

ANALYSIS AND MODELING OF ARSENIC ACTIVATION
AND DEACTIVATION IN SILICON

By

HACI OMER DOKUMACI

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HACI OMER DOKUMACI

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Heavily doped layers are one of the basic components of semiconductor device technology. As device dimensions shrink, higher electrically active dopant concentrations are required to fabricate devices with desirable properties. However, clustering and precipitation limit the obtainable active dopant concentration. Because of its high solubility and low diffusivity, arsenic is the most commonly used dopant for the fabrication of n^+ layers in silicon. The electrical activation and deactivation process of arsenic needs to be understood to assess its effects on the electrical properties of devices.

The focus of this thesis is analysis and modeling of phenomena related to electrical activation and deactivation of arsenic. The properties of the dislocation loops formed during arsenic deactivation were investigated with transmission electron microscopy. The loops are confined inside the arsenic layer, suggesting a strong link between loop formation and inactive arsenic. The reduction in buried boron layer diffusivity can be explained by the increase in the number of atoms bound by the loops. Transient enhanced

diffusion after high dose arsenic implantation was quantified using buried boron layers. Dislocation loops were also studied in these samples. The enhancement in boron diffusivity decreases at higher arsenic doses. The effect of arsenic activation on vacancy population was investigated with antimony marker layers. There is not any observable vacancy injection during arsenic activation in the presence of dislocation loops. Small enhancements in antimony diffusion were observed after the loops had dissolved.

An arsenic deactivation model that takes into account the size distribution of inactive arsenic structures was developed in FLOOPS. The model successfully reproduces the initial rapid deactivation of arsenic and the slow deactivation after the first few minutes. Various numerical methods were evaluated for the numerical solution of the rate equations that describe the size evolution of extended defects. The logarithmic rediscritization method was found to be the most accurate and stable technique for reducing the number of rate equations. The inclusion of the interactions between the arsenic-vacancy complexes, interstitials and dislocation loops led to a more general and physical arsenic deactivation model which can account for several experimental trends.

CHAPTER I

INTRODUCTION

Heavily doped layers are one of the basic components of semiconductor device technology. As semiconductor devices are scaled down to sub-micron dimensions, the design and the development of these regions become increasingly complex. Figure 1.1 illustrates various heavily doped layers in a typical BiCMOS process. The source/drain regions of the MOS transistors are doped with a high concentration of dopants in order to obtain a low sheet resistance. The buried layers below the MOS devices are used to minimize latch-up. For the bipolar transistor, heavy doping is utilized in the emitter to increase the current gain. The heavily doped extrinsic base and buried collector regions reduce the parasitic resistances associated with the bipolar transistor.

As device dimensions shrink, the absolute value of the threshold voltage of short-channel MOS transistors decreases. One way to reduce this effect is to fabricate shallower source/drain junctions. The resulting increase in the source/drain sheet resistance should be countered by increasing the electrically active dopant concentration. As the device dimension is reduced, the metal/silicon contact resistance also increases due to the reduction in the area of the contact. The contact resistance can be decreased by utilizing higher active dopant concentrations. However, the active dopant concentration does not increase indefinitely as the

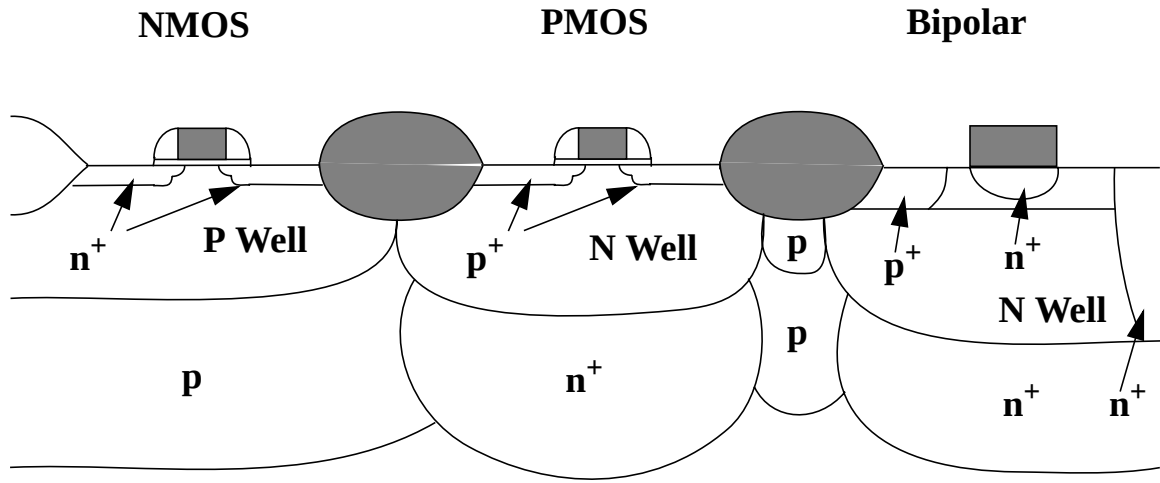


Figure 1.1 A cross-section of the active layers in a typical BiCMOS process.

dopant concentration is increased, because it is limited by the precipitation and clustering processes. These processes determine the electrical activation/deactivation behavior of dopants. They need to be understood in order to obtain lower sheet and contact resistances and to assess their effects on other electrical properties of the devices.

Arsenic is the most commonly used dopant in the fabrication of n-type layers because of its high electrical activation and low diffusivity, making it a suitable candidate for shallow junction technology. In this chapter, a review of literature on dopant activation/deactivation in silicon will be provided with an emphasis on arsenic. Some of the phenomena related to activation/deactivation and their effects on silicon devices will be discussed. The reasons of why a further understanding

and modeling of arsenic activation/deactivation processes is needed will be explained. Finally, the organization of this dissertation will be given.

1.1 Dopant Activation/Deactivation

Semiconductor technology relies on the ability to fabricate two types of electrically different layers: n-type and p-type. These layers are obtained by doping the semiconductor with electrically active donor or acceptor atoms. An electrically active dopant atom provides a free carrier to the conduction or valence band. When a dopant atom occupies a substitutional site, it creates an energy level that is very close to one of the bands, making it electrically active.

There are several ways of introducing dopant atoms into the semiconductor lattice. Ion-implantation is the most widely used technology for this purpose because of its excellent controllability and reproducibility which are required by today's integrated circuit technology.

During ion-implantation into silicon, the dopant atoms are accelerated to a certain energy and targeted to the silicon substrate. They penetrate through the surface, colliding with many host atoms before losing all their energy and coming to rest. These collisions disturb the crystalline nature of silicon and create disorder in the lattice in the form of point defects and amorphous zones. Most of the implanted dopant atoms do not occupy substitutional sites in such a disordered state. In order to transfer the dopants to substitutional sites and activate them, the substrate is subjected to a temperature treatment at several hundreds degrees Celsius.

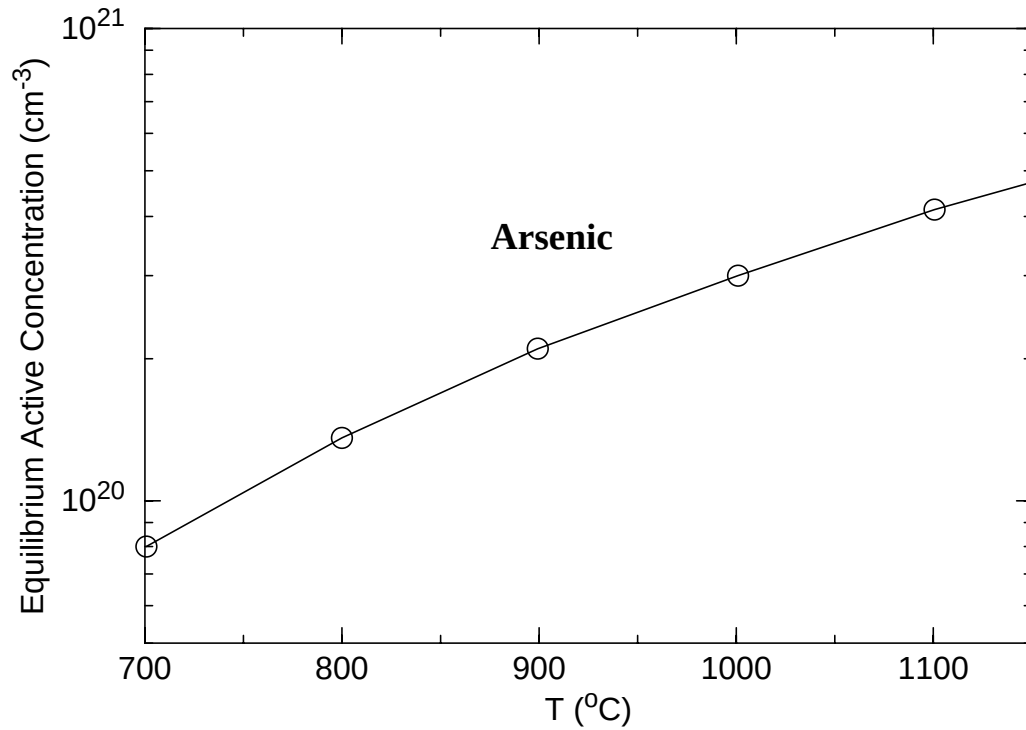


Figure 1.2 The temperature dependence of the equilibrium active concentration of arsenic [1].

The electrically active dopant concentration in high concentration layers is determined by the activation/deactivation processes during thermal anneal. Generally speaking, it is a function of the anneal temperature and time, the dopant, the chemical dopant concentration, and the state of the surface layer just after the ion-implantation (amorphous or non-amorphous). Under equilibrium conditions, the active concentration of dopant atoms in silicon, such as arsenic and boron, has been found to exhibit an Arrhenius dependence on temperature. For example, Figure 1.2 shows the equilibrium active concentration of arsenic as a function of temperature [1]. Today's integrated circuit processing conditions usually keep the silicon-dopant system away from equilibrium. Therefore, it is not simply possible to accurately model the active dopant concentration just as a function of temperature.

The following sections will describe various phenomena which are related to dopant activation/deactivation in silicon.

1.1.1 Electrically Active Dopant Concentration

When the ion-implantation damage exceeds a certain level, an amorphous layer is formed. Dopants in amorphous layers can be electrically activated up to a concentration many times higher than their equilibrium activation levels. During thermal annealing, arsenic has been observed to activate up to $5 \times 10^{20} \text{ cm}^{-3}$ at 560°C [2] even though the equilibrium active concentration of arsenic at 700°C is around $1 \times 10^{20} \text{ cm}^{-3}$ (Figure 1.2). The carrier concentration increases until the amorphous layer crystallizes completely. Further annealing causes arsenic to deactivate rapidly [2,3]. Non-equilibrium activation is also observed for boron [4,5] and antimony [6] in amorphized layers. In the case of boron, a preamorphization step is done since impractical high doses of boron are necessary to get an amorphous layer during boron implantation.

The higher activation effect is totally reversed when the sample is not amorphized by the implant. There are several reports indicating that active boron concentration remains much below its equilibrium activation level after ion-implantation and a low temperature anneal [7-9]. As shown in Figure 1.3, the tail of the boron profile undergoes an enhanced diffusion due to ion-implant damage. The peak is immobile, because boron at the peak region is either in the form of clusters or precipitates which can not diffuse through the lattice. The suppressed activation

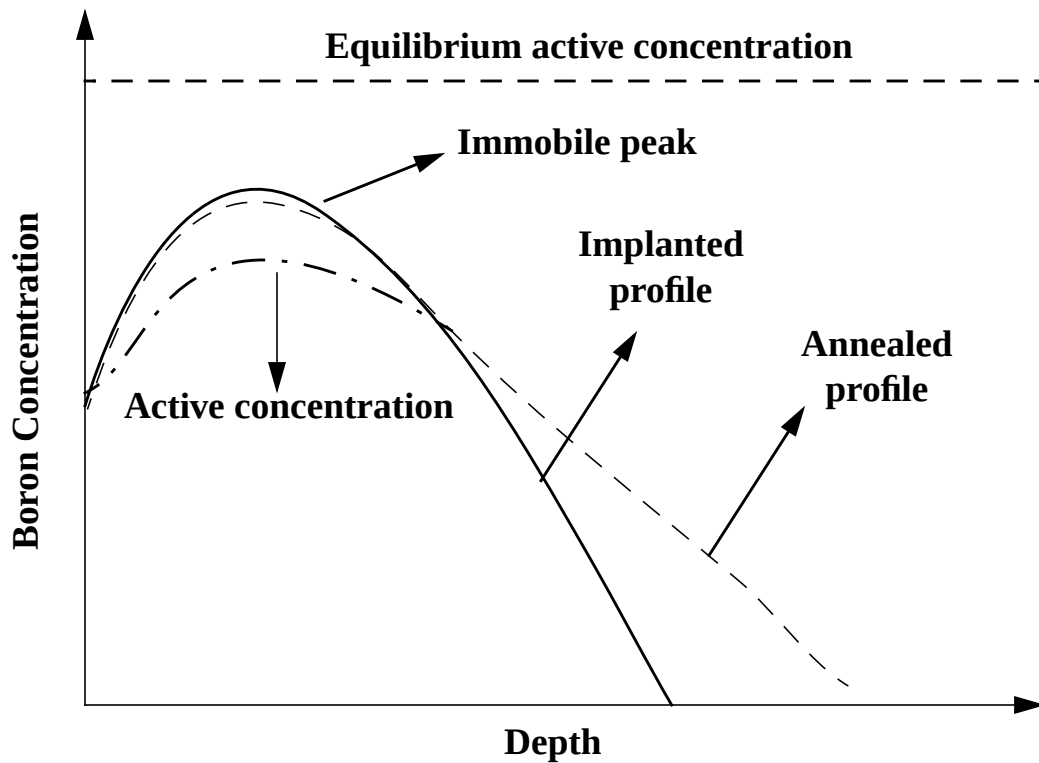


Figure 1.3 Representative boron profiles after ion-implantation and diffusion. The profile is not completely electrically active although the peak concentration is much below the equilibrium active concentration.

of boron at the peak has been attributed to the large supersaturation of interstitials just after ion-implantation [9-11]. If boron atoms are assumed to form clusters through a reaction with silicon interstitials, a high supersaturation of interstitials will increase the rate of formation of boron clusters, thus decreasing the electrically active boron concentration. Precipitation has been another explanation for boron deactivation in implanted samples [7].

Arsenic and phosphorus have been shown to exhibit a phenomenon called reverse annealing [12-14] (Figure 1.4). After being annealed at 650°C, high concentration arsenic samples have been subsequently annealed at 750°C [12].

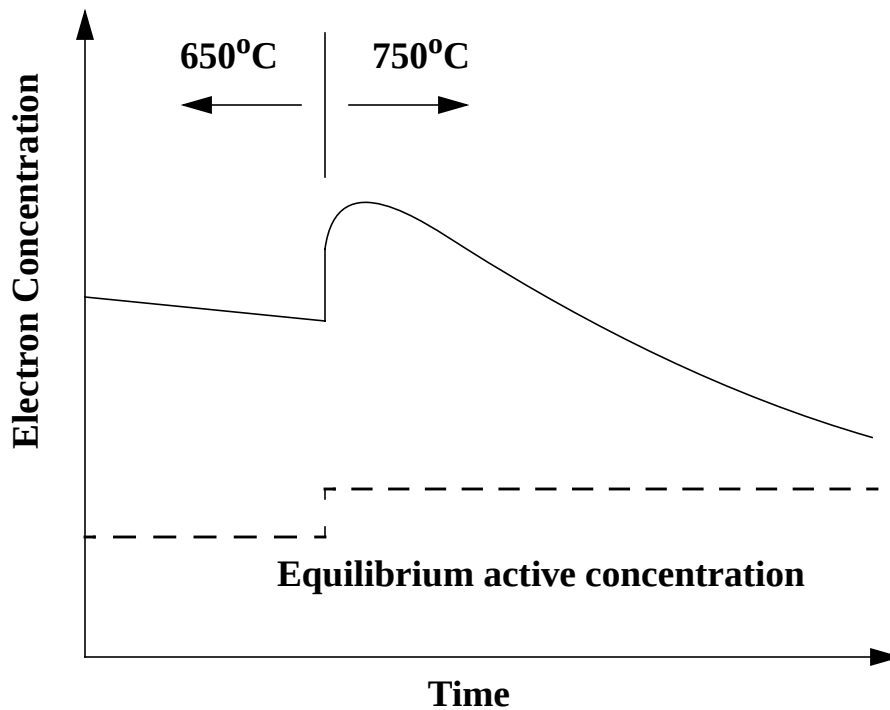


Figure 1.4 Illustration showing the reverse annealing phenomenon in arsenic and phosphorus doped samples.

Although the carrier concentration at the end of the 650°C anneal is above the equilibrium active concentration of arsenic at 750°C, it still increases at the beginning of the 750°C anneal to a maximum. Normally, one would expect a faster rate of deactivation upon increasing the temperature, since the electrically active concentration is above the equilibrium value at that temperature. This phenomenon has been claimed to be a solid proof that the electrically inactive dopant is in the form of precipitates rather than a cluster.

In terms of activation/deactivation, arsenic has been the most studied dopant in silicon because of its peculiar properties. Various studies [15-17] have reported incomplete arsenic deactivation for concentrations below the equilibrium activation

level. The deactivation is observed both at the tail and the peak of the profiles. It was suggested that inactive arsenic is in the form of arsenic-point defect pairs [15]. Another explanation has recently been given: Although the electrically active arsenic concentration is below its equilibrium value and no deactivation is expected, significant deactivation will still take place if the free energy of formation of very small inactive arsenic clusters is small enough [18]. The electrically active arsenic concentration is also dependent on the rate of ramp-down at the end of a thermal anneal. A slower ramp-down rate has been observed to increase the arsenic sheet resistance by 30% [19]. In a BiCMOS process, it was demonstrated that the sheet resistance of arsenic doped polysilicon increases upon doubling the ramp-down time [20]. It was also shown in the same study that a subsequent 15 second RTA step significantly reduces n^+ silicon and polysilicon sheet resistances and the poly/mono silicon contact resistance by dissolving the precipitates formed during ramp-down.

Laser annealing is another way of activating dopants in semiconductors. Although it is not widely used by industry, it has proved to be a very useful research tool. During laser annealing, a laser beam is directed to the silicon surface, melting the surface layer to a depth which is dependent on the incident laser power. The melt layer regrows very rapidly, incorporating nearly all of the dopant atoms onto substitutional sites. Therefore, up to a certain concentration, dopants can be totally activated with laser annealing. For example, phosphorus has been shown to activate up to a concentration of $5 \times 10^{21} \text{ cm}^{-3}$ and arsenic up to $3 \times 10^{21} \text{ cm}^{-3}$ [21]. Laser annealing also wipes out implantation damage and prevents the formation of extended defects like dislocation loops and stacking faults.

Because of this macroscopically clean state of silicon just after laser annealing, laser annealing and subsequent thermal annealing have been used numerous times to investigate the deactivation kinetics of dopants [3,5,6,12,13,21-23]. Subsequent thermal annealing deactivates dopants at temperatures as low as 300°C [12]. Since laser annealing activates all of the dopants, there is no uncertainty concerning the initial activation conditions. In one of the studies, box-shaped profiles have been created by repeated laser pulse annealing [23]. This allows one to interpret the electrical measurements as characteristic of a single doping concentration. This is not possible with simple thermal annealing since the dopant concentration is a function of depth in that case.

1.1.2 Dopant Diffusion

Substitutional dopants in silicon, such as arsenic, phosphorus and boron, are believed to diffuse via interactions with point defects: interstitials and vacancies [24]. These point defects can exist in various charge states. A chemical reaction between the substitutional dopant and point defects can be envisioned that converts the immobile substitutional dopant to a mobile dopant-defect pair. For a donor atom, this reaction can be written as:



where A^+ represents the substitutional donor atom, X^c represents a point defect with charge c . Since the point defects are charged, their concentration will depend on free carrier concentrations. For example, the concentration of negatively charged point defects with respect to their intrinsic values is given by [24]:

$$\frac{C_{X^{-c}}}{(C_{X^{-c}})^i} = \left(\frac{n}{n_i}\right)^c \quad 1-2$$

where $C_{X^{-c}}$ denotes the concentration of X^{-c} defects, $(C_{X^{-c}})^i$ their concentration in intrinsic silicon, n the electron and n_i the intrinsic electron concentration. This equation has been written under the assumptions that the environment is inert and the reactions between point defects and electrons are so fast that they may be considered in chemical equilibrium.

The diffusivity of a dopant is proportional to the concentration of the mobile dopant-defect pairs. Since the number of dopant-defect pairs is proportional to the number of point defects and the number of point defects depend on the free carrier concentration, the diffusivity depends on the free carrier concentration under extrinsic conditions. Actually, if the dopant-defect reactions and the defects are in equilibrium, the diffusivity for a donor atom can be written as:

$$D = D_o + D_- \left(\frac{n}{n_i}\right) + D_+ \left(\frac{n}{n_i}\right)^2 \dots \quad 1-3$$

where D_o is the diffusivity due to uncharged point defects, D_- due to negatively charged defects, etc. At high concentrations and under the condition of charge neutrality, for a single dopant:

$$n = C_{A^+} \quad 1-4$$

where C_{A^+} is the active dopant concentration. So, ultimately the diffusivity depends on the active dopant concentration under extrinsic conditions.

In so-called isoconcentration studies, the dopant under study is diffused in a region which is homogeneously doped with either another dopant or an isotope of the same dopant at a much higher concentration. This way, the carrier concentration is controlled independently of the diffusing species. The isoconcentration experiments have shown that arsenic [25], phosphorus [26], and antimony [27,28] diffusion are enhanced with increasing electron concentration. Also, boron [29,30] diffusivity is observed to increase with hole concentration.

Recent isoconcentration study by Larsen *et al.* [31] has revealed an even stronger dependence of arsenic and antimony diffusion on donor concentration than that expressed by Equations 1-3 and 1-4. The diffusivities of arsenic and antimony have been found to be proportional to the third to fifth power of the background phosphorus donor concentration for phosphorus concentrations greater than $2 \times 10^{20} \text{ cm}^{-3}$. At the highest donor concentrations, the diffusion coefficients are identical for arsenic, antimony and tin, although these dopants have different diffusivities at lower electron concentrations.

All the results mentioned above indicate that dopant diffusivities get increasingly sensitive to the amount of electrically active dopant concentration as the concentration is increased. Therefore, high concentration dopant diffusion is tightly coupled to the dopant activation/deactivation phenomena which determine the electrically active dopant concentration. From a modeling point of view, even small errors in the prediction of the electrically active dopant concentrations can result in a big error in dopant diffusivities and make the diffusion simulations unreliable. This point may become more and more important in the future as the IC technology requires higher carrier concentrations and therefore higher temperatures in the sub-micron regime.

1.1.3 Point Defect Injection

A recent study by Rousseau *et al.* [32] confirmed the interaction between point defects and dopant activation/deactivation (Figure 1.5). Boron buried layers were used as markers of interstitial supersaturation in the bulk. These layers were obtained by first growing a boron doped silicon epi-layer on silicon and then growing an undoped silicon layer on top of it. Arsenic was implanted and the wafers were laser annealed. The laser annealing achieved full electrical activation of arsenic and a flat arsenic concentration, and destroyed the implant damage by melting the surface layer. For control purposes, another wafer was doped with germanium in exactly the same way. Germanium is similar to arsenic in size and mass. Next, the wafers were annealed at 750°C in an inert ambient for 15s and 2 h.

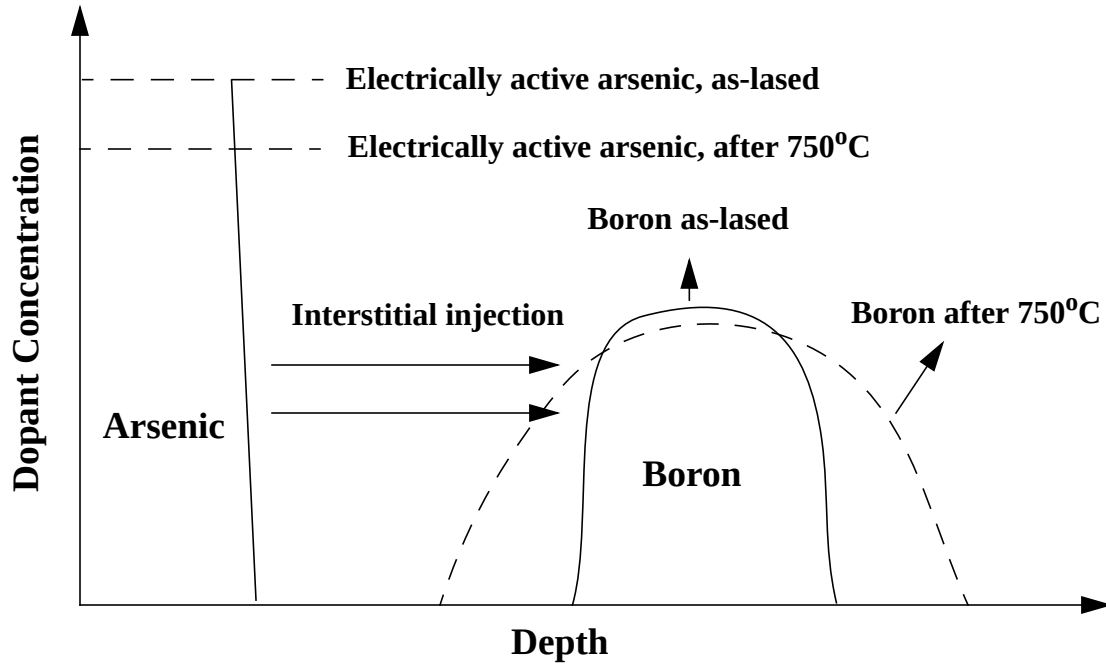


Figure 1.5 Representative arsenic and boron profiles in Rousseau *et al.*'s experiment. Boron diffusivity is enhanced up to a factor of 460 when arsenic is deactivated.

Normally, these anneals will not cause any significant diffusion of boron. But, the diffusivity of the boron buried layer was enhanced by a factor of up to 460 for the 2h anneal. Arsenic deactivation occurred in parallel to the enhancements in boron diffusivity.

Extended X-ray Absorption Fine Structure (EXAFS) measurements [33] and theoretical calculations [34] suggest that arsenic deactivates in the form of arsenic-vacancy complexes. Since the equilibrium concentration of vacancies is much smaller than the concentration of inactive arsenic, a huge amount of vacancies should be generated in the bulk. These vacancies have been postulated to come from arsenic deactivation assisted interstitial-vacancy pair generation. The generated

vacancies are incorporated in the inactive arsenic-vacancy complexes and the interstitials diffuse towards the surface and the bulk, and enhance boron diffusion.

Another study has shown the importance of this phenomenon in bipolar transistors [35]. After arsenic was implanted to form the emitter of the device, it was activated at 1100°C for 10s. The wafer was then cut in two, with one half undergoing a deactivation anneal at 750°C for 2h. The two halves were then annealed at 1000°C for 15s so that the final active arsenic concentration in both halves would be equal. There should not be any difference in the electrical characteristics of these two transistors since the inert diffusion of boron or arsenic is negligible at 750°C with respect to 1000°C or 1100°C. However, the electrical measurements show that the Gummel number is considerably reduced in the transistors that have received the 750°C anneal, because the interstitial injection during arsenic deactivation enhances the diffusion of both arsenic and boron. Therefore, the devices exhibit higher beta, lower output resistance and earlier punchthrough breakdown (Figure 1.6).

Shibayama *et al.* [36] were the first to observe the diffusivity enhancement underneath a high concentration arsenic layer. In their study, arsenic was diffused into silicon from an arsenosilicate glass at 1000°C. The diffusivity of both arsenic and boron were enhanced upon a low temperature anneal between 500-800°C.

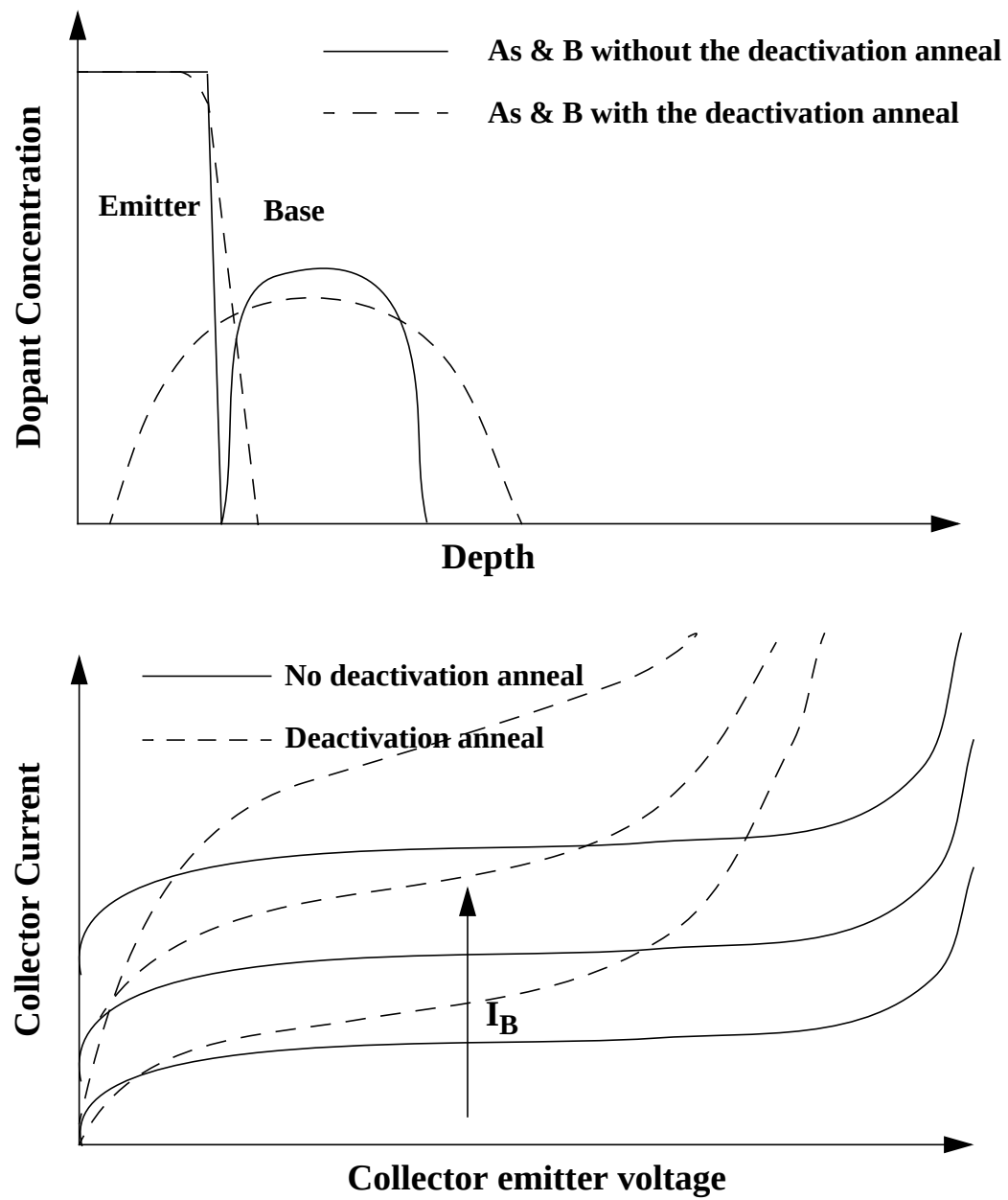


Figure 1.6 Schematic representation of the emitter and base profiles, and electrical characteristics of an npn bipolar transistor with and without a deactivation anneal.

1.1.4 Dislocation Loops

A dislocation loop is an extra layer of silicon atoms having a disc shape. Dislocation loops form when there is a high supersaturation of silicon interstitials during thermal annealing. The major cause of excess interstitials and dislocation loops is ion-implantation. Ion-implantation induced dislocation loops have been extensively studied [37]. Dislocation loops act as sinks and sources for interstitials and vacancies, affecting point defect concentrations and dopant diffusion as a result [38]. They increase the p-n junction leakage current by gettering metallic impurities along their peripheries. The stress fields that they generate in silicon also affect dopant redistribution [38]. The analysis of dislocation loops is therefore crucial in understanding and interpreting the effect of processing conditions on device electrical characteristics.

Since arsenic deactivation injects a huge amount of excess interstitials, one may expect dislocation loop formation as a result. In fact, several Transmission Electron Microscopy (TEM) observations have revealed dislocation loops in laser and then thermally annealed high concentration arsenic samples [21,22,39-42]. These loops have been found to be composed of silicon atoms [42]. It was suggested in the same work that arsenic clustering injects the excess silicon interstitials needed to form the loops. Nearly all studies have concluded that the number of atoms bound by the loops or any other extended defects is much smaller than the inactive arsenic dose. When an electron beam was used for initial annealing instead of a laser, dislocation loops were still observed after thermal annealing. In Chapter

II, the dislocation loops formed after laser and subsequent thermal annealing will be discussed in more detail.

On the other hand, in implanted and thermally annealed high concentration arsenic samples, a band of arsenic-related precipitates and dislocation loops were detected [37,44,45]. These defects lie at the projected range of the implant where arsenic concentration is at its maximum. They form when arsenic concentration exceeds its equilibrium active concentration. The defects that form at the peak of the implanted profile have been classified as type-V defects [37]. It is interesting to note that type-V dislocation loops are observed only in arsenic-implanted samples [37].

Upon high temperature annealing ($>900^{\circ}\text{C}$), end-of-range (type-II) dislocation loops dissolve much faster in the presence of gallium, phosphorus and arsenic if their concentrations exceed their solid solubility [46]. During enhanced elimination of type-II loops, the precipitates were also observed to be dissolving.

1.2 Organization

The focus of this thesis is analysis and modeling of the phenomena related to the arsenic activation/deactivation process. Chapter II presents the extended defects that form as a result of the interstitial supersaturation during arsenic deactivation. Understanding the mechanism of these defects is important for both defect engineering and an evaluation of their effect on arsenic deactivation induced interstitials and, therefore, dopant diffusion near high concentration arsenic layers. Chapter II reports the results of TEM observations on samples which were doped

with different arsenic doses above the equilibrium active concentration and received a laser anneal to activate all of the dopant, followed by thermal annealing. Various characteristics of the observed defects are evaluated and comparisons with published data are made.

Chapter III presents the results of boron enhanced diffusion due to high dose arsenic implantation in silicon. This study is made to investigate the possible effects of arsenic deactivation on implant damage enhanced diffusion. The behavior of both type-V and type-II loops is studied with TEM. Reduction in enhanced diffusion is observed with increasing arsenic dose at three different temperatures. The possible explanations for this reduction are also included in Chapter III.

Chapter IV contains an investigation of the vacancy population during arsenic activation. Since arsenic is believed to deactivate through the formation of arsenic-vacancy complexes, these complexes are expected to dissolve and generate free vacancies during arsenic activation. The vacancy population is monitored using antimony buried layers.

Chapter V presents a general kinetic model for extended defects. This model is applied to arsenic deactivation in silicon. The model calculates the evolution of the arsenic precipitate size density. It reproduces various trends and a good agreement is obtained between the simulations and the experiments.

In Chapter VI, various numerical methods are evaluated for the solution of the rate equations in extended defect simulation. The derivations of these methods are presented. The accuracies of these methods are evaluated using the arsenic deactivation model in Chapter V.

Chapter VII presents an arsenic deactivation model including dislocation loop formation and the interaction of the interstitials with the inactive arsenic structures. The model shows quantitative agreement with the arsenic deactivation and boron enhancement data. It is also in qualitative agreement with the properties of the loops in the deactivated layer. Finally, Chapter VIII presents the conclusions of this dissertation and recommendations for future experimental and modeling efforts.

CHAPTER II

TRANSMISSION ELECTRON MICROSCOPY ANALYSIS OF EXTENDED DEFECTS IN HEAVILY ARSENIC DOPED, LASER, AND THERMALLY ANNEALED LAYERS IN SILICON

2.1 Introduction

Arsenic is the most commonly used dopant for creating n^+ layers in silicon, such as the source/drain regions in a MOSFET and the emitter of a bipolar transistor. In order to get high conductivity, arsenic is often incorporated into these layers in excess of its equilibrium active concentration. Subsequent thermal annealing gives rise to inactive arsenic. As mentioned in Chapter I, deactivation of arsenic is accompanied by silicon interstitial injection and the enhancement of the boron layers underneath the arsenic layer [32]. This reaction can be written as:



where As represents a substitutional arsenic atom, As_mV_n the inactive arsenic complex, V a vacancy and I an interstitial. The reaction can be modified accordingly if the inactive arsenic complex also includes silicon.

Several transmission electron microscopy (TEM) observations have revealed precipitate-like defects, rod-shaped structures and/or dislocation loops in laser and

thermally annealed samples which have been doped with arsenic in excess of its equilibrium active level [21,22,39-42]. Lietoila *et al.* [22] have suggested that rod-like defects may be arsenic precipitates, whereas Armigliato *et al.* [40] have reported that all defects observed by TEM cannot explain the amount of electrically inactive arsenic in their experiments. No extended defects were detected by Lietoila *et al.* for a much smaller arsenic dose. Parisini *et al.* [41] measured the number of atoms bound by various types of interstitial-type defects at different annealing temperatures and confirmed the large discrepancy between the concentration of inactive arsenic and the concentration of atoms in observable defects. They proposed that the extended defects are formed as a result of agglomeration of silicon interstitials which are created during laser annealing. In a later work [42], based on double-crystal x-ray diffractometry (DCD) and extended x-ray absorption fine structure analysis (EXAFS) measurements, they suggested that deactivation of arsenic is the cause of excess interstitials. They also found that the dislocation loops are composed of silicon atoms. When an electron beam was used for annealing instead of a laser, similar defects were observed upon subsequent thermal treatment between 600-900°C [43].

On the other hand, a band of arsenic related precipitates and dislocation loops were detected after solid phase epitaxy of arsenic layers doped in excess of its equilibrium active level [37,44,45]. These defects were shown to lie at a depth corresponding to the projected range of the implant. In addition, half-loop dislocations that are located near the surface were observed to grow during arsenic precipitate dissolution even after 72h at 900°C [37]. Jones *et al.* found that the

elimination of end-of-range damage (category-II dislocation loops) is enhanced in the presence of a high concentration arsenic layer [46]. Both half-loop formation and enhanced elimination of category-II loops occur when arsenic peak concentration exceeds its solid solubility.

Understanding the mechanism of these defects is important for both defect engineering and an evaluation of the effects of arsenic deactivation on point defects and, therefore, dopant diffusion underneath high concentration arsenic layers. This chapter reports the results of TEM observations on samples which were doped with different arsenic doses above the equilibrium active concentration, received a laser anneal to activate all of the dopant and finally thermally annealed.

2.2 Experiment

Arsenic was implanted into $\langle 100 \rangle$, 10 Ω -cm p-type silicon substrates at doses ranging from 4×10^{15} to 3.2×10^{16} cm^{-2} with an energy of 35 keV. Completely active, box-shaped profiles were obtained by repeated laser pulse annealing (308 nm XeCl, 35 ns FWHM pulses, silicon melt duration 75 ns). The melt-region thickness of about 200 nm was considerably larger than the depth of the implant; thus any major implant damage in the as-implanted layer was effectively annealed out. The samples then received additional rapid thermal anneals at 700 or 750°C for durations that resulted in no appreciable diffusion. Further experimental details about the preparation of these samples can be found in Rousseau *et al.* [13] and Luning *et al.*[23].

The defects were studied by TEM using both bright field and weak beam conditions. Both plan-view and cross-section samples were analyzed with a JEOL 200 CX electron microscope operating at 200 keV. All micrographs were taken with a g_{220} condition.

The quantification of the defects on the TEM pictures were done by counting them and measuring the longest dimension of the defect. The density of the defects can be found from the following expression:

$$D = \frac{NM^2}{A_p} \quad 2-2$$

where D is the areal density of the defects, N is the number of defects in the area of interest, M is the magnification, and A_p is the analyzed area on the picture. The loops are assumed to lie on $[111]$ planes where the picture shows the defects through $\langle 100 \rangle$ direction. The areal density of the atoms bound by the loops was found by measuring the largest dimension of the loops and using the following formula:

$$N_{bound} = \frac{\pi \sum r^2}{\sqrt{3}A_p} d_{111} \quad 2-3$$

where r is the radius of a loop and is equal to half of the largest dimension, and d_{111} is the areal density of silicon on the $[111]$ plane. The $\sqrt{3}$ factor projects the

analyzed area onto the [111] plane. So, Equation 2-3 effectively calculates the areal density of the bound atoms on the [111] plane.

2.3 TEM Results

The as-lased samples were completely free of any visible defects. Subsequent thermal annealing revealed a very strong dose dependence of the defect structure in the arsenic doped layer. This phenomenon can be seen in Figure 2.1 to Figure 2.4 which show plan-view TEM micrographs of samples after a thermal treatment at 750°C for 2h. Density and size information about the defects are listed in Table 2.1 along with the inactive arsenic dose.

In contrast to the absence of any extended defects at the lowest dose ($4 \times 10^{15} \text{ cm}^{-2}$), large dislocation loops and rod-like defects are observed upon increasing the dose by just a factor of two. For the next two doses, only dislocation loops are detected. Upon increasing the arsenic dose, the density of the loops increases dramatically. Especially, the $1.6 \times 10^{16} \text{ cm}^{-2}$ sample exhibits almost fifty times more loops than the $8 \times 10^{15} \text{ cm}^{-2}$ sample. The concentration of atoms bound by the loops was found to be around 30-50 times smaller than the inactive arsenic concentration and is insufficient to directly account for most of the inactive arsenic.

Figure 2.5 and Figure 2.6 show the plan-view micrographs of the samples which were doped with a dose of $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 700°C for 15s (short-time) and 100 min (long-time). Very dense fine particles appear after the short-time anneal whereas the long-time sample exhibits a high density of loops.

Figure 2.1 Plan-view TEM micrograph of the sample implanted with $4 \times 10^{15} \text{ cm}^{-2}$ and annealed at 750°C (bright field).

Figure 2.2 Plan-view TEM micrograph of the sample implanted with $8 \times 10^{15} \text{ cm}^{-2}$ and annealed at 750°C (weak beam dark field).

Figure 2.3 Plan-view TEM micrograph of the sample implanted with $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 750°C (weak beam dark field).

Figure 2.4 Plan-view TEM micrograph of the sample implanted with $3.2 \times 10^{16} \text{ cm}^{-2}$ and annealed at 750°C (weak beam dark field).

Figure 2.5 Plan-view TEM micrograph of the sample implanted with $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 700°C for 15s (weak beam dark field).

Figure 2.6 Plan-view TEM micrograph of the sample implanted with $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 700°C for 100 min (weak beam dark field).

Table 2.1: Summary of TEM observations made on the samples annealed at 750°C for 120 minutes.

Dose (cm ⁻²)	Surface Conc. (cm ⁻³)	Defect Type	Size (Å)	Density (cm ⁻²)	Density of Bound Atoms (cm ⁻²)	Inactive As Dose (cm ⁻²)
4x10 ¹⁵	2.3x10 ²⁰	None	-	-	-	2.2x10 ¹⁵
8x10 ¹⁵	4.5x10 ²⁰	Dislocation loops	200 - 1200	3.3x10 ⁹	1.2x10 ¹⁴	4.9x10 ¹⁵
		Rod-like defects	400 - 2800	1.8x10 ⁹	-	
1.6x10 ¹⁶	9.1x10 ²⁰	Dislocation loops	50 - 350	1.3x10 ¹¹	3.5-4.5x10 ¹⁴	1.3x10 ¹⁶
3.2x10 ¹⁶	1.9x10 ²¹	Dislocation loops	100 - 400	> 2.5x10 ¹¹	> 6x10 ¹⁴	2.9x10 ¹⁶

Further analysis showed that the defects in the short-time sample are dislocation loops with a density of around $6 \times 10^{11} \text{ cm}^{-2}$ and average size of 90 Å. Recently, Rutherford back-scattering (RBS) measurements were made on the same samples [47]. It was demonstrated that the backscattered angular-scan spectra for silicon have the same minimum in both the as-lased and short-time samples whereas the minimum yield of arsenic increases. Furthermore, silicon minimum yield was

shown to increase appreciably in the long-time sample, and both arsenic and silicon angular-scan spectra were characteristic of a large degree of dechanneling.

Figure 2.7 to Figure 2.10 show the cross-section views of the samples implanted with doses of 8×10^{15} and $1.6 \times 10^{16} \text{ cm}^{-2}$. For the higher dose, the defects lie uniformly in a region from the surface down to a depth of about 180 nm, which coincides well with the junction depth. The uniformity of the defects in the arsenic layer is in contradiction with an earlier TEM work where dislocation loops were observed to lie at the amorphous-crystalline interface for a similar surface concentration [41,42]. Except for the intrusion of rod-like defects to a depth of 230-250 nm in the $8 \times 10^{15} \text{ cm}^{-2}$ sample, the confinement of the defects to the arsenic layer suggests that inactive arsenic complexes reduce the formation energy of the loops.

In a similar study [42], it has been found that the loops are composed of silicon atoms. It has been suggested in the same work that arsenic clustering injects the excess silicon interstitials needed to form the loops. As mentioned before, buried boron layers show enhanced diffusion as a result of arsenic deactivation, suggesting that arsenic deactivation is accompanied by interstitial injection [32]. TEM observations in this study involve exactly the same samples for the 750°C, 2h anneal. The enhancements for these samples are shown in Table 2.2. There is a large increase in boron diffusivity at an arsenic concentration of $4.5 \times 10^{20} \text{ cm}^{-3}$ and the enhancement keeps decreasing as the dose is increased. The TEM results show that the number of atoms bound by the loops increases with arsenic concentration. Therefore, the loops seem to be responsible for the reduction in boron diffusivity.

Figure 2.7 Cross-section TEM micrograph of the sample implanted with $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 700°C for 15 s (weak beam dark field).

Figure 2.8 Cross-section TEM micrograph of the sample implanted with $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 700°C for 100 min (weak beam dark field).

Figure 2.9 Cross-section TEM micrograph of the sample implanted with $8 \times 10^{15} \text{ cm}^{-2}$ and annealed at 750°C for 2h (weak beam dark field).

Figure 2.10 Cross-section TEM micrograph of the sample implanted with $1.6 \times 10^{16} \text{ cm}^{-2}$ and annealed at 750°C for 2h (weak beam dark field).

Table 2.2: Enhancement of buried boron layer diffusivity for various arsenic doses [32].

Dose (cm^{-2})	Surface Concentration (cm^{-3})	Enhancement	Inactive As dose (cm^{-2})
4×10^{15}	2.3×10^{20}	30	2.2×10^{15}
8×10^{15}	4.5×10^{20}	460	4.9×10^{15}
1.6×10^{16}	9.1×10^{20}	230	1.3×10^{16}
3.2×10^{16}	1.9×10^{21}	110	2.9×10^{16}

The dislocation loop density gets higher as the arsenic dose is increased, although the interstitial supersaturation decreases. From nucleation theory, the loop density is expected to decrease as the interstitial supersaturation gets smaller, which seems to contradict these experimental observations. But, since loop nucleation occurs at the very early stages of the deactivation anneal, the density of the loops is determined by the interstitial supersaturation at the beginning of the anneal. Instead of the time averaged interstitial supersaturation, it is enough that the initial interstitial supersaturation be higher at higher arsenic concentrations for the loops to be denser.

At the lowest arsenic concentration ($2.3 \times 10^{20} \text{ cm}^{-3}$), the enhancement is 15 times smaller than the one at the next higher concentration ($4.5 \times 10^{20} \text{ cm}^{-3}$), although the inactive arsenic doses are comparable. Also, no dislocation loops are observed at the lowest concentration. This suggests that another deactivation mechanism may be dominant in this sample, such as the simultaneous formation of arsenic-interstitial pairs.

2.4 Conclusions

The properties of the extended defects that are formed during arsenic deactivation were investigated. The density of the dislocation loops depends on the chemical arsenic concentration. As the arsenic concentration increases, more interstitials are injected during deactivation, and, therefore, a higher density of loops form. The number of atoms bound by the loops is much smaller than the inactive arsenic dose. The loops are confined in the arsenic layer, indicating that the inactive arsenic reduces the formation energy of the loops. Finally, the increase in the number of the atoms bound by the loops explains the reduction in the buried boron layer diffusivity at higher arsenic concentrations.

CHAPTER III

HIGH DOSE ARSENIC IMPLANTATION INDUCED TRANSIENT ENHANCED DIFFUSION

3.1 Introduction

Ion implantation of dopants into silicon introduces damage in the form of interstitials and vacancies. If the damage is above a certain level, an amorphous layer forms. Upon thermal annealing, the amorphous layer grows back into crystalline silicon. If arsenic has been implanted at high doses, end-of-range loops appear below the original amorphous/crystalline (a/c) interface, whereas type-V loops form at the projected range (Figure 3.1). When a dopant layer is present beyond the a/c interface, its diffusion is enhanced because of the ion-implant damage. It has been previously suggested that the damage beyond the a/c interface is the main cause of the enhanced diffusion of dopants after amorphizing implants [48,49].

As mentioned in Chapter II, arsenic deactivation is accompanied by interstitial injection. Buried boron layers have been observed to exhibit enhanced diffusion when arsenic is deactivated at the surface [32]. In Chapter II, the high level of interstitial injection is also confirmed by TEM studies of type-V dislocation loops formed during arsenic deactivation in initially defect-free laser annealed samples [39].

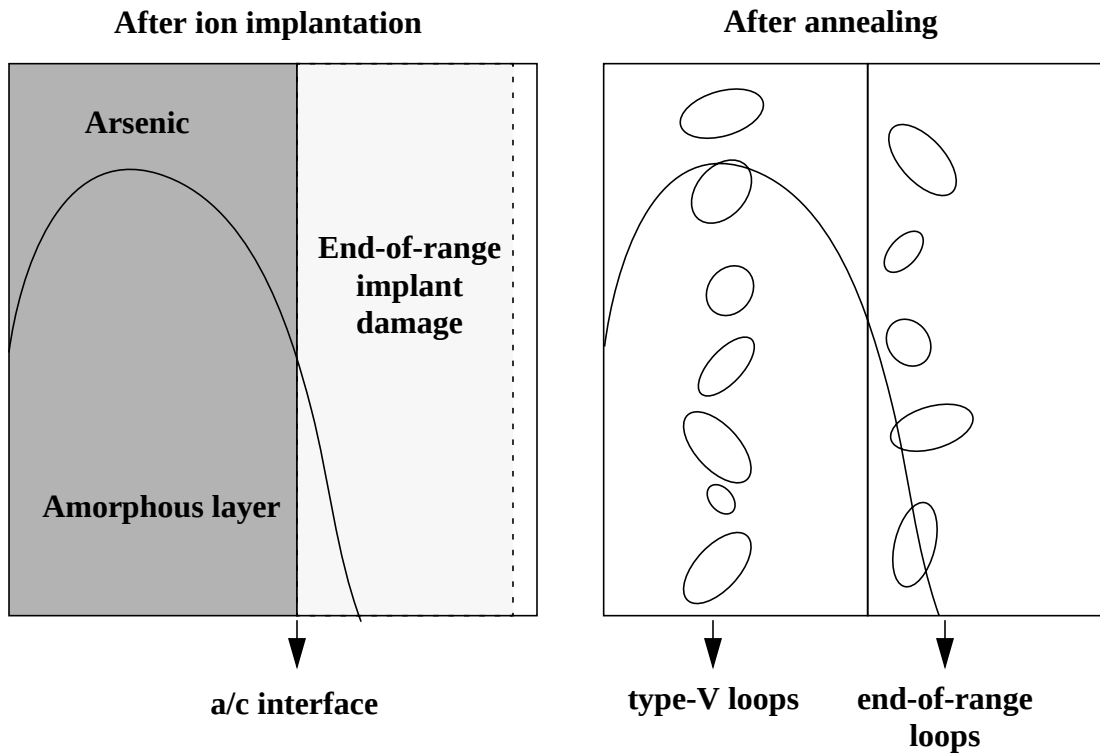


Figure 3.1 Schematic representation of damage and loop formation in high dose arsenic implanted silicon.

Although arsenic deactivation creates excess interstitials and causes dislocation loop formation, it is not yet clear how much effect it has on the enhanced diffusion caused by high dose arsenic implantation. While excess interstitials should contribute to the implant damage enhanced diffusion, type-V loops may decrease the amount of enhanced diffusion by absorbing the interstitials. In this work [50], arsenic was implanted into silicon at various doses with the same energy. Buried boron layers were used as markers of interstitial supersaturation. Most of the chosen doses give rise to peak arsenic concentrations above the equilibrium active concentration. The density of type-V loops is a very strong function of the arsenic concentration, and the interstitial supersaturation during arsenic deactivation

increases abruptly above a certain arsenic concentration. Hence, an abrupt change in the diffusivity of the buried boron layer can be expected if arsenic deactivation has an appreciable effect on damage enhanced diffusion.

3.2 Experiment

The boron buried layers were prepared in Texas Instruments. After depositing 200 Å of oxide on <100> silicon to reduce ion channeling, boron was implanted at 10 keV with a dose of $3 \times 10^{12} \text{ cm}^{-2}$. The oxide was then etched with an HF solution and an approximately 0.6 µm thick epi layer was grown. Arsenic was implanted at 50 keV at 7° tilt with doses ranging from 4×10^{14} to $4 \times 10^{15} \text{ cm}^{-2}$. The peak arsenic concentrations determined from SIMS are shown in Table 3.1 along with the implanted doses. The arsenic concentrations were normalized to the implanted dose. The samples were annealed at three different times temperatures: 750°C 2h, 900°C 1min, and 1050°C 15s. It has been previously reported that the damage enhanced diffusion due to interstitial cluster dissolution is complete for boron implants within the anneal times selected for each temperature [7,51].

Arsenic and boron profiles were obtained by secondary ion mass spectrometry (SIMS) using an oxygen beam. Since the boron dose was low, the sample was tilted at an angle so that the boron yield was higher during sputtering. The defects were studied by transmission electron microscopy with a JEOL 200 CX electron microscope operating at 200 keV. Plan-view and cross-section samples were analyzed in g_{220} and g_{111} conditions.

Table 3.1: Peak arsenic concentration vs. arsenic implant dose

Dose (cm ⁻²)	4x10 ¹⁴	8x10 ¹⁴	1.6x10 ¹⁵	2.4x10 ¹⁵	4x10 ¹⁵
Peak Concentration (cm ⁻³)	1.1x10 ²⁰	2x10 ²⁰	4x10 ²⁰	6.4x10 ²⁰	1x10 ²¹

3.3 Results and Discussion

The annealed profiles of the boron buried layer are shown in Figure 3.2 for different arsenic doses at 750°C. The doses of the original boron SIMS profiles were normalized to that of the unannealed sample. The damage enhanced diffusion of the boron buried layer is reduced as the arsenic dose is increased. This trend is also observed after the 900°C and 1050°C anneals. The reduction in the diffusivity is also supported by the arsenic SIMS profiles. After the 750°C anneal, the highest dose arsenic profile moves 200 Å less than the 8x10¹⁴ cm⁻² profile. The enhancements in the boron diffusivity can be seen in Figure 3.3 to Figure 3.5. The enhancement was found by finding the diffusivity that best matches the experimental profile and dividing it by the reference inert diffusivity which is given by:

$$D = 0.757 \exp\left(-\frac{3.46}{kT}\right) \quad 3-1$$

At both 750°C and 900°C, the boron diffusivity drops nearly by a factor of 2 from the lowest to the highest arsenic dose. The cross-sectional TEM (XTEM)

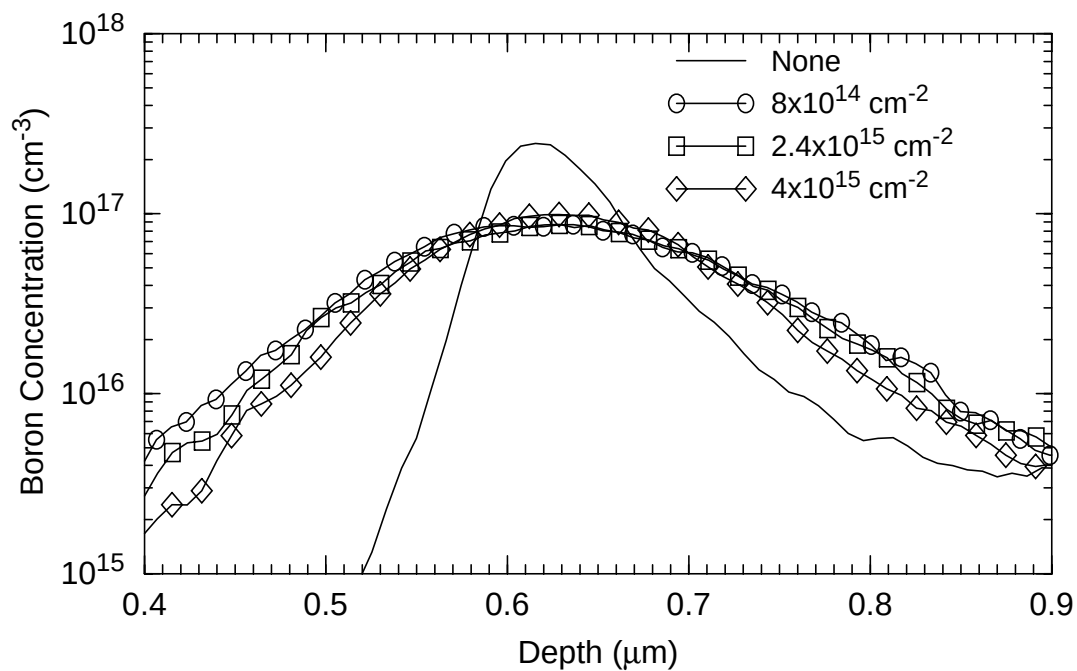


Figure 3.2 Buried boron profiles for different arsenic doses after the 750°C, 2hr. anneal.

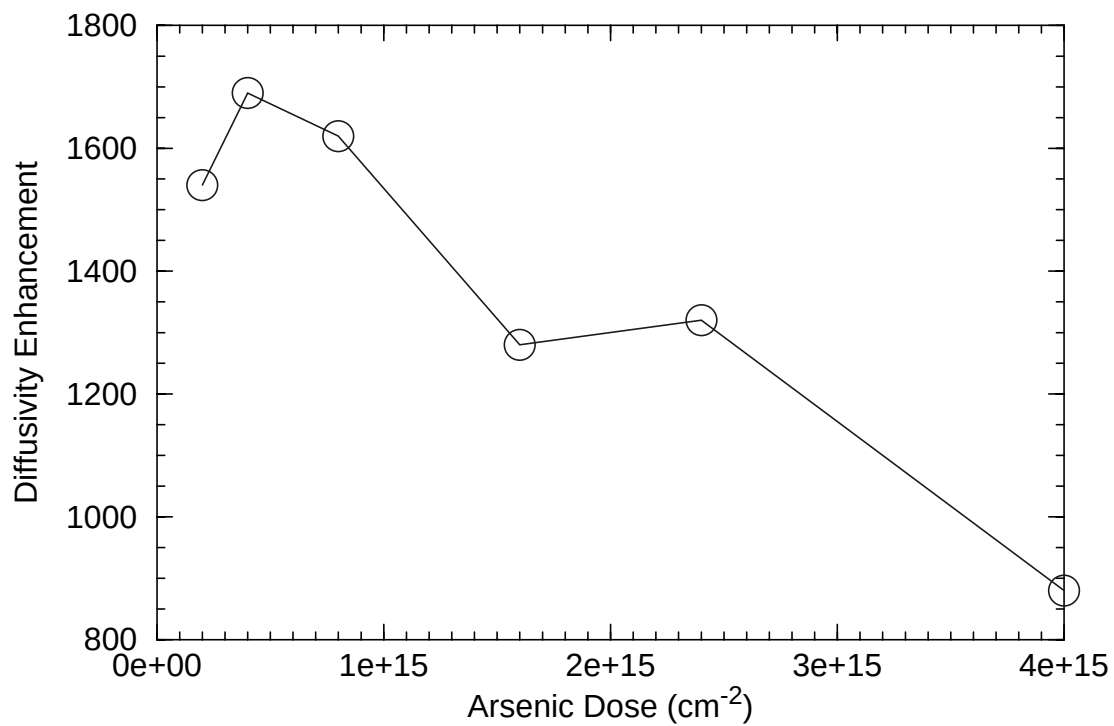


Figure 3.3 The enhancement of boron diffusivity as a function of arsenic dose at 750°C.

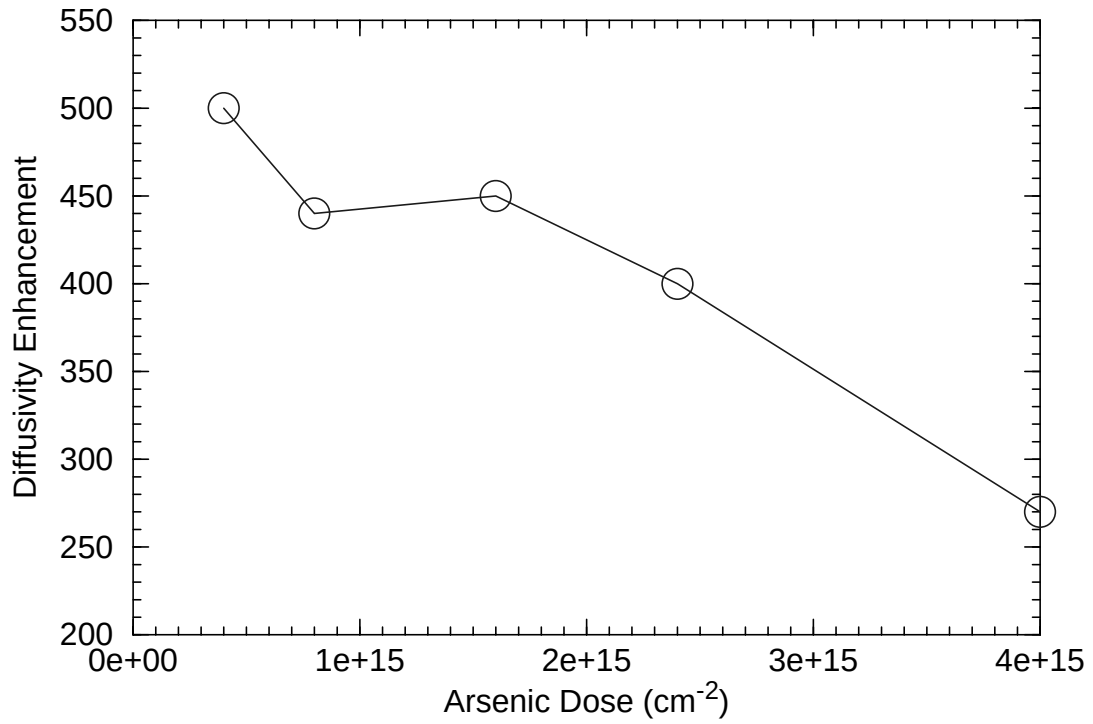


Figure 3.4 The enhancement of boron diffusivity as a function of arsenic dose at 900°C.

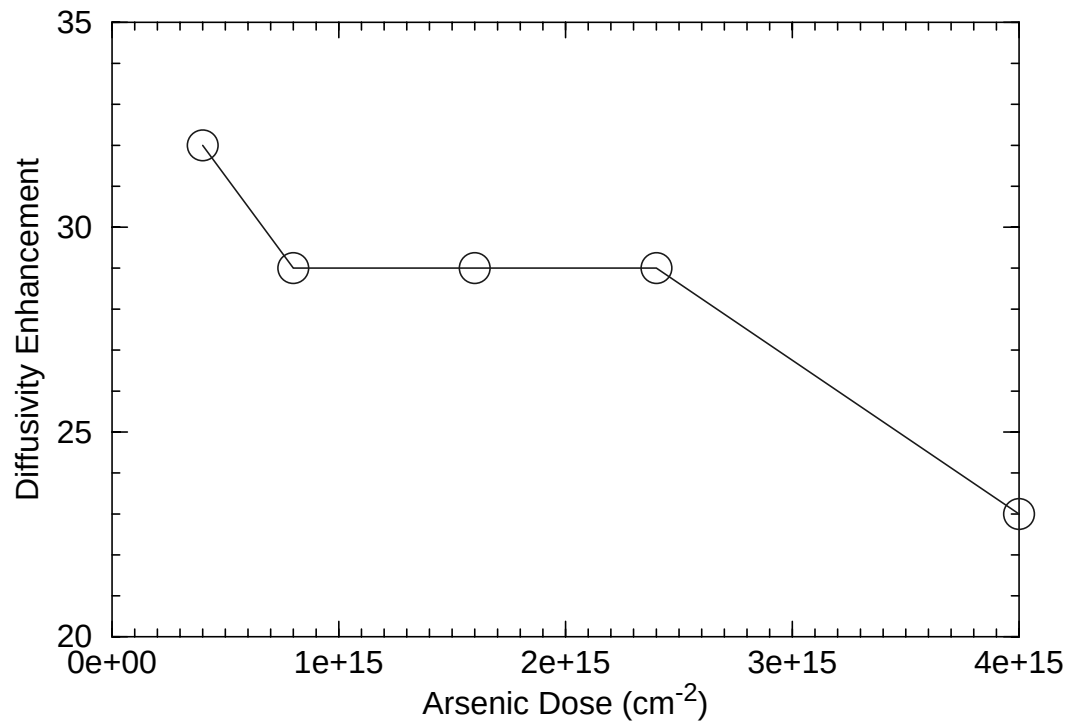
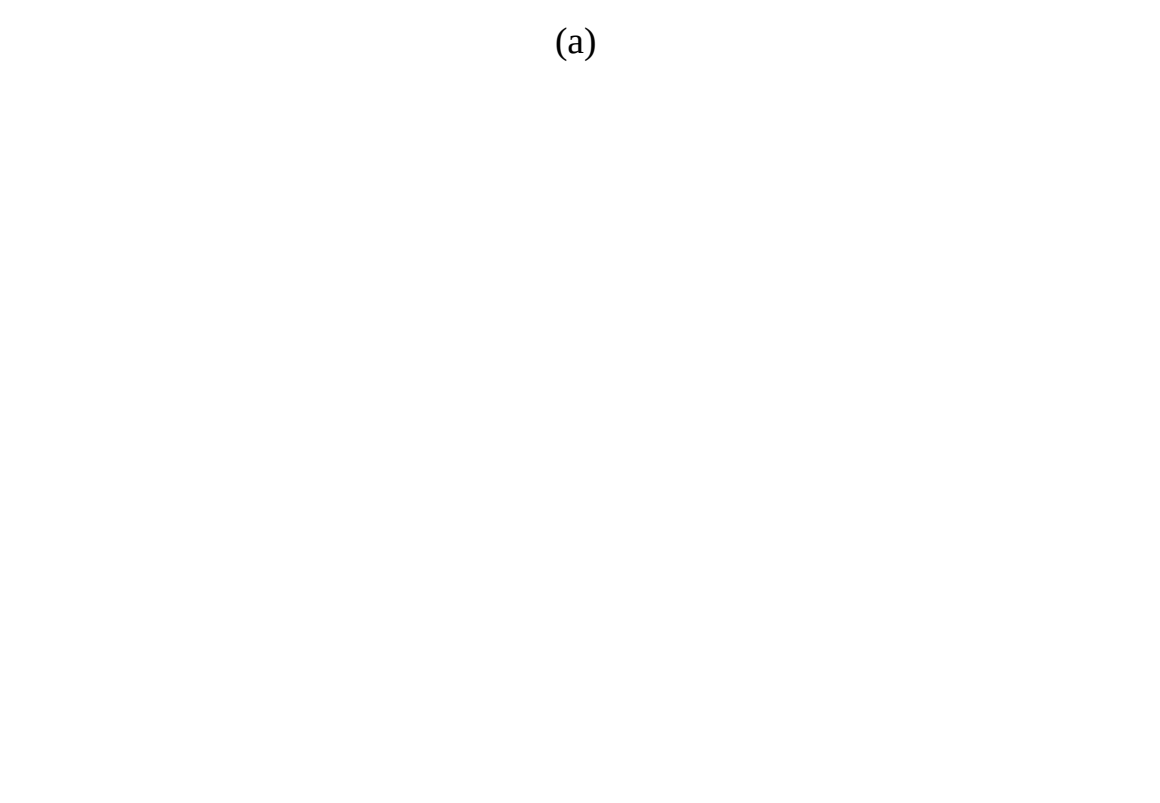


Figure 3.5 The enhancement of boron diffusivity as a function of arsenic dose at 1050°C.



(a)



(b)

Figure 3.6 Weak beam-dark field cross-section TEM micrographs of the sample implanted with an arsenic dose of (a) $1.6 \times 10^{15} \text{ cm}^{-2}$, (b) $2.4 \times 10^{15} \text{ cm}^{-2}$ and annealed at 750°C .

analysis of the samples reveals that a high density of type-V loops forms when the peak arsenic concentration is $6.4 \times 10^{20} \text{ cm}^{-3}$ at both 750°C and 900°C. On the other hand, only a very low density of type-V loops form at a peak concentration of $4 \times 10^{20} \text{ cm}^{-3}$ (Figure 3.6). These results are consistent with the dislocation loop results in Chapter II. The diffusivity data shows that the abrupt appearance of a high density of type-V loops does not have a drastic effect on damage enhanced diffusion. It has been previously suggested that the enhanced diffusion after amorphizing implants is mainly caused by the damage beyond the a/c interface [48,49]. Since type-V loops form at the projected range, they may not absorb an appreciable amount of the interstitials that are beyond the a/c interface and blocked by the end-of-range loops (Figure 3.1). Moreover, XTEM micrographs show that there is not any intrusion of the type-V loops into the end-of-range loop layer even at the highest dose, suggesting a lack of strong interaction between type-V loops and end-of-range damage. Still, type-V loops may be contributing to the decrease in the enhanced diffusivity, although the decrease in the enhanced diffusivity starts before their formation. It is interesting that the buried layer diffusivity does not increase at the arsenic peak concentration of $4 \times 10^{20} \text{ cm}^{-3}$ although a great amount of interstitial supersaturation is expected [52] and nearly no type-V loops form at this concentration. The end-of-range loops should be acting as very efficient sinks for these excess interstitials and preventing them to contribute to the enhanced diffusion.

The density and the number of atoms bound by both the type-V and the end-of-range loops are plotted in Figure 3.7 for 750°C and 1050°C. Both the density and

the number of bound atoms show an increase as the arsenic dose is increased, suggesting that the loops are responsible for the reduction in boron diffusivity. A low density of rod-like defects ($6 \times 10^8 \text{ cm}^{-2}$) was observed at the dose of $8 \times 10^{14} \text{ cm}^{-2}$ along with the loops. For the 1050°C anneal, no type-V loops were observed in the XTEM micrographs for all the doses. So, the abrupt increase in the loop density at this temperature is only due to end-of-range loops.

Two mechanisms may exist if the reduction in the enhanced diffusivity is caused only by the dose dependence of the implant damage below the a/c interface. The depth of the amorphous layer has been observed to increase with dose [53]. More of the implant damage beyond the a/c interface may be incorporated into the amorphous layer at higher doses. This mechanism may reduce the enhanced diffusion. However, a possible decrease in the implant damage below the a/c interface is inconsistent with our experimental loop data where both the loop density and the number of bound atoms increase even when only end-of-range loops exist. So, the damage and therefore the excess interstitials beyond the a/c interface are actually increasing with higher arsenic doses. This may not necessarily mean a larger interstitial supersaturation during the whole enhanced diffusion. A higher interstitial supersaturation at the beginning of the anneal can cause a higher density of end-of-range dislocation loops, which in turn can capture more interstitials during the anneal, decreasing the enhanced diffusion. This statement is supported by the results of other experiments, such as the decrease in enhanced diffusion at higher arsenic concentrations during arsenic deactivation in laser annealed samples [52] and the reduction in boron diffusion with increasing boron dose [8]. Arsenic

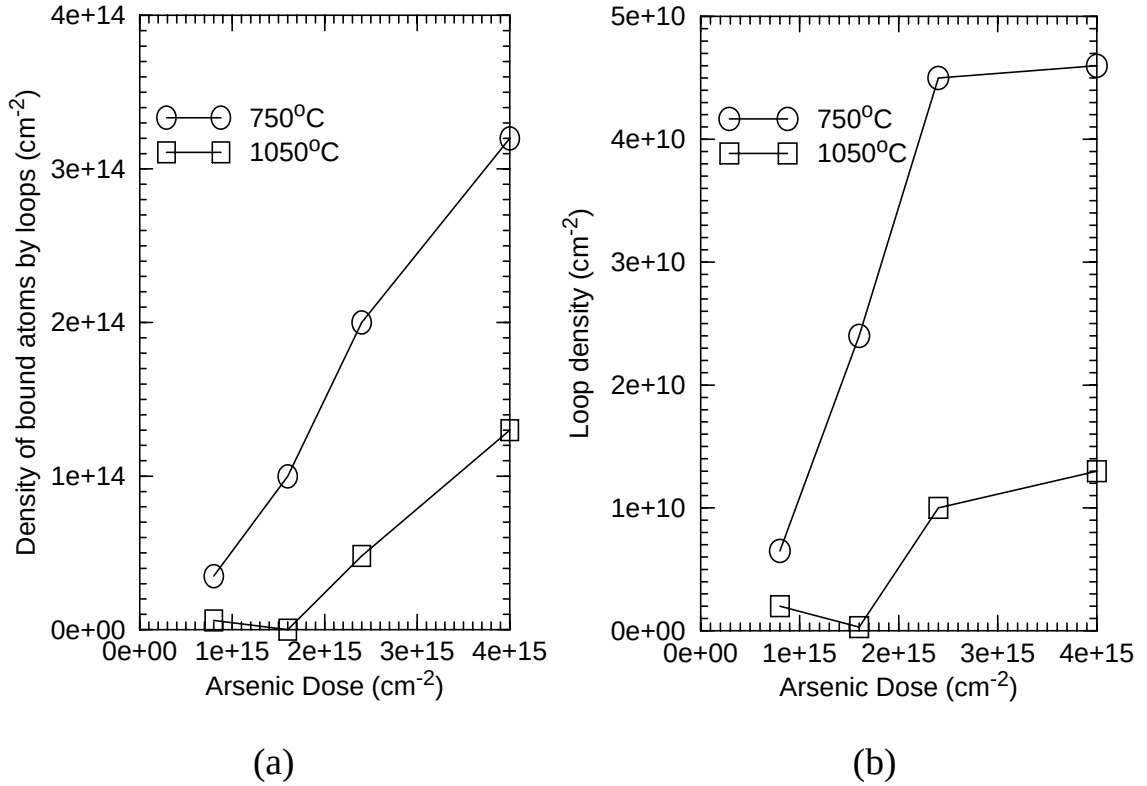


Figure 3.7 Arsenic dose dependence of (a) the density of the bound atoms by loops, and (b) the density of the loops.

deactivation induced interstitials may also contribute to the supersaturation and increase the density of end-of-range loops, besides nucleating the type-V loops.

3.4 Conclusions

Buried boron layers were used to quantify the transient enhanced diffusion after high-dose arsenic implantation. The enhancement in boron diffusivity decreases with increasing arsenic dose at 750, 900 and 1050°C. At the same time, the number of atoms bound by the loops increase, suggesting that the dislocation

loops are responsible for the reduction in boron diffusivity. Finally, arsenic deactivation induced interstitials do not increase the enhanced diffusion.

CHAPTER IV

INVESTIGATION OF VACANCY POPULATION DURING ARSENIC ACTIVATION IN SILICON

Recent experimental investigations have shown that electrical deactivation of arsenic in silicon creates excess silicon interstitials [52]. This has been attributed to the formation of arsenic-vacancy clusters and generation of silicon interstitials during this process. As pointed out in Chapter II, this high level of interstitial injection is also confirmed by TEM studies of type-V dislocation loops formed during arsenic deactivation in the same initially defect-free laser annealed samples [39].

The formation of a large number of arsenic-vacancy clusters has been confirmed with positron annihilation measurements [54]. Furthermore, extended x-ray absorption fine-structure (EXAFS) results combined with Rutherford BackScattering (RBS) measurements also indicate that the deactivation of arsenic proceeds through the formation of arsenic vacancy complexes below 750°C [55]. Upon electrical activation of arsenic, these complexes are expected to dissolve and generate free vacancies. In this work [56], antimony doping superlattice (DSL) structures were used to detect any possible vacancy injection into the bulk during the activation of arsenic. Since antimony diffuses predominantly through a vacancy mechanism, its diffusion is enhanced when there is a supersaturation of vacancies [24].

4.1 Experimental Details

The DSL structures used in the experiment contained six narrow antimony buried marker layers with 10 nm widths, peaks spaced 100 nm apart and doped to a concentration of $1.5 \times 10^{19} \text{ cm}^{-3}$. They were grown by low temperature molecular beam epitaxy on Si(100) floatzone substrates [57]. The samples were split into three during ion-implantation: no implant, arsenic implant, and germanium implant. Since germanium is similar to arsenic in mass and size, it allows us to monitor any possible effects of similar ion-implantation damage on antimony diffusion if the damage is not completely wiped out during the damage anneal. Arsenic was implanted at 50 keV at 7° tilt with doses of $3 \times 10^{15} \text{ cm}^{-2}$ and $8 \times 10^{15} \text{ cm}^{-2}$, while germanium was implanted at only $8 \times 10^{15} \text{ cm}^{-2}$. All the samples were capped with an approximately 2000 Å layer of oxide and then a nitride layer to prevent the evaporation of arsenic. They were annealed at 1150°C for 5s in order to eliminate the implantation damage. After the samples were subjected to a deactivation anneal at 750°C for 2h, some of them were further annealed either at 850°C for 4 h or 950°C for 30 min to electrically activate some of arsenic. The unimplanted, arsenic and germanium doped samples were annealed very close to each other during each thermal cycle so that there would not be any thermal variations between these splits. Figure 4.1 shows a flowchart of the experimental steps.

Chemical arsenic and antimony concentrations were measured by SIMS. Plan-view samples were studied by TEM with a JEOL electron microscope

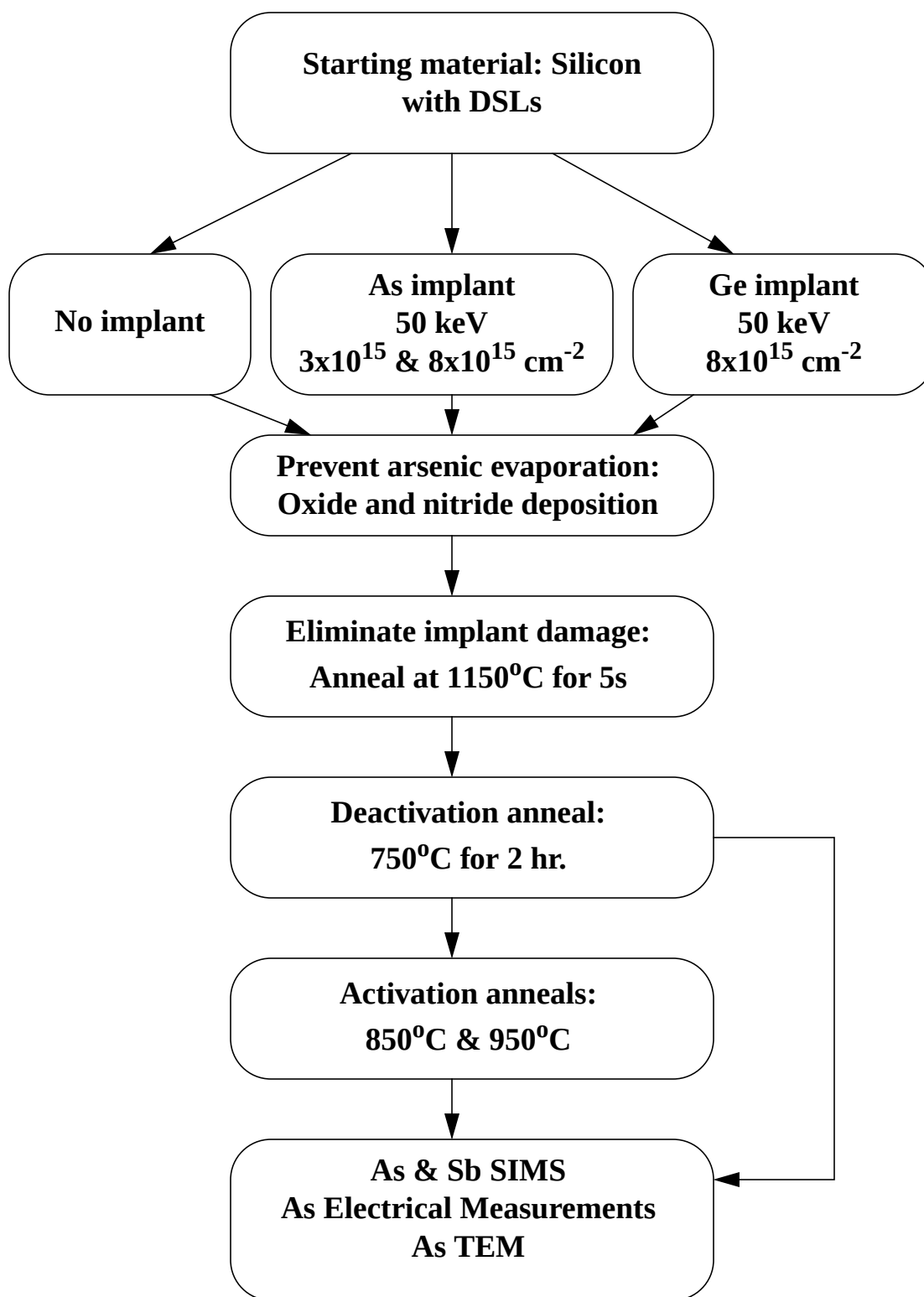


Figure 4.1 A flowchart of the experiment.

operating at 200 keV. Spreading and sheet resistance measurements were made on arsenic doped samples.

In order to find the antimony diffusivity during the activation anneals, the following procedure was employed: For each spike, the SIMS profile after the deactivation anneal was supplied as an initial profile to the process simulation program FLOOPS. The antimony diffusivity was assumed to have the form $D_{Sb} = \alpha D_{Sb}^{ref}$, where α is an enhancement factor and the reference diffusivity D_{Sb}^{ref} is the default inert antimony diffusivity in FLOOPS, and is given by:

$$D_{Sb}^{ref} = 0.21 \exp\left(-\frac{3.65}{kT}\right) + (n/n_i) 15 \exp\left(-\frac{4.08}{kT}\right) \quad 4-1$$

The diffusion of the initial profile was simulated with FLOOPS for different values of α until the error between the simulated and the experimental profiles was minimized. The enhancement or the retardation in antimony diffusivity in the arsenic or germanium doped samples was found by dividing the diffusivity in these samples to the diffusivity extracted from the unimplanted samples which were annealed under the same conditions.

4.2 Results and Discussion

Figure 4.2 shows the antimony SIMS profiles in the as-deposited DSL sample, and in the high dose ($8 \times 10^{15} \text{ cm}^{-2}$) arsenic sample which has been subjected to the 950°C,

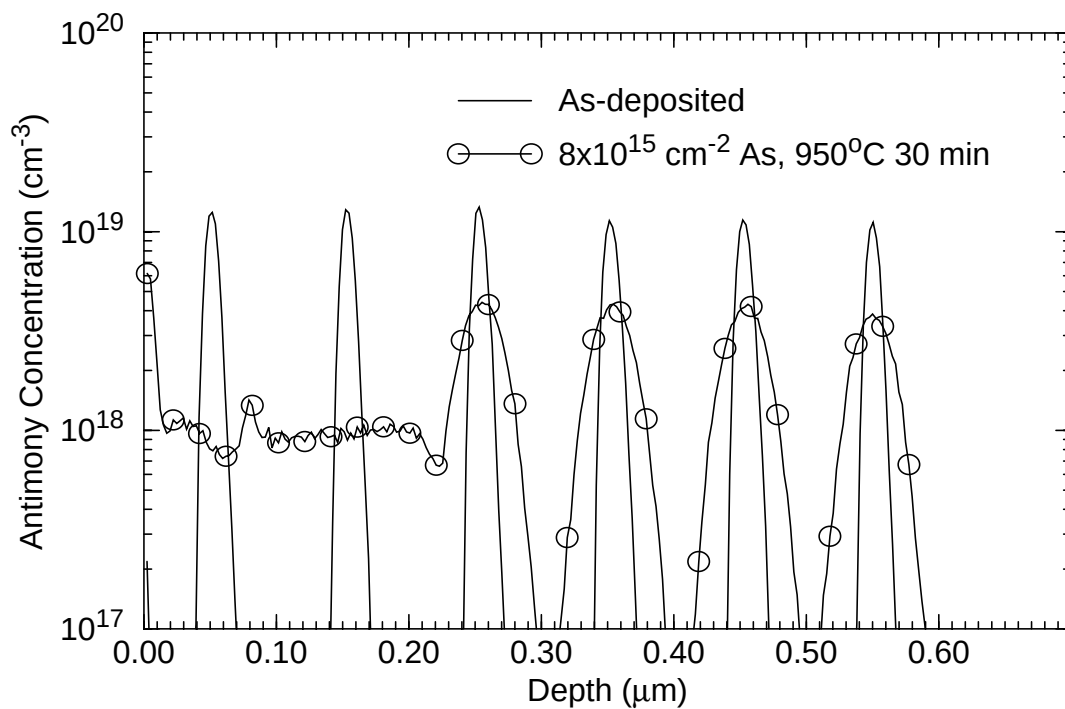


Figure 4.2 Antimony SIMS profiles in the as-deposited DSL sample and the sample implanted with $8 \times 10^{15} \text{ cm}^{-2}$ arsenic and annealed at 950°C for 30 min after the damage and deactivation anneals.

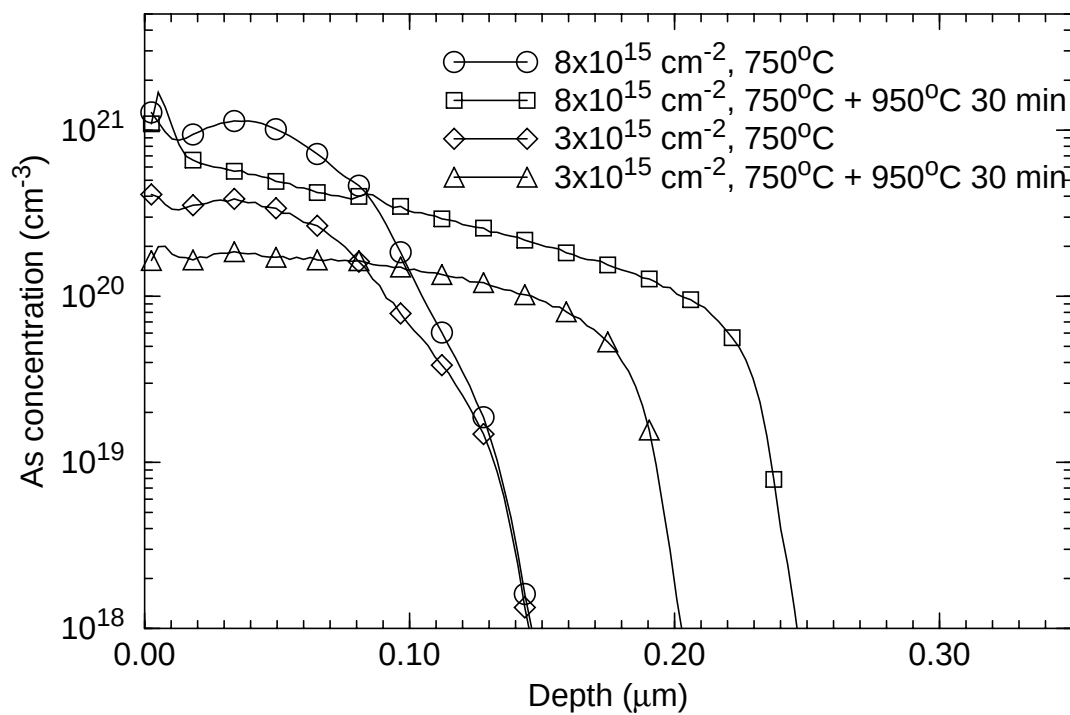


Figure 4.3 Arsenic SIMS profiles. The temperatures in the legends represent the anneals after the damage anneal at 1150°C .

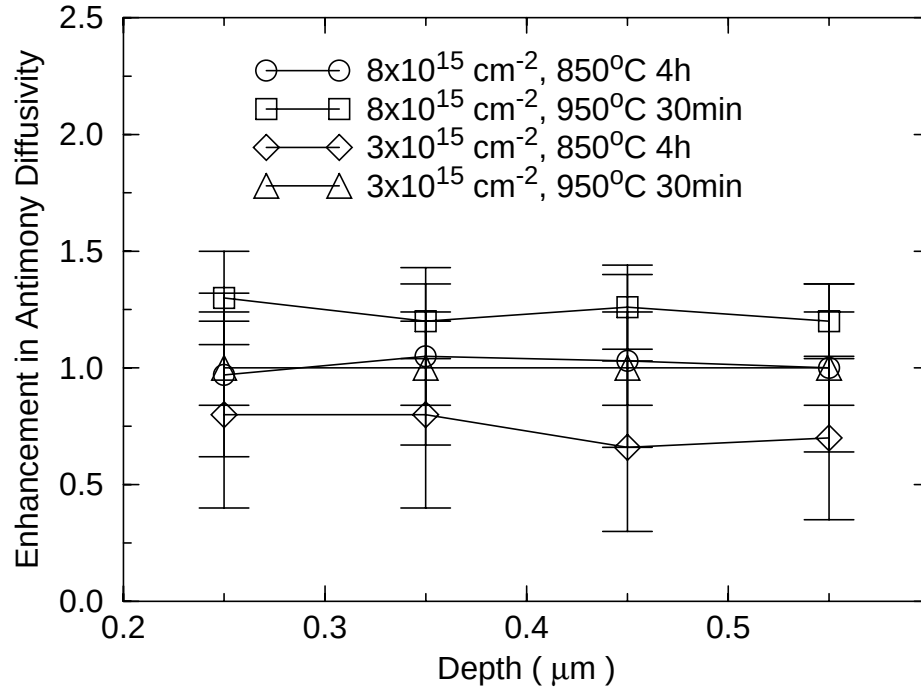


Figure 4.4 Enhancement in the antimony diffusivity as a function of depth in the arsenic doped samples. The thermal cycles shown in the legends represent only the activation anneals.

30 min activation anneal. Antimony inside the arsenic layer exhibits considerable amount of more diffusion than antimony outside the arsenic layer. This can be attributed to an increase in the equilibrium concentration of free vacancies inside the arsenic layer. Figure 4.3 presents the arsenic profiles in the both the high ($8 \times 10^{15} \text{ cm}^{-2}$) and low ($3 \times 10^{15} \text{ cm}^{-2}$) dose samples after the deactivation and the 950°C , 30 min activation anneal. A significant amount of arsenic diffusion takes place during the activation anneal.

Figure 4.4 shows the enhancement in the antimony diffusivity during the activation anneals in the arsenic doped samples. This enhancement was calculated by dividing the antimony diffusivity in the arsenic doped samples to the inert antimony diffusivity extracted from the unimplanted samples. The inert antimony diffusivity was found to be around 40% less than the default diffusivity in FLOOPS

(Equation 4-1) at 850°C and 5% less at 950°C. The enhancements in antimony diffusivity are very close to unity, indicating that there is no observable vacancy supersaturation during arsenic activation in these samples. The activation of arsenic was confirmed by both sheet resistance (Table 4.1) and spreading resistance measurements (Figure 4.5). The spreading resistance data shows that diffusion of arsenic into the bulk as well as the higher activation level of arsenic at 950°C contribute to the amount of more electrically active arsenic.

The positron annihilation experiments show that the average number of vacancies per inactive arsenic atom is between 1/2 and 1/4 in an arsenic doped silicon sample which has been laser annealed and then thermally annealed at 750°C (concentration of arsenic = $8 \times 10^{20} \text{ cm}^{-3}$) [54]. RBS and EXAFS measurements have led Brizard *et al.* to propose the existence of arsenic-vacancy clusters which have a vacancy/arsenic ratio of around 1/3 [55]. Thus, it is unexpected that there is not any significant enhancement in the arsenic doped samples since a very large amount of free vacancies is expected to be released upon the dissolution of these clusters during the activation anneals.

To investigate the possibility that the generated vacancies may be absorbed by the extrinsic extended defects either left over from the damage anneal or created by the subsequent deactivation anneal, a plan-view TEM study of the arsenic doped samples was undertaken (Table 4.1). Dislocation loops were observed in the samples after the deactivation anneal, and they completely dissolve during the activation anneals with the exception of the 850°C high dose sample where only a very small amount of loops has survived the activation anneal.

Table 4.1: Summary of the electrical and TEM measurements on the arsenic doped samples.

Arsenic dose (10^{15} cm^{-2})	Anneal sequence after the damage anneal ($^{\circ}\text{C}$)	Sheet Resistance (Ω/sq)	Density of atoms bound by dislocation loops (cm^{-2})	The total amount of electrically active arsenic (cm^{-2})
8	750	71.8	1.1×10^{14}	1.1×10^{15}
8	750 + 850 4h	48.7	Very few loops	-
8	750 + 950 30min	30.0	No loops	3×10^{15}
3	750	76.4	2.3×10^{13}	1.1×10^{15}
3	750 + 850 4h	63.4	No loops	1.5×10^{15}
3	750 + 950 30min	50	No loops	2×10^{15}

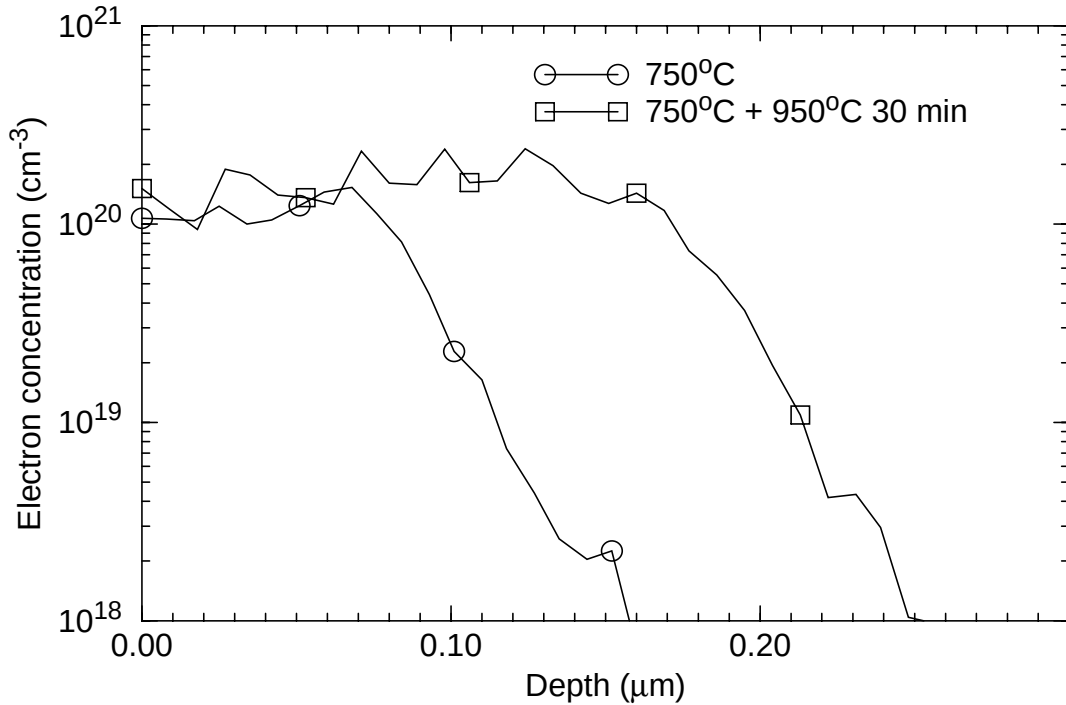


Figure 4.5 Spreading resistance measurements of the arsenic doped layer for the high ($8 \times 10^{15} \text{ cm}^{-2}$) arsenic dose. The temperatures in the legends represent the anneals after the damage anneal at 1150°C .

Table 4.1 also shows the total amount of electrically active arsenic obtained by integrating the electron concentration from the spreading resistance measurements with depth. In the high dose sample, the ratio of the density of atoms bound by the loops to the activated amount of arsenic during the 950°C activation anneal is roughly 1/17, whereas in the low dose sample this ratio is 1/40. These ratios are much smaller than the vacancy/arsenic ratio in the clusters calculated from either the positron annihilation or EXAFS measurements. Therefore, even if the loops are annihilated by only absorbing the vacancies generated by the activation process, this mechanism alone is not enough to explain the lack of vacancy injection into the bulk assuming that vacancies are generated with a ratio indicated by the positron annihilation and EXAFS measurements.

The unaccounted vacancies may be either recombining at the surface or with the interstitials created during the deactivation anneal and possibly trapped by an impurity such as arsenic or carbon. In fact, carbon has been observed to be an efficient sink for excess interstitials. At high enough doses, carbon can mostly eliminate the transient enhanced diffusion [58] which is believed to be caused by excess interstitials. The carbon profiles have also been measured along with arsenic and antimony. Figure 4.6 shows the carbon profiles after the deactivation anneal for the unimplanted and high dose arsenic samples. In the unimplanted sample, a rapidly decreasing carbon concentration can be observed at the surface. This is believed to be caused by carbon-related particles residing on top of the surface. On the other hand, in the high dose arsenic sample, carbon profile exhibits a peak around 80 nm and a deeper penetration at the surface, suggesting that the observed

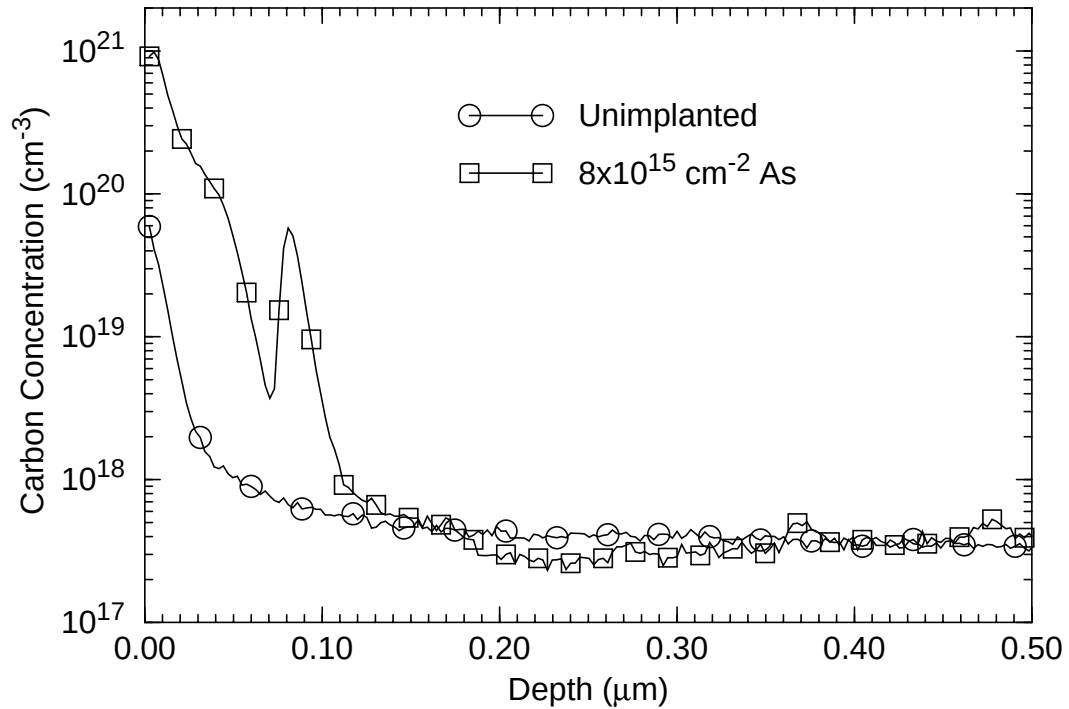


Figure 4.6 Carbon SIMS profiles in the unimplanted and high dose arsenic samples after the deactivation anneal.

carbon in this sample is actually inside silicon, rather than at the top of the surface. This high concentration of carbon may be capturing the excess interstitials injected during the deactivation cycle and creating a sink for excess vacancies.

Another explanation for the unaccounted vacancies is a possible increase in the ratio of the concentration of clusters that have a higher vacancy/arsenic ratio, such as As_2V , to the concentration of higher order clusters which have a smaller vacancy/arsenic ratio, such as As_4V . This can especially happen in the regions where chemical arsenic concentration is not very high (i.e. diffused regions) and the formation of arsenic rich clusters is kinetically limited. Therefore, instead of being injected into the bulk, the excess vacancies may be recaptured by the relatively more vacancy rich arsenic-vacancy complexes.

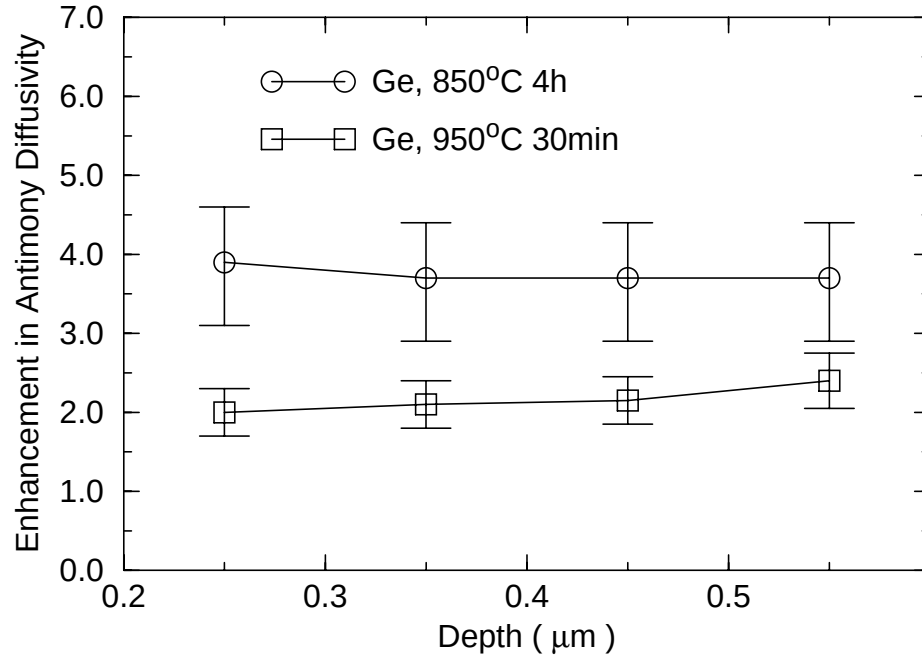


Figure 4.7 Enhancement in the antimony diffusivity as a function of depth in the germanium doped samples. The thermal cycles shown in the legends represent only the activation anneal.

Figure 4.7 shows the enhancement in the antimony diffusivity in germanium doped samples during the activation anneals. Unlike arsenic, antimony diffusion is enhanced by a factor of 2 to 4 in these samples.

4.3 Vacancy Population in the Partial Absence of Dislocation Loops

A second set of samples was prepared in order to find out whether the enhancement in antimony diffusivity increases after the dislocation loops dissolve completely. These samples were prepared like the previous ones (Figure 4.1) except that the activation anneals were done without any oxide or nitride on the surface. The activation anneal conditions were 16 hours at 850°C, and 1 and 2 hours at

950°C. These anneal times were longer than the time when all or most of the dislocation loops had completely dissolved (Table 4.1). Therefore, the vacancy population in the partial absence of the loops can be determined from these samples. The anneals involved either unimplanted or high dose ($8 \times 10^{15} \text{ cm}^{-2}$) arsenic samples.

Figure 4.8 and Figure 4.9 compare the antimony profiles of the unimplanted and high dose arsenic samples at the fourth peak after the deactivation anneal and the activation anneals of 850°C, 16h and 950°C, 1h. Although these profiles are quite similar after the deactivation anneal, the high dose arsenic sample exhibits more antimony diffusion than the unimplanted sample during the activation anneals. This indicates that antimony diffusion is enhanced in the high dose arsenic samples. Figure 4.10 shows the enhancements in the antimony diffusivity which are between 1.5 and 2 at both temperatures.

As discussed before, these enhancements may have been caused by the vacancies injected during the arsenic activation. Non-equilibrium diffusion of arsenic may also have created this enhancement. Since dopant atoms are believed to diffuse by pairing with point defects, rapid dopant diffusion can carry a large number of dopant-defect pairs to the bulk. These dopant-defect pairs can create excess point defects upon dissolution if the recombination of the vacancies and interstitials is not as fast as their generation through dopant diffusion. This effect becomes more significant as the dopant concentration and diffusivity increase. It has been proposed as the mechanism responsible for the enhanced diffusion observed in the tail of the high concentration phosphorus profiles [59-62]. Although the inert

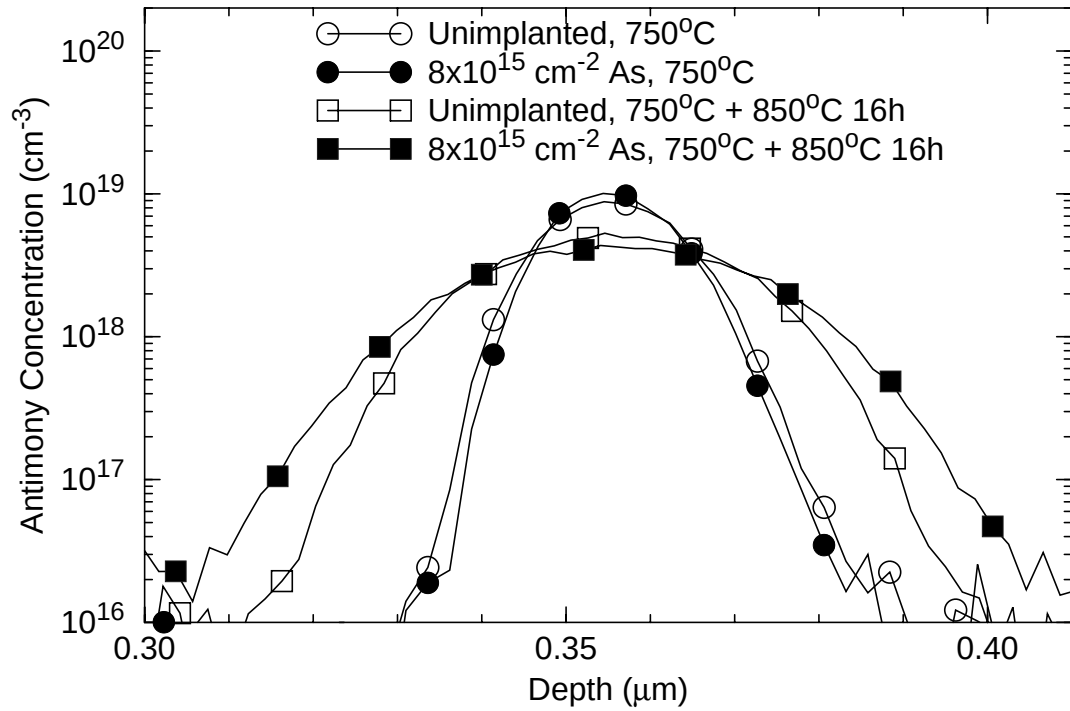


Figure 4.8 Comparison of the antimony profiles of the unimplanted and high dose arsenic samples after the deactivation and activation (850°C , 16h) anneals. During the activation anneal, antimony diffusion is enhanced in the arsenic sample.

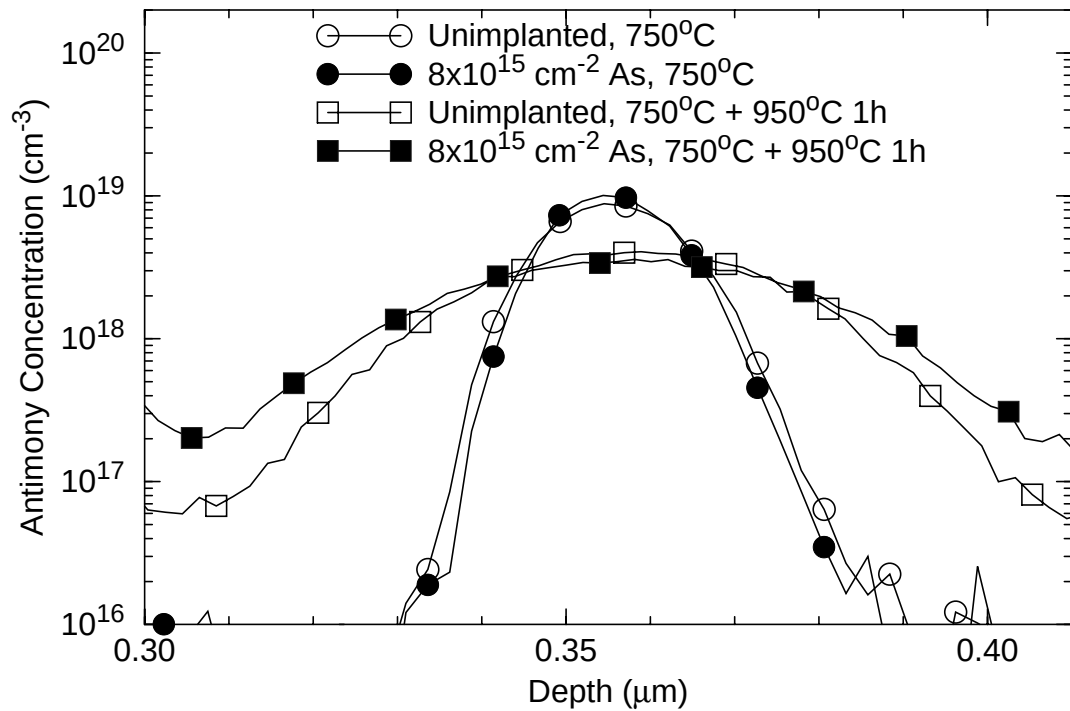


Figure 4.9 Comparison of the antimony profiles of the unimplanted and high dose arsenic samples after the deactivation and activation (950°C , 1h) anneals. During the activation anneal, antimony diffusion is enhanced in the arsenic sample.

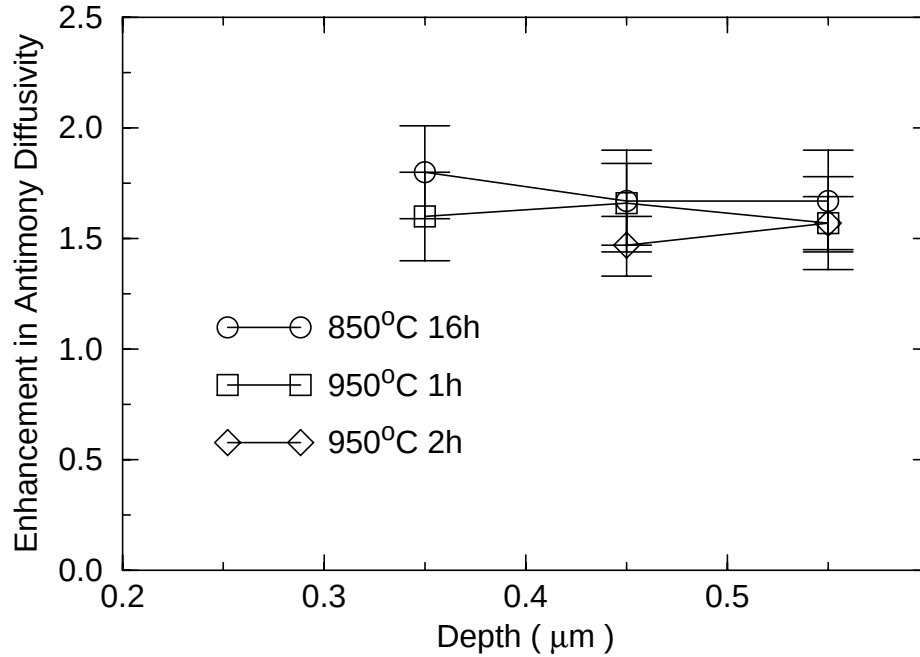


Figure 4.10 Enhancement in the antimony diffusivity as a function of depth in the high dose ($8 \times 10^{15} \text{ cm}^{-2}$) arsenic doped samples. The thermal cycles shown in the legends represent only the activation anneals.

arsenic diffusivity is smaller than that of phosphorus, non-equilibrium diffusion of arsenic may still be responsible for the small enhancements in these samples.

4.4 Conclusions

The effect of arsenic activation on vacancy population has been studied using antimony buried layers. The antimony diffusivity has been found to be very close to its inert diffusivity during arsenic activation in the presence of dislocation loops, indicating that there is no observable vacancy injection under these conditions. The density of the atoms bound by the loops are not sufficient to absorb all the vacancies which are expected to be generated in an amount indicated by the positron

annihilation and EXAFS measurements. Other possible mechanisms that can explain the lack of vacancy injection in the presence of the loops include surface recombination, recombination with trapped interstitials generated during the deactivation anneal and absorption of vacancies by relatively more vacancy rich arsenic defects, such as As_2V clusters. On the other hand, antimony diffusion is enhanced for the same anneals when germanium is present at the surface.

In the partial absence of the loops, antimony diffusion is enhanced by a factor of 1.5-2 during arsenic activation. Vacancy injection during arsenic activation as well as non-equilibrium diffusion may explain this enhancement.

CHAPTER V

A KINETIC MODEL FOR ARSENIC DEACTIVATION

5.1 The Physical Structure of Inactive Arsenic

In the arsenic-silicon phase diagram, monoclinic SiAs phase is the closest one to a dilute arsenic-silicon (solute-solvent) mixture [63]. In this phase, arsenic has three nearest neighbors, whereas silicon has four [64]. The monoclinic phase has also been observed in arsenic implanted silicon at very high arsenic concentrations ($\sim 1 \times 10^{22} \text{ cm}^{-3}$) [65,66]. Nobili *et al.* have determined the solid solubility of arsenic associated with the monoclinic phase [67]. The solid solubility is defined as the equilibrium concentration of the solute (arsenic) when the solid mixture is in contact with an infinitely large film of the second phase. Figure 5.1 shows the solid solubility value along with the equilibrium active concentration of arsenic. The solid solubility of arsenic is about an order of magnitude larger than its equilibrium active level.

At equilibrium, monoclinic SiAs precipitates start to form above solid solubility, whereas arsenic is substitutionally dissolved in silicon below the equilibrium active concentration. The inactive arsenic structure between these two limits has been the subject of much recent research. RBS [55] and X-ray standing wave measurements [68] show that this inactive arsenic structure is coherent with

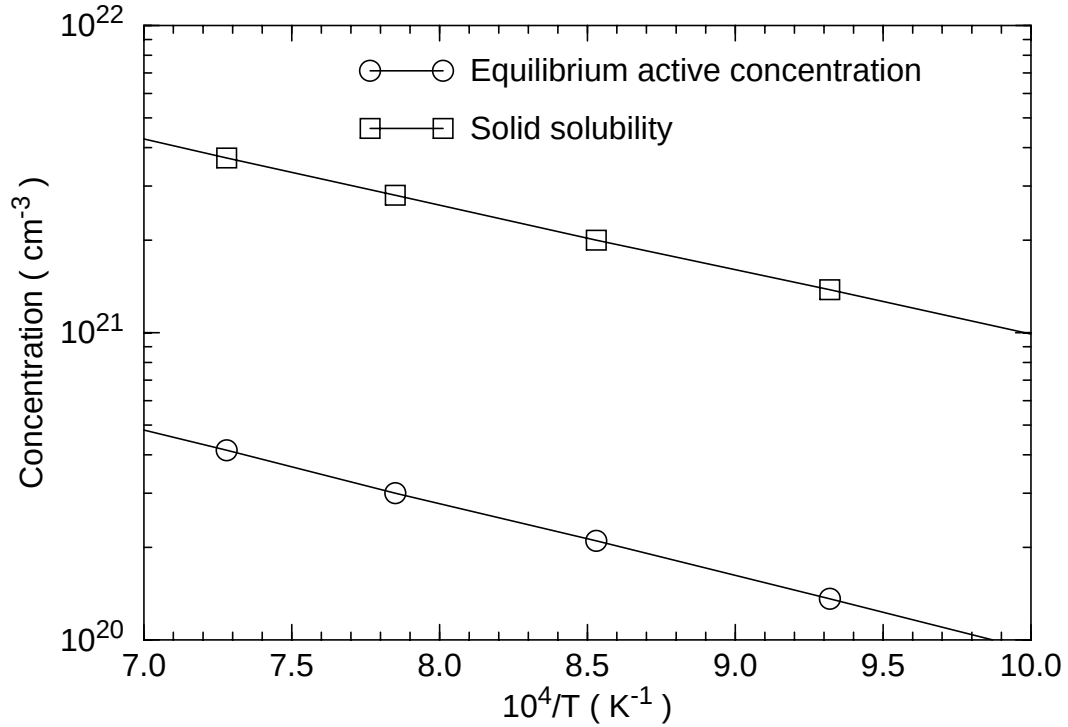


Figure 5.1 The temperature dependences of the solid solubility associated with the monoclinic SiAs phase and the equilibrium active concentration.

the silicon lattice. This result suggests that the inactive arsenic does not have the crystal structure of the monoclinic SiAs phase, since the monoclinic phase, having a crystal structure different from silicon, would create incoherence in silicon [40,52]. EXAFS measurements on high concentration arsenic samples demonstrate that the number of the nearest neighbors of an arsenic atom decreases from four silicon atoms in laser annealed samples to an average of 2.5 to 3.5 in deactivated samples. This result can be explained by the formation of arsenic-vacancy complexes (As_mV_n) in which arsenic has less than four neighbors. Recent positron annihilation experiments have also found evidence of a high density of vacancies related to inactive arsenic [54]. Moreover, theoretical calculations indicate that the formation of arsenic-vacancy complexes is an energetically favorable process [34,69]. The

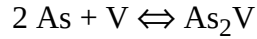
interstitial injection observed during arsenic deactivation also indirectly supports the existence of arsenic- vacancy complexes [32].

Very small ($\sim 15 \text{ \AA}$) precipitates have been identified by TEM in deactivated arsenic samples [40]. These precipitates have been proposed to have a zinc-blende structure. In this structure, every alternating silicon atom is replaced by an arsenic atom and both silicon and arsenic have four nearest neighbors of the other species. The aforementioned EXAFS measurements show that the number of silicon first neighbors of arsenic tends back to four atoms at high temperatures ($>750^\circ\text{C}$) [33]. This observation has been connected to the co-existence of arsenic-vacancy complexes and zinc-blende type AsSi precipitates.

In summary, the inactive arsenic structure that is formed between the limits of solid solubility and equilibrium active concentration is believed to be arsenic-vacancy complexes. At high temperatures, the vacancy content seems to be decreasing with vacancies being replaced by silicon atoms.

5.2 Previous Models for Inactive Arsenic

Clustering and precipitation have been proposed to explain the formation of electrically inactive arsenic in silicon. In clustering models, multiple arsenic atoms are assumed to come together and form a new defect which is electrically inactive at room temperature. These clusters may also contain point defects. For example, an As_2V cluster can be formed by the following reaction:



5-1

On the other hand, precipitation models consider the formation of much larger structures that may contain thousands of dopant atoms. The precipitates may form at any size whereas clusters are assumed to have on the order of a few atoms. The size distribution of precipitates depend on the initial supersaturation of dopant atoms, the time and the temperature of the anneal and other kinetic factors such as diffusivity and reaction rates.

Many TEM observations have concluded that extended defects in high concentration arsenic doped samples are not sufficient enough to account for most of the inactive arsenic [39-41]. This evidence favors the clustering explanation such that most of the inactive arsenic may be in the form of clusters which are too small to be observed by TEM. However, it is also possible that very small coherent silicon-arsenic precipitates can be responsible for the unobserved inactive arsenic.

As mentioned earlier, Armigliato *et al.* [40] have identified very small precipitates in heavily arsenic doped samples. It is well known that the electrically active arsenic concentration at equilibrium (i.e. for long anneal times) is very insensitive to the chemical arsenic concentration [12]. This has been put forward as suggestive evidence for precipitation [12] since cluster models predict that the active arsenic concentration depend on the chemical concentration at equilibrium. However, the equilibrium electron concentration can be made independent of the chemical concentration if one assumes that the clusters are charged at the annealing temperature [70]. As mentioned in Chapter I, reverse annealing [12,13] has been

shown to occur in arsenic implanted samples, suggesting the existence of precipitates having a distribution of sizes of different free energy. But, reverse annealing can also be explained by the existence of multiple clusters [13]. It certainly rules out the single cluster model. All of the experimental data suggests that the most reasonable assumption for inactive arsenic is the coexistence of clusters and precipitates [24,42,55]. The clusters can form at the beginning of the deactivation cycle and act as embryos for larger precipitates.

Most of the previous quantitative models for inactive arsenic has been single cluster models. Sheet resistances and electron concentrations in arsenic doped layers have been fit with various equilibrium cluster models [71-73]. Dynamic clustering models have been used to fit the initial stages of deactivation [42] and the effect of ramp-down on the sheet resistance [19]. Luning *et al.* [23] have pointed out that single clustering models can not at the same time account for the rapid arsenic deactivation at the beginning and the slow one at long times that they observe in their experiments.

Some of the quantitative precipitation models that have been proposed in the literature solve for the whole size distribution of precipitates. This kind of model has been demonstrated for antimony precipitation [74], arsenic and phosphorus precipitation [18], and oxygen precipitation [75]. The dopant precipitation model by S. Dunham [18] has been shown to exhibit reverse annealing. However, it has not been applied extensively to arsenic and does not account for interstitial injection and dislocation loop formation. The oxygen precipitation model includes the interstitial injection and bulk stacking fault growth observed during oxygen

precipitation. A recently proposed precipitation model solves for the first three moments of the precipitate size distribution, making it computationally less intensive [76].

The next section will present a general extended defect model which can be applied to arsenic deactivation as a precipitation model [77]. The model calculates the evolution of the precipitate size distribution and is able to account for various phenomena related to arsenic activation and deactivation. The interaction of arsenic-vacancy complexes with interstitials and dislocation loops will be included into the model in Chapter VII.

5.3 A Kinetic Model for Extended Defects

In the literature, the evolution of extended defects has usually been described by two phases: a nucleation and a growth phase. The nucleation theories study the formation of stable nuclei in a supersaturated solution while the growth theories try to determine the growth rate of these particles after they are formed. This is a somewhat artificial distinction since the nucleation and the growth of an extended defect is a continuous event. However, it makes the modeling problem more tractable and less computation intensive.

The classical nucleation theory was first formulated by Volmer and Weber 70 years ago [78]. It was later developed by several authors [79-82]. In this approach, the defects are assumed to grow or shrink by gaining or losing one atom at a time.

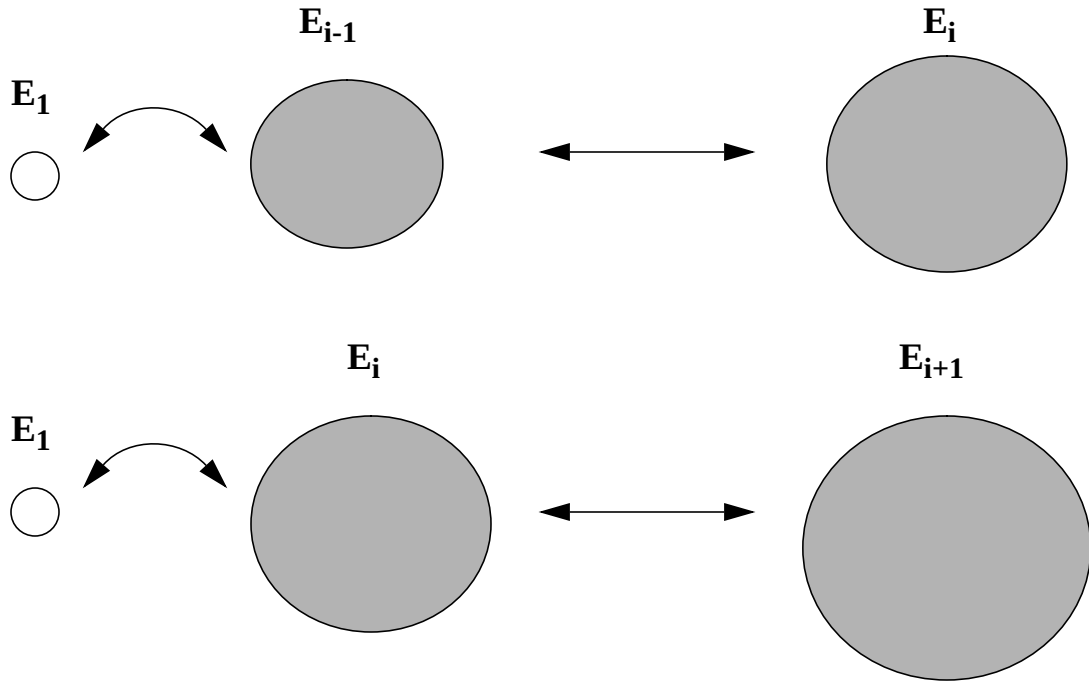
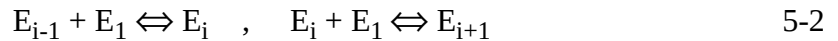


Figure 5.2 Schematic representation of the reactions taking place during extended defect formation. The defects are assumed to grow or shrink by gaining or losing one atom at a time.

This process, as shown in Figure 5.2, can be written as a set of reactions in the following form:



where E_i represents a defect containing i solute atoms and E_1 is a single solute atom. E_1 may be an arsenic atom or a silicon interstitial, where E_i is then an arsenic precipitate (or cluster) or a dislocation loop. In this formulation, the collision and fusion of defects are ignored, as well as the fission of defects into two or more other defects. The formulation may not be valid in non-dilute solutions where the concentration of the solute is comparable to the concentration of solvent.

According to reactions 5-2, the change in the density of the i-sized defect is given by the following equation:

$$\frac{\partial f_i}{\partial t} = (\beta_{i-1} f_{i-1} - \alpha_i f_i) - (\beta_i f_i - \alpha_{i+1} f_{i+1}), i \geq 2 \quad 5-3$$

where β_{i-1} is the forward and α_i is the reverse reaction rates of the first reaction in 5-2. Equation 5-3 can be put in a more convenient form:

$$\frac{\partial f_i}{\partial t} = J_{i-1} - J_i, i \geq 2 \quad 5-4$$

where J_i is the rate at which defects of size i become defects of size i+1 and is defined by:

$$J_i = \beta_i f_i - \alpha_{i+1} f_{i+1} \quad 5-5$$

Equation 5-3 does not apply to the case of i=1, i.e. the single solute atoms. The concentration of the single solute atoms can be found from the mass conversation equation:

$$f_1 + \sum_{i=2}^{\infty} i f_i = C_t \quad 5-6$$

where C_t is the total solute concentration and is a given.

The forward reaction rate can be found by a treatment similar to the one given by Turnbull and Fisher [83]. The free energy diagram of the right hand side of reaction 5-2 is shown in Figure 5.3. Here G_i represents the non-mixing component of the free energy of defect E_i when E_1 is taken as the reference phase. Δg_f is the reaction barrier between $E_1 + E_i$ and the activated complex which turns into E_{i+1} . The forward reaction rate can be written as:

$$\beta_i = A_i \lambda_d C_i^{int} \nu_d \exp\left(-\frac{\Delta g_f}{kT}\right) \quad 5-7$$

where A_i is the surface area of the size- i defect, λ_d is the lattice spacing around the defect, C_i^{int} is the concentration of E_1 atoms at the interface of the defect, ν_d is the vibration frequency and Δg_f is the energy barrier. $A_i \lambda_d C_i^{int}$ is the number of E_1 atoms that are around each E_i defect and are ready to react with E_i . $\nu_d \exp\left(-\frac{\Delta g_f}{kT}\right)$ is the number of times that this reaction takes place per unit time.

The diffusivity of the E_1 atom in the solvent can roughly be written as:

$$D = \lambda^2 \nu \exp\left(-\frac{\Delta g_D}{kT}\right) \quad 5-8$$

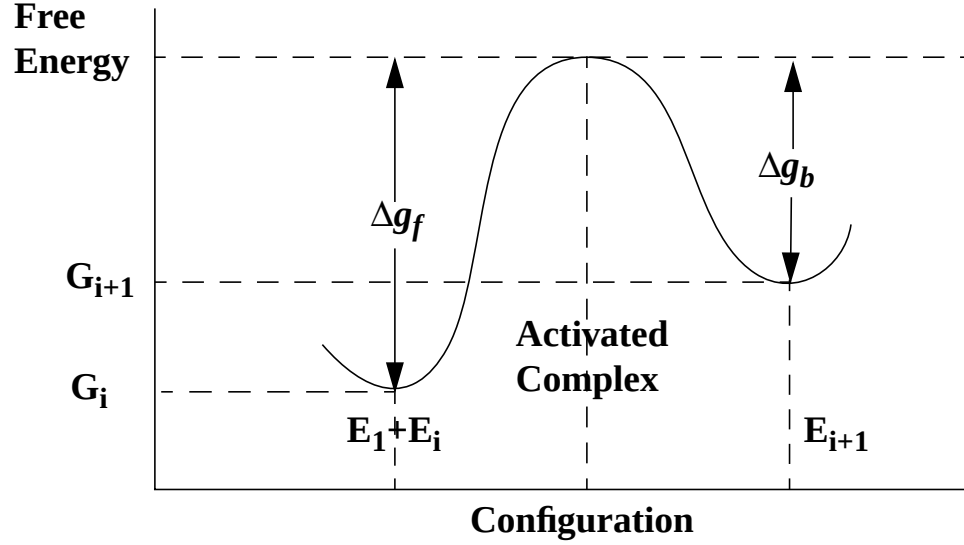


Figure 5.3 Schematic representation of free energies related to the following reaction between the extended defects and a single atom: $E_i + E_1 \rightleftharpoons E_{i+1}$.

where λ is the lattice spacing, ν is the vibration frequency and Δg_D is the migration energy. If the lattice spacing and the vibration frequency do not change near a defect and, most importantly, the migration energy, Δg_D , is equal to the reaction barrier, Δg_f , then

$$\beta_i = A_i \frac{D}{\lambda} C_i^{int} \quad 5-9$$

The interface solute concentration around a defect, C_i^{int} , is not necessarily equal to the far-field solute concentration, f_1 , because the transport of the solute atoms to the defect may not be fast enough to resupply all the solute atoms that have reacted with the defect. So, the solute may be depleted around the defect. For

convenience the diffusion of the solute atoms is assumed to be fast enough so that

$C_i^{int} = f_1$. So the forward reaction rate becomes:

$$\beta_i = A_i \frac{D}{\lambda} f_1 \quad 5-10$$

The reverse reaction rate can be found from the forward reaction rate and the thermal equilibrium condition, as suggested by Katz [81]. At thermal equilibrium, the detailed balance condition requires all fluxes to be equal to zero. So, from Equation 5-5:

$$\alpha_{i+1} = \beta_i \frac{f_i^{eq}}{f_{i+1}^{eq}} \quad 5-11$$

where f_i^{eq} is the density of size-i defects at equilibrium.

Upon minimizing the Gibbs free energy of a system consisting of defects of all sizes, the solute and solvent atoms, one can obtain the following expression for the density of the defects at thermal equilibrium:

$$\frac{f_{i+1}^{eq}}{f_i^{eq}} = \frac{f_1}{C_{sol}} \exp\left(\frac{W_i - W_{i+1}}{kT}\right) \quad 5-12$$

where W_i is the interfacial free energy of a single i -sized defect, C_{sol} is the solubility, k is Boltzmann's constant and T is the absolute temperature. Previously, it has been incorrectly assumed that the solute concentration is equal to its solubility at thermal equilibrium for this system [82,84] although Equation 5-12 is the only result of applying thermodynamics to this system. If the mixture was in touch with an infinitely big film of the second phase of the solute-solvent system, then the solute concentration would reach to its solubility at thermal equilibrium.

The interfacial free energy of a size- i defect, W_i , depends on the size of the defect. In the classical nucleation model, it is proportional to the surface area of the defect if the defect is large:

$$W_i = \sigma A_i \quad 5-13$$

where σ is the interfacial surface energy per area and is defined by this equation. If the defect is spherical:

$$A_i = \left(\frac{36\pi}{C_p^2} \right)^{1/3} i^{2/3} \quad 5-14$$

where C_p is the density of the solute atoms in the defect. For small defects, the interfacial free energy is expected to deviate from the size dependence expressed in Equation 5-13. Terms that are proportional to the linear dimension of the defect plus

other terms may become more important. An empirical relation relating the interfacial free energy to defect size can be used [18]:

$$W_i = c_1 i^{a_1} + c_2 i^{a_2} + \dots \quad 5-15$$

where $a_1, a_2, \dots$ shapes the size dependence of the interfacial free energy and $c_1, c_2, \dots$ are constants. Since the interfacial free energy is proportional to the surface area for large defects, a_1 can be set to 2/3 for spherical defects, to 1/2 for planar ones, etc. If the defect creates stress in the lattice, the strain energy term should also be included in W_i .

5.4 Simulation Results

Equations 5-3, 5-6, 5-10, 5-11, 5-12, 5-14, and 5-15 were implemented into FLOOPS. The interaction between the precipitates and point defects was not included in the model. The simulated experimental data was taken from Luning *et al.* [23]. In that work, arsenic was implanted into silicon at various doses, followed by laser annealing. Then, the samples were subjected to thermal annealing at various temperatures. The laser annealing activated all of the dopant, thus giving a clear initial condition for the simulations, i.e. the active concentration f_1 , is equal to the total dopant concentration, C_t at the beginning. The profiles were box-shaped and no appreciable diffusion of arsenic was observed; therefore a single chemical dopant concentration could

be used instead of the whole arsenic profile for each simulation. The discrete rate equations were solved without any rediscrretization. The initial density of all precipitates was assumed to be very small. As the boundary condition, the density of an arbitrarily large precipitate was taken to be zero.

The arsenic diffusivity used in the simulations has the following form [18]:

$$D_{As} = D_o + D_- \left(\frac{n}{n_i} \right) \left[1 + \left(\frac{f_1}{C_o} \right)^m \right] \quad 5-16$$

where D_o and D_- are the neutral and negative components of inert arsenic diffusivity, n is the electron concentration and n_i is the intrinsic carrier concentration. The term, $\left[1 + \left(\frac{f_1}{C_o} \right)^m \right]$, takes into account the experimentally observed power law dependence of the arsenic diffusivity on the active concentration [31]. D_o , D_- and C_o have Arrhenius dependences on temperature.

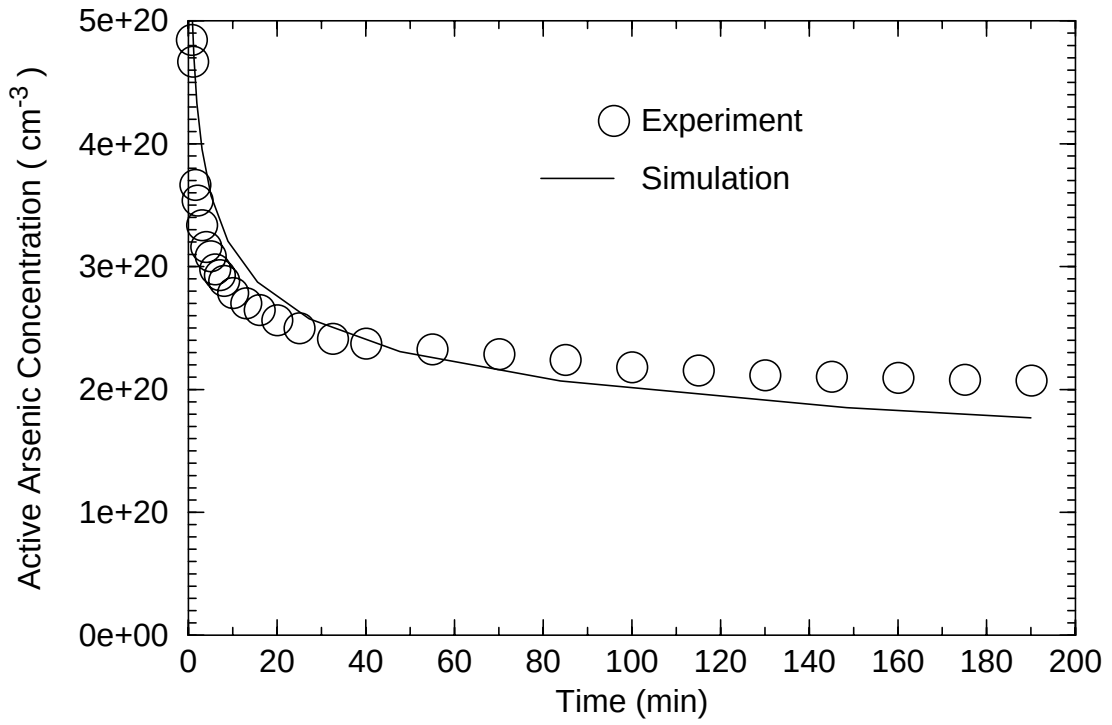
The simulation parameters are given in Table I. The solubility, C_{sol} , is taken to be equal to the equilibrium active concentration of arsenic. The only parameters that were fitted during the simulations are the interfacial energy coefficients c_1 and c_2 , and the reference concentration C_o .

Figure 5.4 to Figure 5.7 show a comparison of simulations with the arsenic deactivation data obtained between 500 and 800°C for chemical arsenic concentrations of $1 \times 10^{21} \text{ cm}^{-3}$ and $4.4 \times 10^{20} \text{ cm}^{-3}$. The simulations successfully reproduce the experimental data. All of the simulations exhibit a very fast deactivation of arsenic at the beginning of the thermal anneal just like the

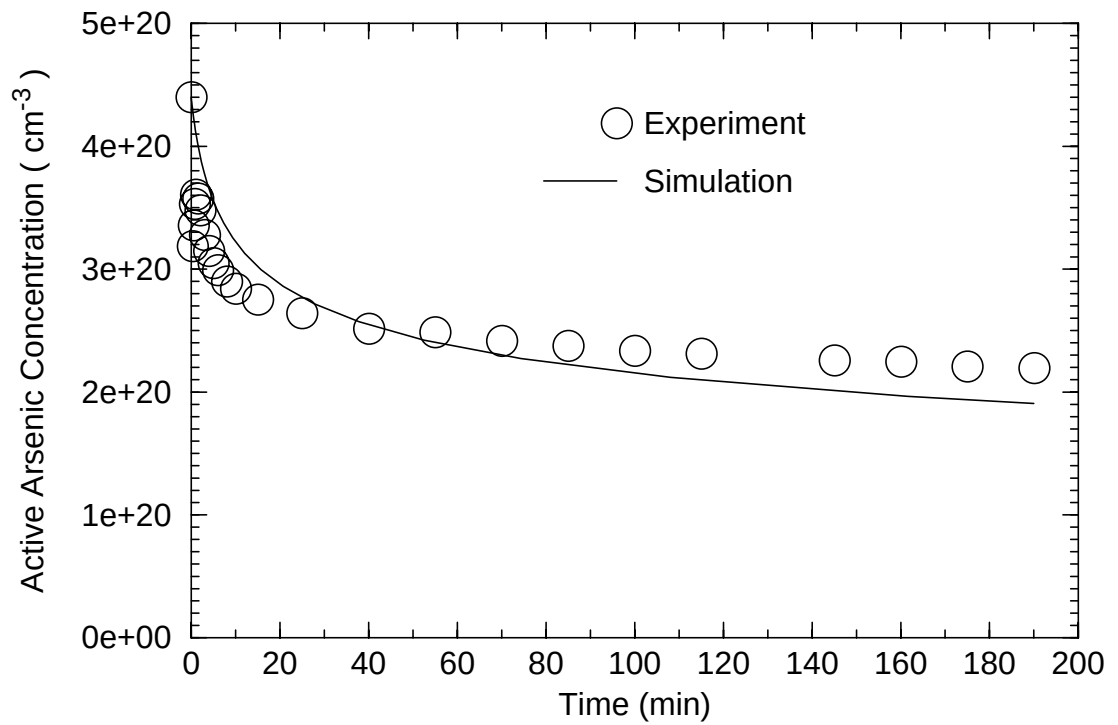
Table 5.1: Parameter values used for simulations of arsenic deactivation

Parameter	Pre-exponential	Activation Energy (eV)
D_o	0.0666 cm ² /s	3.44
D_-	12.8 cm ² /s	4.05
C_o	3x10 ²³ cm ⁻³	0.631
m	3.5	
a_1	2/3	
c_1	0.13 eV	
a_2	1/3	
c_2	0.115 eV	
λ	2.7x10 ⁻⁸ cm	
C_p	2.5x10 ²² cm ⁻³	
C_{sol}	2.2x10 ²² cm ⁻³	0.47

experiments. This is due to the rapid formation of small clusters which have relatively small formation energies. The slow deactivation after around a few minutes is also replicated by the simulations. This slow deactivation could not be reproduced by single size cluster models [23]. Figure 5.8 shows the simulated size distributions of the 1x10²¹ cm⁻³ sample after 5 and 124 minutes at 700°C. The distribution becomes broader for the longer anneal, suggesting that the slow deactivation is due to further precipitation at larger sizes.

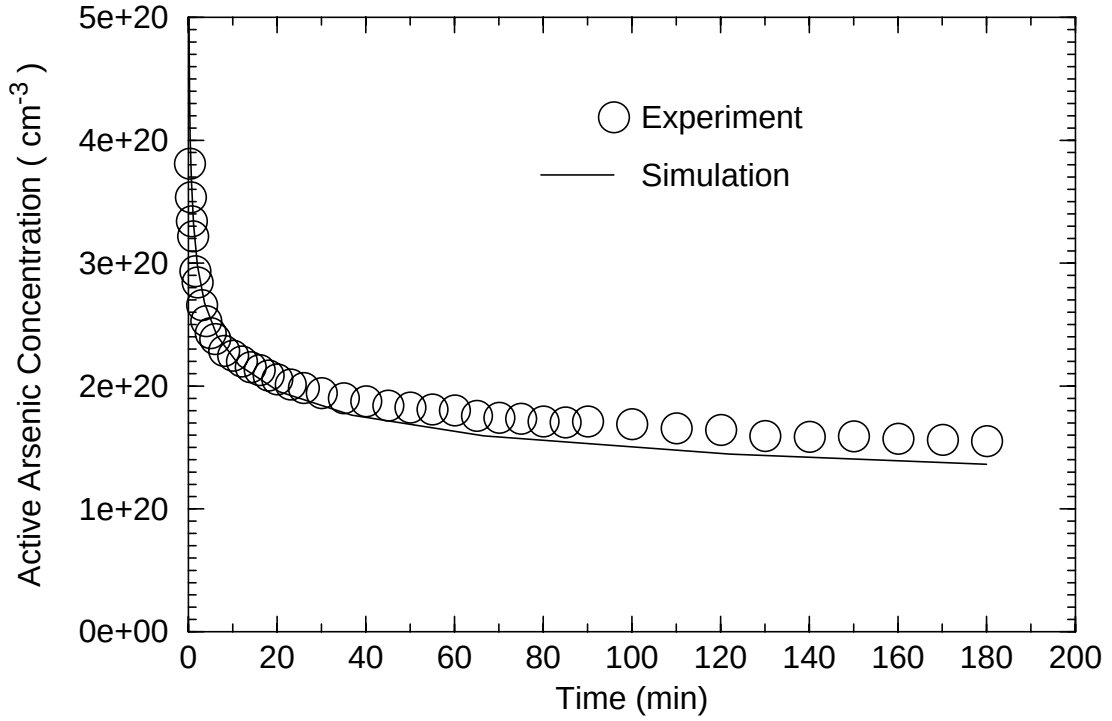


(a)

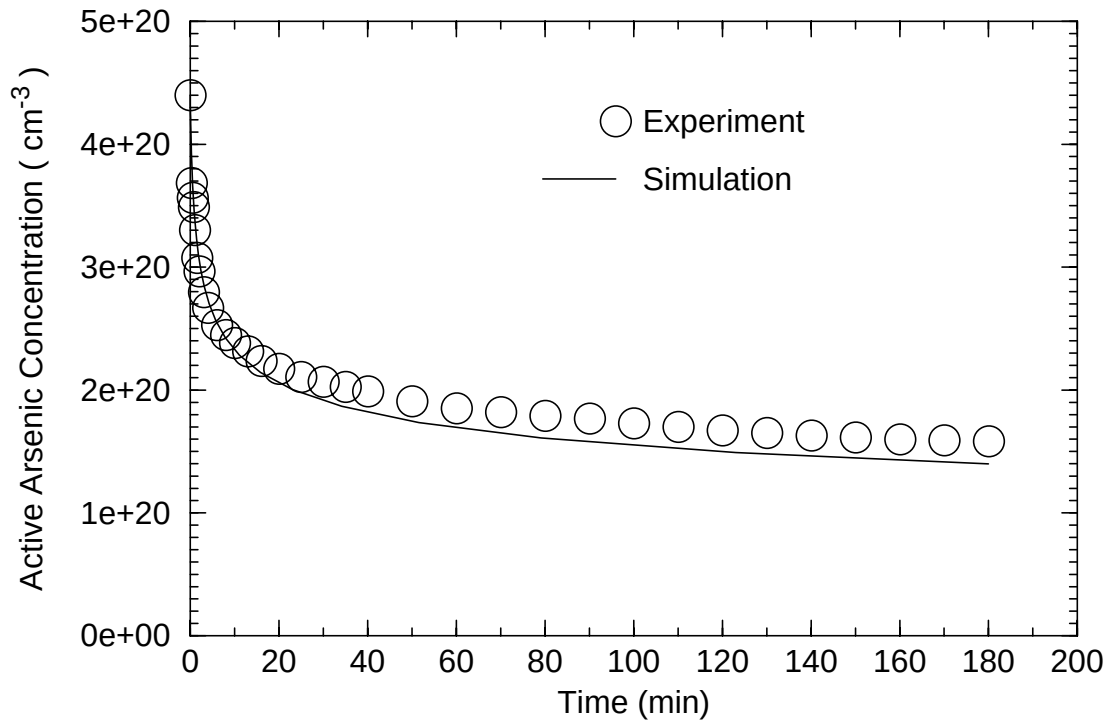


(b)

Figure 5.4 Comparison of experiments and simulation at 500°C at a chemical arsenic concentration of (a) $1 \times 10^{21} \text{ cm}^{-3}$, (b) $4.4 \times 10^{20} \text{ cm}^{-3}$.

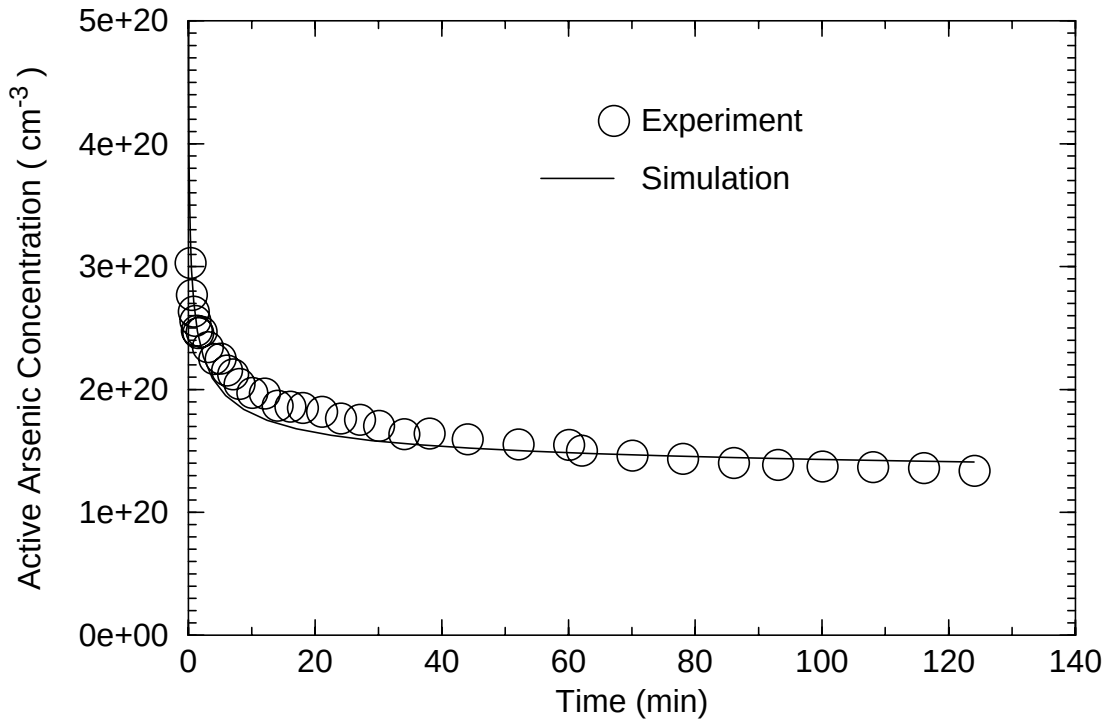


(a)

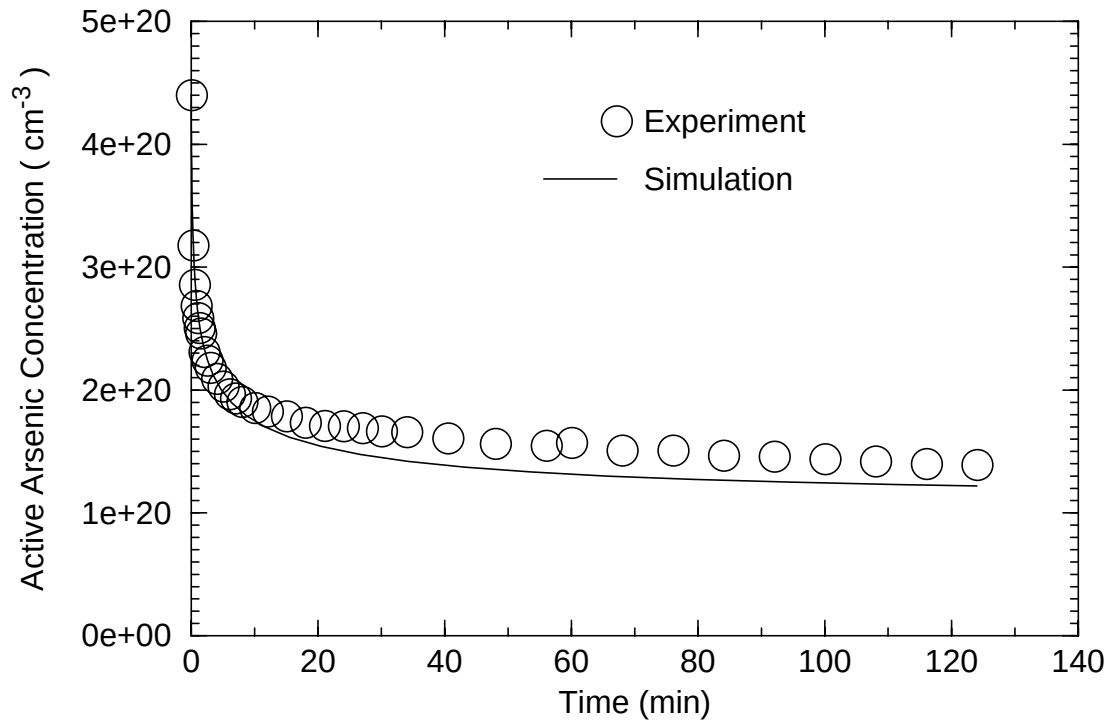


(b)

Figure 5.5 Comparison of experiments and simulation at 600°C at a chemical arsenic concentration of (a) $1 \times 10^{21} \text{ cm}^{-3}$, (b) $4.4 \times 10^{20} \text{ cm}^{-3}$.

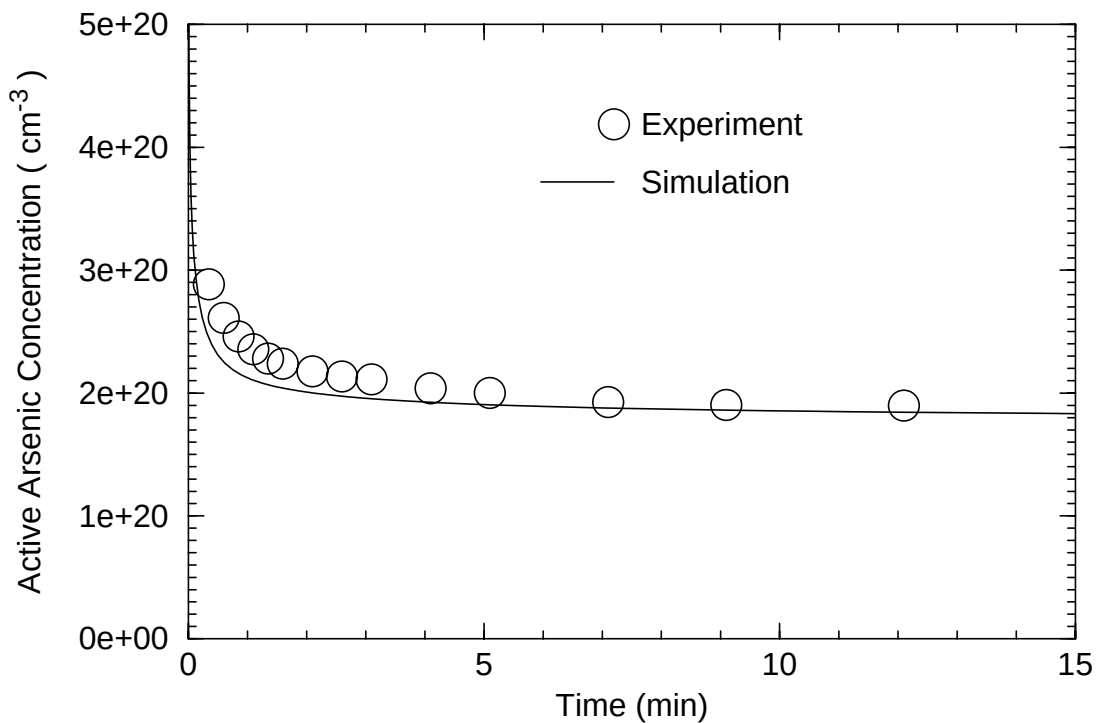


(a)

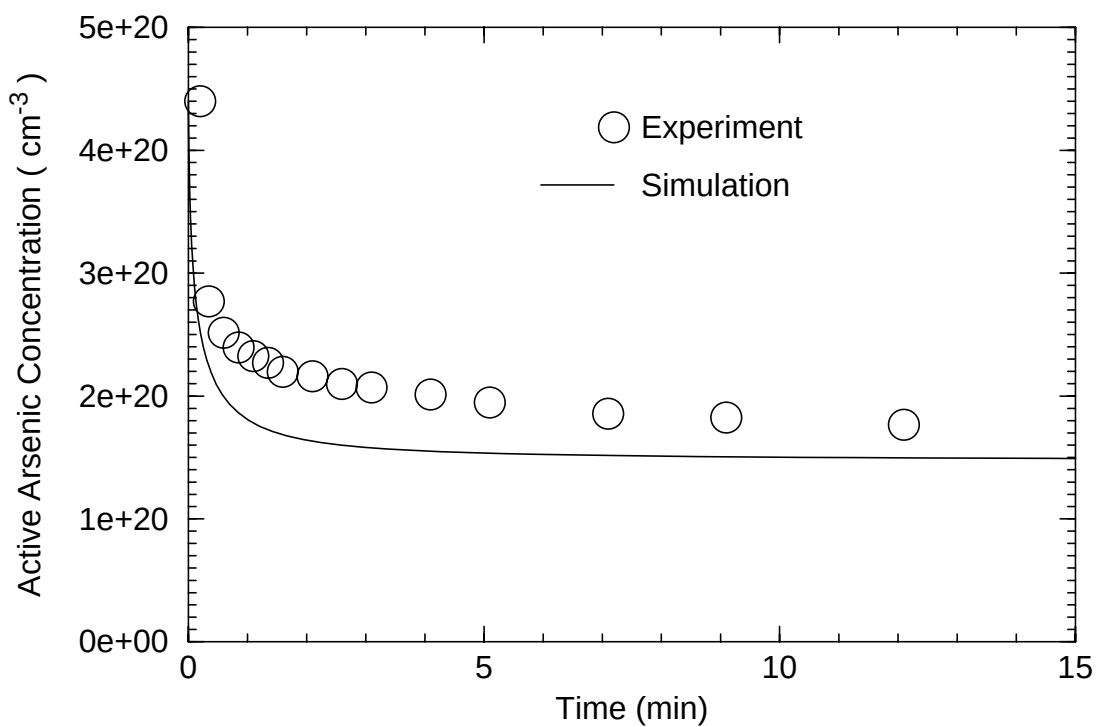


(b)

Figure 5.6 Comparison of experiments and simulation at 700°C at a chemical arsenic concentration of (a) $1\text{e}+21 \text{ cm}^{-3}$, (b) $4.4\text{e}+20 \text{ cm}^{-3}$.



(a)



(b)

Figure 5.7 Comparison of experiments and simulation at 800°C at a chemical arsenic concentration of (a) $1 \times 10^{21} \text{ cm}^{-3}$, (b) $4.4 \times 10^{20} \text{ cm}^{-3}$.

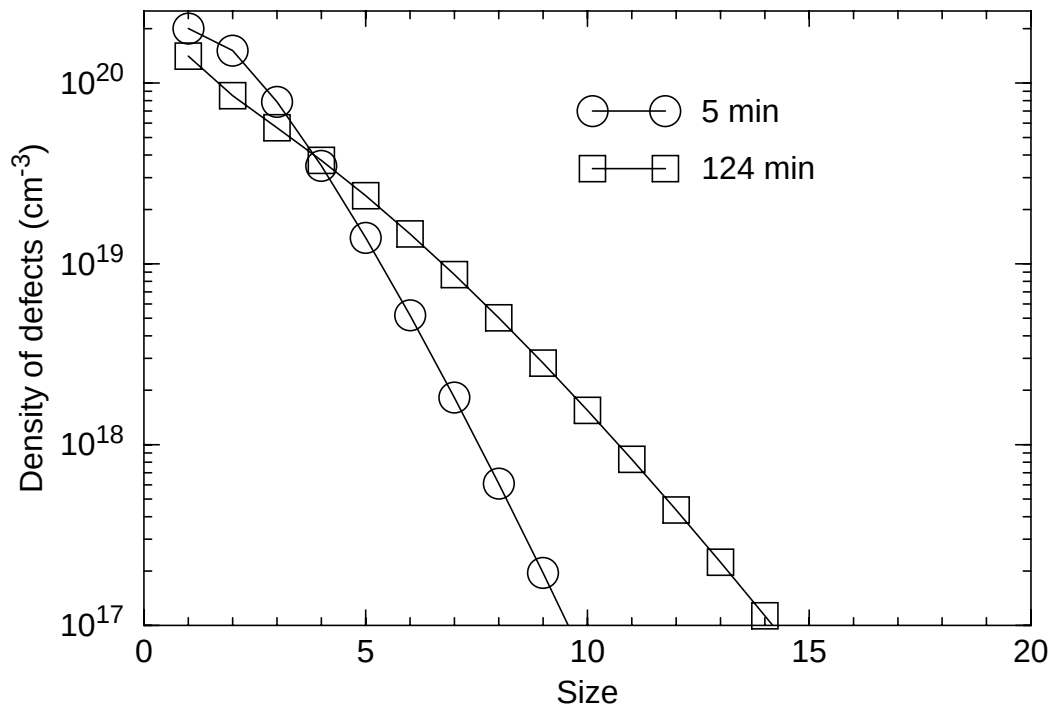


Figure 5.8 Simulated defect size distributions for the $1 \times 10^{21} \text{ cm}^{-3}$ sample after 5 min and 124 min at 700°C .

5.5 Conclusions

An arsenic deactivation model that takes into account the size distribution of inactive arsenic structures was presented. The rate equations that describe the evolution of the size distribution were derived from the kinetic theory and thermodynamics. The model is in good quantitative agreement with the experimental arsenic deactivation data, and successfully reproduces the rapid deactivation at the beginning and the slow deactivation after a few minutes.

CHAPTER VI

A COMPARISON OF VARIOUS NUMERICAL METHODS FOR THE SOLUTION OF THE RATE EQUATIONS IN EXTENDED DEFECT SIMULATION

6.1 Introduction

Extended defects in silicon play an important role in the final electrical characteristics of silicon devices. Precipitation/clustering of dopant atoms determine the carrier concentration in heavily doped regions. Dislocation loops affect the population of point defects and therefore dopant diffusion. {311} defects have recently been identified as an interstitial source during transient enhanced diffusion [85,86]. In general, extended defects form during phase transitions and as a result of aggregation of impurities such as dopants and point defects. The extended defects have been widely studied in the literature. Nucleation of clusters in gases, nucleation of vacancy voids [87,88], crystal nucleation in glasses [89] and crystal nucleation in amorphous silicon [90] are just a few examples.

In Chapter V, arsenic deactivation was simulated by solving the size distribution of electrically inactive arsenic precipitates. The rate equations describing the size distribution were directly solved without the necessity of a numerical method to reduce the number of equations. A small number (~50) of rate equations was enough to get a good fit to the experimental data. In addition, the

experimental arsenic profile was homogenous, so the rate equations which were solved at only one point on the arsenic profile were representative of all the other points.

Other extended defects such as dislocation loops and oxygen precipitates may contain millions of atoms. It is impossible to solve those many rate equations in a reasonable time with today's computer technology. Moreover, the impurity profiles are almost always inhomogenous, creating the necessity of solving different rate equations at each point in space. For these two reasons, the number of equations should be reduced to a reasonable level with an appropriate numerical technique [91].

The size evolution of the extended defects are described by the rate equations (also known as the discrete birth and death equations) which are introduced in Chapter V:

$$\frac{\partial f_i}{\partial t} = J_{i-1} - J_i, i \geq 2 \quad 6-1$$

$$J_i = \beta_i f_i - \alpha_{i+1} f_{i+1} \quad 6-2$$

where f_i is the density of i -sized defect, β_i is the forward and α_{i+1} is the reverse reaction rates. As detailed in Chapter V, the reverse reaction rate can be found from the forward reaction rate and the thermal equilibrium condition:

$$\alpha_{i+1} = \beta_i \frac{f_i^{eq}}{f_{i+1}^{eq}} \quad 6-3$$

where f_i^{eq} is the density of i-sized defects at equilibrium. Upon substituting Equation 6-3 into Equation 6-2, an alternate form for J_i can be obtained:

$$J_i = \beta_i f_i^{eq} \left(\frac{f_i}{f_i^{eq}} - \frac{f_{i+1}}{f_{i+1}^{eq}} \right) \quad 6-4$$

Several researchers [82,84,87,92] have worked on the solution of either the rate equations or its continuous form which is referred as the Fokker-Planck equation:

$$\frac{\partial}{\partial t} f(s, t) = \frac{\partial}{\partial s} [A(s) f(s, t)] + \frac{\partial^2}{\partial s^2} [B(s) f(s, t)] \quad 6-5$$

where s is the continuous size variable, A and B are the drift and diffusion coefficients respectively. In spite of all this work, there still exists the need for a simple numerical method which can reproduce the solution of the rate equations with a sufficient degree of accuracy for large defect sizes (>1000). In this chapter, various numerical methods will be derived and they will be evaluated using the arsenic deactivation model of Chapter V. Two general techniques will be investigated: rediscrization and interpolation.

6.2 Rediscretization

In this approach, the rate equations are first put into a continuous form and then rediscretized. After finding a suitable continuous form, the equations are discretized using two different methods: linear and logarithmic discretization.

6.2.1 Continuous Form for the Rate Equations

The first continuous form for the rate equations has been given by Zeldovich [93] and Frenkel [80]:

$$\frac{\partial}{\partial t} f(s, t) = -\frac{\partial}{\partial s} J(s, t) \quad 6-6$$

$$J(s, t) = -\beta(s) f^{eq}(s) \frac{\partial}{\partial s} \left(\frac{f}{f^{eq}} \right) \quad 6-7$$

These equations can be obtained by expanding Equations 6-1 and 6-4 into a Taylor series about i and keeping only the first two terms (the constant and the first derivative). This approach was later criticized by Goodrich [82]. He approximated the rate equations at the mid-points, rather than at the end-points. However, he used Equation 6-2 instead of Equation 6-4 in his derivation. Therefore, his analysis led to an equilibrium condition that is different from that of the discrete rate equations

(Equation 6-3). In contrast, the Frenkel-Zeldovich equation automatically contains the exact equilibrium conditions, because the starting point is Equation 6-4 which already includes the discrete equilibrium conditions. Shizgal and Barrett [84] suggested another methodology to approximate the rate equations with a continuous form and compared all three methods to the exact solution. They found that their and Goodrich's approaches are more accurate than Frenkel's.

In order to approximate the rate equations with a continuous form, the mathematical procedure suggested by Goodrich will be followed. First, the right hand side of Equation 6-1 is expanded into a Taylor series around $i - \frac{1}{2}$ up to the second term. The resulting equation is:

$$\left. \frac{\partial}{\partial t} f(s) \right|_{s=i} = - \left. \frac{\partial}{\partial s} J(s) \right|_{s=i-\frac{1}{2}} \quad 6-8$$

where s is the continuous size variable. The implicit dependences of f and J on t are not shown in order to make the derivation more clear. The same mid-point expansion is then applied to Equation 6-4, rather than Equation 6-2. As discussed in the previous paragraph, Equation 6-4 already contains the exact equilibrium conditions, therefore its continuous form will also preserve them. Rewriting Equation 6-4 by substituting $i - \frac{1}{2}$ in place of i , the following expression is obtained:

$$J_{i-\frac{1}{2}} = \beta_{i-\frac{1}{2}} f_{i-\frac{1}{2}}^{eq} \left(\frac{f_{i-\frac{1}{2}}}{f_{i-\frac{1}{2}}^{eq}} - \frac{f_{i+\frac{1}{2}}}{f_{i+\frac{1}{2}}^{eq}} \right) \quad 6-9$$

Expanding β , f^{eq} , and $\frac{f}{f^{eq}}$ separately into Taylor series around i , and keeping the first two terms for β and $\frac{f}{f^{eq}}$, and the first three terms for f^{eq} , the following equation is obtained:

$$J(s) \Big|_{s=i-\frac{1}{2}} = - \left[\beta(s) - \frac{1}{2} \frac{\partial}{\partial s} \beta(s) \right] \left[f^{eq}(s) - \frac{1}{2} \frac{\partial}{\partial s} f^{eq}(s) + \frac{1}{8} \frac{\partial^2}{\partial s^2} f^{eq}(s) \right] \quad 6-10$$

$$\frac{\partial}{\partial s} \left(\frac{f}{f^{eq}} \right) \Big|_{s=i} \quad -$$

Substituting this equation into Equation 6-8, the following differential equations can be written for the discrete rate equations:

$$\frac{\partial}{\partial t} f(s) = - \frac{\partial}{\partial s} J(s) \quad 6-11$$

$$J(s) = - \left[\beta(s) - \frac{1}{2} \frac{\partial}{\partial s} \beta(s) \right] \left[f^{eq}(s) - \frac{1}{2} \frac{\partial}{\partial s} f^{eq}(s) + \frac{1}{8} \frac{\partial^2}{\partial s^2} f^{eq}(s) \right] \frac{\partial}{\partial s} \left(\frac{f}{f^{eq}} \right) \quad 6-12$$

f^{eq} was expanded up to the second derivative for the following reason: As mentioned in Chapter V, f^{eq} can be written as:

$$\frac{f^{eq}(s+1)}{f^{eq}(s)} = \frac{f_1}{C_{sol}} \exp\left(\frac{W(s) - W(s+1)}{kT}\right) \quad 6-13$$

for $s = i$. f_1 represents the solute concentration, C_{sol} is the solubility and W is the interfacial free energy. From this iteration, f^{eq} can be found to be an exponential function of size s . If only the first two terms in the Taylor expansion are kept for f^{eq} , namely $f^{eq} - \frac{1}{2} \frac{\partial^2 f^{eq}}{\partial s^2}$, this term will become negative if:

$$f^{eq} < \frac{1}{2} \frac{\partial^2 f^{eq}}{\partial s^2} \quad 6-14$$

After finding an expression for f^{eq} from Equation 6-13 and inserting it into this inequality, the condition above can be rewritten as:

$$\ln\left(\frac{f_1}{C_{sol}}\right) - \frac{1}{kT} \frac{\partial^2 W(s)}{\partial s^2} > 2 \quad 6-15$$

This condition can be met at large supersaturations or slowly changing interfacial free energy values. Then, the flux $J(s)$ will be positive, which is completely non-physical. The sign of the flux should only be decided by the $\frac{\partial}{\partial s} \left(\frac{f}{f^{eq}} \right)$ term, as in the discrete rate equations. A similar analysis shows that the inclusion of the second derivative term in the expansion of f^{eq} guarantees that the approximate Taylor series for f^{eq} will always be positive as long as f^{eq} is expressed as similar to Equation 6-13 and W similar to 5-15.

Now that a continuous form has been derived for the rate equations, the next step will be to discretize it for an arbitrary size spacing. Figure 6.1 shows an arbitrary segment of the size space for which Equations 6-11 and 6-12 will be discretized. For size l , the right hand side of Equation 6-11 can be approximated as:

$$\frac{\partial f_l}{\partial t} = -\left(\frac{J_{l'} - J_{k'}}{\Delta}\right) \quad 6-16$$

where l' and k' are the mid-points in the respective interval and Δ is the size difference between the mid-points. The task is now reduced to finding an appropriate discrete expression for J at l' and k' . Two discretization schemes will be investigated for this purpose: linear and logarithmic.

6.2.2 Linear Discretization

In this method, the function to be discretized, $y(s)$, is assumed to be linear in size at each interval $[k, l]$:

$$y(s) = as + b \quad 6-17$$

The value of this function and its derivative at the mid-point, k' , can be approximated with the values of the function at the end-points, k and l :

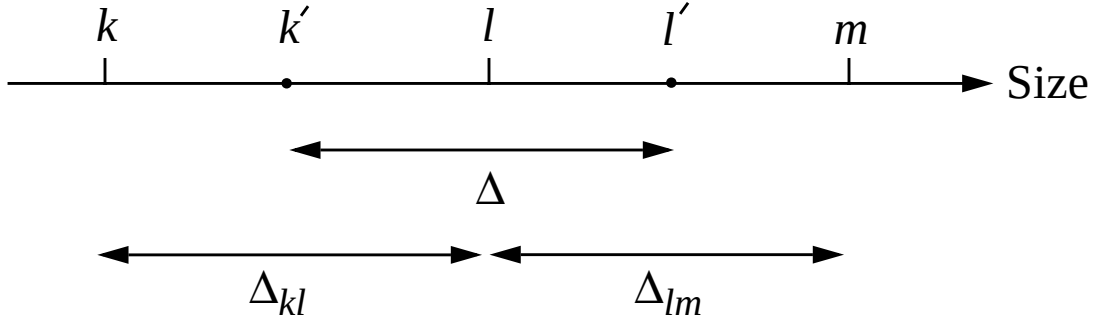


Figure 6.1 An arbitrary interval in the size space for which the continuous rate equations are discretized.

$$y_{k'} = \frac{y_k + y_l}{2} \quad 6-18$$

$$\left. \frac{\partial y}{\partial s} \right|_{k'} = \frac{y_l - y_k}{\Delta_{kl}} \quad 6-19$$

If β , f^{eq} , and $\frac{f}{f^{eq}}$ are assumed to be linear functions of size, one can obtain a discrete equation for $J_{k'}$ by substituting these relations into Equation 6-12. Repeating the same procedure in the interval $[l, m]$, a similar expression can be derived for $J_{l'}$.

6.2.3 Logarithmic Discretization

In this scheme, the function to be discretized is assumed to be an exponential function of size:

$$y(s) = ae^{bs} \quad 6-20$$

Similar to linear discretization, the value of the function and its derivative at the mid-point can be evaluated in terms of the values of the function at the end-points:

$$y_{k'} = \sqrt{y_k y_l} \quad 6-21$$

$$\left. \frac{\partial y}{\partial s} \right|_{k'} = \frac{\sqrt{y_k y_l}}{\Delta_{kl}} \ln\left(\frac{y_l}{y_k}\right) \quad 6-22$$

$$\left. \frac{\partial^2 y}{\partial s^2} \right|_{k'} = \sqrt{y_k y_l} \left[\frac{\ln\left(\frac{y_l}{y_k}\right)}{\Delta_{kl}} \right]^2 \quad 6-23$$

If β , f^{eq} , and $\frac{f}{f^{eq}}$ are assumed to be exponential in size, a discrete equation can be obtained for $J_{k'}$ by substituting these relations into Equation 6-12.

There is one important problem with the logarithmic discretization method. The derivative of $\frac{f}{f^{eq}}$ with respect to size is approximated as:

$$\left. \frac{\partial}{\partial s} \left(\frac{f}{f^{eq}} \right) \right|_{k'} = \frac{1}{\Delta_{kl}} \sqrt{\frac{f_l}{f_l^{eq}} \frac{f_k}{f_k^{eq}}} \ln\left(\frac{f_l f_k^{eq}}{f_k f_l^{eq}} \right) \quad 6-24$$

As one of the densities, such as f_l , decreases, the derivative also decreases, eventually approaching zero for very small values of f_l . This causes the flux, $J_{k'}$, to

get smaller, which in turn decreases the rate of change of f_l (Equation 6-16). This result is both counter-intuitive and incompatible with the original discrete rate equations. In the rate equations, the rate of change of f_l increases as f_l gets smaller (Equations 6-1 and 6-4).

This difficulty can be overcome by exploiting a technique that has been widely used in diffusion simulations and FLOOPS. This method works by mixing a small part of f_k into f_l and vice versa:

$$f_k \rightarrow \alpha f_k + (1 - \alpha) f_l \quad 6-25$$

$$f_l \rightarrow \alpha f_l + (1 - \alpha) f_k \quad 6-26$$

where α is close to unity. If these substitutions are put into Equation 6-24, it can be found that Equation 6-24 is now compatible with the rate equations in the limit of small f_l . In this work, the natural logarithm term in the derivative has not been changed in order to preserve the equilibrium conditions.

6.3 Interpolation

Figure 6.2 shows a segment of the size space where a solution for the discrete rate equations is desired. The rate equation for size l can be rewritten as:

$$\frac{\partial f_l}{\partial t} = \beta_{l-1} f_{l-1}^{eq} \left(\frac{f_{l-1}}{f_{l-1}^{eq}} - \frac{f_l}{f_l^{eq}} \right) - \beta_l f_l^{eq} \left(\frac{f_l}{f_l^{eq}} - \frac{f_{l+1}}{f_{l+1}^{eq}} \right) \quad 6-27$$

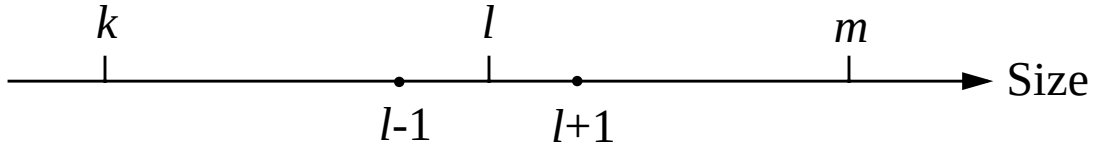


Figure 6.2 An arbitrary interval in the size space. In the interpolation method, the density f_{l-1} is interpolated with f_k and f_l and the density f_{l+1} with f_l and f_m .

These equations include the densities for sizes $l-1$ and $l+1$, i.e. f_{l-1} and f_{l+1} . If only the solutions for f_k , f_l and f_m are desired, f_{l-1} and f_{l+1} can be interpolated using these densities. Then, the rate equations will have only the densities whose solutions are desired.

In the linear interpolation case, the densities are assumed to be linear in size at each interval such as $[k, l]$. f_{l-1} can be interpolated as:

$$f_{l-1} = \frac{(l-k-1)f_l + f_k}{l-k} \quad 6-28$$

A similar expression can be obtained for f_{l+1} . If these interpolations are substituted in Equation 6-27, the rate equations will only have f_k , f_l and f_m as unknowns.

The exponential interpolation is similar to the linear one, except the densities are assumed to be exponential in size at each size interval. The exponential interpolation expression for f_{l-1} is given by:

$$f_{l-1} = (f_l^{(l-k-1)} f_k)^{\frac{1}{l-k}} \quad 6-29$$

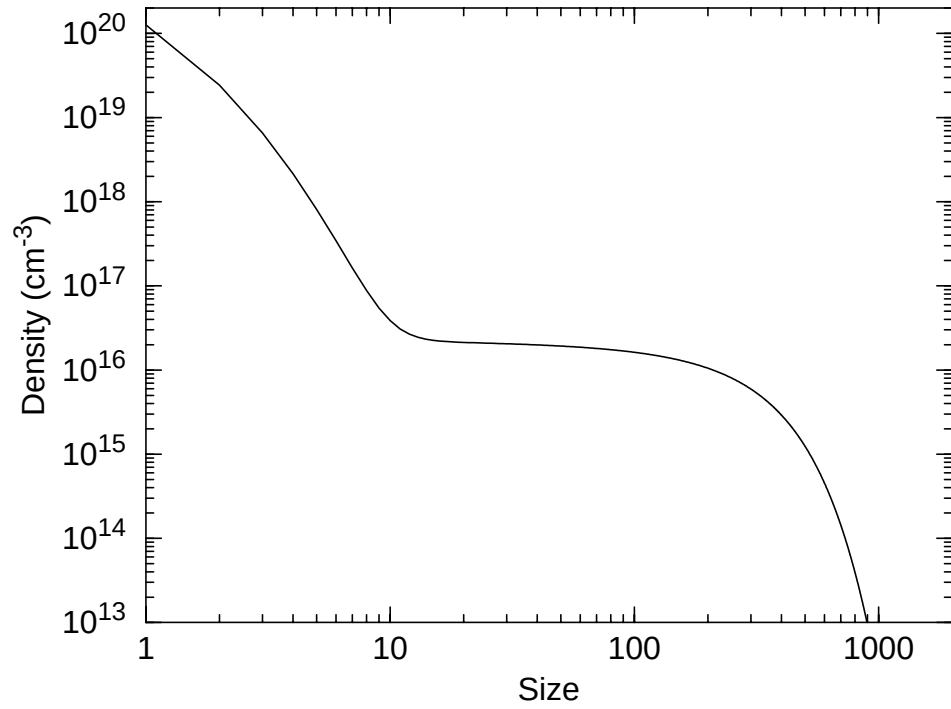
6.4 Comparison of Numerical Methods

The numerical techniques described in the previous sections were implemented in FLOOPS. Their accuracies in the solution of the rate equations were evaluated using the arsenic deactivation model in Chapter V. The chemical arsenic concentration was taken to be $1 \times 10^{21} \text{ cm}^{-3}$. Table 6.1 shows the simulation parameters that are different than the ones used in Chapter V.

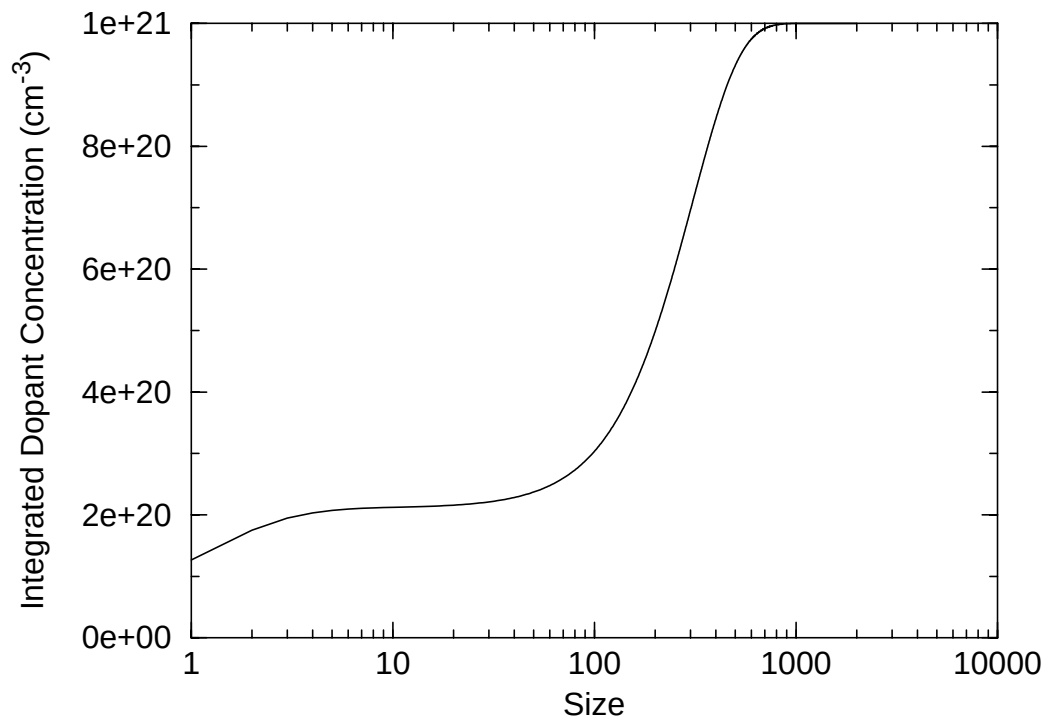
Figure 6.3 (a) shows the exact solution of the original discrete rate equations with these parameters. The equations have been solved up to size 2000. The exact solution will be a reference point in comparing the different numerical techniques. Figure 6.3 (b) shows the integrated dopant concentration in the precipitates. This concentration has been calculated by taking the sum of the dopant concentration up to the size shown in the x-axis. Most of the dopant atoms are located between the

Table 6.1: Simulation parameters that are different from the ones in Chapter V.

Parameter	Pre-exponential	Activation Energy (eV)
C_o	$4.8 \times 10^{21} \text{ cm}^{-3}$	0.4
c_1	0.3 eV	
c_2	0.0 eV	



(a)



(b)

Figure 6.3 (a) Exact solution of the rate equations for the simulation described in the text. (b) The integrated dopant concentration for the exact solution.

sizes 50-700. Therefore, the accuracy of a numerical method will mostly depend on how well it can reproduce the size distribution in this range.

Table 6.2 shows the grids used in the simulations. Thirteen different grids have been tried. The grids are defined such that a size step of 1 is used up to size SZ1 and a size step of Δ up to size 2000. A size step of 1 represents the size step in the discrete rate equations. The number of equations (N_{eq}) that has resulted from each grid is also shown in Table II.

6.4.1 Comparison of Size Distributions

Figure 6.4 shows a comparison of the size distributions obtained by the linear and logarithmic rediscritization methods. For a size spacing of 4 ($\Delta=4$), the linear rediscritization technique reproduces the exact solution accurately except at the tail of the profile. But, when Δ is increased to 20, it becomes completely unstable and gives a completely different size distribution. On the other hand, the logarithmic rediscritization method fits the exact solution very accurately for the same size spacing.

Figure 6.5 shows a comparison of the linear interpolation with the logarithmic rediscritization method. Since logarithmic rediscritization has been found to be the most accurate and stable method in the simulations, all the other techniques are compared to this method. The linear interpolation method reproduces the exact solution fairly accurately for $\Delta=20$. This is the same size spacing for which the linear discretization technique has failed. As Δ is increased and the

Table 6.2: The grids used in the simulations. A size step of 1 is used up to size SZ1 and a size step of Δ is used up to size 2000.

Grid #	SZ1	Size Step (Δ)	Number of equations (N_{eq})
1	100	2	1050
2	100	3	734
3	100	4	575
4	100	5	480
5	100	10	290
6	100	20	195
7	100	50	138
8	100	100	119
9	50	50	89
10	50	100	70
11	20	50	60
12	20	100	40
13	10	200	20

number of equations is decreased, the linear interpolation method becomes much less accurate ($\Delta=50$, $N_{eq}=60$). The logarithmic rediscrization technique produces a much better solution for the same grid.

Figure 6.6 shows the size distribution obtained with the exponential interpolation and logarithmic rediscrization methods. For $N_{eq}=70$, logarithmic rediscrization is more accurate. However, it has been found that the accuracy of the exponential interpolation technique is not proportional to the number of

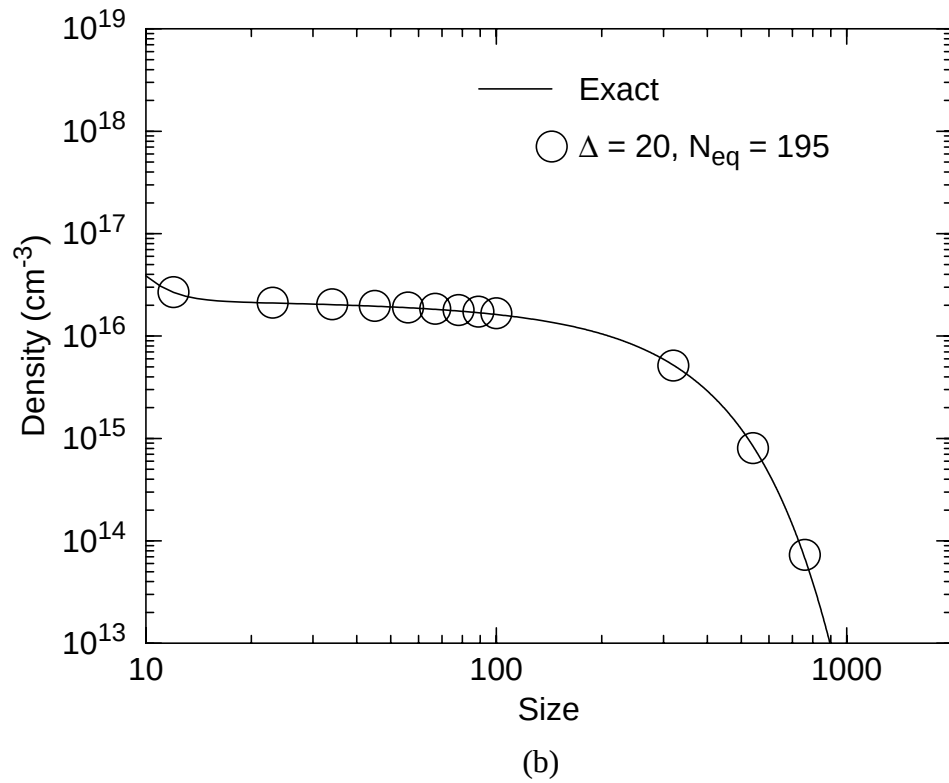
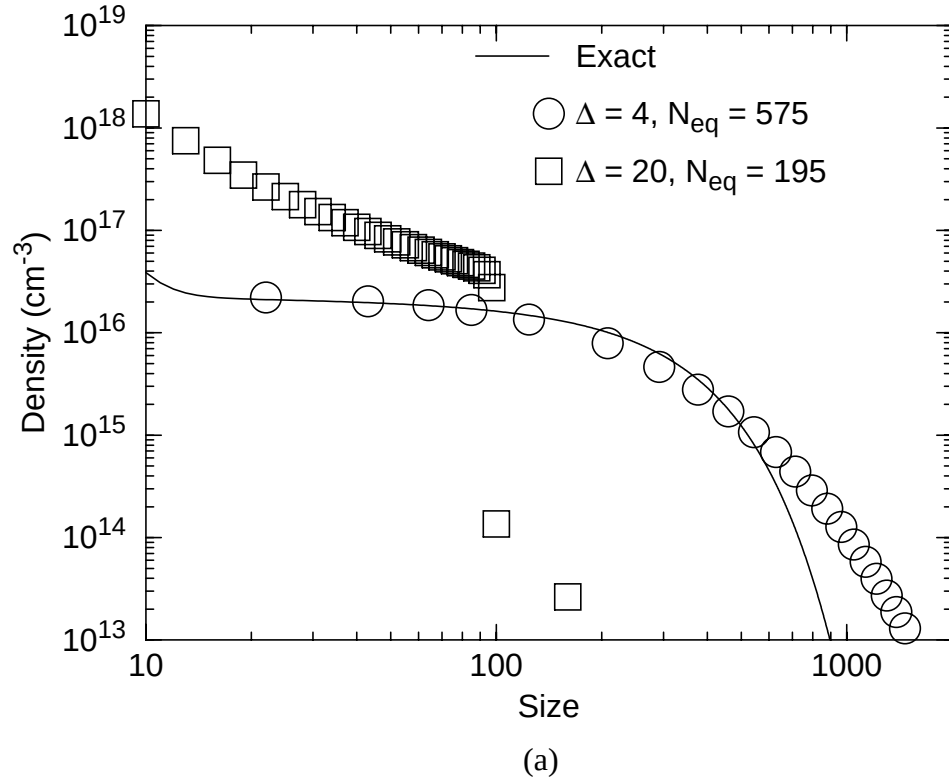


Figure 6.4 A comparison of the size distributions obtained by (a) the linear rediscritization, and (b) the logarithmic rediscritization methods.

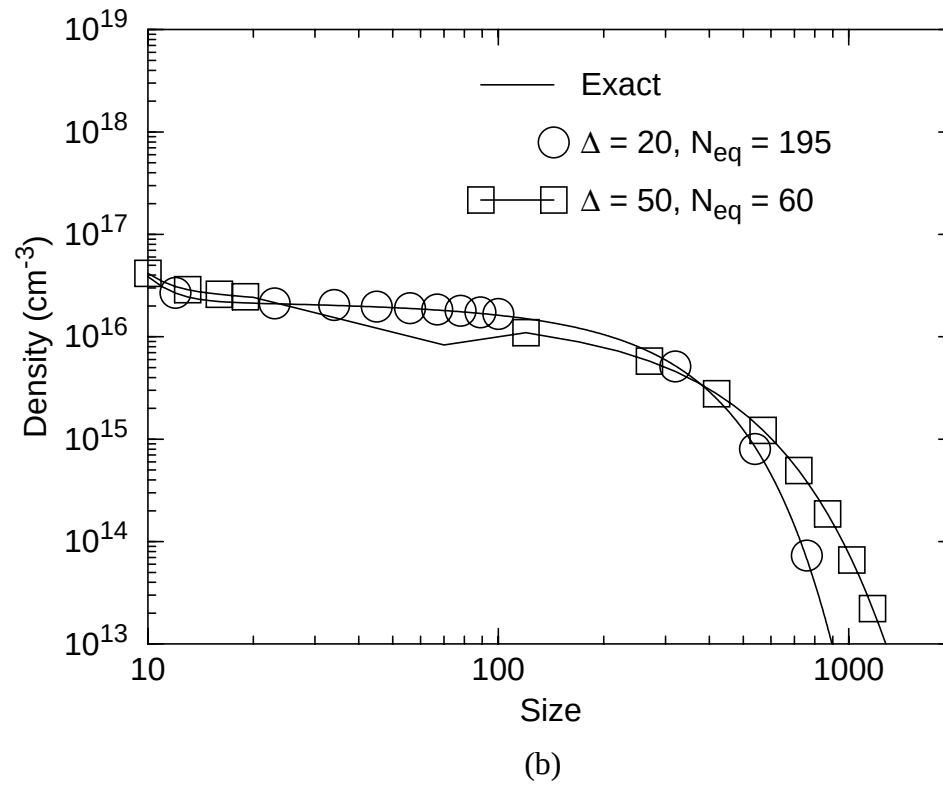
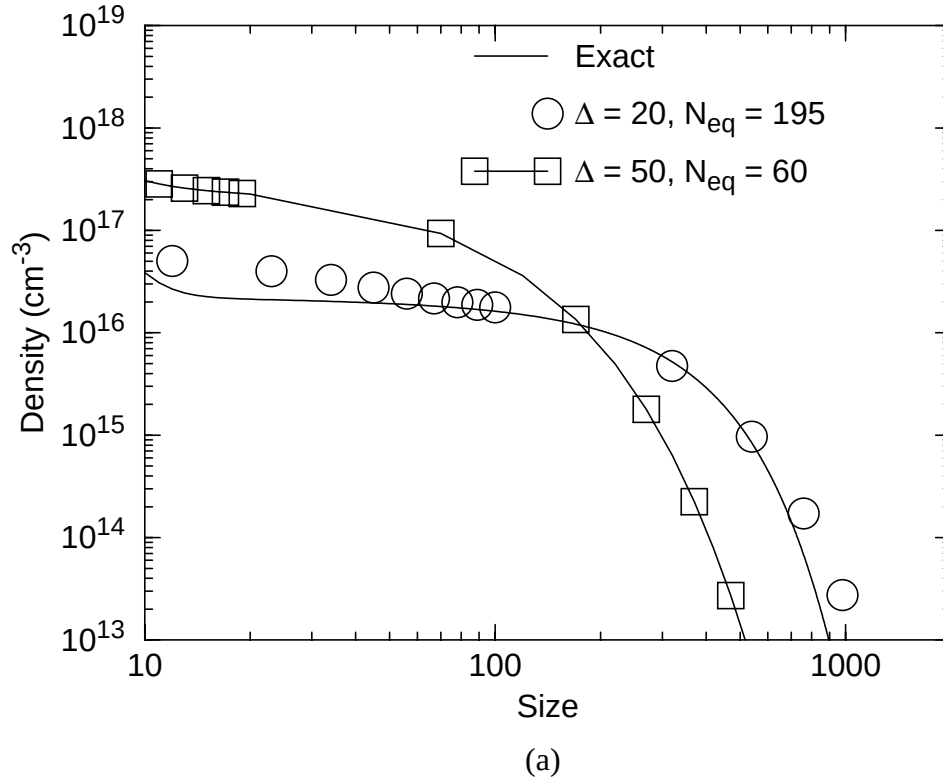


Figure 6.5 A comparison of the size distributions obtained by (a) the linear interpolation, and (b) the logarithmic rediscritization methods.

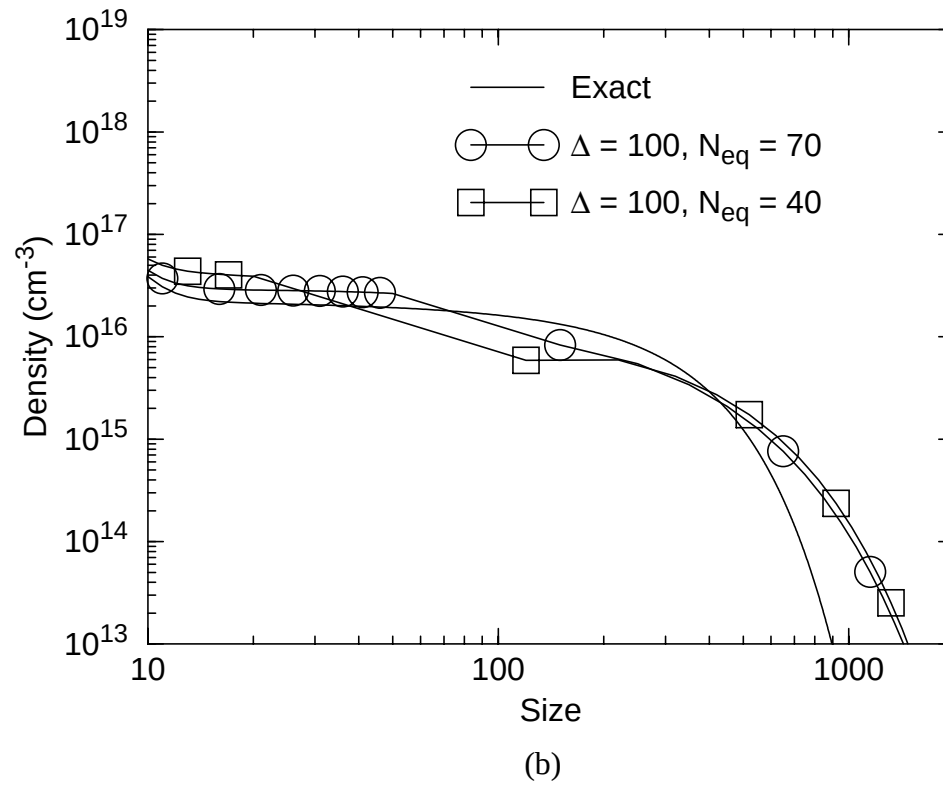
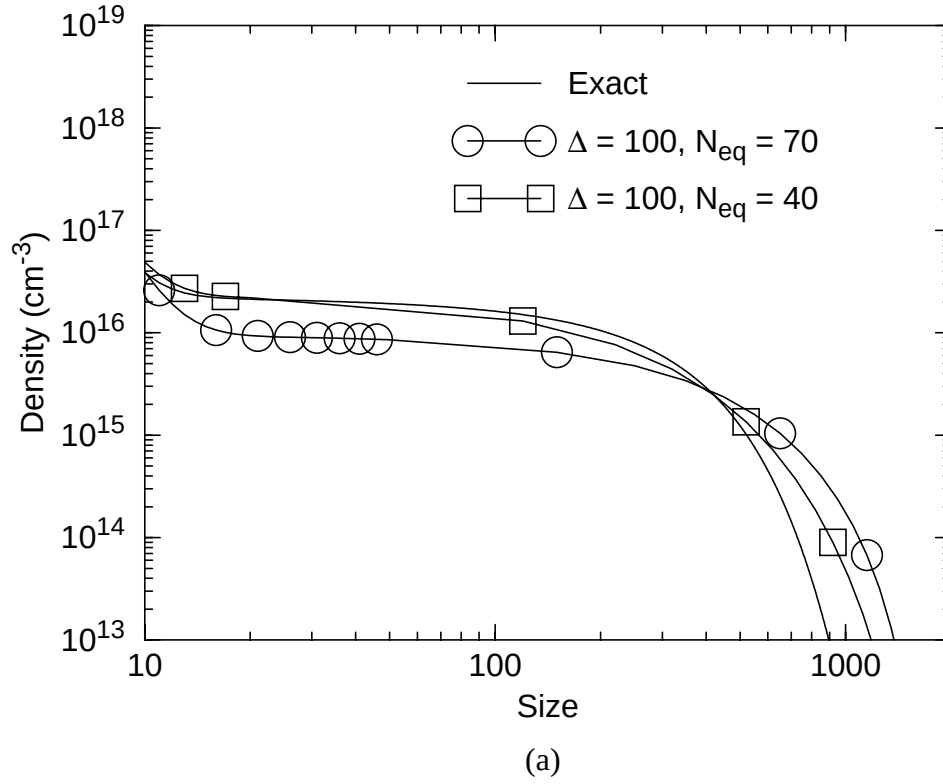


Figure 6.6 A comparison of the size distributions obtained by (a) the exponential interpolation, and (b) the logarithmic rediscritization methods.

equations. For example, it produces a more accurate solution for $N_{eq}=40$. In spite of being more accurate in some cases, it will be shown in the next section that the exponential interpolation method is unstable and produces oscillations in the active concentration for a small number of equations.

6.4.2 Comparison of Active Concentrations

As mentioned in Chapter V, the active concentration is obtained from the following relationship:

$$f_1 = C_t - \sum_{i=2}^{\infty} i f_i \quad 6-30$$

where C_t is the chemical dopant concentration, and f_i is the density of the i -sized precipitates. From a process modeling point of view, the solution of the active concentration is more important than the size distribution of the precipitates. The final judgment on a numerical method should be based on how accurate it can reproduce the active concentration, although there may be inaccuracies in the solution of the size distribution.

Figure 6.7 and Figure 6.8 compare the evolution of the active concentration obtained with different numerical methods for $\Delta=20$ and $N_{eq}=195$. The linear rediscritization technique completely fails to reproduce the exact solution. A denser grid should be used if this method is to be utilized in the solution of the rate

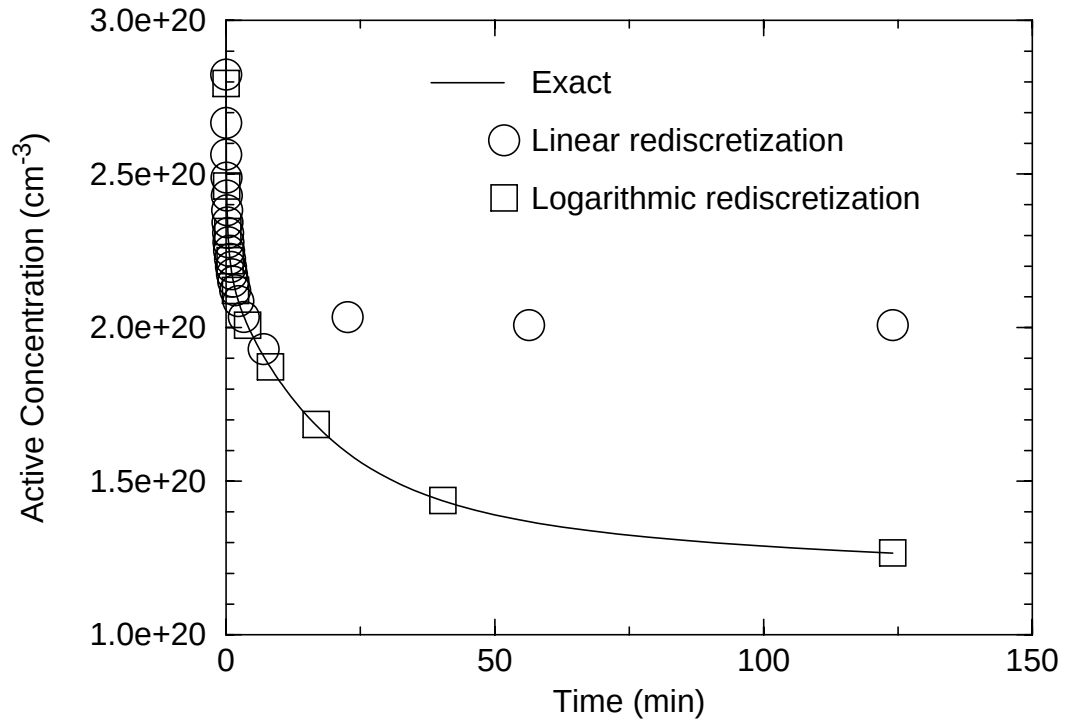


Figure 6.7 Comparison of the active concentrations for $\Delta=20$ and $N_{\text{eq}}=195$, obtained with the (a) linear rediscretization, and (b) logarithmic rediscretization methods.

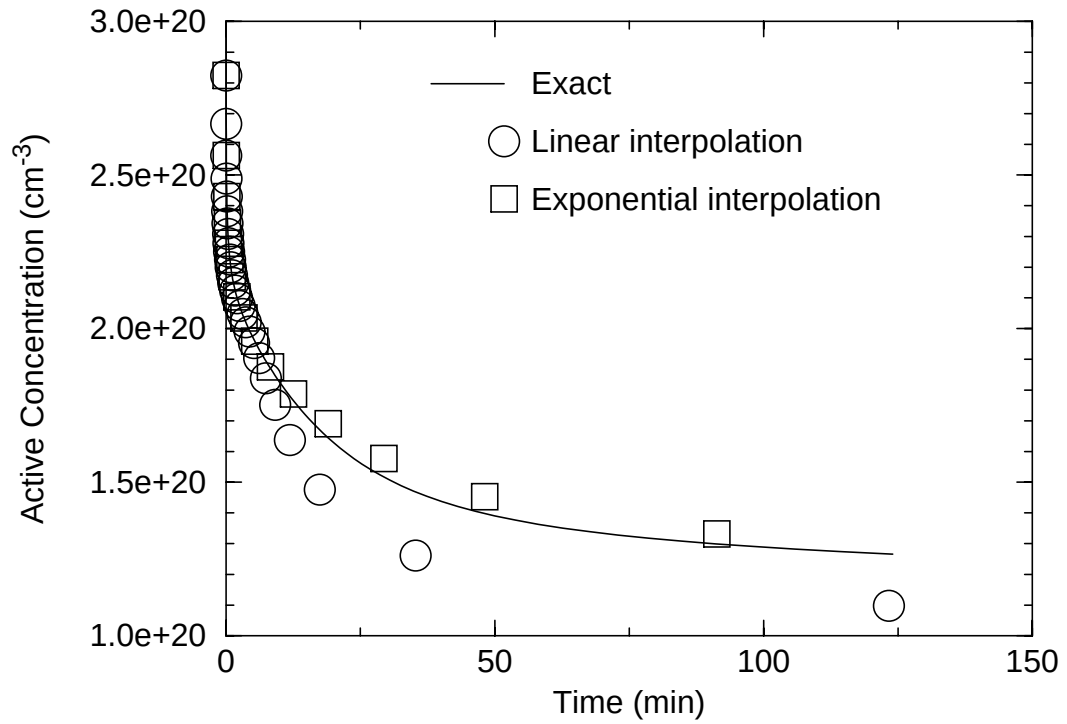


Figure 6.8 Comparison of the active concentrations for $\Delta=20$ and $N_{\text{eq}}=195$, obtained with the (a) linear interpolation, and (b) exponential interpolation methods.

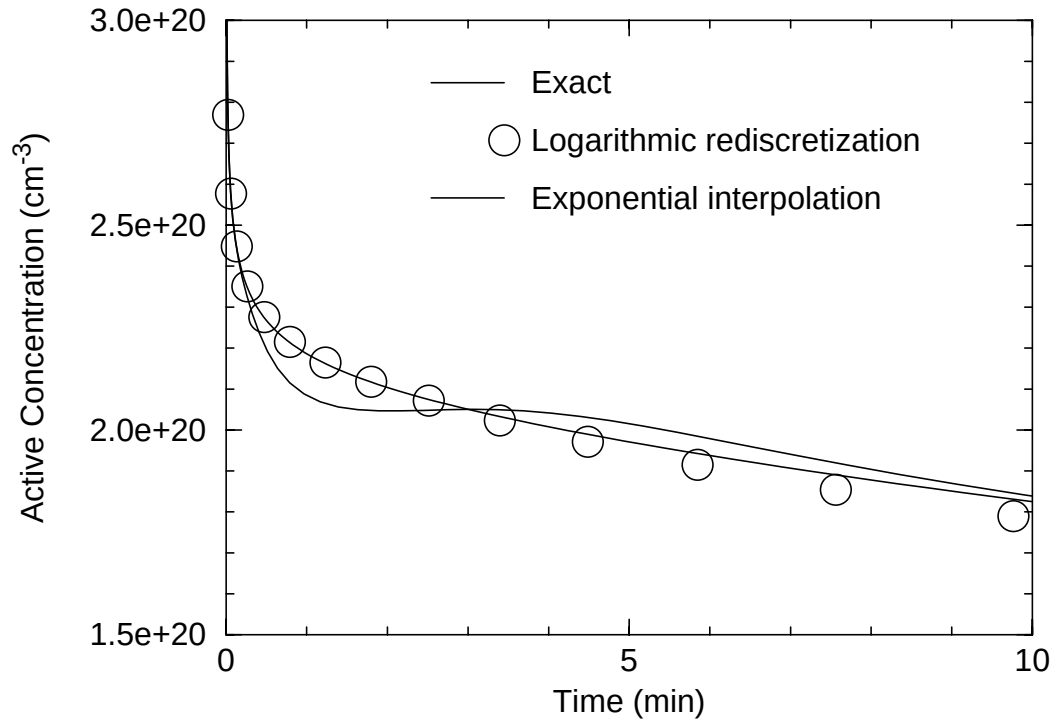


Figure 6.9 Comparison of the active concentrations for $\Delta=50$ and $N_{\text{eq}}=60$, obtained with the logarithmic rediscrctization, and the exponential interpolation methods.

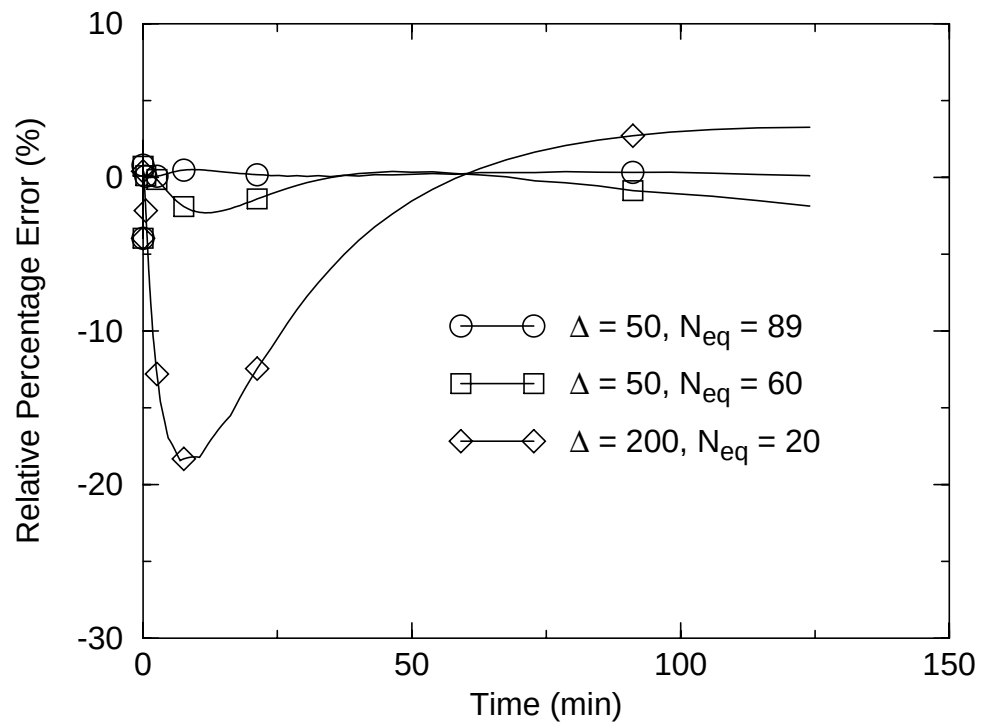


Figure 6.10 Percentage error in the active concentration obtained with the logarithmic rediscrctization method relative to the exact solution

equations. The linear interpolation method can reproduce the shape of the evolution curve, but it is much less accurate than either the exponential interpolation or the logarithmic discretization technique. As the number of equations is reduced, the linear interpolation method gets consistently more inaccurate.

Figure 6.9 shows a comparison of the logarithmic rediscretization and the exponential interpolation techniques for $N_{eq}=60$. The exponential interpolation method causes oscillations in the active concentration at small times. It is also less accurate than the logarithmic rediscretization method. So, the summation $\sum_{i=2}^{\infty} i f_i$ seems to be conserved better in the logarithmic rediscretization technique for small grids, making it more accurate in representing the active concentration.

Figure 6.10 shows the percentage error in the active concentration obtained with the logarithmic rediscretization method relative to the exact solution. For the smallest grid used in the simulations ($N_{eq}=20$), the relative error does not exceed 20%. Therefore, the logarithmic rediscretization method performs satisfactorily for the solution of the active concentration even for a reduction of 100 in the number of rate equations.

6.5 Conclusions

Various numerical methods were evaluated for the solution of the rate equations that describe the size evolution of extended defects. These methods include linear and logarithmic rediscretization, and linear and exponential interpolation. A new continuous form was derived for the rate equations. The

accuracy of the numerical methods was evaluated using the arsenic deactivation model in Chapter V. The logarithmic rediscretization method was found to be the most accurate and stable numerical technique for the representation of both the size distribution of defects and the active concentration.

CHAPTER VII

AN ARSENIC DEACTIVATION MODEL INCLUDING THE INTERACTION OF ARSENIC DEACTIVATION WITH INTERSTITIALS AND DISLOCATION LOOPS

7.1 Introduction

As mentioned in Chapter V, arsenic deactivates with vacancies. During the formation of arsenic-vacancy complexes, interstitials are injected into the bulk, and boron diffusion is enhanced underneath the arsenic layers (Figure 7.1). The reaction for the formation of arsenic-vacancy complexes can be written as:



The enhanced diffusion due these excess interstitials have been shown to affect the device characteristics significantly [35,52]. In Chapter II, several properties of the dislocation loops that are formed during arsenic deactivation were investigated. The density of atoms bound by the loops increases at higher arsenic concentrations. This explains the reduction in the boron diffusivity at higher arsenic concentrations. Dislocation loops can also indirectly influence the arsenic deactivation process by absorbing interstitials and thereby affecting reaction 7-1. In order to accurately predict the arsenic deactivation process and its effects on the

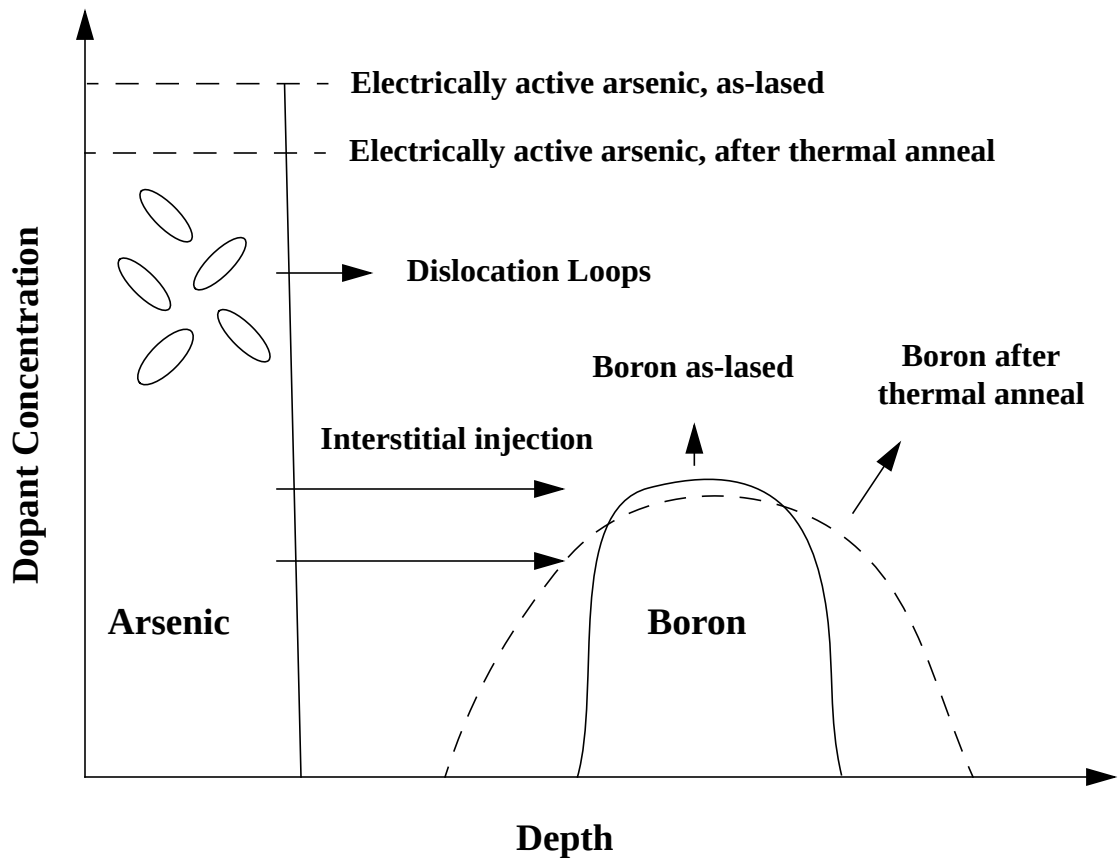


Figure 7.1 An illustration of the phenomena observed during arsenic deactivation. The samples have been laser annealed and then thermally annealed. This is the simulated structure in this chapter.

surrounding doped layers, interstitial injection and dislocation loop formation should also be included in an arsenic deactivation model.

A recent dopant precipitation model takes into account the interaction of point defects with precipitates [94]. It keeps track of the first three moments of the precipitate size distribution instead of the whole distribution. It has not been applied to a wide range of experimental arsenic deactivation data and does not include dislocation loop formation. A recently proposed oxygen precipitation model [75] takes into account the influence of point defects and bulk stacking faults on the

precipitation of oxygen. This model solves for the whole size distribution of both the oxygen precipitates and stacking faults, and is able to account for a wide range of experiments.

In this chapter, an arsenic deactivation model including the generation of interstitials and formation of dislocation loops will be presented. The model will be shown to predict several qualitative features related to the arsenic deactivation process.

7.2 Model for the Inactive Arsenic-Vacancy Complexes

The following reaction will be considered between the arsenic-vacancy complexes, substitutional arsenic, and the point defects:



where P_i is an arsenic-vacancy complex including i As atoms, and I is the silicon interstitial. It is assumed that the growth of arsenic-vacancy structures proceeds through the release of interstitials. This model is intended to be used for the laser and then thermally annealed samples. The initial conditions are taken to be the conditions just after the laser anneal. Since positron annihilation measurements suggest that there is not a significant amount of free vacancies left behind after the laser anneal [54], the free vacancies have not been considered in reaction 7-2. The surface may be a source of free vacancies during thermal annealing, but the very fast

initial deactivation of arsenic at low temperatures (500-800°C) in laser annealed samples suggests that the deactivation proceeds through bulk processes, i.e. through the generation of interstitial-vacancy pairs in the bulk [32] if the vacancy diffusivity is relatively low.

The positron annihilation experiments also show that the average number of vacancies per inactive arsenic atom is between 1/2 and 1/4. Based on EXAFS and RBS measurements, Brizard *et al.* have proposed the existence of arsenic-vacancy clusters which have a vacancy/arsenic ratio of around 1/3 [55]. In the model, this number will be assumed to be 1/4. Since all the vacancies in the arsenic-vacancy complexes are assumed to be generated through the formation of interstitial-vacancy pairs, the number of injected interstitials will be equal to the number of generated vacancies. Thus, α is taken to be 1/4.

The size evolution of the arsenic-vacancy complexes is modeled using the rate equations derived in Chapter V. The rate of change in the density of P_i is given by:

$$\frac{\partial}{\partial t} f_P(i) = J_P(i-1) - J_P(i) \quad 7-3$$

$$J_P(i) = \beta_P(i) f_P^{eq}(i) \left[\frac{f_P(i)}{f_P^{eq}(i)} - \frac{f_P(i+1)}{f_P^{eq}(i+1)} \right] \quad 7-4$$

where β_P is the forward reaction rate, and f_P^{eq} is the equilibrium concentration of i -sized arsenic-vacancy complexes. The forward reaction rate can be written as:

$$\beta_P(i) = A_P(i) \frac{D_{As}}{\lambda} f_P(1) \quad 7-5$$

$A_P(i)$ is the surface area of P_i , D_{As} is the diffusivity of arsenic, λ is the lattice spacing, and $f_P(1)$ is the substitutional arsenic concentration.

Since there is a large supersaturation of interstitials during arsenic deactivation, D_{As} should depend on this supersaturation. If the vacancy component of the arsenic diffusivity can be neglected when there is a large supersaturation of interstitials, D_{As} can be expressed as:

$$D_{As} = D_{As}^{in} f_I \frac{C_I}{C_I^*} \quad 7-6$$

where C_I is the interstitial concentration, C_I^* is the equilibrium interstitial concentration, and f_I represents the interstitial component of arsenic diffusivity.

The equilibrium ratio of the defects includes the interaction with interstitials:

$$\frac{f_P^{eq}(i+1)}{f_P^{eq}(i)} = \frac{f_P(1)}{C_{sol}} \left(\frac{C_I}{C_I^*} \right)^{-\alpha} \exp\left(\frac{W_P(i) - W_P(i+1)}{kT} \right) \quad 7-7$$

C_{sol} is taken to be the equilibrium active concentration, and W_P is the interfacial free energy. For simplicity, W_P is taken to be proportional to the surface area of the defect:

$$W_p(i) = c_1 i^{2/3} \quad 7-8$$

where c_1 is kept as a fitting parameter.

7.3 Model for Dislocation Loops

The evolution of dislocation loops can be described by the following reaction:



where L_i represents a loop containing i silicon atoms. Similar to arsenic-vacancy complexes, the size evolution of the loops is calculated using the rate equation formalism in Chapter V. Namely:

$$\frac{\partial}{\partial t} f_L(i) = J_L(i-1) - J_L(i) \quad 7-10$$

$$J_L(i) = \beta_L(i) f_L^{eq}(i) \left[\frac{f_L(i)}{f_L^{eq}(i)} - \frac{f_L(i+1)}{f_L^{eq}(i+1)} \right] \quad 7-11$$

In this case, the forward reaction rate is given by:

$$\beta_L(i) = A_L(i) \frac{D_I}{\lambda} C_I \quad 7-12$$

where D_I is the diffusivity of interstitials. Since dislocation loops grow along their edges, the sink area for the interstitials is taken to be the cross-sectional area of the surrounding edge of a loop. Assuming circular disc-shaped loops, this sink area can be written as:

$$A_L(i) = 2\pi r_L(i) b \quad 7-13$$

where r_L is the radius of the loop, and b is the magnitude of the Burger's vector representing the thickness of the loop.

The equilibrium ratio of the loops is given by:

$$\frac{f_L^{eq}(i+1)}{f_L^{eq}(i)} = \frac{C_I}{C_I^*} \exp\left(\frac{W_L(i) - W_L(i+1)}{kT}\right) \quad 7-14$$

W_L includes both strain and stacking fault energy terms [95,96]:

$$W_L(i) = \frac{\mu b^2 r_L(i)}{2(1-\nu)} \left[\ln\left(\frac{8 r_L(i)}{b}\right) - 2 + \frac{3-2\nu}{4(1-\nu)} \right] + iE_\gamma \quad 7-15$$

where μ is the shear modulus, ν is the Poisson's ratio, and E_γ is the internal energy associated with the stacking fault. Chapter II shows that dislocation loops are formed only in the arsenic layer during deactivation, suggesting a reduction in the formation energy of the loops due to the presence of arsenic. This reduction is accounted by simply multiplying $W_L(i)$ by a constant factor c_2 , which is less than unity. c_2 is kept as a fitting parameter.

7.4 Point Defect Continuity Equations

The continuity equations for interstitials and vacancies can be written as:

$$\frac{\partial C_I}{\partial t} = \frac{\partial}{\partial x} \left(D_I C_I^* \frac{\partial}{\partial x} \left(\frac{C_I}{C_I^*} \right) \right) - k_B (C_I C_V - C_I^* C_V^*) + \alpha \frac{\partial N_P}{\partial t} - \frac{\partial N_L}{\partial t} \quad 7-16$$

$$\frac{\partial C_V}{\partial t} = \frac{\partial}{\partial x} \left(D_V C_V^* \frac{\partial}{\partial x} \left(\frac{C_V}{C_V^*} \right) \right) - k_B (C_I C_V - C_I^* C_V^*) \quad 7-17$$

The first terms on the right hand side of Equations 7-16 and 7-17 represent the diffusion of the defects, while the second terms take into account the bulk recombination of interstitials with vacancies. The third and the fourth terms on the right hand side of the interstitial continuity equation represent the generation of interstitials by the arsenic-vacancy complexes, and the absorption of interstitials by the dislocation loops, respectively. N_P and N_L are the concentration of arsenic in

the arsenic-vacancy complexes, and the density of the atoms bound by the loops, respectively. They are defined by:

$$N_P = \sum_{i=2}^{\infty} i f_P(i) \quad 7-18$$

$$N_L = \sum_{i=2}^{\infty} i f_L(i) \quad 7-19$$

The interstitials satisfy the following boundary condition at the surface:

$$J_I = k_S^I (C_I - C_I^*) \quad 7-20$$

where J_I is the interstitial flux, and k_S^I is the surface recombination velocity. A similar equation can be written for vacancies.

7.5 Simulation Parameters

The equations presented in the previous sections were implemented in FLOOPS. The simulated structure is shown in Figure 7.1. The simulations involved a thermal anneal at 750°C for 2h for three different arsenic concentrations: 4.5×10^{20} , 9.1×10^{20} , and $1.9 \times 10^{21} \text{ cm}^{-3}$. The dislocation loop rate equations were solved using the linear interpolation method. The most important parameters were found to be the interface energy coefficients of the arsenic-vacancy complexes, and

the dislocation loops, c_1 and c_2 respectively, and the equilibrium interstitial concentration, C_I^* . The dislocation loop properties, such as the peak loop radius and the density of the atoms in the loops are very sensitive to c_2 and C_I^* . The enhancement in the buried boron layer diffusivity also depends on these parameters.

However, there is orders of magnitude difference in the reported values of C_I^* under intrinsic conditions [97-99]. In addition, C_I^* depends on the carrier concentration under extrinsic conditions. Since our simulations involve high concentration arsenic layers, C_I^* has to be modified to take into account this dependence, which can be expressed as:

$$C_I^* = (C_I^*)^{int} \frac{\sum_c K_I^c \left(\frac{n_i}{n}\right)^c}{\sum_c K_I^c} \quad 7-21$$

where $(C_I^*)^{int}$ is the intrinsic equilibrium interstitial concentration, K_I^c represent the equilibrium constants, and c is the charge state of the interstitials. Values for K_I^c have been extracted from the simulations of oxidation enhanced and transient enhanced diffusion of dopants under extrinsic conditions [100-102]. But, there is not a good agreement between these values. For simplicity, the interstitials are assumed to be either positively or double negatively charged. Then, Equation 7-21 can be rewritten as:

$$C_I^* = (C_I^*)^{int} \frac{K_I^+ \left(\frac{n_i}{n}\right) + K_I^- \left(\frac{n}{n_i}\right)^2}{K_I^+ + K_I^-} \quad 7-22$$

The ratio K_I^- / K_I^+ is kept as a fitting parameter, while $(C_I^*)^{int}$ is taken from Zimmermann *et al.* [97]. Finally, all the parameter values are listed in Table 7.1. The fitted parameters are shown in the first four columns. The common parameters with the model of Chapter V can be found in Table 5.1.

Table 7.1: Parameter values for simulations of arsenic deactivation

Parameter	Pre-exponential	Activation Energy (eV)
$c1$	0.3	
$c2$	0.86	
K_I^- / K_I^+	1.6×10^{-4}	
k_S^I	0.1 cm/s	
$(C_I^*)^{int}$	$1.94 \times 10^{27} \text{ cm}^{-3}$	3.835
D_I	$2.58 \times 10^{-2} \text{ cm}^2/\text{s}$	0.965
f_I	0.5	
b	3.14 Å	
μ	$7.55 \times 10^{11} \text{ dynes/cm}^2$	
v	0.3	
E_γ	0.028 eV	
$(C_V^*)^{int}$	$2.3 \times 10^{21} \text{ cm}^{-3}$	1.08
k_B	$8.16 \times 10^{-4} \text{ cm}^3/\text{s}$	3.19

7.6 Comparison with Experiments

The boron enhancement and arsenic deactivation data was taken from Rousseau *et al.* [32], and the dislocation loop data was obtained from Chapter II. Since arsenic is totally active after the laser anneal, the initial active concentration is equal to the chemical concentration. The formation of arsenic-vacancy complexes is simulated for a single arsenic chemical concentration since arsenic is homogeneously distributed. Similarly, for the interstitial concentration in the loop equations, the value in the middle of the arsenic profile is used. Although the interstitial concentration changes with depth because of surface recombination, it is fairly homogenous except very close to the surface. In addition, the cross-section TEM results of Chapter II show that dislocation loops are homogeneously distributed throughout the arsenic layer, justifying our procedure.

Figure 7.2 shows the size distribution of dislocation loops for two different arsenic concentrations. As the arsenic concentration increases, the density of the loops increases and the peak loop radius decreases. This is in good qualitative agreement with the experimental loop data. The simulations show that the initial interstitial supersaturation increases as the arsenic concentration is increased since deactivation of arsenic produces more interstitials (reaction 7-2). As a result, a higher density of loops form (reaction 7-9).

Figure 7.3 and Figure 7.4 show comparisons of the simulations with the experimental active arsenic concentration and the boron diffusivity enhancement data. The simulations predict the active arsenic concentration within 20% of the

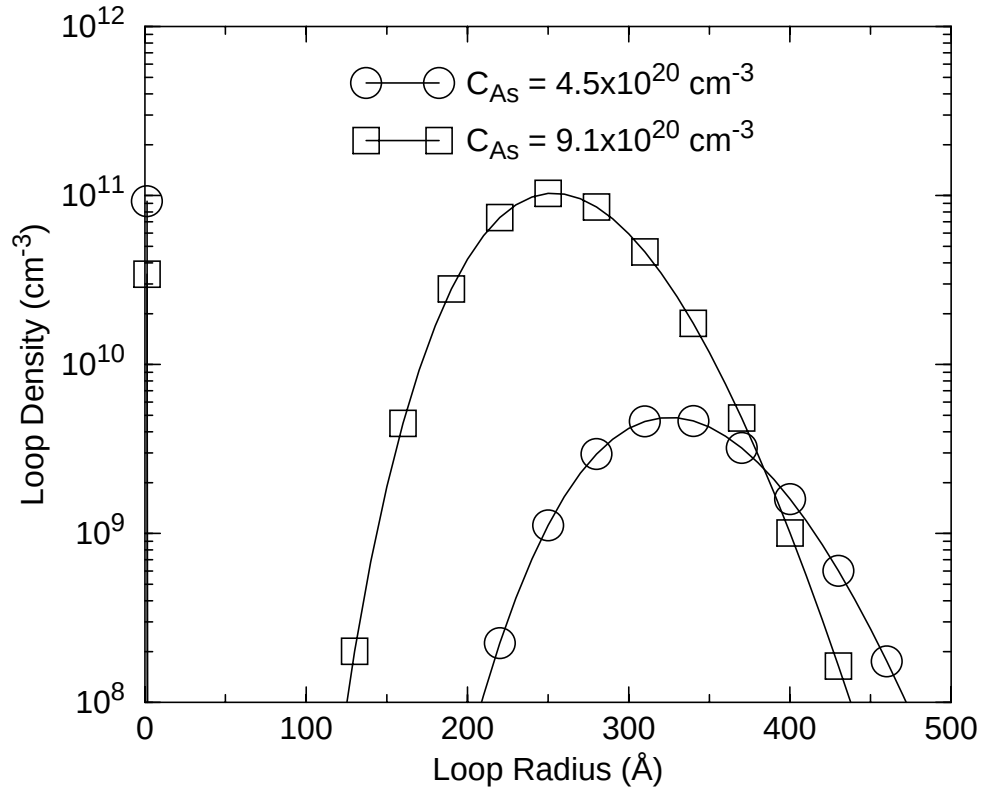


Figure 7.2 Comparison of loop size distributions for two different arsenic concentrations.

measurements. In addition, the model shows good agreement with the enhancement in boron diffusivity, which decreases with increasing arsenic concentration. Since a higher density of loops forms at the beginning of the anneal for a higher arsenic concentration, the loops capture more interstitials during the rest of the deactivation process. This results in a lower enhancement in the boron buried layer diffusivity.

Figure 7.5 and Figure 7.6 show the comparisons for the loop properties. The model completely overestimates the density of the atoms bound by the loops. This can be understood by interpreting the interstitial continuity equation (Equation 7-16) and the surface recombination term in Equation 7-20. The interstitials generated by the deactivation process can be annihilated in the bulk or at the surface, can be

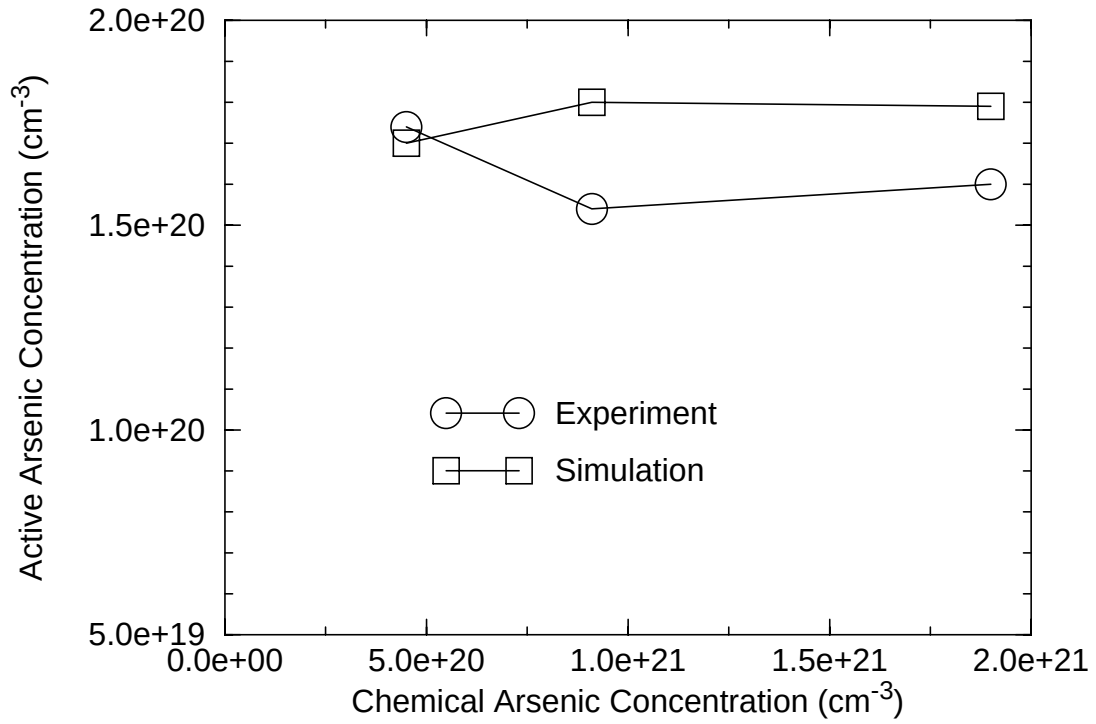


Figure 7.3 Comparison of simulations with experiments for the active arsenic concentration after the 750°C, 2h anneal.

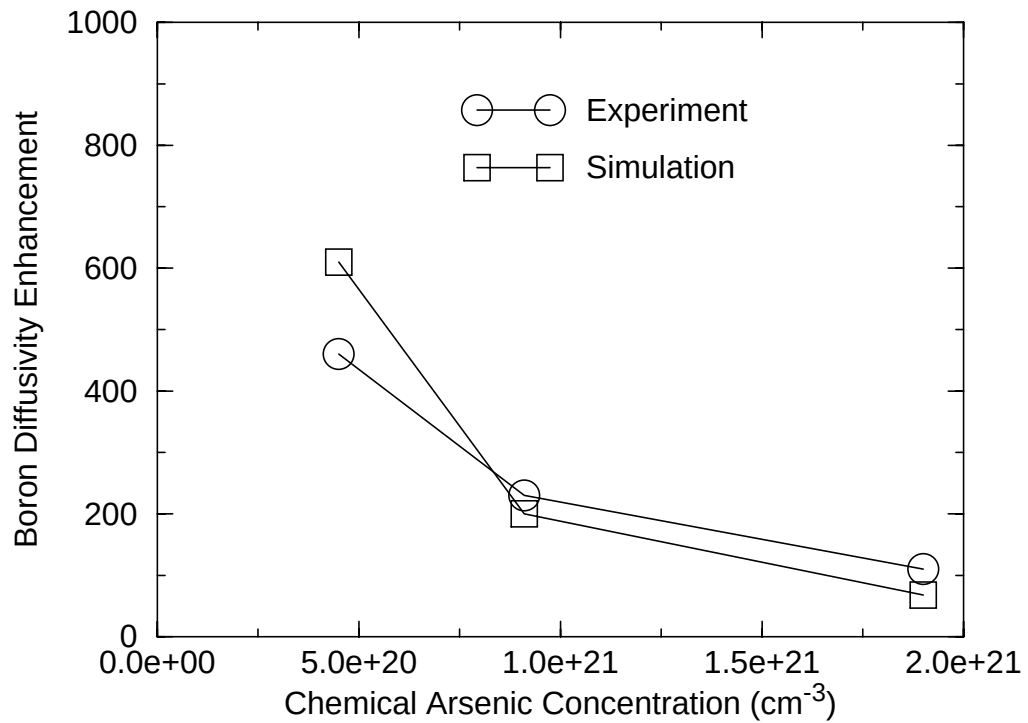


Figure 7.4 Comparison of simulations with experiments for the boron diffusivity enhancement after the 750°C, 2h anneal.

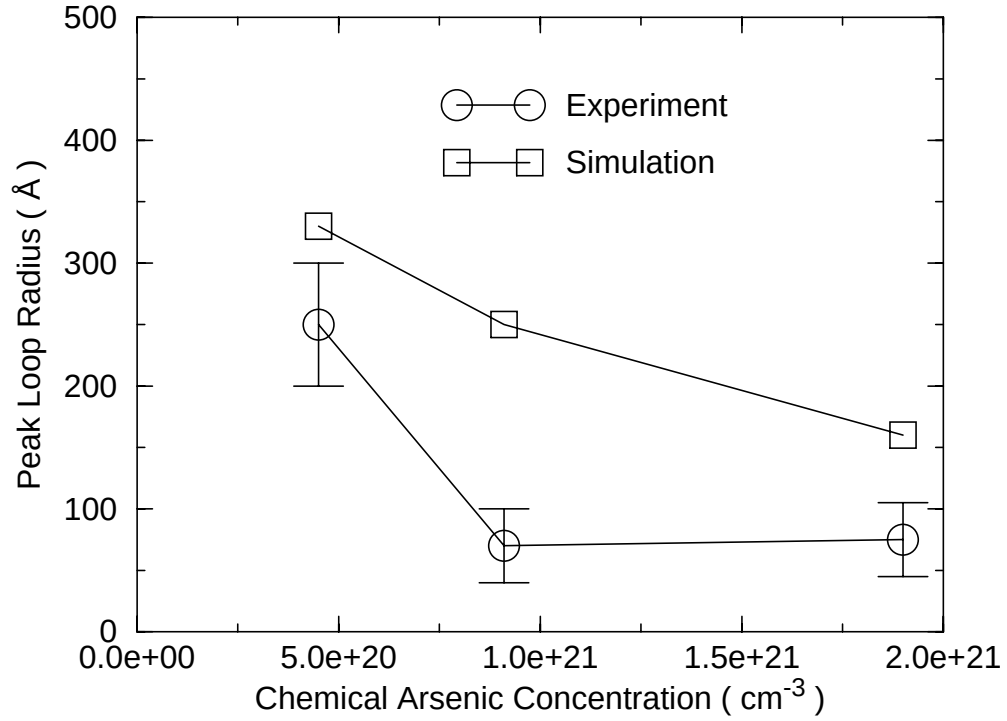


Figure 7.5 Comparison of simulations with experiments for the peak loop radius after the 750°C, 2h anneal.

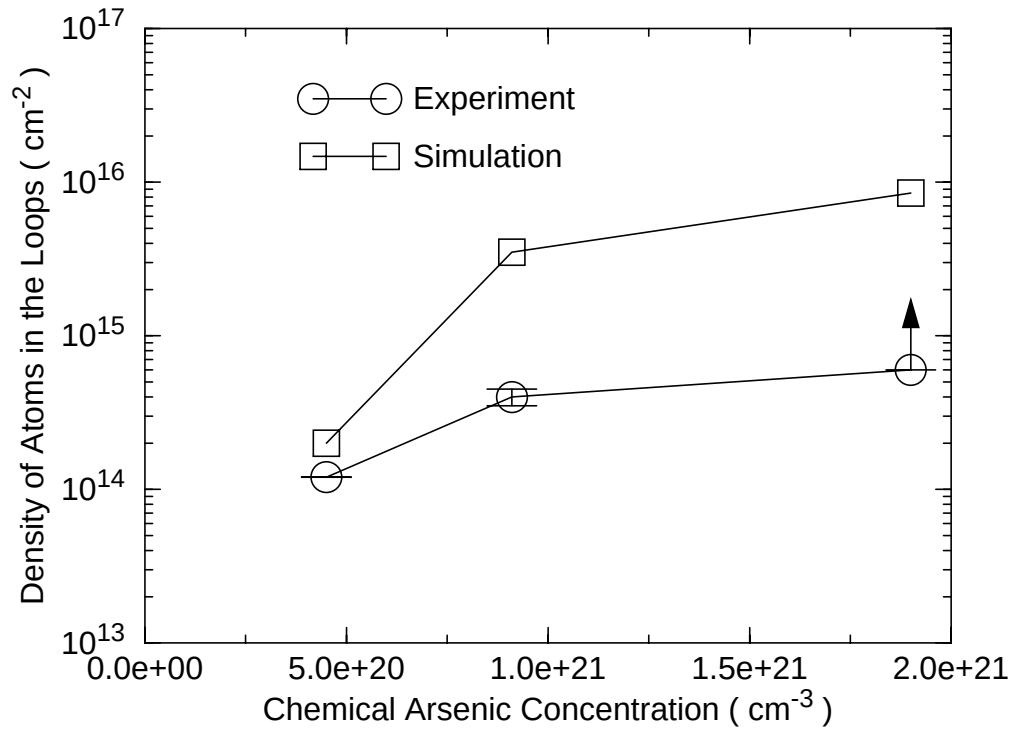


Figure 7.6 Comparison of simulations with experiments for the density of atoms bound by the loops after the 750°C, 2h anneal.

absorbed by the loops or can diffuse into the bulk. The simulations show that the diffusion flux to the bulk, which is limited by the enhancement in boron diffusivity, is negligible. The bulk recombination is also insignificant, since the vacancies are depleted very quickly at the beginning of the anneal due to a high concentration of interstitials. This leaves only the surface recombination and loop absorption terms. There is not a general agreement on the value of the recombination velocity in the literature [62,103,104]. Although a value that is much greater than the one obtained from oxidation enhanced diffusion simulations is used, the surface recombination is still negligible at the two higher arsenic concentrations. Thus, in the simulations, the loops capture most of the interstitials for these arsenic concentrations. The generated interstitial/deactivated arsenic ratio was taken to be 1/4 based on EXAFS and positron annihilation experiments. But, the experiments show that the density of atoms bound by the loops is 30-50 times smaller than the inactive arsenic concentration. This explains the discrepancy between the experiments and our simulations for the density of atoms in the loops. From a modeling point of view, this discrepancy may be minimized if a different surface recombination or the fully coupled diffusion model is used.

In order to model the arsenic deactivation better, one should understand the discrepancy between the number of atoms bound by the loops and the number of generated interstitials as suggested by the EXAFS and positron annihilation measurements. Either the recombination of interstitials or the generation of vacancies at the surface may be playing an important role during arsenic deactivation. The role of the surface on the recombination and generation of point

defects should be experimentally determined. Actually, a buried high concentration arsenic layer can be used to separate the surface from the bulk processes occurring during arsenic deactivation. Two buried phosphorus layers, one between the arsenic layer and the surface, the other deeper than the arsenic layer can be utilized to quantify the interstitial diffusion flux to the surface and to the bulk. Similarly, the vacancy fluxes can be measured with antimony buried layers. If the density of interstitials bound by the loops in the arsenic layer increases significantly, this will mean that surface has an important role during arsenic deactivation in the simulated samples.

7.7 Conclusions

An arsenic deactivation model that includes the interaction of arsenic-vacancy complexes with interstitials and dislocation loops was presented. The model shows good quantitative agreement with the experimental results of active arsenic concentration and buried boron layer diffusivity for a thermal anneal at 750°C for 2h. It is also in good qualitative agreement with the peak loop radius and the density of atoms bound by the loops. There is a big discrepancy between the simulations and the experiments for the density of atoms bound by the loops. In order to model the arsenic deactivation better, one should first understand the discrepancy between the number of atoms bound by the loops and the number of interstitials that are expected to be generated in an amount as indicated by the

positron annihilation and EXAFS measurements. The role of the surface on the recombination and generation of point defects should also be determined.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

This dissertation focused on the issues related to the analysis and modeling of arsenic deactivation in silicon. Chapter II shows the properties of the extended defects that are formed during arsenic deactivation in laser and then thermally annealed samples at 700 and 750°C. The density of the dislocation loops shows a strong dependence on the chemical arsenic concentration. As the arsenic concentration increases, more interstitials are injected during arsenic deactivation, and, therefore, a higher density of loops form. The density of atoms bound by the loops is much smaller than the inactive arsenic dose. The loops are confined in the arsenic layer, indicating that the inactive arsenic reduces the formation energy of the loops. The increase in the density of atoms bound by the loops explains the reduction in the buried boron layer diffusivity at higher arsenic concentrations. More TEM work on similar samples is necessary to further confirm these conclusions. Additional TEM studies can also be correlated to extended investigations on enhanced diffusion of boron [52].

In Chapter III, buried boron layers were used to quantify the transient enhanced diffusion after high-dose arsenic implantation. The enhancement in boron diffusivity decreases with increasing arsenic dose at 750, 900 and 1050°C. At the same time, the density of atoms bound by the loops increase, suggesting that the

dislocation loops are responsible for the reduction in boron diffusivity. Arsenic deactivation induced interstitials did not increase the transient enhanced diffusion. In order to further understand the effects of arsenic deactivation on transient enhanced diffusion, a comparison study with germanium or silicon can be done. This study may separate the effects of type-V loops from those of end-of-range loops. A better study would be to implant germanium or silicon into laser annealed arsenic samples and measure the enhanced diffusion. This way, one can change the amount of arsenic-induced interstitials and the amount of end-of-range implant damage independently of each other.

In Chapter IV, the effect of arsenic activation on vacancy population was studied using antimony marker layers. The antimony diffusivity was found to be very close to its inert value during arsenic activation in the presence of dislocation loops, indicating that there is no observable vacancy injection under these conditions. The density of atoms bound by the loops is not sufficient to absorb all the vacancies which are expected to be generated in an amount as indicated by the positron annihilation and EXAFS measurements. Other possible mechanisms that can explain the lack of vacancy injection in the presence of the loops include surface recombination, recombination with trapped interstitials generated during the deactivation anneal and absorption of vacancies by relatively more vacancy rich arsenic defects, such as As_2V clusters. On the other hand, antimony diffusion is enhanced for the same anneals when germanium is present at the surface. In the partial absence of the loops, antimony diffusion is enhanced by a factor of 1.5-2 during arsenic activation. Vacancy injection during arsenic activation as well as

non-equilibrium diffusion may explain this enhancement. In order to eliminate the effect of any trapped interstitials, this study can be repeated in samples which are not contaminated with carbon. Also, positron annihilation measurements can provide information on the vacancy/inactive arsenic ratio after partial arsenic activation.

In Chapter V, an arsenic deactivation model that takes into account the size distribution of inactive arsenic structures was presented. The rate equations that describe the evolution of the size distribution were derived from the kinetic theory and thermodynamics. The model is in good quantitative agreement with the experimental arsenic deactivation data, and successfully reproduces the rapid deactivation at the beginning and the slow deactivation after a few minutes. Although this model is quite sufficient for thermal annealing of laser annealed samples, its range of validity should be checked by comparing the model predictions with the active arsenic concentration in ion-implanted samples.

In Chapter VI, various numerical methods were evaluated for the solution of the rate equations that describe the size evolution of extended defects. These methods include linear and logarithmic rediscrretization, and linear and exponential interpolation. A new continuous form for the rate equations was derived. The accuracy of the numerical methods was evaluated using the arsenic deactivation model in Chapter V. The logarithmic rediscrretization method was found to be the most accurate and stable numerical technique for the representation of both the size distribution of defects and the active concentration. Higher order discrretization methods can increase the accuracy of the simulation [105].

Chapter VII presented an arsenic deactivation model that includes the interaction of arsenic-vacancy complexes with interstitials and dislocation loops. The model shows good quantitative agreement with the experimental results of active arsenic concentration and buried boron layer diffusivity as a function of chemical arsenic concentration for a thermal anneal at 750°C for 2h. It is also in good qualitative agreement with the peak loop radius and the density of atoms bound by the loops. However, there is a big discrepancy between the simulations and the experiments for the density of atoms bound by the loops. In order to model the arsenic deactivation better, one should first understand the discrepancy between the density of atoms bound by the loops and the number of interstitials that are expected to be generated in an amount as indicated by the positron annihilation and EXAFS measurements. The role of the surface on the recombination and generation of point defects should also be experimentally determined. A buried high concentration arsenic layer can be used to separate the surface from the bulk processes occurring during arsenic deactivation. Two buried phosphorus layers, one between the arsenic layer and the surface, the other deeper than the arsenic layer can be utilized to quantify the interstitial diffusion flux to the surface and to the bulk. The number of interstitials bound by the loops can then give information on how important the surface is in generating or annihilating point defects.

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BIOGRAPHICAL SKETCH

Haci Omer Dokumaci was born in Kahramanmaras, Turkey, in 1970. He received his B.S. degree both in electrical engineering and physics from Bogazici University, Turkey, in 1991 and his M.S. degree in electrical engineering from the University of Florida, Gainesville, Florida in 1993. Since then, he has been pursuing a Ph.D. degree in electrical engineering at the University of Florida. His research interests are semiconductor process modeling, simulation, and integration, with emphasis on physical models for dopant diffusion and activation.