

## Mechanisms of arsenic clustering in silicon

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(Received 25 October 2005; revised manuscript received 6 May 2006; published 18 July 2006)

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  $(DAs_1)^-$ ,  $(DAs_1)^{2-}$ ,  $(DAs_2)^-$ ,  $(DAs_2)^{2-}$ ,  $(DAs_3)^-$ ,  $(DAs_3)^{2-}$ ,  $(DAs_4)^-$ , and  $(DAs_4)^{2-}$  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  $(DAs_2)^{2-}$ , 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  $(DAs_2)^{2-}$  gives the best fit to the experimental data and can be used in simulation of high concentration arsenic diffusion.

DOI: 10.1103/PhysRevB.74.035205

PACS number(s): 61.72.Ji, 61.72.Tt, 61.72.Ss, 85.40.Ry

### 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.<sup>1-11</sup> 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.<sup>12-14</sup> 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.<sup>4,7,15-19</sup> Moreover, a reverse annealing or transient increase of the carrier density can be observed if a doped specimen, previously annealed at temperature  $T_1$ , is further annealed at higher temperature  $T_2$ .<sup>20</sup> It is supposed that transient dissolution of a part of the clusters occurs during such a reverse annealing.<sup>20</sup>

At very high dopant concentrations exceeding the solid solubility of As in Si, a significant fraction of arsenic atoms can form precipitates.<sup>3-6,8,10,15,21,22</sup> The typical distributions of the total dopant concentration and electron density after

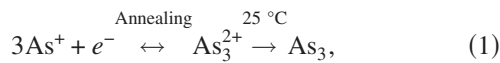
thermal annealing of silicon substrates heavily implanted by As were presented by Nobili *et al.*<sup>4</sup> (Fig. 7 from Ref. 4) and by Solmi<sup>10</sup> [Fig. 1(c) from Ref. 10]. As can be seen from Fig. 1(c) of Ref. 10, the carrier concentration reaches its saturation value  $n_e = 3.57 \times 10^{20} \text{ cm}^{-3}$ , whereas the total arsenic concentration increases to the solubility limit<sup>9</sup>  $C_{\text{sol}} = 3.27 \times 10^{21} \text{ cm}^{-3}$  and continues to increase in the region adjoint to the surface. It is supposed that the cluster formation occurs at high dopant concentrations,<sup>1-3,7,9,10,12,15,16</sup> more precisely, at the dopant concentrations approximately ranging from  $n_e$  to  $10n_e$ . If dopant concentration exceeds the solubility limit  $C_{\text{sol}}$ , precipitation occurs.<sup>4,10</sup> 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

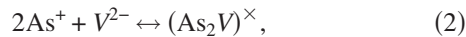
A great number of clustering models with different types of clusters have been developed and proposed since 1973.<sup>1-3,12,15,16,23,25,26</sup> The variety of the proposed models reflects discrepancies in the experimental results<sup>21</sup> and a great uncertainty in the nature of the clusters discussed. For example, inactive cluster  $VAs_2$  was considered in Ref. 12 to explain the difference 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.<sup>1</sup> According to Tsai *et al.*,<sup>2</sup> who have also investigated diffusion in the ion-implanted layers, clustering of arsenic may be expressed as



where  $As^+$  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 Ref. 8 that the formation of clusters  $(As_2V)^\times$  occurs due to the following reaction:



which is most liable to cause deactivation because the concentration of inactive As species increases to the fourth power of the active As concentration.<sup>1,14</sup> 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

$$C_{AC} = A \tilde{C}_{V^\times} \chi^2 C^2, \quad (3)$$

where

$$A = K_{AC} C_{V^\times}^{\text{eq}} n_i^2, \quad (4)$$

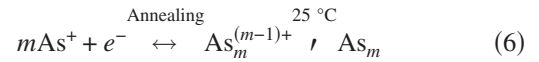
$$\tilde{C}_{V^\times} = \frac{C_{V^\times}}{C_{V^\times}^{\text{eq}}}, \quad \chi = \frac{n}{n_i}, \quad (5)$$

$C_{AC}$  and  $C$  are the concentrations of the impurity atoms incorporated into clusters and substitutionally dissolved arsenic atoms, respectively;  $K_{AC}$  is the constant of the local equilibrium for reaction (2);  $C_{V^\times}$  and  $C_{V^\times}^{\text{eq}}$  are the actual and the equilibrium concentrations of neutral vacancies, respectively;  $n$  is the electron density during thermal treatment normalized to the concentration of intrinsic charge carriers in a semiconductor at the annealing temperature  $n_i$ .

One would expect from (3) that reaction (2) yields the fourth power dependence  $C_{AC} \propto C^4$ , since for high concentrations  $C \gg n_i$  it might be reasonable to assume  $\chi = n/n_i \approx C/n_i$ . However, as seen from Ref. 4 (Fig. 7) and Ref. 10 [Fig. 1(c)], the electron density at room temperature  $n_R \approx \text{const}$  in the region of concentrations associated with active clustering. Consequently, reaction (2) yields the second

power dependence  $C_{AC} \sim C^2$ , which contradicts the experimental data.<sup>1,14</sup>

The model<sup>2</sup> was generalized by Solmi and Nobili<sup>5</sup>

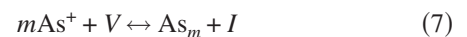


to take into account a saturation behavior of the carrier density with increasing dopant concentration. For diffusion at a temperature of 1050 °C, the best agreement between the modeled and experimental curves describing diffusivity against total arsenic concentration was achieved for  $m=4$ . And at 900 °C, the neutral cluster model<sup>12</sup> provided a better agreement with the experimental data. The reaction (6) was also used in Ref. 9 to describe deactivation in the arsenic-doped layers, which were formed by ion implantation and high temperature annealing of silicon-on-insulator specimens.

It is important to note that reaction (6) was first theoretically studied by Guerrero *et al.* in Ref. 23, which will be considered below.

Because of the vacancy participating in cluster formation, silicon self-interstitials were in turn ejected or left behind during clustering.<sup>6</sup> This assumption had been made much earlier in the study<sup>15,17</sup> of impurity deactivation within the laser-annealed layers. However, the results obtained in Ref. 6 show that the point defects induced during clustering and/or precipitation make no contribution to the enhanced transient diffusion of arsenic implanted at low energy, while these defects did coalesce to form extended defects at the projected range. Analysis of the defect microstructure has revealed that the transition between arsenic clustering and SiAs precipitation is not abrupt, pointing to possible coexistence of arsenic clusters and SiAs precipitates (although precipitates are not directly observed).<sup>6</sup>

Taking into account the self-interstitial injection, Solmi *et al.*<sup>11</sup> have recently used the following reaction:

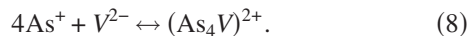


to model the transient arsenic diffusion. Here  $m$  is assumed to have the values between 2 and 4 to take into account the fact that the As cluster was formed around a vacancy with the subsequent injection of the self-interstitial.

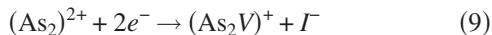
### B. Clustering during deactivation of supersaturated arsenic layers formed by laser annealing

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 Ref. 16 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.*<sup>24</sup> 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.<sup>16</sup> Using this cluster species, a single-step clustering reaction was postulated in Ref. 16,



The assumption of self-interstitial ejection during clustering was supported by the experimental data obtained by Parisini *et al.*<sup>15</sup> who have observed that extended defects at the projected range were extrinsic or interstitial in nature. The reaction



was proposed in Ref. 15 only for the initial step of the deactivation process in arsenic implanted silicon specimens, first laser-annealed and then thermally annealed. Here  $\text{I}^-$  is the negatively charged self-interstitial. The results obtained by Rousseau *et al.*<sup>17</sup> 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 in Ref. 18, 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.

As presented above, the existing explanations of the experiments concerning deactivation in the supersaturated arsenic layers does not allow one to make the exact conclusion about cluster structure and to describe the effect of electron density saturation. However, these experiments give very useful information for developing the future clustering model. For example, it follows from Ref. 16 that a thermal treatment of laser-melted layers at the temperature of 800 °C results in a quick deactivation of a certain fraction of impurity atoms, moreover the main amount of these atoms is deactivated due to clustering for 30 seconds after annealing start (see Fig. 4 from Ref. 16). The following slow change in the arsenic activation can be attributed to changes in the defect subsystem, which simultaneously causes a transient enhanced diffusion. These results are confirmed indirectly by the experiments of Ref. 18 where it was shown that carrier concentrations in laser-melted layer after annealing at the temperature of 750 °C for 15 seconds and for 2 hours were practically the same (see Fig. 7 from Ref. 18). Thus, for high temperature annealing (1000 °C and higher), the experimental data show that a local thermodynamic equilibrium between clusters and substitutional arsenic atoms is established during several seconds or even during the time less than 1 second.

### C. Experimental investigations of defect subsystem

The methods of transmission electron spectroscopy (TEM),<sup>4,6,15,22,27</sup> extended x-ray-absorption fine-structure (EXAFS),<sup>15,28–30</sup> Rutherford backscattering (RBS),<sup>22,31</sup> positron lifetime measurements<sup>32–35</sup> combined with the measurements of electron momentum distributions,<sup>36–40</sup> and other methods<sup>21,41</sup> are commonly used to investigate silicon speci-

mens doped by As. The analysis of these experimental data shows that complexing of As atoms with vacancies occurs in the layers heavily doped by arsenic. Based on the experimental data, various  $\text{V}_m\text{As}_n$  clusters are possible but  $\text{VAs}_2$  and  $\text{VAs}_3$  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,  $\text{VAs}_3$  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<sup>29</sup> at temperatures higher than 750 °C. At the same time, clustering occurs at temperatures higher than 750 °C as well.<sup>10</sup> This means that such a high temperature clustering is hardly explained by  $\text{VAs}_3$  complexes.

### D. First principles studies

Along with various experimental investigations, a number of the theoretical *ab initio* calculations have been performed to explain deactivation of arsenic atoms in silicon. From the calculations of Pandey *et al.*,<sup>24</sup> it follows that  $\text{VAs}_4$  complex including a vacancy surrounded by four arsenic atoms is energetically favored over both substitutional, isolated As in Si and substitutional Si-As<sub>4</sub> configurations. This cluster is electrically inactive, being responsible for arsenic deactivation and structural changes in heavily doped silicon. Larger defect clusters (e.g.,  $\text{V}_2\text{As}_4$ ) should also form during annealing, whereas  $\text{VAs}_4$  is only the first step in the clustering process. These investigations were continued in Ref. 42, where general  $\text{V}_n\text{As}_m$  complexes have been considered. The formation energies of the vacancy-donor complexes  $\text{VAs}_1$ ,  $\text{VAs}_2$ ,  $\text{VAs}_3$ , and  $\text{VAs}_4$  were found to be 2.47, 0.82, -0.53, and -2.39 eV, respectively. Moreover, it was proposed that the complex  $\text{VAs}_2$  was mobile, as were the  $\text{VAs}_1$  pairs. As these pairs moved, they reacted with other defects to form larger, immobile complexes. When considering the mobile  $\text{VAs}_2$  complexes, Ramamoorthy and Pantelides<sup>42</sup> have tried to explain the coupled diffusion phenomena and clustering. It was supposed that  $\text{VAs}_2$  and  $\text{VAs}_3$  were the dominant complexes in the deactivated specimens near the enhanced-diffusion threshold.<sup>43,44</sup> A high rate of As diffusion observed during rapid thermal annealing<sup>43</sup> was due to  $\text{VAs}_2$  migration over a very short time period (6–60 s), when no extensive clustering could occur. During their motion,  $\text{VAs}_2$  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, in Refs. 45 and 46 it was stated that the formation of  $\text{VAs}_3$  or  $\text{VAs}_4$  defects was exothermic, but, according to the first-principles calculations,<sup>42</sup> buildup of  $\text{VAs}_1$  or  $\text{VAs}_2$  structures was endothermic. This means that even at low arsenic concentrations all impurity atoms must form  $\text{VAs}_3$  or  $\text{VAs}_4$  clusters after long-time treatment. In point of fact, at low dopant concentrations, one can observe intensive diffusion by means of  $\text{VAs}_1$  pairs rather than clustering.

Berding *et al.*<sup>25</sup> and Berding and Sher<sup>47</sup> have used the electronic quasichemical formalism to calculate a free energy of various clusters, including  $\text{AsSi}_4$ ,  $\text{VAs}_4$ ,  $\text{VAs}_3\text{Si}_1$ ,



$VAs_2Si_2$ . 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.*<sup>45</sup> as an alternative to exothermic  $VAs_4$ . The clusters DP(2),  $V_2As_6$ , and  $Si_8$  were also included in the calculations performed in Ref. 47. In contrast to Ref. 42, Berding *et al.*<sup>25</sup> and Berding and Sher<sup>47</sup> take into account the ionized states and entropy of the cluster formation. The entropy is unfavorable for the formation of a large defect complex such as  $VAs_4$ . Therefore, the complete free-energy calculation is needed to determine the role of  $VAs_4$  in deactivation. Based on the complete free-energy calculation, it was found that cluster  $VAs_4$  was neutral, in agreement with the previous findings.<sup>24</sup> Also, the energy of this complex ( $-1.62$  eV) was in a rough agreement with the value given in Ref. 24. The  $VAs_3$  and  $VAs_2$  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.

In Refs. 25 and 47 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  $2 \times 10^{21} \text{ cm}^{-3}$  at a temperature of  $700^\circ\text{C}$ , which is in disagreement with the experimental data (see Fig. 2 from Ref. 25). It is important that, according to Ref. 47, DP(2) clusters proposed by Chadi *et al.* in Ref. 45 may be present as a deactivating species, insignificantly contributing to the deactivation under conditions of full equilibration.

These new defects, first mentioned in Ref. 45 and called DP, represent a pair of two threefold 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  $\langle 110 \rangle$  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 Ref. 45 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 Ref. 45 were further developed in Ref. 46. Citrin *et al.*<sup>46</sup> 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.<sup>48</sup> 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 cal-

culations, Voyles *et al.*<sup>48</sup> 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.<sup>46</sup> 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 Ref. 19. Nevertheless, as follows from the experimental data,<sup>10</sup> a deactivation mechanism can be different in the As- and Sb-doped silicon. The mechanism of arsenic clustering calls for further investigation. In Ref. 26, Mueller *et al.* 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 Refs. 24, 25, 42, and 47, Mueller *et al.*<sup>26</sup> 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 Ref. 25, the cluster  $VAs_2$  has two acceptor levels, whereas Solmi *et al.*<sup>20</sup> have found from the carrier mobility measurements that the complex to be electrically neutral at room temperature. In Ref. 49 the first-principles calculations were performed to explain the coupled diffusion phenomena and clustering in heavily arsenic-doped silicon. In contrast to Ref. 42, 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. The models of clustering used in the first-principles calculations often contradict with each other and the experimental data. 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.<sup>2,12,13,23</sup> 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.*<sup>2</sup> was the first to account for the saturation of the charge carriers at increasing doping levels.<sup>23</sup> 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<sup>2</sup>

$$C_{Cl} = K_{Cl} n^C, \quad (10)$$

where  $C_{Cl}$  and  $n$  are the concentrations of clusters and electrons at the annealing temperature, respectively;  $K_{Cl}$  is the

constant of local thermodynamic equilibrium. After cooling, all clusters become neutral and  $C \approx n_R$  if  $C \gg n_i$ . 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

$$n \approx C + 2C_{Cl} = C + 2K_{Cl}nC^3. \quad (11)$$

Solving this equation, Tsai *et al.*<sup>2</sup> obtained

$$n = \frac{C}{1 - 2K_{Cl}C^3} \quad (12)$$

and

$$C_T = C + \frac{3K_{Cl}C^4}{1 - 2K_{Cl}C^3} = \frac{C + K_{Cl}C^4}{1 - 2K_{Cl}C^3}, \quad (13)$$

where  $C_T$  is the total arsenic concentration.

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

$$C = C_{\text{sat}} = \frac{1}{\sqrt[3]{2K_{Cl}}} \quad (14)$$

both the concentration of arsenic atoms incorporated into clusters and the total concentration of arsenic atoms approach infinity. The value  $n_e = C_{\text{sat}}$  is interpreted in Ref. 2 as a maximum level of electron concentration at room temperature. From the experimental data it is seen that a maximum equilibrium carrier concentration in the arsenic implanted layers  $n_e$  may be described by the following relation:<sup>10</sup>

$$n_e = 2.2 \times 10^{22} \exp\left(-\frac{0.47 \text{ eV}}{k_B T}\right), \quad (15)$$

where  $T$  is the temperature of annealing.

Using Eqs. (15) and (14), the value of  $K_{Cl}$  may be derived to be

$$K_{Cl} = \frac{1}{2n_e^3}. \quad (16)$$

To illustrate,  $n_e = 3.57 \times 10^{20} \text{ cm}^{-3}$  for annealing at a temperature of 1050 °C and  $K_{Cl} = 1.10 \times 10^{-62} \text{ cm}^9$ .

The values of electron density at room temperature  $n_R$  as a function of the total arsenic concentration calculated by the model of Tsai *et al.*<sup>2</sup> are shown in Fig. 1. The experimental values of  $n_R$  based on the data from Ref. 5 are also given for comparison. As seen from Fig. 1, saturation of the electron concentration for the model<sup>2</sup> is observed at the extremely high total As concentrations, whereas the experimental data show that the carrier concentration reaches its maximum at  $C_T \approx 8 \times 10^{20} \text{ cm}^{-3}$ . Thus, the model<sup>2</sup> is inconsistent with the experimental data. Moreover, as follows from the experimental data of Solmi and Nobili,<sup>5</sup> 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 was concluded in Ref. 5 that  $n_e$  had a physical meaning. Thus, the model<sup>2</sup> 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

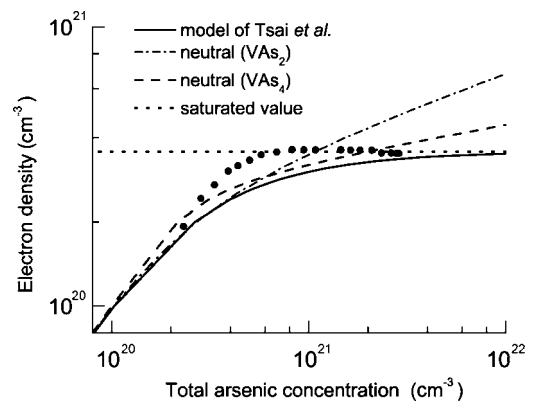
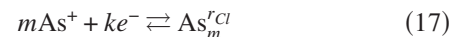


FIG. 1. Calculated electron concentration against the total arsenic concentration for different models of clustering: solid line, model of Tsai *et al.* (Ref. 2); dashed-dotted line, neutral clusters  $VAs_2$ ; and dashed line, neutral clusters  $VAs_4$ . The experimental data (circles) are taken from Solmi and Nobili (Ref. 5) for the diffusion at a temperature of 1050 °C.

model and associated with the peculiarity of the diffusivity is three times greater than  $n_e$ .

Figure 1 presents the functions  $n = n(C_T)$  calculated for the cases when neutral clusters  $VAs_2$  and  $VAs_4$  are formed. In these cases, saturation of the electron density is not observed and the calculations do not agree with the experimental data. The absence of saturation for the electron concentration corresponds to the first-principles calculations in Ref. 25 (Fig. 2 from Ref. 25) and Ref. 47 (Fig. 3 from Ref. 47). As seen from these figures, no saturation is observed at arsenic concentrations when  $VAs_4$  clustering is prevailing.

The reactions



were used in the basic model for the clustering of As in silicon proposed by Guerrero *et al.*<sup>23</sup> Here  $m$  and  $k$  are the numbers of arsenic atoms and electrons participating in the clustering process;  $As_m^{r_{Cl}}$  is the arsenic cluster in the charge state  $r_{Cl}$ . The dependence  $C = C(C_T)$  was analyzed by using the mass action law combined with the assumption of local charge neutrality

$$n = C + r_{Cl}C_{Cl} = C + r_{Cl}K_{Cl}C^m n^k. \quad (18)$$

It was supposed in Ref. 23 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  $n_R$  in the sample at room temperature;  $K_{Cl}$  is the constant of local thermodynamic equilibrium for reaction (17). 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.,  $r_{Cl}=0$ ,  $C$  is a monotonically increasing function of  $C_T$  and also there is no finite limit to  $C$  and electron density  $n_R$  at room temperature.

(2) If the clusters are positively charged at a high temperature ( $r_{Cl} \geq 1$ ) and exactly one electron takes part in the

reaction (18), i.e.,  $k=1$ ,  $C$  is a monotonically increasing function of  $C_T$ , which approaches a finite “saturation” value  $C_{\max}$  with increasing  $C_T$ .

As can be seen from the reaction (1), the model of Tsai *et al.*<sup>2</sup> 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 ( $r_{Cl} \geq 1$ ) 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  $C_{T \max}$ . A maximum concentration value  $C = C_{\max}$  is observed for  $C_T = C_{T \max}$ . With further increase in the total arsenic concentration  $C_T > C_{T \max}$  the concentration of the substitutionally dissolved arsenic atoms  $C$  and hence electron density  $n_R$  at room temperature are decreased.

This behavior of  $n_R$  is at variance with the experimental data, because experimentally measured  $n_R$  is approximately constant with increasing  $C_T$  (see Fig. 1).

(4) If the clusters are negatively charged at high temperatures ( $r_{Cl} \leq -1$ ), then  $C = C(C_T)$  behaves as in case (1), i.e.,  $C$ , and hence electron density  $n_R$  at room temperature, monotonically increase without limit for increasing  $C_T$ . This behavior of  $n_R$  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.<sup>23</sup> 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 Ref. 23 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 Ref. 5, 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.<sup>5,10</sup> 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 Refs. 25 and 26. It has been shown by Berd-

ing *et al.*<sup>25</sup> that clusters  $VAs_3$  and  $VAs_2$  have one and two acceptor levels, respectively. The calculations carried out by Mueller *et al.*<sup>26</sup> also show that for the electron densities  $n > 10^{16} \text{ cm}^{-3}$  the majority of complexes  $VAs_2$  will be negatively charged. According to Ref. 26, the complex  $VAs_3$  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  $VAs_3$  aggregate.

The saturation of the electron density is also observed in the layers heavily doped by Sb. To explain this phenomenon, it was supposed in Ref. 50 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. 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,<sup>10</sup> 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 Ref. 51 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 Refs. 2 and 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  $D_1^{r_1}$  can be involved in the cluster formation and another defect  $D_2^{r_2}$  can be generated during clustering. Here  $r_1$  and  $r_2$  are the charge states of defect  $D_1^{r_1}$  and defect  $D_2^{r_2}$ , respectively. In this case, a reaction for the formation and dissolution of clusters can be written as



where  $As^+$  is the substitutionally dissolved arsenic atom;  $e^-$  is the electron;  $(DAs_m)^{r_{Cl}}$  is the cluster formed;  $r_{Cl}$  is the charge state of cluster  $(DAs_m)^{r_{Cl}}$  incorporating a lattice defect  $D$ ;  $m_1$  and  $m_2$  are, respectively, the numbers of defects  $D_1^{r_1}$  and  $D_2^{r_2}$  participating in the cluster formation.

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

$$m + m_1r_1 - k = r_{Cl} + m_2r_2. \quad (20)$$

The mass action law for reaction (19) yields

$$K_L C^m (C_{D1r_1})^{m_1} \chi^k n_i^k = K_R C_{Cl} (C_{D2r_2})^{m_2}, \quad (21)$$

where  $K_L$  is the rate of 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);  $C_{D1r_1}$  is the concentration of defects  $D_1^{r_1}$  in the charge state  $r_1$  participating in the cluster formation;  $C_{D2r_2}$  is the concentration of defects  $D_2^{r_2}$  in the charge state  $r_2$  generated during clustering;  $C_{Cl}$  is the concentration of the clusters  $(DAs_m)^{r_{Cl}}$  in the charge state  $r_{Cl}$ .

Due to a high dopant concentration, the approximation of local charge neutrality can be used for the evaluation of normalized electron density  $\chi$ ,

$$\chi = \frac{n}{n_i} = \frac{1}{2n_i} [C + r_{Cl}C_{Cl} - C_B + \sqrt{(C + r_{Cl}C_{Cl} - C_B)^2 + 4n_i^2}], \quad (22)$$

where  $C_B$  is the summarized concentration of acceptors.

It follows from Eq. (19) that the concentration of impurity atoms incorporated into clusters  $C_{AC} = mC_{Cl}$ . Moreover, considering highly mobile electrons, the mass action law for the reaction of defect conversion between the charge states is valid

$$C_{D1r_1} = K_{D1r_1} n^{-r_1} C_{D1\times} = K_{D1r_1} n_i^{-r_1} \chi^{-r_1} C_{D1\times}, \quad (23)$$

$$C_{D2r_2} = K_{D2r_2} n^{-r_2} C_{D2\times} = K_{D2r_2} n_i^{-r_2} \chi^{-r_2} C_{D2\times}, \quad (24)$$

where  $K_{D1r_1}$  and  $K_{D2r_2}$  are the constants for the local thermodynamic equilibrium in the reactions when neutral defects  $D_1^\times$  and  $D_2^\times$  are converted into charge states  $r_1$  and  $r_2$ , respectively.

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

$$C_{AC} = K \tilde{C}_D \chi^{-(r_1 m_1 + k + r_2 m_2)} C^m, \quad (25)$$

where

$$K = \frac{m K_L (h_{D1r_1})^{m_1} n_i^{-(r_1 m_1 + k + r_2 m_2)} (C_{D1\times}^{eq})^{m_1}}{K_R (h_{D2r_2})^{m_2} (C_{D2\times}^{eq})^{m_2}}, \quad (26)$$

$$\tilde{C}_D = \frac{(\tilde{C}_{D1})^{m_1}}{(\tilde{C}_{D2})^{m_2}}, \quad \tilde{C}_{D1} = \frac{C_{D1\times}}{C_{D1\times}^{eq}}, \quad \tilde{C}_{D2} = \frac{C_{D2\times}}{C_{D2\times}^{eq}}. \quad (27)$$

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  $C_{D1\times}^{eq}$  and  $C_{D2\times}^{eq}$  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  $C = C(C_T)$ ,  $C_{AC} = C_{AC}(C_T)$ , and  $n = n(C_T)$  for this case are presented in Fig. 2. For comparison with the experimental data,<sup>5</sup> the processing temperature was chosen to be 1050 °C ( $n_i = 1.1665 \times 10^{19} \text{ cm}^{-3}$ ). To calculate the functions  $C(C_T)$ ,  $C_{AC}(C_T)$ , and  $n(C_T)$ , a system of nonlinear equations (22) and (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  $m_1 = 1$ . Equation (20) for  $m = 1$  yields that  $-r_1 m_1 - r_2 m_2$

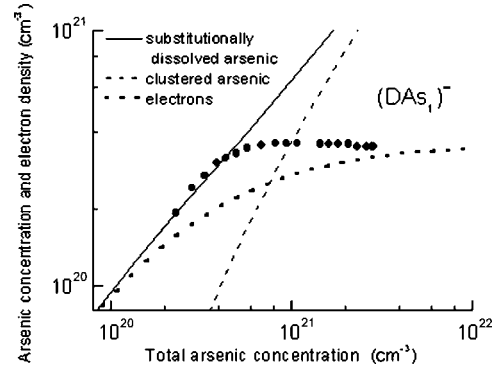


FIG. 2. Calculated concentrations of substitutionally dissolved arsenic atoms (solid line), clustered arsenic atoms (dashed line), and electron density (dotted line) against the total dopant concentration for the formation of singly negatively charged clusters incorporating one arsenic atom. The measured electron density (circles) is taken from Solmi and Nobili (Ref. 5) for the diffusion at a temperature of 1050 °C.

+ $k=2$ , and the system (25) and (22) becomes

$$C_{AC} = K \tilde{C}_D \chi^2 C, \quad (28)$$

$$\chi = \frac{1}{2n_i} [C - K \tilde{C}_D \chi^2 C - C_B + \sqrt{(C - K \tilde{C}_D \chi^2 C - C_B)^2 + 4n_i^2}]. \quad (29)$$

As can be seen from Fig. 1, the concentration of charge carriers in the saturation region is approximately equal to the value  $n_e = 3.5665 \times 10^{20} \text{ cm}^{-3}$ . In Fig. 2 for  $C_T \rightarrow +\infty$ , the electron concentration reaches saturation at the value  $n \sim 3.765 \times 10^{20} \text{ cm}^{-3}$  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  $n_e$ . As seen from Fig. 2, the function  $n = n(C_T)$  is similar to that predicted by the model of Tsai *et al.*<sup>2</sup> 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. 3(a) the system of nonlinear equations (22) and (25) is solved numerically for the formation of singly negatively charged clusters  $(DAs_2)^-$  incorporating a lattice defect and two arsenic atoms ( $r_{Cl} = -1$ ,  $m_1 = 1$ , and  $m = 2$ ). Then from (20), (22), and (25), it follows:

$$C_{AC} = K \tilde{C}_D \chi^3 C^2, \quad (30)$$

$$\chi = \frac{1}{2n_i} \left[ C - \frac{1}{2} K \tilde{C}_D \chi^3 C^2 - C_B + \sqrt{\left( C - \frac{1}{2} K \tilde{C}_D \chi^3 C^2 - C_B \right)^2 + 4n_i^2} \right]. \quad (31)$$

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  $n_{\max} = 3.750 \times 10^{20} \text{ cm}^{-3}$  at  $C_{T \max} \sim 1.634 \times 10^{21} \text{ cm}^{-3}$  and then



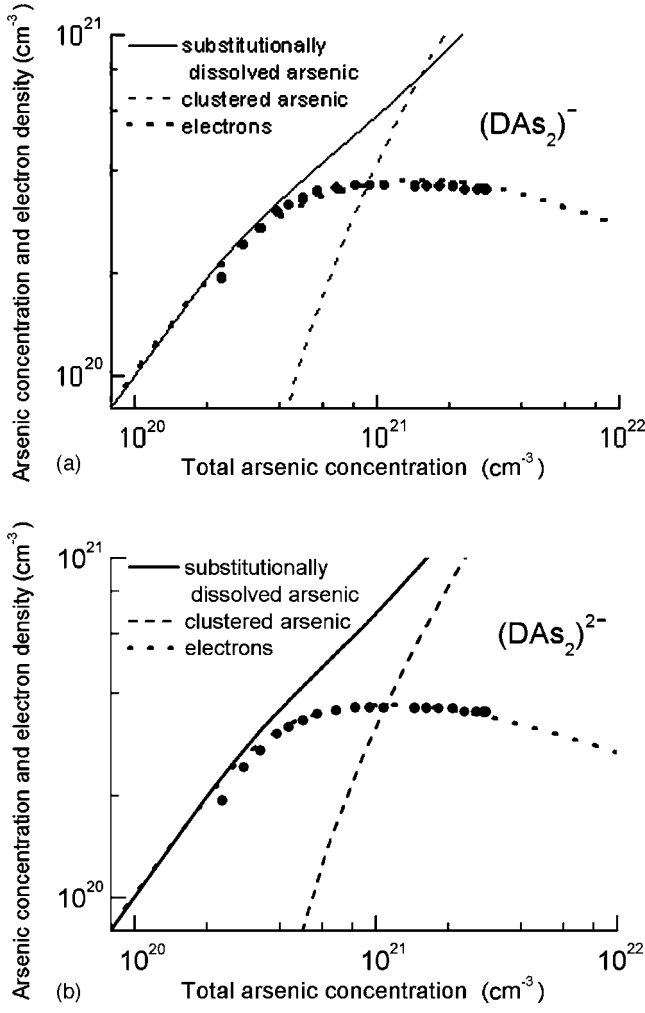


FIG. 3. Calculated concentrations of substitutionally dissolved arsenic atoms (solid line), clustered arsenic atoms (dashed line), and electron density (dotted line) against the total dopant concentration for the formation of singly (a) and doubly (b) negatively charged clusters incorporating two arsenic atoms. The measured electron density (circles) is taken from Solmi and Nobili (Ref. 5) for the diffusion at a temperature of 1050 °C.

decreases monotonically. At maximum of  $n$  the concentration of the substitutionally dissolved arsenic atoms  $C_{\max}$  is  $7.943 \times 10^{20} \text{ cm}^{-3}$ . The parameter  $K\tilde{C}_D$  used in this calculation is equal to  $4.0 \times 10^{-26} \text{ cm}^3$ . The calculated curve agrees with the experimental function  $n=n(C_T)$  much better than those obtained by the model of Tsai *et al.*<sup>2</sup> and the models of neutral  $(DAs_2)$  and neutral  $(DAs_4)$  clusters.

The calculations of  $n=n(C_T)$  and  $C_{AC}=C_{AC}(C_T)$  were also performed for the clusters  $(DAs_2)^{2-}$ ,  $(DAs_3)^-$ ,  $(DAs_3)^{2-}$ ,  $(DAs_4)^-$ , 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 shifted to smaller dopant concentrations with increases in the negative charge of the cluster.

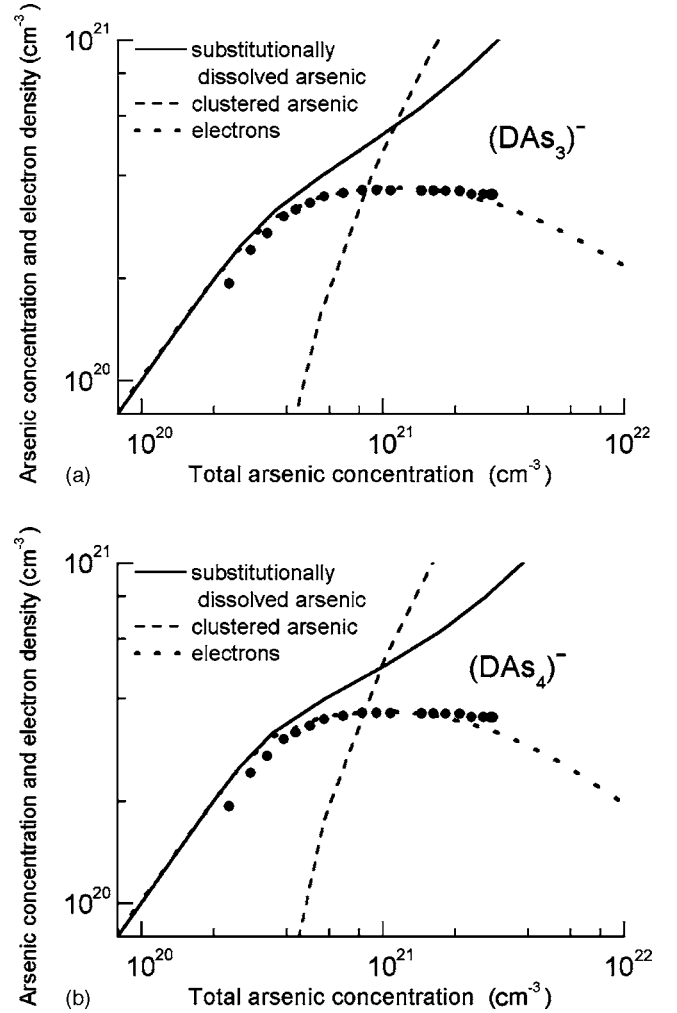


FIG. 4. Calculated concentrations of substitutionally dissolved arsenic atoms (solid line), clustered arsenic atoms (dashed line), and electron density (dotted line) against the total dopant concentration for the formation of singly negatively charged clusters incorporating three (a) and four (b) arsenic atoms. The measured electron density (circles) are taken from Solmi and Nobili (Ref. 5) for the diffusion at a temperature of 1050 °C.

From comparing the calculated distributions  $n(C_T)$  with the experimental data, it follows that the best fit is observed for the doubly negatively charged cluster  $(DAs_2)^{2-}$  [see Fig. 3(b)]. To obtain the curves shown in Fig. 3(b), we solve the system (22) and (25), having the following form for the clusters  $(DAs_2)^{2-}$ :

$$C^A = K\tilde{C}_D\chi^4 C^2, \quad (32)$$

$$\chi = \frac{1}{2n_i} [C - K\tilde{C}_D\chi^4 C^2 - C_B + \sqrt{(C - K\tilde{C}_D\chi^4 C^2 - C_B)^2 + 4n_i^2}]. \quad (33)$$

At maximum value of  $n_{\max}=3.694 \times 10^{20} \text{ cm}^{-3}$ , the concentration of the substitutionally dissolved arsenic atoms  $C_{\max}$  is equal to  $7.943 \times 10^{20} \text{ cm}^{-3}$ . The calculated curve  $n=n(C_T)$  agrees well with the experimental data, although



only one fitting parameter  $K\tilde{C}_D=0.67\times 10^{-27}\text{ cm}^3$  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  $C_T\leq 1.0\times 10^{21}\text{ cm}^{-3}$ . Minor differences in values of the theoretical curve and experimental data for  $C_T>2.3\times 10^{21}\text{ cm}^{-3}$  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) and (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  $C_T>2.3\times 10^{21}\text{ cm}^{-3}$  may be incorrect.

Figures 4(a) and 4(b) show the functions  $C=C(C_T)$ ,  $C_{AC}=C_{AC}(C_T)$ , and  $n=n(C_T)$  calculated for clusters  $(DAs_3)^-$  and  $(DAs_4)^-$ , respectively. As can be seen from these figures, fitting to the experimental data is worse in comparison with Fig. 3(b), especially for the total concentrations greater than  $2.0\times 10^{21}\text{ cm}^{-3}$ .

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  $(DAs_1)^-$  and  $(DAs_2)^-$  or clusters in different charge states  $(DAs_2)^\times$ ,  $(DAs_2)^-$ , and  $(DAs_2)^{2-}$  can coexist. As follows from the calculated curves for the electron density, when clusters  $(VAs_1)^-$  (Fig. 2) and  $(VAs_2)^\times$  (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 previously developed clustering models fail to explain the available experimental data, especially the effect of electron density saturation at high arsenic concentrations. Therefore, a model of 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  $(DAs_1)^-$ ,  $(DAs_1)^{2-}$  or more arsenic atoms  $(DAs_2)^-$ ,  $(DAs_2)^{2-}$ ,  $(DAs_3)^-$ ,  $(DAs_3)^{2-}$ ,  $(DAs_4)^-$ , and  $(DAs_4)^{2-}$  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  $(DAs_1)^{2-}$  and clusters incorporating more than one arsenic atom, the electron density reaches its maximum value, then slowly decreases monotonically as the total arsenic concentration increases. The electron density calculated for the formation of  $(DAs_2)^{2-}$  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  $C_T>2.3\times 10^{21}\text{ cm}^{-3}$  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  $(DAs_2)^{2-}$ . 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  $(DAs_2)^{2-}$  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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