Mechanisms of arsenic clustering in silicon

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A model of arsenic clustering in silicon is proposed and analyzed. The main feature of the proposed model is the assumption that negatively charged arsenic complexes play a dominant role in the clustering process. To confirm this assumption, electron density and concentration of impurity atoms incorporated into the clusters are calculated as functions of the total arsenic concentration at a temperature of 1050°C. A number of the negatively charged clusters incorporating a point defect and one or more arsenic atoms (DA(2)−), (DA(2)2−), (DA(3)−), (DA(3)2−), (DA(4)−), and (DA(4)2−) are investigated. It is shown that for the doubly negatively charged clusters or for clusters incorporating more than one arsenic atom the electron density reaches a maximum value and then monotonically and slowly decreases as total arsenic concentration increases. In the case of cluster (DA(2)2−), the calculated electron density agrees well with the experimental data. Agreement with the experiment confirms the conclusion that two arsenic atoms participate in the cluster formation. Among all present models, the proposed model of clustering by formation of (DA(2)2−) gives the best fit to the experimental data and can be used in simulation of high concentration arsenic diffusion.

I. INTRODUCTION

Using low energy high dose arsenic ion implantation, one can produce the active regions of modern integrated microcircuits characterized by very shallow junctions and high dopant concentrations. Thermal annealing is applied after implantation for the arsenic activation and damage reduction. During the initial stage of annealing, the arsenic atoms become electrically active, occupying the substitutional positions. Then a fraction of impurity atoms incorporates into the clusters, thereby decreasing the layer conductivity.1,2,3,4,5,6,7,8,9,10,11 Due to clustering, the concentration of charge carriers is less than the total impurity concentration because the clustered dopant atoms do not serve as a source of free charge carriers. We can observe the clustering phenomenon in many cases of the formation of highly doped semiconductor structures; for example, in the region with high impurity concentration during thermal diffusion of arsenic atoms.12,13,14 Deactivation of the electrically active dopant atoms also indicates that clustering can occur during thermal treatment of the supersaturated arsenic layers created by ion implantation with subsequent thermal or laser annealing.15,16,17,18,19 Moreover, a reverse annealing or transient increase of the carrier density can be observed if a doped specimen, previously annealed at temperature T1, is further annealed at higher temperature T2.20 It is supposed that transient dissolution of a part of the clusters occurs during such a reverse annealing.20

At very high dopant concentrations exceeding the solid solubility of As in Si, a significant fraction of arsenic atoms can form precipitates.3,4,5,6,8,10,15,21,22 The typical distributions of the total dopant concentration and electron density after thermal annealing of silicon substrates heavily implanted by As were presented by No-
arsenic may be expressed as gated diffusion in the ion-implanted layers, clustering of neutral at room temperature. are electrically active at annealing temperatures, but are participating in the cluster formation; $\text{As}^{+}$ can be seen from Fig. 1c, $\text{As}^{2+}$ and $\text{As}_{3}^{2+}$ more precisely, at the dopant concentrations approximately ranging from $n_{e}$ to 10 $n_{e}$. If dopant concentration exceeds the solubility limit $C_{\text{sol}}$, precipitation occurs. Arsenic clustering and precipitation have attracted evergrowing attention of the researchers, as they are greatly important for the silicon integrated circuits technology. Both clusters and precipitates do not serve as a source of charge carriers and the total arsenic concentration may be higher than the electron density by about two orders of magnitude. The clusters and precipitates are metastable and can dissociate under subsequent thermal treatments. This means that stringent requirements should be placed upon the accuracy of the clustering models used to calculate the carrier concentrations in heavily doped silicon layers.

II. ANALYSIS OF CLUSTERING PHENOMENA

The development of a model for As clustering necessitates a consistent analysis of the experimental data and theoretical substantiation of the processes proceeding in heavily doped silicon layers.

A. Clustering during thermal diffusion and annealing of ion-implanted layers

A great number of clustering models with different types of clusters have been developed and proposed since 1973. The variety of the proposed models reflects discrepancies in the experimental results and a great uncertainty in the nature of the clusters discussed. For example, inactive cluster $\text{VA}_{2}$ was considered in to explain the differences between the total and electrically active dopant concentrations for arsenic thermally diffused from a constant source. For the best fit to the diffusion profiles of ion-implanted arsenic, it was suggested that the electrically inactive arsenic atoms were incorporated into the clusters with four arsenic atoms per cluster. According to Tsai et al. who have also investigated diffusion in the ion-implanted layers, clustering of arsenic may be expressed as

$$3\text{As}^{+} + e^{-} \xrightarrow{\text{Annealing}} \text{As}_{3}^{2+} \xrightarrow{25^\circ\text{C}} \text{As}_{3},$$

where $\text{As}^{+}$ is the substitutionally dissolved arsenic atom participating in the cluster formation; $e^{-}$ is the electron.

As follows from reaction (1), the clustered As atoms are electrically active at annealing temperatures, but are neutral at room temperature.

It was found in that the formation of clusters $(\text{As}_{2}V)^{x}$ occurs due to the following reaction, which

$$2\text{As}^{+} + \text{V}^{2-} \leftrightarrow (\text{As}_{2}V)^{x}$$

is most liable to cause deactivation because the concentration of inactive As species increases to the fourth power of the active As concentration. Here $V^{2-}$ is the doubly negatively charged vacancy participating in the clustering.

Indeed, if a local equilibrium is assumed, it follows from the mass action law for reaction (2) that

$$C^{A} = AC^{\chi}C^{2},$$

$$A = H^{A}C^{\chi}n_{i}^{2},$$

$$\tilde{C}^{\chi} = \frac{C^{\chi}}{C_{i}^{\chi}}.$$
The model was generalized by Solmi and Nobili
\[ m\text{As}^+ + e^- \xrightleftharpoons{\text{Annealing}} \xrightarrow{25^\circ\text{C}} \text{As}^{(m-1)+} \]  
(6)
to take into account a saturation behavior of the carrier density with increasing dopant concentration. For diffusion at a temperature of 1050°C, the best agreement between the modeled and experimental curves describing diffusivity against total arsenic concentration was achieved for \( m = 4 \). And at 900°C, the neutral cluster model provided a better agreement with the experimental data. The reaction (6) was also used to describe deactivation in the arsenic-doped layers, which were formed by ion implantation and high temperature annealing of silicon-on-insulator specimens. However, Solmi et al. have recently used the following reaction
\[ m\text{As}^+ + V \longleftrightarrow \text{As}_m + I \]  
(7)
to model the transient arsenic diffusion. Here \( m \) is assumed to have the values between 2 and 4 to take into account the fact that the As cluster was formed around a vacancy with the subsequent injection of the self-interstitial.

It is important to note that reaction (6) was first theoretically studied by Guerrero et al. in paper, which will be considered below.

## B. Clustering during deactivation of supersaturated arsenic layers formed by laser annealing

Let us consider the clustering models used for the explanation of deactivation in the supersaturated arsenic layers formed by ion implantation and subsequent laser annealing. In it was found that a cluster consisting of four positively charged arsenic atoms and two additional negative charges gave the best least-squares fit with respect to the experimental data obtained in the case of deactivation within the supersaturated arsenic layers created by ion implantation and subsequent laser annealing. If two negative charges are associated with a doubly charged vacancy, this model gains support from the theoretical calculations of Pandey et al. Such a cluster has an intuitive geometrical and structural appeal — four arsenic atoms tetrahedrally arranged around a vacancy may relax inward, thus relieving lattice strains due to the As size effect. Using this cluster species, a single-step clustering reaction was postulated in.

\[ 4\text{As}^+ + V^{2-} \longleftrightarrow (\text{As}_4V)^{2+}. \]  
(8)

The assumption of self-interstitial ejection during clustering was supported by the experimental data obtained by Parisini et al. who have observed that extended defects at the projected range were extrinsic or interstitial in nature. The reaction
\[ (\text{As}_2)^{2+} + 2e^- \rightarrow (\text{As}_2V)^+ + I^- \]  
(9)
was proposed only for the initial step of the deactivation process in arsenic implanted silicon specimens, first laser-annealed and then thermally annealed. Here \( I^- \) is the negatively charged self-interstitial. The results obtained by Rousseau et al. confirm the conclusion that arsenic is indeed deactivated by vacancies, with a concurrent injection of self-interstitials. The latter follows from the observed significant enhancement of the diffusion in the buried boron layer underneath the As structure subjected to deactivation. Investigations of the enhanced diffusion in buried boron layers were continued where it was proposed that small arsenic clusters of various sizes were formed around a vacancy during deactivation with injection of the associated interstitial into the bulk.

Considering that the majority of the models described in this section are based essentially on the experimental investigations of the defect subsystem, we first concern ourselves with these experimental results.

## C. Experimental investigations of defect subsystem

The methods of transmission electron spectroscopy (TEM), extended x-ray-absorption fine-structure (EXAFS), Rutherford backscattering (RBS), positron lifetime measurements, combined with the measurements of electron momentum distributions and other methods are commonly used to investigate silicon specimens doped by As. For example, TEM observations show that As-lased samples are completely free of any visible defects. On the other hand, TEM analysis reveals the presence of extended defects after subsequent thermal treatment. For example, small \{113\} interstitial loops begin to appear beyond the plateau region of the As profile after low-temperature treatment. After high-temperature thermal treatment (>850°C), a low density of very small As-related precipitates (about 2 nm in diameter) is observed. The precipitated As fraction cannot be responsible for the total amount of inactive As.

It was established that EXAFS measurements provided particular details about the local atomic structure around the dopant and confirmed the fact that As atoms are substitutional after laser annealing. Note that, according to the x-ray standing-wave spectroscopy measurements, the As atoms remained at the substitutional positions even after 85% of the electrical activity has been lost due to thermal annealing of the laser melted layers.

On the other hand, a large amount of nonsubstitutional arsenic was detected by Rutherford back-scattering after
diffusion from TiSi$_2$ source. These defects are interpreted as precipitates, probably formed due to the stress induced by TiSi$_2$ layer. Indeed, when thermal annealing is carried out after the complete removal of titanium silicide (i.e., without stress), one can observe the activation of all the arsenic atoms diffused in the silicon substrate. Thus, such full activation indicates the significant influence of stress on the formation of precipitates.

According to EXAFS measurements, subsequent thermal annealing (350 – 750°C) of the As-lased layers leads to the formation of V$_n$As$_m$ clusters including up to 7 $\pm$ 4 As atoms around the vacancy. However, at high temperatures it was observed that the number of the first neighbors of Si has tended back to 4 atoms. This is probably due to the precipitates observed by TEM over this temperature range. Quantitative analysis of EXAFS data for the ultra-low energy implanted layers after rapid or spike annealing has revealed a site for As that was different from the pure substitutional one, suggesting the presence of clusters of As atoms coupled to vacancies. All the observed phenomena, namely, a low value of the total coordination number in the annealed samples, small As–Si bond length, and the presence of As–As coordination, may be explained by the assumption that clustering of As ions with vacancies takes place to form V$_n$As$_m$ structures.

Ion channeling and RBS were used to complement the EXAFS and electron microscopy results. In has been found that the deactivated As atom is displaced with respect to the lattice sites and, moreover, the average displacement is constant over the temperature range 450 – 900°C, being equal to 0.23 $\pm$ 0.06 Å. Also, in it was proposed that the formation of larger clusters V$_n$As$_m$ ($n \approx 5$ and $m \approx 10$) occurred starting from V$_2$As$_{2}$ or VAs$_4$. The formation of these larger clusters is in agreement with a decrease in the first nearest neighbors of As. At higher temperatures, an increase in the number of the first nearest neighbors of As to 4 was observed by EXAFS measurements. This means that the cluster species may differ at intermediate (350 – 750°C) and higher temperatures.

Very interesting information about clustering was obtained during the experimental investigations of the doped layers by positron annihilation spectroscopy and positron annihilation spectroscopy combined with the Hall-effect/resistivity measurements. The defect subsystem was generally investigated before and after thermal treatment. To support these measurements, the positron lifetimes and core electron momentum distributions were calculated for different vacancy-donor complexes. Lawther et al. have investigated the doped layers melted by an excimer laser to obtain the profile with constant As concentration and a sharp fall-off at a depth of 0.2 μm. Arsenic deactivation was initiated by annealing at 750°C for 15 s or by conventional thermal treatment for 2 h. It was found that V$_n$As$_m$ complexes with the average values of $m$ greater than 2 caused arsenic deactivation in heavily doped Si. Myler et al. have studied the silicon layers (with arsenic concentration 4$\times$10$^8$ μm$^{-3}$) fully activated by laser melting and subsequently annealed for 15 s at 500 and 750°C. The changes in the positron annihilation spectra after the thermal treatment at 500 or 750°C were also attributed to the formation of As$_m$Si$_{12}$–nV$_{ac}$ complexes. In this experiment, the impossibility of determining the number of impurity atoms incorporated in the impurity-vacancy complex was established. Ranki et al. have studied the samples implanted by As during MBE growth at 450°C. The samples were annealed in N$_2$, either by RTA at 900°C for 10 – 170 s or furnace annealing at 800 – 900°C for two minutes. Based on the positron annihilation and Hall-effect/resistivity experiments, Ranki et al. have concluded that the dominant defect in As-grown samples was V$_2$As$_{2}$. The measurements demonstrated high concentrations (above 10$^5$ μm$^{-3}$) of V$_2$As$_{3}$ complexes in heavily-doped silicon. Moreover, larger V-As complexes, probably V$_2$As$_5$, may occur together with V$_2$As$_{3}$ at high As concentrations. A relative amount of V$_2$As$_{3}$ increases with annealing. This cluster is even dominant after annealing at 800°C. The V$_2$As$_{3}$ and V$_2$As$_5$ complexes become unstable at 800°C and 900°C, respectively, then their concentrations decrease. Cluster reconstruction may occur during cooling, starting from V$_2$As$_1$ to V$_2$As$_2$ and then to V$_2$As$_3$. The clusters V$_2$As$_2$ and V$_2$As$_3$ may be in turn transformed to the V$_2$As$_5$ complexes. Moreover, some V$_2$As$_4$ and other vacancy complexes may be also formed, but with much lower concentrations.

High energy electron irradiation is commonly used in positron experiments for the generation of nonequilibrium vacancies, mobile even at room temperature and liable to interact with the dopant atoms. For example, positron experiment were performed both with the As-grown samples doped by arsenic in concentrations of 10$^7$ and 10$^8$ μm$^{-3}$ and samples subjected to 2 MeV electron irradiation at 300 K. It was established that heavily As-doped silicon contained V$_2$As$_3$ complex as a native defect. Before irradiation, the concentration of V$_2$As$_3$ was equal to $\sim$ 10$^7$ μm$^{-3}$ at a doping level of 10$^8$ μm$^{-3}$. After electron irradiation, one can observe the pairs (VAs$_1$) formed by a vacancy and a single impurity atom. It was demonstrated that the migration of these VAs$_1$ defects started at around 450 K, leading to formation of VAs$_2$ defects. And, in turn, these defects were transformed to VAs$_3$ defects at 700 K. The VAs$_3$ defects were stable at 700 K, representing the dominant vacancy-impurity cluster in heavily doped n-type Si at this temperature. The formation of larger VAs$_2$ and VAs$_3$ complexes was significantly dependent on the As concentration. This interpretation of the experimental data was confirmed by the results obtained in. In these experiments, the electron irradiated samples were annealed isochronally (30 min) at 300 – 1220 K. Irradiation of the heavily doped Si samples has produced mainly the vacancy-donor pairs (VAs$_1$) with a small concentration of divacancies. Considering that, after irradiation,
VA$_3$ concentration was much higher than the initial concentration of VA$_8$, no signals from VA$_8$ were observed for the As-irradiated As-doped sample. From the core-region electron momentum distribution measurements, it was found that defects in As-irradiated samples may be identified as VA$_1$, in samples annealed at 600 K — as VA$_2$, and in those annealed at 775 K — as VA$_3$. It is well known that a drastic drop in the conductivity occurs when heavily doped Si is annealed at temperatures between 400°C and 500°C. This deactivation of the dopants is partially reversible by annealing at 800 – 1000°C. Taking into account these experimental data, Ranki et al. have suggested that the formation and annealing of VA$_3$ at 700 and 1100 K, respectively, are responsible for the observed behavior of the conductivity. The experiments conducted in were completed by studies associated with thermal treatment up to 1220 K. It has been found that dissociation of VA$_3$ began at 1100 K, and at 1220 K these defects were annealed away.

Thus, the analyzed data show that complexing of As atoms with vacancies occurs in the layers heavily doped by arsenic. Based on the experimental data, various VA$_m$As$_n$ clusters are possible but VA$_2$ and VA$_3$ are the most likely. Taking clustering into account, one can explain the phenomenon of compensation at high doping levels. Nevertheless, some aspects are not clearly understood. For example, VA$_3$ starts to dissociate at 1100 K. This annealing temperature agrees well with the observation that the number of Si first neighbors tends back to 4 atoms at temperatures higher than 750°C. At the same time, clustering occurs at temperatures higher than 750°C as well. This means that such a high-temperature clustering is hardly explained by VA$_3$ complexes.

### D. First principles studies

Along with various experimental investigations, a number of the theoretical calculations have been performed to explain deactivation of arsenic atoms in silicon. From the calculations of Pandey et al. it follows that VA$_4$ complex including a vacancy surrounded by four arsenic atoms is energetically favored over both substitutional, isolated As in Si and substitutional Si-As$_4$ configurations. This cluster is electrically inactive, being responsible for arsenic deactivation and structural changes in heavily doped silicon. Larger defect clusters (e.g., VA$_3$) should also form during annealing, whereas VA$_4$ is the only step in the clustering process. These investigations were continued where general VA$_m$As$_n$ complexes have been considered. The formation energies of the vacancy-donor complexes VA$_3$, VA$_2$, VA$_3$, and VA$_4$ were found to be 2.47, 0.82, -0.53, and -2.39 eV, respectively. Moreover, it was proposed that the complex VA$_2$ was mobile, as were the VA$_3$ pairs. As these pairs moved, they reacted with other defects to form larger, immobile complexes. When considering the mobile VA$_2$ complexes, Ramamoothy and Pantelides have tried to explain the coupled diffusion phenomena and clustering. It was supposed that VA$_2$ and VA$_3$ were the dominant complexes in the deactivated specimens near the enhanced-diffusion threshold. A high rate of As diffusion observed during rapid thermal annealing was due to VA$_2$ migration over a very short time period (6 - 60 s), when no extensive clustering could occur. During their motion, VA$_2$ complexes reacted with other defects and formed larger, immobile complexes, which decreased the As diffusivity.

Nevertheless, further investigation is necessary because some theoretical results disagree with the experimental data. For example, it was stated that the formation of VA$_3$ or VA$_4$ defects was exothermic, but, according to the first-principles calculations, buildup of VA$_1$ or VA$_2$ structures was endothermic. This means that even at low arsenic concentrations all impurity atoms must form VA$_3$ or VA$_4$ clusters after long-time treatment. In point of fact, at low dopant concentrations, one can observe intensive diffusion by means of VA$_1$ pairs rather than clustering.

Berding et al. and Berding and Sher have used the electronic quasichemical formalism to calculate a free energy of various clusters, including AsSi$_4$, VA$_4$, VA$_3$Si$_3$, VA$_2$Si$_2$. Here AsSi$_4$ is the arsenic atom in the substitutional position. The neutral cluster composed of threefold-coordinated second-neighbor arsenic atoms DP(2) was proposed by Chadi et al. as an alternative to exothermic VA$_4$. The clusters DP(2), VA$_2$As$_6$, and Si$_8$ were also included in the calculations performed. In Berding et al. and Berding and Sher, take into account the ionized states and entropy of the cluster formation. The entropy is unfavourable for the formation of a large defect complex such as VA$_4$. Therefore, the complete free-energy calculation is needed to determine the role of VA$_4$ in deactivation. Based on the complete free-energy calculation, it was found that cluster VA$_4$ was neutral, in agreement with the previous findings. Also, the energy of this complex (-1.62 eV) was in a rough agreement with the value given in. The VA$_3$ and VA$_2$ clusters were found to have one and two acceptor levels within the energy gap. Consequently, their formation energy may be effectively decreased when the Fermi energy is near the conduction-band edge. The equilibrium cluster concentrations depending on the temperature and concentration of dopant atoms are obtained using the minimized free energy of the system. For all the dopant concentrations and temperatures considered (400 – 1000°C), three classes of clusters are dominant under equilibrium conditions: Si$_8$, AsSi$_4$, and VA$_4$. If the Fermi energy was near the conduction-band edge. Predominantly, VA$_3$ and VA$_2$ were singly and doubly ionized, respectively. At low arsenic concentrations (up to ~ 5 × 10$^6$ µm$^{-3}$), noticeable deactivation was absent for temperatures higher than 500°C. With the arsenic concentration raised to 5 × 10$^7$ µm$^{-3}$ and higher, significant deactivation was predicted, mainly due to the formation of VA$_4$ clusters. Both concentration
and temperature influenced the contributions of different defects. For example, the concentration of VAs$_2$ clusters has reached the concentration of isolated arsenic atoms in the lattice As$_x$Si$_{4-x}$ for $\sim 5 \times 10^8 \, \mu\text{m}^{-3}$ at a temperature of $700 \, ^\circ\text{C}$ and for $\sim 2 \times 10^9 \, \mu\text{m}^{-3}$ at a temperature of $1000 \, ^\circ\text{C}$.

In$^{25,48}$ the authors have attempted to explain the effect of the electron concentration saturation at high doping levels. However, the calculations performed in these papers show that saturation is not reachable even at very high arsenic concentrations. For example, saturation was not reached with the arsenic concentration of $2 \times 10^9 \, \mu\text{m}^{-3}$ at a temperature of $700 \, ^\circ\text{C}$, which is in disagreement with the experimental data (see Fig. 2 from$^{44}$). It is important that, according to$^{44}$, DP(2) clusters proposed by Chadi et al.$^{44}$ may be present as a deactivating species, insignificantly contributing to the deactivation under conditions of full equilibration.

These new defects, first mentioned in$^{44}$ and called DP, represent a pair of two three-fold coordinated donor atoms. The lowest energy DP structures are DP(2) and DP(4), where the donor atoms occupy either second- or fourth-neighbor Si sites along the $<110>$ direction. It was shown that DP(2) exist in the stable electrically active 2+ charge state that is donating electrons to the conduction band or in the metastable neutral charge state capturing two electrons from the Fermi sea. A very important conclusion made in$^{44}$ is a threefold coordination of each dopant atom in DP(2) in the neutral trap state. Thus, relaxation of the neighboring Si atoms creates an increased volume, which is consistent with the experimental observations. Therefore, such an increased volume around the donor atoms is possible without vacancies. The main ideas of$^{44}$ were further developed in$^{25}$. Citrin et al.$^{25}$ have proposed a new class of defects, called the donor-pair-vacancy-interstitials and composed of two dopant donor atoms near the displaced Si atom that is forming a vacancy-interstitial pair. This defect, which is like a hybrid of the donor-pair and Frenkel-pair defects, is denoted DP(i)V-I. For the case of Sb, the data of annular dark-field (“Z-contrast”) scanning transmission electron microscopy (ADF-STEM) clearly demonstrate that, in heavily Sb-doped silicon grown at low temperatures, the primary deactivating defect contains only two Sb atoms.$^{49}$ Thus, energetically favorable VSb$_3$ and VSb$_4$ may be ruled out from the deactivation process. Only VSb$_2$, DP(2), and DP(4) may be considered as liable candidates. Using additional STEM measurements, x-ray absorption data, and first-principles calculations, Voyles et al.$^{49}$ have shown that neither VSb$_2$ nor DP(2) and DP(4) defects are important in heavily Sb-doped Si. At that time, DP(2)V-I and DP(4)V-I were in line with the available experimental results, including positron annihilation spectroscopy data.$^{25}$ Both DP(2)V-I and DP(4)V-I are independent out of the pre-existing vacancy population, which is in conformity with the observations of$^{49}$.

Nevertheless, as follows from the experimental data,$^{49}$ a deactivation mechanism can be different in the As- and Sb-doped silicon. The mechanism of arsenic clustering calls for further investigation. In$^{25,48}$, Mueller et al.$^{48}$ have investigated the electronic structure and charge states of various vacancy-impurity clusters using the first-principles density-functional theory (DFT). It was found that the VAs$_1$ complex can trap up to two conduction electrons at a high n-doping level. Both VAs$_2$ and VAs$_3$ act as a single-electron trap center. In agreement with$^{25,48}$, Mueller et al.$^{48}$ have found that in VAs$_4$ the fifth valence electrons of all four As atoms are strongly bound and the complex is expected to remain neutral for any position of the Fermi level. Note that according to the calculations of$^{48}$ the cluster VAs$_2$ has two acceptor levels, whereas Solmi et al.$^{20}$ have found from the carrier mobility measurements that the complex to be electrically neutral at room temperature. In$^{20}$ the first-principles calculations were performed to explain the coupled diffusion phenomena and clustering in heavily arsenic-doped silicon. As contrast to$^{48}$ it was found that the VAs$_2$ cluster is less mobile due to its high migration barrier. However, these clusters can contribute to the diffusion of As at elevated temperatures.

Proceeding from the presented analysis, our understanding of the clustering mechanisms is neither complete nor firmly established. This concerns the number of arsenic atoms in the cluster as well as its structure. However, a study based on the first-principles shows that clusters of a certain kind have an acceptor level and can be negatively charged. Let us consider the models for the clusters with different charge states.

### E. Models based on the mass action law

The models based on thermodynamic formalism are usually used for simulation of high concentration dopant diffusion taking place during semiconductor processing. Assuming a local thermodynamic equilibrium among substitutionally dissolved arsenic, the dopant atoms incorporated into clusters, and electrons, one can use the mass action law to calculate the concentration of clustered dopant atoms.$^{2,12,13,23}$ The charge conservation law for the reaction of cluster formation under the assumption of local charge neutrality is also useful for describing the clustering phenomenon. A widespread model of Tsai et al.$^{2}$ was the first to account for the saturation of the charge carriers at increasing doping levels.$^{23}$ It is interesting to compare this model with the latest experimental data. The mass action law for the reaction (1) at the diffusion temperature yields$^{2}

$$C^{\text{Cl}} = A^{\text{Cl}} n C^3,$$

(10)

where $C^{\text{Cl}}$ and $n$ are the concentrations of clusters and electrons at the annealing temperature, respectively; $A^{\text{Cl}}$ is the constant of local thermodynamic equilibrium. After cooling, all clusters become neutral and $C \approx n_R$ if
was concluded that \( n_e \) had a physical meaning. Thus, the model that includes cluster neutralization during cooling is also inconsistent with the experimental data for arsenic diffusivity. Indeed, the electron concentration at the annealing temperature calculated by this model and associated with the peculiarity of the diffusivity is three times greater than \( n_e \).

\( C \gg n_i \). Here \( n_R \) is the concentration of electrons at room temperature. It follows from the assumption of local charge neutrality that the electron concentration at the annealing temperature for \( C \gg n_i \) is

\[
n = C + 2C^{Cl} = C + 2A^{Cl}nC^3.
\]  

(11)

Solving this equation, Tsai et al. obtained

\[
n = \frac{C}{1 - 2A^{Cl}C^3}
\]  

(12)

and

\[
C^T = C + \frac{3A^{Cl}C^4}{1 - 2A^{Cl}C^3} = \frac{C + A^{Cl}C^4}{1 - 2A^{Cl}C^3}.
\]  

(13)

From Eq. (13) it is inferred that under condition

\[
C = C_{sat} = \frac{1}{\sqrt{2}A^{Cl}}
\]  

(14)

both the concentration of arsenic atoms incorporated into clusters and the total concentration of arsenic atoms approach infinity. The value \( n_{Re} = C_{sat} \) is interpreted as a maximum level of electron concentration. From the experimental data it is seen that a maximum equilibrium carrier concentration at the annealing temperature in the arsenic implanted layers may be described by the following relation:

\[
n_e = 1.3 \times 10^{11} \exp \left( -\frac{0.42eV}{k_BT} \right).
\]  

(15)

Using Eqs. (13) and (14), the value of \( A^{Cl} \) may be derived to be

\[
A^{Cl} = \frac{1}{2n_e^2}.
\]  

(16)

To illustrate, \( n_e \) is 3.57 \( \times \) 10\(^8\) \( \mu \text{m}^{-3} \) at a temperature of 1050 °C and \( A^{Cl} \) is 1.10 \( \times \) 10\(^{-20}\) \( \mu \text{m}^9\).

The values of \( n_R \) as a function of the total arsenic concentration calculated by the model of Tsai et al. are shown in Fig. 1. The experimental values of \( n_R \) based on the data from Solmi and Nobili are also given for comparison. As seen from Fig. 1, saturation of the electron concentration for the model is observed at the extremely high total As concentrations, whereas the experimental data show that the carrier concentration reaches its maximum at \( C^T \approx 8 \times 10^8 \mu \text{m}^{-3} \). Thus, the model is inconsistent with the experimental data. Moreover, as follows from the experimental data of Solmi and Nobili, the value of \( n_e \) obtained at room temperature corresponds to the peculiarity of the curve for diffusivity as a function of the total arsenic concentration. Because this feature characterizes impurity diffusion at the annealing temperature, it

FIG. 1: Calculated electron concentration against the total arsenic concentration for different models of clustering: solid line — model of Tsai et al. (Ref.2), dash-dotted line — neutral clusters VAs\(_{2}\), and dashed line — neutral clusters VAs\(_4\). The experimental data (circles) are taken from Solmi and Nobili for the diffusion at a temperature of 1050 °C.

It was supposed that the charge of clusters becomes zero when the sample is cooled down to room temperature. Therefore, \( C \) is interpreted as the concentration of electrically active arsenic at room temperature,
which equals the electron density \( n \) in the sample at room temperature. Four main conclusions have been drawn from the basic model:

1. When the electrons do not participate in the reaction (17), i.e., \( k = 0 \), or the clusters are electrically neutral at high temperature, i.e., \( r = 0 \), \( C \) is a monotonically increasing function of \( C^T \) and also there is no finite limit to \( C \) and electron density \( n \) at room temperature.

2. If the clusters are positively charged at a high temperature \( (r \geq 1) \) and exactly one electron takes part in the reaction (17), i.e., \( k = 1 \), \( C \) is a monotonically increasing function of \( C^T \), which approaches a finite “saturation” value \( C_{\text{max}} \) with increasing \( C^T \).

As can be seen from the reaction (1), the model of Tsai et al.\(^22\) satisfies these conditions. On the other hand, from our calculations for this model (see Fig. 1), it follows that saturation of the electron concentration is observed at extremely high total As concentrations. It means that the saturation value obtained in such a manner is inconsistent with the experimental data.

3. Provided that the clusters are positively charged at high temperatures \( (r \geq 1) \) and there are two or more electrons taking part in the reaction (17), i.e., \( k \geq 2 \), \( C \) increases with increasing \( C^T \) only up to a finite value \( C_{\text{max}}^T \). A maximum concentration value \( C = C_{\text{max}} \) is observed for \( C^T = C_{\text{max}}^T \). With further increase in the total arsenic concentration \( C^T > C_{\text{max}}^T \) the concentration of the substitutionally dissolved arsenic atoms \( C \) and hence electron density \( n \) at room temperature, are decreased.

This behavior of \( n \) is at variance with the experimental data, because experimentally measured \( n \) is approximately constant with increasing \( C^T \) (see Fig. 1).

4. If the clusters are negatively charged at high temperatures \( (r \leq -1) \), then \( C = C(C^T) \) behaves as in case 1, i.e., \( C \), and hence electron density \( n \) at room temperature, monotonically increase without limit for increasing \( C^T \). This behavior of \( n \) also conflicts with the experimental data.

In what follows, the basic model is extended to take into account the different charge states of vacancies participating in the cluster formation.\(^28\) It is shown that the main conclusions from the basic model are valid for the case when vacancy is involved in the formation of clusters. Thus, the generalized model of arsenic clustering proposed in\(^22\) is not in agreement with the experimental data for all possible cases of the cluster formation considered in this model. In our opinion, this contradiction is due to the assumption that charged clusters become neutral during cooling. As follows from\(^2\) the hypothesis that deactivation is taking place during cooling of the substrates contradicts the experimental data.

Evidently, the models of arsenic clustering should give an adequate explanation not only for saturation of the electron density, but also for the plateau formed on the carrier concentration profile after annealing of the ion implanted layers.\(^2,10\) As follows from the above analysis, there is no model satisfying these requirements.

The performed analysis enables us to formulate the purpose of this study: the development of a more adequate model to explain the plateau phenomenon of the charge carrier profile at high concentration arsenic diffusion.

## III. Model

To develop a model for arsenic clustering that can describe the saturation phenomenon of the electron density, we assume that not only neutral, but also negatively charged, arsenic clusters are formed. The possibility for the formation of the negatively charged arsenic clusters is confirmed by the calculations in\(^25,26\). It has been shown by Berding et al.\(^25\) that clusters \( V\text{As}_2 \) and \( V\text{As}_3 \) have one and two acceptor levels, respectively. The calculations carried out by Mueller et al.\(^26\) also show that for the electron densities \( n > 10^4 \text{ cm}^{-3} \) the majority of complexes \( \text{VA}_2 \) will be negatively charged. According to\(^26\) the complex \( \text{VA}_3 \) exhibits an acceptor level. This cluster is singly ionized at elevated Fermi levels, resulting in a loss of four mobile carriers for the formation of a \( \text{VA}_3 \) aggregate.

It is interesting that saturation of the electron density is observed in the layers of GaAs heavily doped by silicon. To explain this phenomenon, it was supposed (see, for example\(^22,23\)) that silicon atoms in heavily doped GaAs are dissolved substitutionally not only in the Ga sublattice (donor \( \text{Si}^{+}_{\text{Ga}} \)), but also in the As sublattice (acceptor \( \text{Si}^{-}_{\text{As}} \)). It was supposed in\(^23\) that a maximum electrical conductivity in Sb-doped silicon is limited by the defect formation at high dopant concentrations. The Sb-vacancy pairs were considered as defect dominating at high doping levels. Also, it was supposed that this defect acts as an electron acceptor and is responsible for saturation of charge carriers at high doping levels. Although a mechanism of such a saturation of the electron density in silicon heavily doped by Sb is different from that in As-doped silicon,\(^10\) the idea of the limited electron density due to compensation by the acceptors is a very fruitful one. For example, it has been supposed in\(^24\) that phosphorus clusters are negatively charged. Due to this assumption, saturation of the electron density during high concentration phosphorus diffusion was explained.

As distinct from the models of arsenic clustering considered in\(^22,23\) we assume that arsenic clusters have the same negative charge both at high diffusion temperatures and at room temperature. As follows from the analysis of the experimental data and theoretical investigations, the structure of arsenic clusters under diffusion temperature is still not conclusively established. Therefore, it is assumed that a point defect \( D_1 \) can be involved in the cluster formation and another defect \( D_2 \) can be generated during clustering. In this case, a reaction for the formation and dissolution of clusters can be written as

\[
m\text{As}^+ + m_1D^{r_1} + k e^- \leftrightarrow \Phi^{r_1} + m_2D^{r_2},
\]  

(19)
where \( A \) is the substitutionally dissolved arsenic atom \( \text{As}^+; \) \( e^- \) is the electron; \( \Phi \) is the cluster formed; \( m_1 \) and \( m_2 \) are respectively the numbers of defects \( D_1 \) and \( D_2 \) participating in the cluster formation; \( r_1 \), \( r_2 \), and \( r_{Cl} \) are the charge states of defect \( D_1 \), defect \( D_2 \), and cluster \( \Phi^{rc_1} \), respectively.

The charge conservation law for the chemical reaction (19) is of the form

\[
m + m_1 z_1 - k = z_{Cl} + m_2 z_2,
\]

where \( z_1 \) and \( z_2 \) are the charges of defects \( D_1 \) and \( D_2 \), respectively; \( z_{Cl} \) is the charge of cluster \( \Phi^{rc_1} \) in terms of the elementary charge.

The mass action law for reaction (19) yields

\[
K_L C^n \frac{(C_{r_1}^1)^{m_1}}{k} \frac{1}{n_i} = K_R C_{\Phi} \frac{(C_{r_2}^2)^{m_2}}{k},
\]

where \( K_L \) is the rate of the chemical reaction (19) in the forward direction; \( K_R \) is the rate of this reaction in the opposite direction; \( C \) is the concentration of impurity atoms participating in reaction (19); \( C_{r_1}^1 \) is the concentration of defects in the charge state \( r_1 \) participating in the cluster formation; \( C_{r_2}^2 \) is the concentration of defects in the charge state \( r_2 \) generated during clustering; \( C_{\Phi} \) is the concentration of the clusters in the charge state \( r_{Cl} \); \( \chi \) is the electron density normalized to the concentration of the intrinsic charge carriers in a semiconductor during diffusion \( n_i \).

Due to a high dopant concentration, the approximation of local charge neutrality can be used for the evaluation of \( \chi \)

\[
\chi = \frac{n}{n_i} = \frac{1}{2n_i} \left[ C + z_{Cl} C_{\Phi} - N_B \right] + \sqrt{(C + z_{Cl} C_{\Phi} - N_B)^2 + 4n_i^2},
\]

where \( N_B \) is the summarized concentration of acceptors; \( n_i \) is the effective concentration of the intrinsic charge carriers at a diffusion temperature calculated for a high doping level.

It follows from equation (19) that the concentration of impurity atoms incorporated into clusters \( C^A = m C_{\Phi} \). Moreover, considering highly mobile electrons, the mass action law for the reaction of defect conversion between the charge states is valid

\[
C_{r_1}^1 = h_{r_1} C_{r_1}^1 \frac{n^{-z_1} C_{r_1}^1}{n_i} = h_{r_1} C_{r_1}^1 \frac{n^{-z_1} C_{r_1}^1}{n_i},
\]

\[
C_{r_2}^2 = h_{r_2} C_{r_2}^2 \frac{n^{-z_2} C_{r_2}^2}{n_i} = h_{r_2} C_{r_2}^2 \frac{n^{-z_2} C_{r_2}^2}{n_i},
\]

where \( h_{r_1} \) and \( h_{r_2} \) are the constants for the local thermodynamic equilibrium in the reactions when neutral defects \( D_1^r \) and \( D_2^r \) are converted into charge states \( r_1 \) and \( r_2 \), respectively.

Substituting (23) and (24) into (21) and taking into consideration that \( C_{AC} = m C_{Cl} \), we obtain

\[
C_{AC} = K \chi \frac{(k + r_2 m_2 - r_1 m_1)}{C^m},
\]

where

\[
K = \frac{m K_L (h_{r_1} r_1)^{m_1}}{K_R (h_{r_2} r_2)^{m_2}} \left( \frac{C_{eq}^1}{C_{eq}^2} \right)^{m_1},
\]

\[
\frac{\tilde{C}_D}{C_{eq}^1}, \quad \frac{\tilde{C}_D}{C_{eq}^2} = \frac{C_{eq}^1}{C_{eq}^2}.
\]

Here \( C_{AC} \) is the concentration of clustered arsenic atoms and \( C_T = C + C_{AC} \) is the total arsenic concentration. The parameter \( K \) has a constant value depending on the temperature of diffusion. This value can be extracted from the best fit to the experimental data. The quantities \( C_{eq}^1 \) and \( C_{eq}^2 \) are the equilibrium concentrations of corresponding defects in the neutral charge state.

IV. RESULTS OF CALCULATIONS

Analysis of Eqs. (22) and (25) shows that saturation of the electron density will be observed for the formation of singly negatively charged clusters incorporating one arsenic atom and a lattice defect. The calculations of the functions \( C = C(C_T) \), \( C^A = C^A(C_T) \), and \( n = n(C_T) \) for this case are presented in Fig. 2. For comparison with the experimental data, the processing temperature was chosen to be \( 1050^\circ \text{C} \) \((n_i = 1.1665 \times 10^9 \text{ mm}^{-3})\). To calculate the functions \( C = C(C_T) \), \( C^A(C_T) \), and \( n(C_T) \), a system of nonlinear equations (22), (25) was solved numerically by Newton’s method. In the case of singly negatively charged clusters (DAs) incorporating a lattice defect and one arsenic atom we adopt \( r_{Cl} = 1 \) and \( m_1 = 1 \). Eq. (21) for \( m = 1 \) yields that \( -z_1 m_1 - z_2 m_2 + k = 2 \), and the system (25), (22) is of the form:

\[
C^A = K \tilde{C}_D \chi^2 C,
\]

\[
\chi = \frac{1}{2n_i} \left[ C - K \tilde{C}_D \chi^2 C - N_B + \sqrt{(C - K \tilde{C}_D \chi^2 C - N_B)^2 + 4n_i^2} \right].
\]

As can be seen from Fig. 1, the concentration of charge carriers in the saturation region is approximately equal to the value \( n_e = 3.5665 \times 10^9 \text{ mm}^{-3} \). In Fig. 2 for \( C^T \to +\infty \), the electron concentration reaches saturation at the
value $n \sim 3.765 \times 10^8 \ \mu m^{-3}$ associated with the plateau of the charge carrier profile given in Fig. 1. The value of parameter $K\tilde{C}_D$ for this case was chosen as $1.0698 \times 10^{-4}$ a. u. to provide a fit to the experimental value of $n_c$. As seen from Fig. 2, the function $n = n(C^T)$ is similar to that predicted by the model of Tsai et al. Saturation of the electron density occurs at extremely high values of the total impurity concentration $C^T$, which is in conflict with the experimental data.

In Fig. 3a the system of nonlinear equations (22), (25) is solved numerically for the formation of singly negatively charged clusters incorporating one arsenic atom. The measured electron density (circles) is taken from Solmi and Nobile.

$$C^A = K\tilde{C}_D \chi^3 C^2,$$

$$\chi = \frac{1}{2n_i} \left[ C - \frac{1}{2} K\tilde{C}_D \chi^3 C^2 - N_B + \sqrt{\left(C - \frac{1}{2} K\tilde{C}_D \chi^3 C^2 - N_B\right)^2 + 4n_i^2} \right].$$

The calculations for $n = n(C^T)$ show that, with the increasing total concentration of impurity atoms $C^T$, the concentration of charge carriers $n$ reaches its maximum value $n_{\text{max}} = 3.750 \times 10^8 \ \mu m^{-3}$ at $C^T_{\text{max}} \sim 1.634 \times 10^9 \ \mu m^{-3}$ and then decreases monotonically. At maximum the concentration of the substitutionally dissolved arsenic atoms $C_{\text{max}}$ is $7.943 \times 10^8 \ \mu m^{-3}$. The parameter $K\tilde{C}_D$ used in this calculation is equal to $4.0 \times 10^{-14} \ \mu m^3$.

The calculated curve agrees with the experimental function $n = n(C^T)$ much better than those obtained by the model of Tsai et al. and the models of neutral (DAs$_2$) and neutral (DAs$_4$) clusters.

![Graph](image-url)

**FIG. 2:** Calculated concentrations of substitutionally dissolved arsenic atoms (solid line), clustered arsenic atoms (dashed line), and electron density (dotted line) against the total dopant concentration for the formation of singly negatively charged clusters incorporating one arsenic atom. The measured electron density (circles) is taken from Solmi and Nobile for the diffusion at a temperature of 1050°C.

**FIG. 3:** Calculated concentrations of substitutionally dissolved arsenic atoms (solid line), clustered arsenic atoms (dashed line), and electron density (dotted line) against the total dopant concentration for the formation of singly (a) and doubly (b) negatively charged clusters incorporating two arsenic atoms ($r_{\text{Cl}} = -1$, $m_1 = 1$, and $m = 2$). Then, from (20), (22), and (25) it follows that:

The calculations of $n = n(C^T)$ and $C^A = C^A(C^T)$ were also performed for the clusters (DAs$_2$)$^-$, (DAs$_4$)$^-$, (DAs$_3$)$^{2-}$, (DAs$_4$)$^{-}$, and (DAs$_4$)$^{2-}$. And similar behavior of $n = n(C^T)$ was observed for all these cases. Also, the concentration of charge carriers increases with increasing $C^T$, reaches a maximum, and then decreases monotonically. This decrease is more pronounced with an increased number of arsenic atoms in the cluster. Besides, the position of maximum carrier concentration is
It follows from comparison of the calculated distributions \( n(C^T) \) with the experimental data that the best fit is observed for the doubly negatively charged cluster \((\text{DAs}_2)^{2-}\) (see Fig. 3b). To obtain the curves shown in Fig. 4, we solve the system (22), (25) having the following form for the clusters \((\text{DAs}_2)^{2-}\) :

\[
C^A = K \tilde{C}_D \chi^A C^2 , \tag{32}
\]

\[
\chi = \frac{1}{2n_i} \left[ C - K\tilde{C}_D \chi^A C^2 - N_B + \sqrt{ \left( C - K\tilde{C}_D \chi^A C^2 - N_B \right)^2 + 4n_{ie}^2} \right] . \tag{33}
\]

At maximum value of \( n_{max} = 3.694 \times 10^8 \mu m^{-3} \), the concentration of the substitutionally dissolved arsenic atoms \( C_{max} \) is equal to \( 7.943 \times 10^8 \mu m^{-3} \). The calculated curve \( n = n(C^T) \) agrees well with the experimental data, although only one fitting parameter \( KC\tilde{C}_D = 0.67 \times 10^{-15} \mu m^{-3} \) has been used. Full agreement is reached in the region of the transition to saturation of the electron density \( n \). This means that two arsenic atoms are incorporated in the cluster, and this arsenic cluster is doubly negatively charged, at least at the total dopant concentrations \( C^T \leq 1.0 \times 10^9 \mu m^{-3} \). Minor differences in values of the theoretical curve and experimental data for \( C^T > 2.3 \times 10^9 \mu m^{-3} \) can arise due to heavy doping effects (change of the silicon zone structure, changes in the constants of forward \( K_L \) and backward \( K_R \) reactions, etc). It is clear from expressions (22), (25) that variation of the defect concentration \( \tilde{C}_D \) in the region of high impurity concentrations also influences the concentration of impurity atoms incorporated in the clusters and, hence, the concentration of charge carriers. A change of \( \tilde{C}_D \) due to generation (absorption) of the defects in the region with high arsenic concentration is quite possible. For example, such a generation can occur due to the lattice expansion. Besides, it is possible that a high doping level leads to error in the determination of the experimental values for electron density, and the data for \( C^T > 2.3 \times 10^9 \mu m^{-3} \) may be incorrect.

Figs. 4 and b show the functions \( C = C(C^T) \), \( C^A = C^A(C^T) \), and \( n = n(C^T) \) calculated for clusters \((\text{DAs}_3)^-\) and \((\text{DAs}_4)^-\), respectively. As can be seen from these figures, fitting to the experimental data is worse in comparison with Fig. 3b, especially for the total concentrations greater than \( 2.0 \times 10^9 \mu m^{-3} \).

Note that multiple clustering can occur, too, and different clusters can coexist in the equilibrium state. For example, the clusters incorporating different numbers of arsenic atoms \((\text{DAs})^-\) and \((\text{DAs}_2)^-\) or clusters in different charge states \((\text{DAs}_2)^{\times}\), \((\text{DAs}_2)^-\), and \((\text{DAs}_2)^{2-}\) can coexist. As follows from the calculated curves for the electron density, when clusters \((\text{VAs}_1)^-\) (Fig. 2) and \((\text{VAs}_2)^{\times}\) (Fig. 1) are formed, it may be expected that the fall of the electron density in the plateau region will be less pronounced in the case of multiple clustering. However, this problem requires further investigation.

V. CONCLUSIONS

Based on analysis of the experimental results and theoretical calculations for clustering of arsenic atoms in silicon, it was shown that the developed clustering models fail to explain the available experimental data, especially the effect of electron density saturation at high
arsenic clustering was proposed and analyzed. The main feature of the proposed model is the assumption that negatively charged arsenic complexes play a dominant role in the clustering process. To confirm this assumption, the concentration of the impurity atoms incorporated in clusters and electron density were calculated as a function of the total arsenic concentration at a temperature of 1050 °C. Different cases of the formation of negatively charged clusters incorporating a point defect and one arsenic atom (DAs\(^{1−}\)), (DAs\(^{2−}\)) or more arsenic atoms (DAs\(^{2−}\)), (DAs\(^{3−}\)), (DAs\(^{3−}\)), (DAs\(^{4−}\)), and (DAs\(^{4−}\)) were investigated. It was shown that in the case of (DAs\(^{1−}\)) the concentration of charge carriers reaches saturation with increase in the total arsenic concentration and concentration of the substitutionally dissolved impurity atoms. However, saturation was observed for very high values of the total arsenic concentration, conflicting with the experimental data. In the cases of doubly negatively charged cluster (DAs\(^{2−}\)) and clusters incorporating more than one arsenic atom, the electron density reached its maximum value, then decreased monotonically and slowly with an increase in the total arsenic concentration. The electron density calculated for the formation of (DAs\(^{2−}\))− clusters agrees well with the experimental data and confirms the conclusion that two arsenic atoms participate in the cluster formation. Minor difference between the theoretical curve and experimental values for \(C^∗ > 2.3 \times 10^9 \mu m^{-3}\) may be explained by various heavy doping effects or uncertainty due to the experimental errors.

Thus, the plateau on the experimental distribution of the charge carriers, characterized by a practically constant value of the electron density in the region of high doping level, may be attributed to the negatively charged clusters (DAs\(^{2−}\)). The parameters describing arsenic clustering at a temperature of 1050 °C were determined by fitting the calculated values of the electron density to the experimental data. The proposed model of clustering by the formation of the negatively charged (DAs\(^{2−}\))− system gives the best fit to the experimental data among all the present-day models and may be used in simulation of high concentration arsenic diffusion.
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