. \quad (1)$$

Here, the I species are defined very broadly to include every unique type of occupation of a site, including occupation by no atoms. Similarly, the sites are also defined very broadly to include what are usually thought of as lattice sites as well as interstitial positions that can be separately occupied. As an example, for the problem of point defects in a zinc-blende compound AB , one might choose five distinguishable classes of sites in the lattice: the anion sublattice, the cation sublattice, the two types of tetrahedral interstitial sublattices, and the sublattice consisting of hexagonal interstitial sites. For the same problem, the species might include a lattice vacancy on the A sublattice, an antisite of an A atom occupying the B sublattice, an interstitial of an A atom at a tetrahedral site, an interstitial of an A atom at a hexagonal site, and one or more classes of interstitialcies (pair of A atoms sharing a lattice site), and the corresponding defects for the B atoms.

The system is further divided into M independent clusters, each containing n sites. Defining p as the net number of sites per cluster such that $p \equiv N/M$, then $n = p$ corresponds to nonoverlapping space-filling clusters and $n > p$ corresponds to overlapping clusters for which sites are shared between clusters. J is defined as the number of distinguishable classes of clusters, with M_j clusters of class j , such that

$$\sum_{j=1}^J M_j = M. \quad (2)$$

Each of the n cluster sites is associated with one of the distinguishable classes of sites, k , with n^k sites of class k per cluster. For the j th cluster, the number of sites of class k occupied by species i is given by n_{ij}^k , with

$$\sum_{k=1}^K \sum_{i=1}^I n_{ij}^k = \sum_{i=1}^I n_{ij} = \sum_{k=1}^K n^k = n. \quad (3)$$

Consider the system in contact with reservoirs for the I' unique atomic species of the system, and which define the chemical potentials $\mu_{i'}$. A distinction is made between atomic species, for which there is a unique chemical potential defined by the reservoir, and the set of species that can occupy the N sites. The free energy of the system in equilibrium with the reservoirs can be written as

$$F(\{M_j\}, \{N_i^k\}) = \sum_{j=1}^J f_j M_j - k_B T \ln \Omega - \sum_{i'=1}^{I'} N_{i'} \mu_{i'}. \quad (4)$$

The f_j are the cluster free energies. Ω is the number of ways of configuring the system with the set of clusters $\{M_j\} = M_0, M_1, \dots, M_J$ and site occupations $\{N_i^k\} = N_1^1, N_2^1, \dots, N_J^1, N_1^2, N_2^2, \dots, \dots, N_J^K$. Assuming that the clusters are independent, Ω can be obtained by a generalization of the expression derived by Sher *et al.*,² that is,

$$\Omega = \left[\prod_{k=1}^K \left(\frac{N^k!}{\prod_i (N_i^k!)} \right) \right] \left[\frac{M!}{\prod_j (M_j!)} \right] \left[\prod_{j=1}^J (y_j^0)^{M_j} \right]. \quad (5)$$

The term in the first set of square brackets represents the total number of distinguishable ways of simultaneously arranging the sets of $\{N_i^k\}$ species on the $\{N^k\}$ sites. Because only configurations that are consistent with a particular set of clusters $\{M_j\}$ are to be included, this first term is multiplied by the probability of finding the set of clusters $\{M_j\}$. The probability of having the set of clusters $\{M_j\}$, subject to a particular set $\{N_i^k\}$, is given by the *a priori* probability of having a particular arrangement on the lattice of the set $\{M_j\}$ (the term in the third square brackets), times the number of ways of arranging the set $\{M_j\}$ on the M available cluster sites (the term in the second square brackets). The *a priori* probability of finding the j th cluster y_j^0 can be factored into sublattice contributions by

$$y_j^0 = \prod_{k=1}^K y_j^{k0}, \quad (6)$$

where y_j^{k0} is the *a priori* probability of finding the configuration on the k th sublattice. If each member of the set $\{y_j^{k0}\}$ is normalized when the product is taken over distinguishable configurations on the k th sublattice, while keeping the configurations on all other sublattices fixed, then $\{y_j^0\}$ will be

normalized when summed over all clusters $j=1$. Each of the y_j^{k0} can be written in the general form

$$y_j^{k0} = g_j^k \prod_{i=1}^I \left(\frac{N_i^k}{N^k} \right)^{n_{ij}^k}, \quad (7)$$

where g_j^k is the degeneracy of the j th configuration of the k th sublattice, for fixed configurations on all $k' \neq k$ sublattices. When all clusters with a given set of $\{n_{ij}^k\}$ are degenerate, the corresponding degeneracy factors g_j^k are binomial coefficients.²

Equilibrium cluster populations $\{\bar{M}_j\}$ and corresponding equilibrium site occupations $\{\bar{N}_i^k\}$ are obtained by minimizing the free energy of the system according to

$$0 = \frac{dF}{dM_j} \Big|_{\bar{M}_j, \bar{N}_i^k} = \left(\frac{\partial F}{\partial M_j} + \sum_{i=1}^I \sum_{k=1}^K \frac{\partial F}{\partial N_i^k} \frac{\partial N_i^k}{\partial M_j} \right)_{\bar{M}_j, \bar{N}_i^k}. \quad (8)$$

N_i^k and M_j are related by

$$N_i^k = \frac{p^k}{n^k} \sum_{j=1}^J n_{ij}^k M_j, \quad (9)$$

where $p^k \equiv N^k/M$ is the net number of sites of class k in the clusters. The term p^k/n^k corrects the counting of sites in cases where sites are shared between clusters, and reduces to unity when no sites of class k are shared among clusters. Expanding $\ln(\Omega)$ using Sterling's approximation, and taking the partial derivatives, an expression for the equilibrium cluster populations in terms of the equilibrium site occupations $\{\bar{N}_i^k\}$ is obtained from Eq. (8),

$$\begin{aligned} \bar{M}_j = M g_j \left(\prod_{i=1}^I \prod_{k=1}^K \left(\frac{\bar{N}_i^k}{N^k} \right)^{n_{ij}^k [(p^k/n^k) - 1]} \right) \\ \times \exp \left(\frac{-f_j + \sum_k \sum_i n_{ij}^k (p^k/n^k) \sum_{i'} m_{ii'}^k \mu_{i'}}{k_B T} \right), \end{aligned} \quad (10)$$

where

$$g_j = \prod_{k=1}^K g_j^k \quad (11)$$

and $m_{ii'}^k$ is the number of unique atomic species of type i' in the i th defect of the k th sublattice. The corresponding equilibrium fractional cluster populations are

$$y_j = \frac{\bar{M}_j}{M} = g_j b_j \prod_{i=1}^I \prod_{k=1}^K \left[(z_i^k)^{n_{ij}^k [(p^k/n^k) - 1]} \prod_{i'=1}^{I'} \eta_{i'}^{n_{ij}^k (p^k/n^k) m_{ii'}^k} \right], \quad (12)$$

where $b_j = \exp(-f_j/k_B T)$ and $z_i^k = \bar{N}_i^k/N^k$ are the fractional site occupations on the k th sublattice. $\eta_{i'} = \exp(\mu_{i'}/k_B T)$ is the activity of the i' th atomic species. For $K=1$ and $I=2$, Eq. (12) reduces to the expression derived by Sher *et al.*²

with the zero of energy chosen so that the chemical potential of one of the two constituents is identically zero.

III. EQC FORMALISM INCLUDING ELECTRONIC DISORDER

Clusters may have associated with them states of electronic excitations. In such cases, the populations of clusters of type j with charge q (assumed to be integral in units of $|e|$) $M_{j,q}$ can be determined from a generalization of the above derivation. For example, one of the clusters considered in the second half of this paper consists of a substitutional arsenic atom surrounded by silicon atoms. Although the wave function of the hydrogeniclike shallow donor state formed by arsenic will extend beyond the five-atom cluster used, the cluster containing an ionized arsenic will be assigned the full, integral charge associated with the ionized arsenic wave function.

The free energy of the system containing electronic excitations can be written as a generalization of Eq. (4):

$$F(\{M_{j,q}\}, \{N_i^k\}) = \sum_{j=1}^J \sum_q (f_{j,q} + q\mu_F) M_{j,q} - k_B T \ln \Omega - \sum_{i'=1}^{I'} N_{i'} \mu_{i'}, \quad (13)$$

where \sum_q runs over all excitation states of the j th cluster. The cluster free energies have been generalized to include the contributions from the electronic excitations with $f_{j,q} = f_j + E_{j,q}$, where $E_{j,0} = 0$. The interaction of the system with the finite temperature bandlike electronic excitations of the solid are captured in the Fermi energy μ_F , which is required to be the same for both cluster and bandlike excitations, and is discussed further in Sec. IV. The number of ways of configuring the set $\{M_{j,q}\}$ now becomes

$$\Omega = \left[\prod_{k=1}^K \left(\frac{N^k!}{\prod_i (N_i^k!)} \right) \right] \left[\frac{M!}{\prod_j \prod_q (M_{j,q}!)} \right] \times \left[\prod_{j=1}^J \prod_q (y_{j,q}^0)^{M_{j,q}} \right], \quad (14)$$

where

$$y_{j,q}^{k0} = g_{j,q}^k \prod_{i=1}^I \left(\frac{N_i^k}{N^k} \right)^{n_{ij}^k}. \quad (15)$$

As above, the set of equilibrium cluster populations are obtained by minimizing the free energy of the system, using Sterling's approximation, to obtain

$$y_{j,q} = \frac{\bar{M}_{j,q}}{M} = g_{j,q} b_j \zeta_{j,q} \eta_0^{-q} \times \prod_{i=1}^I \prod_{k=1}^K \left[(z_i^k)^{n_{ij}^k} [(p^k n^k) - 1] \prod_{i'=1}^{I'} \eta_{i'}^{n_{ij}^k (p^k/n^k) m_{ii'}^k} \right], \quad (16)$$

where $\zeta_{j,q} = \exp(E_{j,q}/k_B T)$, $\eta_0 = \exp(\mu_F/k_B T)$ is the electron activity, and $g_{j,q} = \prod_k g_{j,q}^k$. Equation (16) reduces to Eq. (12) when the set $\{E_{j,q}\}$ are all zero, so that $y_{j,q} = 0$ for $q \neq 0$. The total population of the j th class of cluster is given by the sum over all charge states

$$y_j = \sum_q y_{j,q}. \quad (17)$$

IV. SOLUTION OF THE EQC EQUATIONS

From Eqs. (16) and (17), a set of J equations for the cluster populations $\{y_j\}$ is obtained. Assuming that the cluster free energies and degeneracies can be determined — for example, from *ab initio* calculations or from experiment — the cluster populations $y_{j,q}$ are functions of the I' constituent chemical potentials $\{\mu_{i'}\}$, temperature T , and pressure P , and for systems with electronic excitations, the electron chemical potential μ_F , for a total of $I' + 3$ unknowns (or $I' + 2$ unknowns when electronic excitations are excluded). For a system of H phases, there are H Gibbs-Duhem relations, one for each phase. Thus, one obtains Gibbs' phase rule that relates the number of degrees of freedom θ to the number of phases and unknowns, via $\theta = I' - H + 3$, or $\theta = I' - H + 2$ when electronic excitations are excluded. The $H + 1$ (or H for no electronic excitations) remaining unknowns are determined by constraint equations. One constraint equation comes from the normalization of the cluster populations in the phase of interest:

$$\sum_q \sum_{j=1}^J y_{j,q} = \sum_{j=1}^J y_j = 1. \quad (18)$$

For systems with electronic excitations, a second constraint equation is given by the condition of overall charge neutrality. For semimetals, semiconductors, and insulators, this is given by

$$\sum_{j=1}^J \sum_q \frac{q M_{j,q}}{V} + N_h - N_e = 0, \quad (19)$$

where V is the volume of the phase of interest, N_e is the electron density in the conduction band, and N_h is the hole density in the valence band. N_e and N_h can be calculated in the usual manner from

$$N_e = \int_{E_c}^{\infty} N_c(E) F(E) dE \quad (20)$$

and

$$N_h = \int_{-\infty}^{E_v} N_v(E) (1 - F(E)) dE, \quad (21)$$

where $F(E)$ is the Fermi-Dirac distribution function. N_c and N_v are the conduction- and valence-band density of states, respectively, and for parabolic bands are given by

$$N_c = \frac{M_c 2^{1/2} (E - E_c)^{1/2} (m_e^* m_0)^{3/2}}{\pi^2 \hbar^3} \quad (22)$$

and

$$N_v = \frac{2^{1/2}(E_v - E)^{1/2}(m_h^* m_0)^{3/2}}{\pi^2 \hbar^3}. \quad (23)$$

E_c and E_v are the energies at the bottom of the conduction band and top of the valence band, respectively; M_c is the number of inequivalent minima in the conduction band; m_0 is the electron mass; and m_e^* and m_h^* are the electron and hole effective masses in units of m_0 . The Fermi-Dirac distribution function $F(E)$ is the probability of a state at energy E being occupied and is given by

$$F(E) = \frac{1}{1 + \exp\left(\frac{E - \mu_F}{k_b T}\right)}. \quad (24)$$

For each phase in addition to the one of interest, one additional equation must be specified. The problem of interest will in part determine which degrees of freedom will be specified, but they will often include the temperature and the pressure. In some cases it will be desirable to specify the concentration of a particular species on a particular sublattice of the system of interest as one of the degrees of freedom. The equation that relates the number of species i on the k th sublattice, N_i^k , or its fractional population $z_i^k = N_i^k/N^k$, to the cluster populations is

$$z_i^k = \sum_{j=1}^J \sum_q \frac{n_{ij}^k}{n^k} y_{j,q}. \quad (25)$$

If Eq. (18) is satisfied, then the z_i^k 's will be normalized to the k th sublattice such that

$$\sum_{i=1}^I z_i^k = z^k = 1. \quad (26)$$

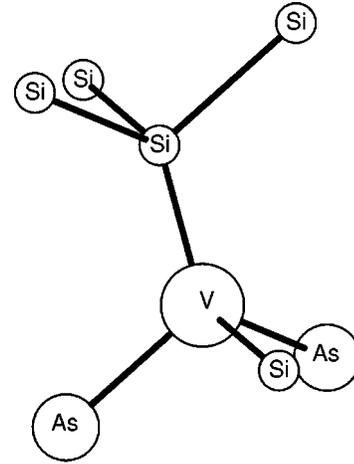
The total fractional population $x_i = N_i/N$ of a species i is related to the $\{z_i^k\}$ by

$$\sum_{k=1}^K z_i^k x^k = x_i. \quad (27)$$

Equations (18), (19), and (25), and equations of states for any external phases will in many problems form the basic set of equations that must be solved for the atomic chemical potentials $\{\mu_i\}$. The solution for the Fermi energy $\{\mu_F\}$ is most easily handled through an iterative numerical procedure, unless Boltzmann statistics for electron populations are known to be applicable *a priori*, in which case Eqs. (20) and (21) reduce to the simpler expressions with $N_e \propto \exp(\mu_F/k_B T)$ and $N_h \propto \exp(-\mu_F/k_B T)$.

A. Calculations for quenched systems

In many cases of interest, equilibration of the system will take place at high temperatures—for example, during growth or processing of a material—but the measurable properties of interest are those of the system at some other lower temperature. If the equilibration of the defect structures at the lower temperature is negligible, the defect structure obtained at high temperature can be assumed to be frozen in, or, if the material is cooled slowly, frozen in at some effective tem-



8-atom cluster

FIG. 1. Typical eight-atom cluster included in the analysis. Example shown here is for the VAs_2 cluster.

perature where diffusion effectively stops. The electronic subsystem can equilibrate rapidly and thus must be allowed to reequilibrate at the lower temperature. This means a recalculation of the Fermi energy, keeping the cluster populations fixed, such that

$$\sum_q y_{j,q}^{LT} = \sum_q y_{j,q}^{HT}, \quad (28)$$

where $y_{j,q}^{LT}$ is the population of the j th class of cluster at low temperature and $y_{j,q}^{HT}$ is the population at high temperature where full equilibration can occur. To calculate $\{y_{j,q}^{LT}\}$, a new Fermi energy μ_F^{LT} is determined by applying the cluster neutrality condition, Eq. (19), subject to the constraints imposed by Eq. (28).

V. APPLICATION OF THE EQC FORMALISM TO ARSENIC IN SILICON

We now turn to an application of the above statistics: the behavior of arsenic in silicon. The problem is formulated quite generally, so that the equilibrium properties for all temperatures and arsenic concentrations up to the solubility limit can be examined. The problem of whether equilibrium is achievable in real experiments is discussed in Sec. VII.

A. Cluster selection and ground-state energies

For the statistics, the real-space lattice is divided into non-overlapping clusters containing eight lattice sites, as illustrated in Fig. 1. The cluster size has been chosen to be large enough so that the largest defect complex of interest can be described, but small enough so that there is only one defect complex per cluster. Previously, five-atom clusters were chosen so that the family of clusters containing a lattice vacancy surrounded by zero to four arsenic atoms could be modeled.³ Here, eight-atom clusters are used so that more extended

defects can be included — for example, the divacancy surrounded by up to six arsenic atoms.²³

One assumption of the EQC is that the lattice can be divided into clusters with energies that are nearly independent of their specific environment, so that just one energy can be assigned to each cluster. The cluster energies are calculated by embedding each of the defect clusters in a silicon lattice. In practice, supercells are used, as is typical in local density approximation (LDA) calculations, and a repeating array of a given defect cluster embedded in a silicon lattice is constructed. Thirty-two atom supercells have been used in the present calculations, and both the overall relaxation of the unit-cell lattice constant and atomic relaxations of up to the second-neighbor shell about the defect complex have been included. Although calculations will be done for high arsenic concentrations, our calculations are restricted to arsenic occupying less than 10% of the lattice sites. Thus, for example, there are nearly 40 silicon atoms for each VAs_4 complex, and ten silicon atoms for each isolated arsenic atom in the lattice, justifying the approximation of embedding the clusters in the silicon host.

Detailed calculations for the following clusters have been done: Si_8 , pure silicon cluster; $AsSi_4$, arsenic atom surrounded by silicon; VAs_n , lattice vacancy surrounded by n arsenic atoms; V_2As_6 , lattice divacancy, surrounded by six arsenic atoms. In these notations, silicon atoms in the cluster are not specifically identified, unless it is necessary for clarity. For example, the VAs_n cluster is synonymous with the VAs_nSi_{7-n} cluster, and the $AsSi_4$ cluster is the same as the $AsSi_7$ cluster. The properties of several additional clusters have also been calculated: the silicon and arsenic interstitials; the lattice vacancy with one or zero arsenic near neighbors; substitutional arsenic near neighbors; second-neighbor clusters of arsenic about a central silicon atom ($SiAs_n$, akin to the VAs_n clusters, but without the vacancy); and arsenic interstitial arsenic substitutional pairs. These cluster energies were calculated allowing relaxation, but using a less complete basis set. Based on these energies and on conservative error estimates for the small basis set, the densities of these defects were found to be small, and negligible for the present considerations. Some of the minority defects — such as the silicon and arsenic interstitials and the VAs_1 cluster, for instance — should be included in an analysis of arsenic diffusion,²⁴ but are not found to impact the equilibrium.

Two additional clusters are included in the analysis. First, the neutral cluster composed of threefold-coordinated second-neighbor arsenic atoms, as recently discussed by Chadi *et al.*,²² and referred to there as DP(2), is included. This defect was reported to have a binding energy of 0.06 eV relative to the undistorted pair with the Fermi energy at the bottom of the conduction band. Second, the divacancy surrounded by six arsenic atoms, V_2As_6 , discussed by Ramamoorthy and Pantelides,²³ was also included. These authors also considered a whole hierarchy of divacancy complexes, but, as will be shown below, even the most well bound of them (V_2As_6) never dominates the deactivation, thus justifying the neglect of the other clusters.

Electronic contributions to the neutral cluster free energies E_j were obtained from a full-potential version of the linearized muffin-tin orbital (FP-LMTO) method,²⁵ in the local-density approximation (LDA) with the Barth and Hedin

TABLE I. Clusters properties. The arbitrary zero of energy is chosen so that the energy of the Si_8 and As_1Si_4 clusters are zero. Acceptor levels are indicated by a and are referenced to the valence-band edge; donor levels are indicated by d , are referenced to the conduction-band edge, and are positive if they are in the gap. Cluster degeneracies are charge-state dependent.

Cluster	Neutral cluster energy E_j (eV)	Ionization energies $E_{j,q}$ (eV)
Si_8	0	none
$AsSi_4$	0	0.054(d),resonant(d) ^a
VAs_4	-1.62	none
VAs_4Si_1	-0.18	0.5(a)
VAs_2Si_2	1.14	0.4($a1$);0.7($a2$)
V_2As_6	-2.30	none
DP(2) ^b	0.10	none

^aThe isolated arsenic is assumed resonant in the conduction band for $[As] > 10^{18} \text{ cm}^{-3}$, and to have the noted finite activation energy for $[As] < 10^{18}$.

^bThe eight-atom cluster is not the natural choice for the DP(2) complex. Because of the small cluster we are using, the degeneracy used is slightly lower than that used by Chadi *et al.*²² in their analysis.

functional.²⁶ 32-atom supercells were used, each containing the eight-atom cluster of interest surrounded by silicon. To ensure a good fit to the charge density and potential in the interstitial region, empty spheres have been included and orbitals added to the basis by centering them on the empty spheres. The semicore d electrons on the arsenic atoms were treated explicitly as valence states in a second panel. The basis set and charge density representation was chosen to give errors in the cluster energies of less than 0.01 eV. For the highest symmetry cells, relaxation calculations were performed using two special k points, and final energies were calculated using fourteen special k points. More k -points were used for lower symmetry cells. The core was allowed to relax during the self-consistency cycle.

Eight-atom cluster energies are extracted from a 32-lattice-site supercell by subtracting off the energy of the 24 silicon atoms about the cluster. Thus, the neutral cluster energies are given by

$$E_j = \mathcal{E}_j^{32} - \left(\frac{24}{32}\right) \mathcal{E}_{Si}^{32}, \quad (29)$$

where \mathcal{E}_j^{32} is the energy of the 32-atom supercell containing the eight-atom j th cluster and surrounded by silicon, and \mathcal{E}_{Si}^{32} is the energy of the 32-atom supercell containing just silicon. Cluster energies are further reduced by setting the arbitrary zero of energy so that the energy of the Si_8 and As_1Si_4 clusters vanish. Eight-atom cluster energies are given in Table I. The energy of the VAs_4 cluster is in rough agreement with Pandey *et al.*¹⁷ These energies may appear to differ substantially from those those reported by Ramamoorthy and Pantelides,²³ but the differences are due mostly to the different reference they use, that of the corresponding $SiAs_n$ clusters. Discrepancies between our energies and those of Pandey *et al.*¹⁷ and Ramamoorthy and Pantelides²³ can be

attributed to the larger basis set and use of more accurate description of the arsenic d states.

The overall lattice constant of the 32-atom unit cell was allowed to relax during the self-consistency cycles. Atomic relaxations were largely radial about the vacancies. For the pure silicon cluster, the Si-Si distance is 2.34 Å. For the neutral AsSi_4 cluster, the first-neighbor arsenic-silicon distance is 2.41 Å. For the neutral VAs_4 cluster, the arsenic atoms move in toward the vacancy, with an effective As-V distance of 2.11 Å and a first-neighbor As-Si distance of 2.40 Å. For the neutral VAs_3 cluster, the effective Si-V distance is 2.30 Å, the effective As-V distances are 2.13 Å and 2.10 Å (a slight breaking of the C_{3h} symmetry is found), and the As-Si distance is ~ 2.4 Å. A temperature- and arsenic-concentration independent value for the number of lattice sites per volume of $5 \times 10^{22} \text{ cm}^{-3}$ was used.

B. Cluster energies: excited states

Ionization energies were calculated and are summarized in Table I. No negative- U centers were found, and thus the ionization energies can be unambiguously cast as one-electron levels. No *ad hoc* shifts were added to the LDA energy levels. The VAs_4 cluster is found to have no donor or acceptor levels in the gap, in agreement with the previous finding.¹⁷ The VAs_3 and VAs_2 clusters are found to have one and two acceptor levels in the gap, respectively, which will effectively lower their formation energy when the Fermi energy is near the conduction-band edge.

Because the band-gap varies with the temperature, how the ionization energies vary with temperature is uncertain — that is, do they track the conduction or the valence-band edge, or neither? To our knowledge, no theory has yet been designed to map the temperature-dependence of LDA ionization energies. In this work, acceptor levels are assumed to track the valence band and donor levels to track the conduction-band edge.

C. Cluster degeneracies

Cluster degeneracies include both spin degeneracies and configurational degeneracies associated with the number of ways of arranging the defect in the eight-atom cluster. The degeneracy is calculated assuming the cluster is embedded in a silicon host, or that the most probable neighboring clusters are the Si_8 clusters. Thus, for example, for the eight-atom clusters, the degeneracy of the AsSi_4 cluster is eight because all of the eight sites the arsenic can take in the cluster are identical when a silicon host is assumed.

D. Vibrational excitations

A Green's-function method to calculate the vibrational free energies of defects in semiconductors based on a valence force-field model plus a point charge Coulomb model was presented elsewhere.²⁷ These vibrational energies are important when absolute reference to an external phase is desired — for example, in Ref. 27 the mercury vapor was used as an absolute reference for establishing the system chemical potentials. As discussed there, it is also important to include the gradient corrections to the LDA to correct for the overbinding of the solids with respect to the free atoms

when one is interested in using a partial pressure to establish the chemical potential of a constituent. In the present paper, no attempt is made to identify the chemical potentials with reference to another phase, and thus, although the vibrational spectrum will change somewhat depending on the bonding geometry of the arsenic and silicon, these contributions are ignored. Because the vibrational terms are ignored, the cluster free energies include just the electronic piece for the ground state calculated from the LDA,

$$f_j = E_j. \quad (30)$$

E. Band-structure properties

In addition to the inability of LDA to predict correct band gaps in silicon, the equilibrium of interest is at high temperatures and the silicon band gap narrows substantially at these high temperatures. To make the most accurate predictions possible, the experimentally determined, temperature-dependent band gaps are extrapolated to the temperature of interest.²⁸ For $T > 300$ K

$$E_g(\text{eV}) = 1.12 - 2.5 \times 10^{-4}(T - 300) \quad (31)$$

is used, where T is the temperature in kelvin and E_g is the minimum energy gap in eV.²⁸ Density-of-states effective masses and band minimum degeneracies are also taken from experiments.

The low-temperature values for the longitudinal and transverse electron effective masses are²⁸ $m_{el}^* = 0.92$ and $m_{et}^* = 0.19$, and the density of states effective mass m_e^* is obtained from

$$m_e^* = (m_{el}^* m_{et}^* m_{et}^*)^{1/3} = 0.32. \quad (32)$$

The silicon conduction band has six inequivalent minimums, so that $M_c = 6$. Temperature and heavy doping modifications to the conduction band shape have not been included.

Both the conduction and valence bands will be assumed to be parabolic. The low-temperature values for the heavy- and light-hole effective masses are²⁸ $m_{lh}^* = 0.15$ and $m_{hh}^* = 0.54$, and the density-of-states effective mass m_h^* is obtained from

$$m_h^* = (m_{lh}^{*3/2} + m_{hh}^{*3/2})^{2/3} = 0.59. \quad (33)$$

The near-gap valence-band structure may also be modified at the high temperatures considered here.

VI. RESULTS: EQUILIBRIUM BEHAVIOR

In solving for the behavior of arsenic in silicon, a given amount of arsenic is assumed to be frozen into the silicon lattice — for example, by a laser melt anneal following an ion implantation. Appreciable diffusion of the arsenic is not observed during the subsequent equilibration anneals,⁹ and thus the concentration of arsenic in the doped region is assumed to be constant throughout the equilibration. Dislocations, the surface, and the bulk (in the case of a doped surface layer) are considered sources and sinks for silicon atoms. The neutral cluster energies, ionization states, and degeneracies are incorporated into Eq. (16). The five unknowns of the problem are the silicon and arsenic chemical

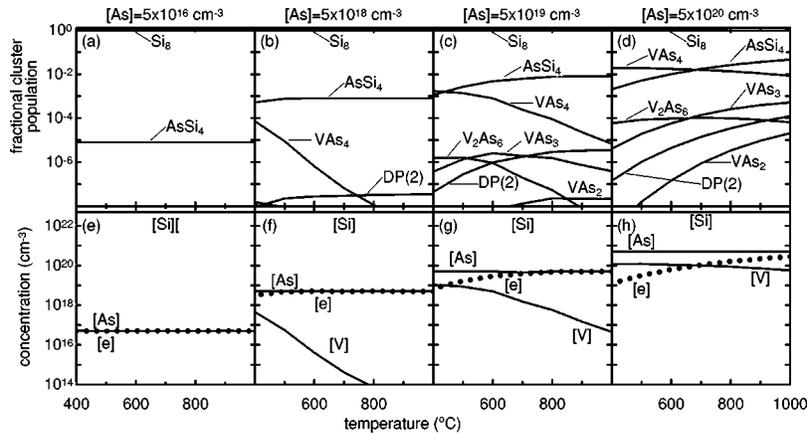


FIG. 2. Fractional cluster populations y for eight-atom clusters, as a function of temperature, for silicon with a total arsenic concentration of (a) $5 \times 10^{16} \text{ cm}^{-3}$, (b) $5 \times 10^{18} \text{ cm}^{-3}$, (c) $5 \times 10^{19} \text{ cm}^{-3}$, and (d) $5 \times 10^{20} \text{ cm}^{-3}$. Cluster populations have been summed over all ionization states; the singly ionized acceptor dominates for VAs_3 , the doubly ionized acceptor dominates for VAs_2 , and the singly ionized donor dominates for $AsSi_4$. Panels (e)–(h) are the total concentration of silicon atoms, arsenic atoms, and vacancies, in equilibrium at the given temperature, for the same arsenic concentrations as in (a)–(d). Also shown in panels (e)–(h) are the electron concentration at 300 K, calculated assuming that the defect structures obtained at the equilibration temperature is frozen in.

potentials μ_{Si} and μ_{As} , the Fermi energy μ_F , the temperature, and the pressure. If the system is treated as a single phase, there will be a total of three degrees of freedom, which are chosen by specifying the temperature, the total pressure, and the total fractional arsenic concentration x_{As} in the lattice. The two additional equations needed to solve for the unknowns are the normalization of the cluster populations and overall charge neutrality. The system also could have been treated as a two-phase system consisting of the solid in equilibrium with its vapor; because the cluster energies are insensitive to realistic pressures, this produces equivalent results to those presented here. Calculation of the vapor pressure would necessitate calculation of vibrational properties of the arsenic in silicon lattice, and also would need to address the over-binding predicted by LDA. A vapor pressure calculation also requires calculation of the properties of the vapor species such as As_2 and As_4 . Such calculations have been done elsewhere for a III-V alloy system.²⁹

Another system of interest is the system in equilibrium with a second solid phase — for example, the monoclinic $SiAs$ phase or pure arsenic solid; such a calculation is needed for determining the equilibrium solubility limit of arsenic in diamond-phase silicon. Accurate prediction of the solubility limit depends on having good estimates for the vibrational terms in the free energy for all phases involved, and is not discussed here.

A. Cluster populations

In Figs. 2(a)–2(d), the cluster populations are plotted as a function of temperature for arsenic concentrations of $5 \times 10^{16} \text{ cm}^{-3}$, $5 \times 10^{18} \text{ cm}^{-3}$, $5 \times 10^{19} \text{ cm}^{-3}$, and $5 \times 10^{20} \text{ cm}^{-3}$, corresponding to 0.0001%, 0.01%, 0.1%, and 1% of the lattice sites in the system. In Figs. 2(e)–2(h), the total concentrations of silicon atoms, arsenic atoms, and vacancies for the same total arsenic concentrations as in Figs. 2(a)–2(d), are plotted, along with the room-temperature electron concentration assuming that the high-temperature defect

structure is frozen in. Because the diffusion rates of the constituents are very low at room temperature, this is a reasonable assumption.

For all concentrations and equilibration temperatures considered, three classes of clusters dominate: Si_8 , $AsSi_4$, and VAs_4 , with the latter being the primary means of nonideal incorporation of arsenic into the lattice. Results shown in Figs. 2(d) are very similar to those reported in Ref. 3, in which five-atom clusters were used and the V_2As_6 and $DP(2)$ clusters were not included. In all cases, the Fermi energy is near the conduction-band edge, and VAs_3 and VAs_2 are predominantly singly and doubly ionized, respectively.

For a low arsenic concentration of $5 \times 10^{16} \text{ cm}^{-3}$, and for equilibration temperatures above $400 \text{ }^\circ\text{C}$, arsenic incorporates into the lattice almost exclusively as isolated arsenic atoms surrounded by silicon, and with negligible binding to lattice vacancies. If this defect structure is quenched in, this corresponds to 100% arsenic activation at room temperature, as is indicated in Fig. 2(e), where the electron concentration is equal to the total arsenic concentration in the lattice. As the temperature is lowered below $400 \text{ }^\circ\text{C}$ (not shown in the figure), the population of VAs_4 clusters increase until they dominate the arsenic incorporation as $T \rightarrow 0 \text{ K}$. Thus, *in equilibrium*, among the complexes considered, VAs_4 represents the lowest free energy state of arsenic at zero kelvin. Because diffusion is very slow at low temperatures, it is unlikely that full equilibrium of the arsenic-silicon system is ever achieved at temperatures much below $300 \text{ }^\circ\text{C}$. The results discussed here are restricted to cases in which second-phase precipitation does not occur. For $[As] = 5 \times 10^{18} \text{ cm}^{-3}$ [Figs. 2(b) and 2(f)], the density of the deactivating VAs_4 cluster is increased significantly relative to the $[As] = 5 \times 10^{16} \text{ cm}^{-3}$ case, but significant deactivation is still not predicted for equilibration temperatures above $\sim 500 \text{ }^\circ\text{C}$. As the arsenic concentration is raised further to $5 \times 10^{19} \text{ cm}^{-3}$ [Figs. 2(b) and 2(g)] and $5 \times 10^{20} \text{ cm}^{-3}$ [Fig. 2(c) and 2(h)], significant deactivation is predicted, largely due to the VAs_4 clusters.

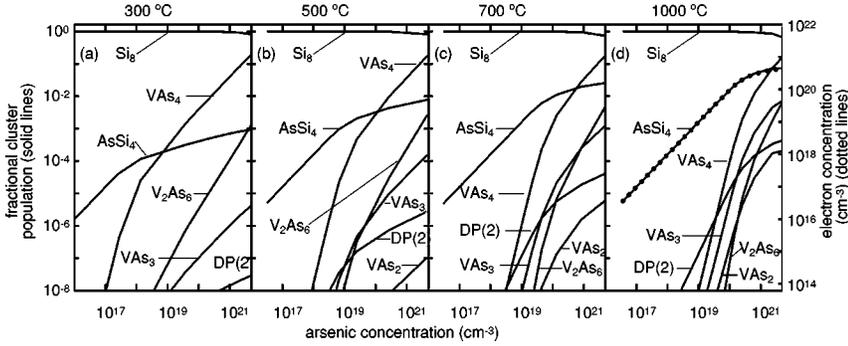


FIG. 3. Solid lines are the fractional eight-atom cluster populations as a function of arsenic concentration, for (a) 300, (b) 500, (c) 700, and (d) 1000 °C. The dotted line in panel (d) is the room-temperature electron concentration, and reads off of the far right axis.

Clearly both concentration and temperature impact the defect distribution: at high temperatures, entropy effects are more important in determining the defect structure and means of incorporating arsenic that increase the system entropy will dominate. Because active arsenic incorporation maximizes the system configurational entropy for a fixed arsenic concentration, this form of incorporation dominates at elevated temperatures, as illustrated in Figs. 2(a)-2(d). For a given temperature, the crossover between incorporation as AsSi_4 and VAs_4 will depend on the total amount of arsenic in the lattice. This is illustrated in Fig. 3; at 300 °C, the concentration at which $[\text{AsSi}_4] = [\text{VAs}_4]$ occurs is $\sim 10^{19} \text{ cm}^{-3}$, and moves to $\sim 10^{20} \text{ cm}^{-3}$, $\sim 5 \times 10^{20} \text{ cm}^{-3}$, and $\sim 2 \times 10^{21} \text{ cm}^{-3}$ for 500 °C, 700 °C, and 1000 °C, respectively. Thus even at 300 °C, entropy still drives arsenic incorporation as isolated active species until total arsenic concentrations are in the range of 10^{19} cm^{-3} . At 1000 °C, a saturation of the active arsenic concentration of about $4 \times 10^{20} \text{ cm}^{-3}$ (dotted line in last panel of Fig. 3) is found, in good agreement with the experimentally determined value of $\sim 3.2 \times 10^{20} \text{ cm}^{-3}$ at this temperature.^{7,9}

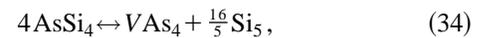
Although the DP(2) cluster proposed by Chadi *et al.*²² is present as a deactivating species, it does not contribute significantly to the deactivation if full equilibration is allowed to occur (the role of DP defects in the approach to equilibrium is discussed in Sec. VII). This is simply due to the larger binding energy of the VAs_4 complex. Although the Fermi energy effect increases the effective binding energy of the DP complexes,²² it also increases the binding of the vacancy complexes by a similar amount per arsenic atom. Note that the present calculation is different from the analysis done by Chadi *et al.*²² In the present calculation, full equilibrium is permitted, with no restrictions to rearrangement of the atoms in the lattice, while the analysis in Ref. 22 assumed that the atoms were frozen into the lattice in random configurations, with no subsequent rearrangements during the deactivation except for the relatively local relaxation about the DP clusters.

Similarly, the V_2As_6 cluster proposed by Ramamoorthy and Pantelides²³ is present, but does not contribute significantly to the deactivation for arsenic concentrations up to $5 \times 10^{20} \text{ cm}^{-3}$. This is due in part to the lower binding energy per arsenic atom of the V_2As_6 compared to the VAs_4 complex, but even if the binding energy per arsenic atom of these complexes was comparable, the VAs_4 complex would still dominate the deactivation because of the higher entropy associated with this complex (it involves the assemblage of fewer arsenic atoms). This was demonstrated by repeating the calculations for $[\text{As}] = 5 \times 10^{20} \text{ cm}^{-3}$, but with only the

Si_8 , AsSi_4 , VAs_4 , and V_2As_6 clusters, and with the energy of the V_2As_6 cluster adjusted so that the binding energy per arsenic was the same as it is for the VAs_4 complex. The density of the Si_8 , AsSi_4 , and VAs_4 clusters is essentially unchanged, and although the density of the V_2As_6 cluster increases by a factor of 10–20 over the given temperature range, it still never dominates the deactivation. Errors in the LDA energies, differences in the vibrational entropy terms of the VAs_4 and V_2As_6 clusters that have not been included here, as well as errors associated with approximations intrinsic to the cluster statistics, which are especially important at very high arsenic concentrations (above $\sim 1 - 10\%$ of the lattice sites), could result in a modification of this conclusion. Unless such errors are very large, clusters containing two or more adjacent vacancies surrounded by arsenic atoms will not dominate the deactivation except at very large arsenic concentrations, perhaps beyond the solid solubility limit.

B. Approximate model of deactivation

Given the large binding energy of the VAs_4 cluster, it may be surprising at first glance that arsenic is ever active in silicon. This result can be understood from a simple analysis of the temperature and arsenic concentration-dependent equilibrium between VAs_4 clusters and isolated arsenic atoms in the lattice AsSi_4 . We emphasize that, with the exception of the present discussion, all results in this paper have relied on the full EQC formalism, as discussed above. The equilibrium reaction can be written as



with a forward reaction energy of $\Delta E = -1.62 \text{ eV}$ taken from Table I. Each complex occupies five regular lattice sites, and there are $\mathcal{N} = 10^{22} \text{ cm}^{-3}$ five-site clusters. The AsSi_4 are assumed to be 100% ionized, and the Fermi energy is assumed to be roughly at the bottom of the conduction band.

From the law of mass action, one obtains

$$\frac{y_{\text{AsSi}_4}^4}{y_{\text{VAs}_4} y_{\text{Si}_5}^{16/5}} = 5^4 \exp\left(\frac{\Delta E}{k_B T}\right), \quad (35)$$

where y_j is the number of j clusters divided by \mathcal{N} . The factor of 5^4 comes from the degeneracy of the AsSi_4 cluster. If the density of other forms of arsenic incorporation in the lattice are small, then

$$x_{\text{As}} \approx \frac{1}{5}y_{\text{AsSi}_4} + \frac{4}{5}y_{\text{VAs}_4}, \quad (36)$$

where x_{As} is the total fractional concentration of arsenic atoms in the lattice, and $1 - x_{\text{As}}$ is approximately the silicon fractional concentration. Defining the activation fraction f as the fraction of arsenic in the lattice in active form, then

$$y_{\text{AsSi}_4} = 5fx_{\text{As}}, \quad (37)$$

$$y_{\text{VAs}_4} = 5(1-f)x_{\text{As}}/4, \quad (38)$$

and

$$y_{\text{Si}_5} = 1 - y_{\text{AsSi}_4} - y_{\text{VAs}_4} = 1 - 5x_{\text{As}}(1-3f)/4. \quad (39)$$

Substituting these expressions into Eq. (35),

$$\frac{4f^4 x_{\text{As}}^3}{5(1-f)[1-5x_{\text{As}}(1-3f)/4]^{16/5}} = \exp\left(\frac{\Delta E}{k_B T}\right). \quad (40)$$

Assuming that no other dopants are present in the lattice and the system is not intrinsic, the free carriers are dominated by the active arsenic concentration, so that $[e] = 5 \times 10^{22} f x_{\text{As}} \text{ cm}^{-3}$, and the total arsenic concentration is given by $[\text{As}] = 5 \times 10^{22} x_{\text{As}} \text{ cm}^{-3}$. The behavior of $[e]$ versus $[\text{As}]$ deduced from this equation is similar to that found using the full EQC formalism. As the temperature is lowered at a fixed arsenic concentration, Eq. (40) shows that the activation fraction decreases, as was found in each of the Figs. 2(f)–2(h). In the limit of $T \rightarrow 0$ K, the right-hand side of Eq. (40) vanishes, and for any finite arsenic concentration the activation fraction vanishes, indicating the VAs_4 cluster as the lowest-energy state at zero temperature. The asymptotic behavior for low arsenic concentrations can be extracted from Eq. (40): as $x_{\text{As}} \rightarrow 0$ (for $T \neq 0$ K) the activation fraction approaches unity and the arsenic is fully active, with $[e] = [\text{As}]$.

C. Comparison with experiment

Extensive research has been conducted into the properties of arsenic in silicon, and no attempt has been made here to provide an extensive critique of the experimental literature. Instead, several experiments to which we can directly compare our results are selected. There are many questions associated with the temporal response of the deactivation, as well as diffusion in heavily doped silicon, which are briefly addressed in the discussion of nonequilibrium behavior in Sec. VII.

Nobili *et al.*⁷ have examined the properties of arsenic-doped silicon in equilibrium with SiAs precipitates. Using their values of the saturated arsenic concentration in the silicon lattice, the corresponding electron concentration has been calculated; results are shown in Fig. 4. Our predicted electron concentrations are within a factor of 2 of the corresponding experimental numbers determined by Nobili *et al.*⁷ over the temperature range $700 < T < 1100$ °C. If the energy of the VAs_4 cluster is reduced by 0.15 eV, our agreement with experiments is excellent; given the accuracy of the LDA energies, as well as uncertainties in the silicon band structure at high doping levels, such a correction is reasonable. This finding of a temperature-dependent, maximum free electron

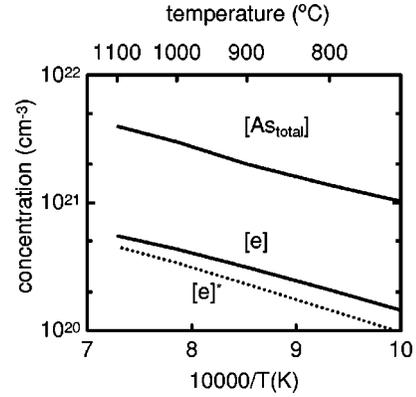


FIG. 4. The saturated total electron concentration in silicon, $[\text{As}]_{\text{total}}$, taken from Ref. 7, and the corresponding electron concentration $[e]$ calculated using our theory. $[e]^*$ is the measured electron concentration for the given $[\text{As}]_{\text{total}}$ and temperature. $[e]^*$ also corresponds to our theory, but calculated with the energy of the VAs_4 cluster reduced by 0.15 eV.

concentration $[e]$ is in contrast to earlier findings³⁰ that observed a temperature-independent $[e]$.

The result that the VAs_4 cluster is responsible for the deactivation is also in agreement with experiments that indicate the presence of vacancies in deactivated material, as discussed in Sec. I. Although some of these experiments may also be consistent with the DP defects identified by Chadi *et al.*,²² a subset of these experiments shows evidence of interstitial generation during the deactivation.¹⁹ This, in turn, is consistent with deactivation accompanied by the generation of vacancies, since the formation of a vacancy-arsenic cluster is most likely via the reaction



where Si_I is the silicon interstitial. In the equilibrium calculations, the interstitial population is allowed to equilibrate with silicon sinks (e.g., dislocations and surfaces) and thus, although the Si_I concentration is not supersaturated in equilibrium, as a transient, one interstitial is generated for each vacancy in the silicon lattice, thus producing a large interstitial flux, as is experimentally observed.

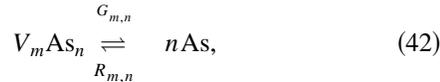
VII. RESULTS: NONEQUILIBRIUM BEHAVIOR

The approach to equilibrium starting from the fully activated material as prepared by, for example, a laser melt anneal, is more difficult to calculate accurately. One concern is the assemblage of the large vacancy arsenic clusters, given that the probability is quite low of randomly freezing in SiAs_4 clusters, out of which vacancies can form to create the VAs_4 complexes in one step. In contrast, the probability of finding SiAs_3Si_1 and SiAs_2Si_2 clusters is significantly higher. If the vacancies can form out of these clusters initially, relatively fast initial deactivation can be explained based on the frozen-in defect concentrations. Subsequent formation of clusters containing more arsenic atoms will be hastened by the Coulombic attraction between the positively ionized active arsenic atoms (AsSi_4) and the negatively charged VAs_3 and VAs_2 clusters. If the Fermi energy is at the bottom of the conduction band, the formation energy of

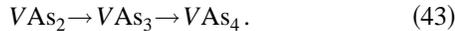
the doubly ionized VAs_2 cluster is roughly zero, similar to the formation energy of the DP clusters discussed by Chadi *et al.*²² An analysis similar to that discussed in Ref. 22 shows that both the DP class of defects and the VAs_2 cluster can form in heavily doped material and can explain some deactivation in material with no rearrangement of the arsenic atoms. Through short-range atomic diffusion, the DP and VAs_2 clusters will eventually evolve into VAs_3 and eventually VAs_4 clusters, until the full equilibrium is reached.

An activation energy of ~ 2 eV for the deactivation process has been measured at low temperatures.⁹ A minimum activation barrier for the formation of the vacancy complexes in heavily doped material can be deduced from our vacancy cluster energies, referenced to the corresponding $SiAs_n$ cluster, and with the formation energy of the silicon interstitial added. Using a value of 3.3 eV for the neutral silicon interstitial,³¹ an activation barrier of $\sim 1-3$ eV for the vacancy clusters in heavily doped material is estimated. These energies are comparable to those reported by Chadi *et al.*²² for the DP structures, and comparable to experiment. Thus, on the basis of the activation barrier, it is not clear whether the DP or VAs_4 defects will dominate the initial deactivation.

An alternative model for the approach to equilibrium involves achievement of a constrained equilibrium in which large clusters are prohibited from forming. For example, consider the reactions



where $G_{m,n}$ and $R_{m,n}$ are the forward and reverse reaction rates, respectively. If $R_{m,n} \ll R_{m,n-1}$, then it is possible that in the approach to equilibrium, the system will pass through a successive set of constrained equilibria involving increasingly larger clusters — for example,



The results of such a calculation were presented in Ref. 4, where it was shown that each successive set of constrained equilibria can explain larger degrees of the deactivation.

In addition to questions concerning the approach to equilibrium starting from the fully activated material, there is an interesting phenomena that occurs when the temperature of deactivated material is changed and the system approaches a new equilibrium condition. When the temperature of an equilibrated (deactivated) sample is stepped to a higher temperature, instead of the electron concentration increasing monotonically toward a new, higher equilibrium value, reactivation can be seen in which the carrier concentration rises above that corresponding to the electrical solubility limit at either temperature.³² Deactivation models that are based on only one deactivating species cannot explain this phenomena; to explain this phenomena and have a physically based model requires either a multiple-cluster model or precipitation.^{32,33}

A model for the transient reactivation is suggested by Fig. 2(d), by noting that as the temperature increases, the equilibrium population of the VAs_4 clusters decreases while that of the VAs_3 clusters increases. When an abrupt change in temperature is introduced, there will be a net breakup of the larger VAs_4 clusters. If the VAs_4 clusters break up quickly

upon a step temperature increase, but the VAs_3 clusters form more slowly (a reasonable assumption, since this involves the assemblage of three arsenic atoms into a cluster), an electron concentration above the electrical solubility limit at either temperature will be obtained as a transient condition, consistent with experimental observation. For quantitative agreement with the transient reactivation experiment, VAs_3 density must be higher and roughly comparable to the VAs_4 density.

VIII. CONCLUSIONS

An EQC formalism to describe the simultaneous equilibration of electronic and chemical (atomic) system in a solid is presented. This formalism has been applied to the problem of arsenic in silicon, and the temperature and concentration dependence has been examined both for full equilibrium and for constrained equilibrium. The quantitative results presented in this paper are sensitive to a number of things, including uncertainties in the temperature- and doping-dependent band structure and ionization energies; inaccuracies in the cluster energies due to the LDA and dispersions owing to the use of supercells; neglect of vibrational free energies (which will be different for threefold- and fourfold-coordinated arsenic); and cluster size effects in the EQC. The sensitivity of our results to variations in these quantities has been examined and it has been found that, although the quantitative agreement with experiment may change, our prediction of the activation being dominated by arsenic clustering about vacancies still holds. One major uncertainty in our calculations comes from the position and temperature dependence of the localized levels of the VAs_3 cluster in the gap. If the localized level at elevated temperatures is different than the value used by several tenths of an eV, our calculations indicate that the VAs_3 may play a greater role in the equilibrium deactivation than the results presented here indicate.

Our theory predicts deactivation in heavily arsenic-doped silicon that is in quantitative agreement with a number of experiments. Fully active arsenic has been shown to be the equilibrium state for lower arsenic doping concentrations for temperatures where equilibrium can be achieved. A temperature and arsenic concentration-dependent electrical solubility limit is predicted that is in good agreement with experiment. Because vacancy clusters with fewer arsenic atoms are nearly as effective at deactivating as is the VAs_4 , fast initial deactivation can be explained via the formation of Frenkel defects in randomly occurring arsenic clusters — for example, $SiAs_2Si_2 \rightarrow VAs_2Si_2 + Si_I$ — with the bulk silicon and the surface serving as a sink for the interstitials; the larger VAs_3 and VAs_4 clusters will subsequently form. Generation of silicon interstitial via the formation of vacancies during the deactivation has also been experimentally seen, and cannot be explained by the neutralizing relaxation of arsenic pairs.²² Furthermore, the presence of more than one cluster (VAs_4 and most likely VAs_3) playing an important role in the deactivation is supported by the observation of transient reactivation upon a temperature increase.^{32,33}

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