GaAs에서의 Si의 擴散機構와 그에 聯關된 格子 缺陷 化學
(Diffusion Kinetics of Si in GaAs and Related Defect Chemistry)

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〈ABSTRACT〉

The diffusion mechanism of Si in GaAs was investigated using different diffusion sources based on the Si－Ga－As ternary phase equilibria. The Si profiles are measured with secondary ion mass spectrometry and differ significantly for sources taken from the different phase fields in the ternary phase diagram. Neutral As vacancy diffusion is proposed for acceptor Si diffusion anneals using a Ga－Si－GaAs source. Donor Si diffusion using As－rich sources and a Si－GaAs tie line source shows concentration dependent diffusion behavior. Concentration dependent diffusion coefficients of donor Si for As－rich source diffusion were found to be related to net ionized donor concentration and showed three regimes of different behavior : saturation regime, intermediate regime, and intrinsic regime. Ga vacancies are proposed to be responsible for donor Si diffusion in GaAs : $Si_{Ga}^{+}V_{Ga}^{-}$(donor Si－acceptor Ga vacancy) complex for the extrinsic regime and neutral V_{Ga} for the intrinsic regime. The Si－GaAs tie line source resulted in two branch profiles, intermediate between the As－rich and the Ga－rich source diffusion cases.

Ⅰ. INTRODUCTION

The diffusion of impurities in semiconductors is of considerable practical relevance for the processing of semiconductor devices. It is also an important indicator of the defect

structure of semiconductors, since diffusion usually proceeds via a vacancy or interstitial mechanism. The defect chemistry of compound semiconductors concerns vacancies, interstitials, antistructure, and impurity defects on both the metal and non metal sublattices. A careful analysis of the defect chemistry reveals that the concentrations of these defects depend on the chemical potentials of the host components (nonstoichoimetry), the impurities, and the electrons and holes (Fermi level). These chemical potentials are all interrelated and can be effectively controlled using a diffusion source that is defined in the sense of the Gibbs phase rule.

Silicon is an important n-type dopant in GaAs, since its low mass is conducive to implantation. It is particularly interesting since it can occupy either sublattice under appropriate conditions and can behave as a donor or an acceptor. The objective of this study is to establish the diffusion mechanism of Si in GaAs using well defined sources, related to the Ga-As-Si ternary phase diagrams. These diffusion sources fix the defect chemistry and the diffusion profiles for the respective conditions and are used to analyze the diffusion mechanism.

Ⅱ. EXPERIMENTAL PROCEDURES

Semi-insulating (100) GaAs wafers were successively cleaned in TCE, acetone, and isopropyl alcohol for 5 min each at 60℃ followed by etching about 2 microns in $NH_4OH : H_2O : H_2O$(1 : 1 : 5 by volume) for 1 min at room temperature, and oxide etching in a $NH_4F : HF$(20 : 1 by volume) buffered oxide etching solution. Ampoules were made of fused silica tubes after cleaning with detergent, acetone, and methanol, followed by a light etch in $HNO_3 : HF$ (9 : 1 by volume) and oven drying. Appropriate silicon diffusion sources were mixed and selaed in quartz ampolules in a vacuum of approximately 10^{-6} torr, and pre-annealed at the diffusion temperatures for several hours and quenched. The binary compounds, SiAs and SiA_2, needed for the Si-SiAs-GaAs and SiAs-$SiAs_2$-GaAs ternary tie triangle sources were synthesized using information on the Si-As binary phase diagram.[1] The arsenic-rich source produced n-type Si incorporation, whereas the Si-Ga-GaAs source produced p-type incorporation. Sources from the Si-GaAs tie-line were also used and produced n-type incorporation. The concentration-depth profiles of Si was determined by CAMECA secondary ion mass spectrometry(SIMS) at Charles Evans and Associates in Redwood City, California. The acceleration energy was about 4.5 keV and the primary beam current was 2.8-3.8 μA.

Ⅲ. RESULTS AND DISCUSSION

1. Arsenic-rich Source Diffusion

Figure 1 is an isothermal section of the Si-Ga-As ternary phase diagram for temperatures below 900℃. The As-rich sources from tie-triangle regions Ⅲ and Ⅳ(Si-SiAs-GaAs and SiAs-$SiAs_2$-GaAs) produce steep bell shaped profiles, typical of concentration-dependent diffusion. Fig. 2 shows 900℃ diffusion profiles for 1, 4, and 9 hours using a region Ⅲ preannealed diffusion source of Si-SiAs-GaAs. Diffusion profiles of Si from region Ⅳ source(SiAs-$SiAs_2$-GaAs mixtures) are similar to the source Ⅲ pro-

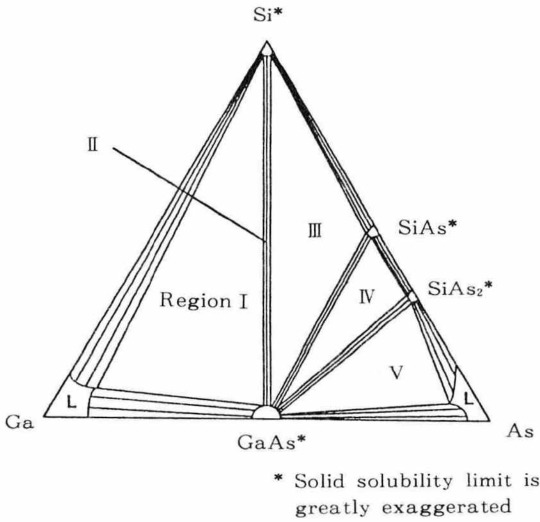


Fig. 1 : Isothermal section of Si−Ga−As ternary phase diagram for temperatures below 900℃

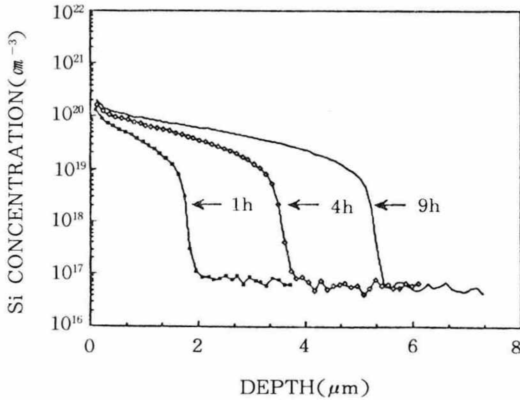


Fig. 2 : Diffusion profiles of Si at 900℃ for 1, 4, and 9 hours. Diffusion sources are from Si−SiAs−GaAs tie−triangle region.

files, but with slightly lower surface solid solubility and a shallower junction depth, as represented in Fig. 3 for a sample annealed at 900℃ for 1 hour. Even though the Ga vacancy concentration is expected to be higher in the region Ⅳ than in region Ⅲ due to a higher As activity, the decrease in the Si

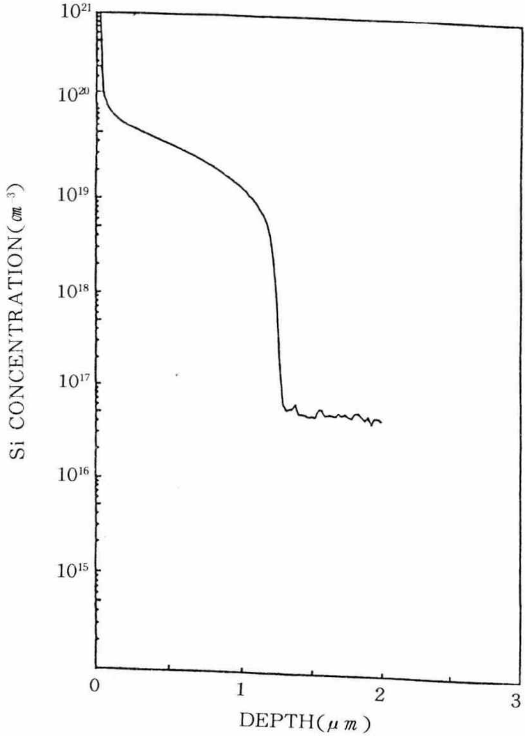


Fig. 3 : Diffusion profile of Si annealed at 900℃ for 1 hour. Diffusion source was from $SiAs-SiAs_2-GaAs$ tie−triangle region(region Ⅳ).

activity evidently causes a decrease in both the surface solid solubility and the diffusivity. The concentration dependent diffusion coefficient of Si (D_{si}) was calculated by the Boltzmann−Matano method.[2] Fig. 4 shows the variation of D_{si} with chemical concentration of Si [Si], for the diffusion at 900℃ for 1hour using a Si−SiAs−GaAs source. D_{si} is essentially constant for $[Si] \geqq 10^{19}$ $㎝^{-3}$, and decreases with [Si] for $[Si] \leqq 10^{19}$ $㎝^{-3}$. The independence of D_{si} on [Si] in the high concentration regime is seen clearly in Fig. 5.

There is evidence from the As pressure dependence that Si diffuses substitutionally in GaAs,[3]−[5] whereas Zn diffuses by an

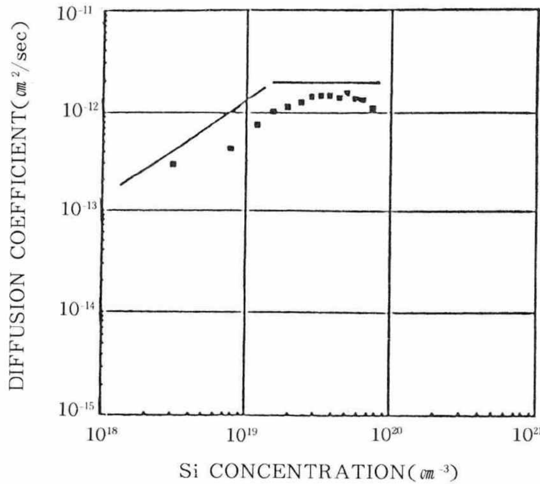


Fig. 4 : D_{Si} vs [Si], for a 900℃−1 hour diffusion anneal using a source from Si−SiAs−GaAs tie−triangle(region Ⅲ). For [Si]≥10^{19}㎝$^{-3}$, D_{Si} becomes constant, and decreases with [Si] for [Si]≤10^{19}㎝$^{-3}$.

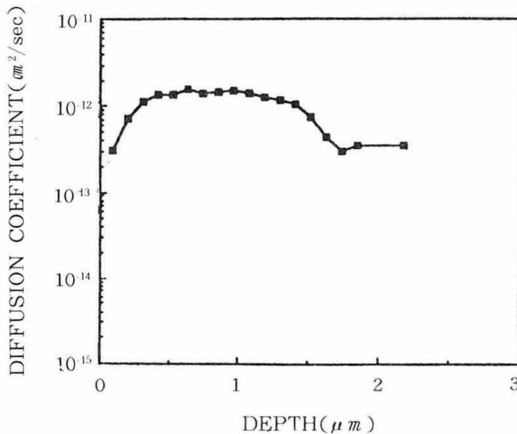


Fig. 5 : D_{Si} vs diffusion depth, x, showing constant D_{Si} for x≤1.5μm, where [Si] is above 10^{19}㎝$^{-3}$ for 900℃−1hour diffusion anneal using a source from Si−SiAs−GaAs tie−triangle(regionⅢ).

interstitial mechanism.[6]-[9] The diffusion coefficient of Si increases with $p^{\frac{1}{4}}_{As_4}$, whereas, that of Zn decreases by the same power.[3] Increasing the As vapor pressure enhances the Ga vacancy concentration which shifts Zn to substitutional sites where it is much less mobile, whereas the diffusion of Si increases with As pressure via the enhanced Ga vacancy concentration. The activation energy for the diffusion coefficient of Si in ths saturation regime (D_{fast}), 2.82eV(Fig. 6), is consistent for a substitutional diffusion mechanism.[10] The concentration dependence of Si diffusivity is discussed in terms of charged vacancies in the next section, assuming a substitutional−vacancy mechanism.

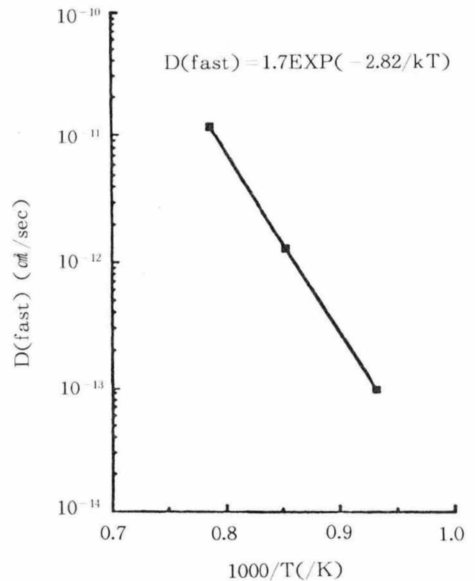


Fig. 6 : D_{fast} with respect to 1/T for temperature range between 800 to 1000℃ for 1 hour anneals using Si−SiAs−GaAs source. D_{fast} is the diffusion coefficient in the saturation regime. The activation energy is 2.82eV and is in the range for the substitutional diffusion mechanism.

2. Diffusion Mechanism of Si Under As−rich Condition

To analyze the dependence of the diffusion

coefficient of Si on the Si concentration, we consider the influence of the Si concentration on the concentration of charged vacancies and the related expression for the effective diffusion coefficient. Electrically active dopants influence the Fermi level and enhance (or depress) the concentration of charged native defects by the self compensation phenomenon. It is generally accepted that Ga vacancies are deep acceptors and As vacancies are deep donors.[11] When charged defects are present, defect species of each charge state contribute to the effective diffusivity of impurities.[12] For the case of vacancy diffusion under extrinsic conditions, the effective diffusion coefficient is enhanced or retarded in comparison to intrinsic conditions,

$$D = \sum_{j=0}^{\pm r} D_i^j \frac{[V^j]_e}{[V^j]_i} \qquad \cdots\cdots\cdots\cdots\cdots (1)$$

where D^j_i is the intrinsic diffusion coefficient corresponding to the jth charge state and $[V^j]_e$ and $[V^j]_i$ are the extrinsic and intrinsic vacancy concentrations of the jth charge state, respectively. The ionized vacancy ratios can be determined using the law of mass action with self compensation models and can be related to the extrinsic carrier concentrations :

$$D = D_i^0 + D_i^+\left(\frac{p}{n_i}\right) + D_i^{2+}\left(\frac{p}{p_i}\right)^2 + D_i^-\left(\frac{n}{n_i}\right) + D_i^{2-}\left(\frac{n}{n_i}\right)^2 + \cdots\cdots\cdots\cdots\cdots (2)$$

$$= D_i^0 + \sum_{j=\pm 1}^{\pm r}\left[D_i^{|j|+}\left(\frac{p}{p_i}\right)^j + D_i^{|j|-}\left(\frac{n}{n_i}\right)^{-j}\right]$$

$$\text{for } j \begin{cases} >0 \ \textit{for } p-type \\ <0 \ \textit{for } n-type \end{cases} \qquad \cdots\cdots\cdots\cdots (3)$$

for charged vacancies up to $\pm r$ states, where r is positive integer, $|j|$ is absolute value of j, $n(n_i)$ and $p(p_i)$ are extrinsic(intrinsic) electron and hole concentrations, respectively. D_i^0 is the intrinsic diffusion coefficient corresponding to neutral vacancies which is constant at a fixed temperature. Positively charged vacancies are enhanced for p-type doping and positive values of j are used in the summation in Eqn. 3, whereas n-type doping conditions enhance the concentrations of negatively charged vacancies and negative values of j are used. The contributions of the charged vacancies to the effective extrinsic diffusion doefficient are a function of the carrier concentration. The correlation factor and the field enhancement factor have been neglected in the above equations. For diffusion of donor Si from an As-rich source with singly ionized gallium vacancies, Eqn. 2 becomes :

$$D_e = D_i^0 + D_i^-\left(\frac{n}{n_i}\right) \cdots\cdots\cdots\cdots (4)$$

For these assumptions, the diffusion coefficient of Si under extrinsic n-type conditions is proportional to the electron concentration, n. It is shown below that D_{Si} is approximately proportional to n over the extrinsic region, and is constant for the intrinsic region and the region of saturated electron concentration. To proceed with the analysis, the relationship between the chemical concentration of Si (C) and the electron concentration due to C must be established. The electron concentration for the case of heavy n-type doping is known to saturate, and is about $4\times10^{18}cm^{-3}$ at 900°C[4] Deal *et al.* provide the following empirical expression for activation efficiency, ε, for Si in GaAs : [13]

$$\varepsilon = \frac{1}{\{1+(\gamma C)^{\beta}\}} \qquad \cdots\cdots\cdots\cdots\cdots (5)$$

where the activation efficiency is the fraction of Si that is ionized donor, C is the chemical concentration of Si, and γ and β are

temperature dependent constants given by :

$$\gamma = 0.038\exp\left(\frac{3500}{T}\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots (6)$$

$$\beta = 1.2 \times 10^{-24}\exp\left(\frac{14600}{T}\right) \quad \cdots\cdots\cdots (7)$$

where T is absolute temperature. Fig. 7 shows the relative values of C and the calculated room temperature net electron concentration (n) for a 1 hour anneal (here n equals the net ionized donor concentration, N_D^+) as a function of depth. At 900°C, the intrinsic electron concentration in GaAs(n_i) is about 3×10^{17} cm^{-3}[10], and above that concentration up to the saturation limit value of $n=4\times10^{18}$ cm^{-3}, D_{Si} is approximately proportional to the net ionized donor concentration(Fig. 8). Since the electron concentration, n, is equal to n_i for $N_D^+ < n_i$, and equal to N_D^+ for $N_D^+ > n_i$, D_{Si} is approximately proportional to n over the whole range. The concentration dependence of Si diffusion for the extrinsic region is therefore consistent with a V_{Ga}^- diffusion mechanism, in accord with Eqn. 4.

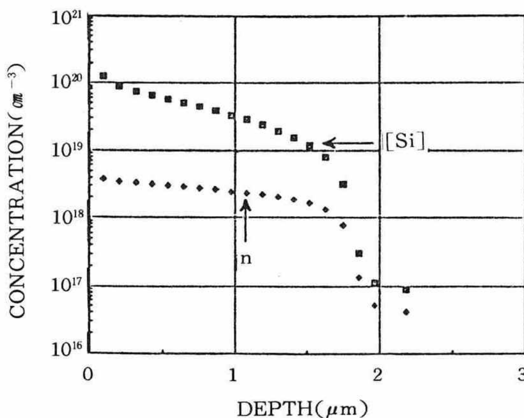


Fig. 7 : Comparison between chemical concentration, C, and calculated room temperature electron concentration, n, with respect to depth, for 900℃−1hour diffusion from Si−SiAs−GaAs source.

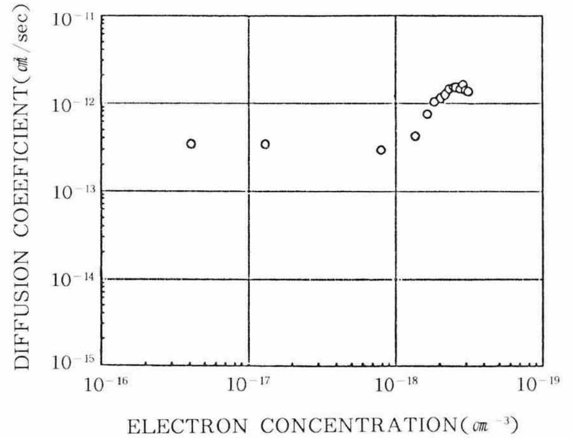
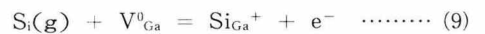


Fig. 8 : The dependence of the diffusion coefficient of Si, D_{Si}, on the calculated room temperature net electron concentration, n, for source Ⅲ diffusion. D_{Si} is constant for intrinsic and saturation regime and approximately proportional to n in intermediate regime.

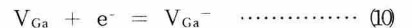
With equilibrium As−rich ternary diffusion sources, there are fluxes of both Si and Ga vacancies from the surface according to the following equilibrium at the surface :

$$\frac{1}{4}As_4(g) = As_{As} + V^0_{Ga} \quad \cdots\cdots\cdots\cdots (8)$$



$$S_i(g) + V^0_{Ga} = Si_{Ga}^+ + e^- \quad \cdots\cdots\cdots (9)$$

where V^0_{Ga} is a neutral Ga vacancy. The electron concentration increases with increasing Si concentration in accord with Eqn. 9 which, in trun, increases $[V_{Ga}^-]$ by the reaction given in Eqn. 10.



$$V_{Ga} + e^- = V_{Ga}^- \quad \cdots\cdots\cdots\cdots\cdots (10)$$

Both Ga vacancies and Si are introduced at the surface and diffuse into the host. When both of these are in sufficiently high concentration, a $Si_{Ga}^+V_{Ga}^-$ complex may form :

$$Si_{Ga}^+ + V_{Ga}^- = Si_{Ga}^+V_{Ga}^- \quad \cdots\cdots\cdots (11)$$

The Coulombic attraction between Si_{Ga}^+ and

V_{Ga}^-, which can be the nearest neighbors on the diffusion plane (*i. e.*, {100} in this study), is considered to be sufficient for weak binding of the complex. The diffusivity of the complex is expected to be much faster than pure substitutional diffusion of Si, since Ga vacancies are always available for exchange with Si. As the Si concentration decreases inside the bulk, the equilibrium in Eqn. 11 is shifted to the left, with slower pure substitutional diffiusion in this regime, as is observed in the present study.

In summary, D_{Si} is constant for $C < n_i$, proportional to n for $C > n_i$, and again constant at high concentrations where n saturates. A $Si_{Ga}^+V_{Ga}^-$ complex formation is proposed as a fast diffusing species in the high Si concentration regime.

3. Gallium-rich Source Diffusion

In contrast to the As-rich diffusion conditions, Si diffusion profiles for p-type sources (source I) are close to ideal complementary error function profiles, as is seen from a 900℃-1hour diffusion profile shown in Fig. 9. D_{Si} is almost constant for the profile, and is approximately 3×10^{-13}㎠/sec. From Eqn. 2, the independence of the diffusion coefficient on the carrier concentration, observed for the Si-Ga-GaAs tie-triangle region, implies the diffusion of neutral As vacancies, namely V^0_{As} ; Si as an acceptor does not appear to produce any significant concentration of compensating charged As vacancies. Information on the energy levels of As vacancies in the band gap is needed to confirm this proposal.

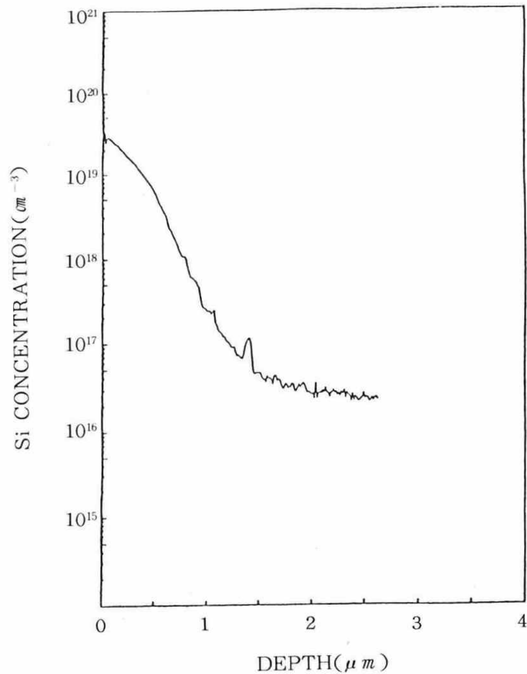


Fig. 9 : Diffusion profile of Si after 900℃-1hour anneal using Ga-rich source of Ga : Si : As = 1.28 : 1 : 1 in mole ratio. The profile is close to an erfc curve.

4. Si-GaAs Tie Line Source Diffusion

The diffusion profiles of Si from the sources on the tie line between Si and GaAs show a diffusion profile that can be represented by two superposed profiles(two-branches). Fig. 10 represents the typical shape of the diffusion profiles arising from source II, Si-GaAs mixtures. Near the surface, the shape of the profiles are close to the erfc behavior with approximately the same diffusion coefficient of Si(about 3×10^{-13}㎠/sec for 900℃-1hour diffusion) as the Ga-rich source diffusion conditions. Inside the bulk where Si concentration reaches approximately 10^{19}㎝$^{-3}$, the profile becomes steep, representative of n-type behavior. Van der pauw measurement of the samples showed overall n-type. The possible explanation for the observations

may be that this type of source provides in-diffusion of both Ga and As vacancies. At the surface, this type of source may not provide a sufficiently high As vapor pressure, so that the As vaporizes producing As vacancies near the surface. Inside the bulk, Ga vacancy diffusion is dominant since Ga vacancies diffuse faster than As vacancies.[14]

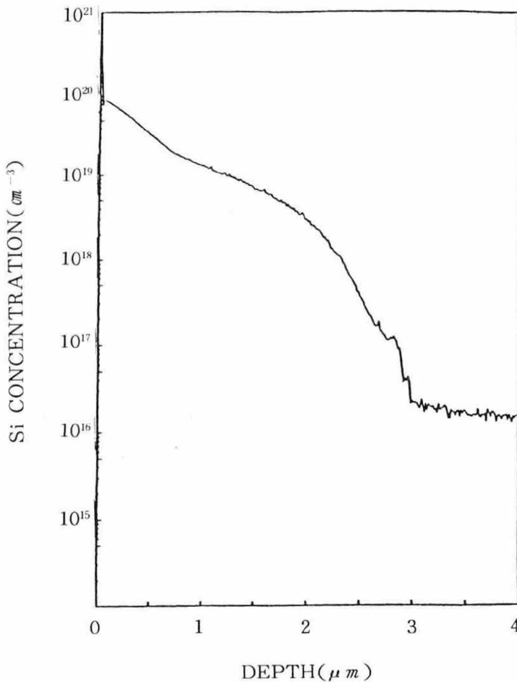


Fig. 10 : Diffusion profile of Si after 900℃-1hour anneal using a source from the tie line Si-GaAs ; the source composition was Si : GaAs=1 : 1 in mole ratio.

Ⅳ. SUMMARY & CONCLUSIONS

The diffusion of Si in GaAs was studied using different diffusion sources based on the Ga-As-Si ternary phase diagram. Diffusion of Si from As-rich sources results in donor behavior for Si with three different regimes for the diffusion behavior of Si related to the net electron concentration, n : at high Si concentrations (saturation regime, above $5\times10^{18}cm^{-3}$), n is saturated and D_{Si} attains a constant maximum value ; for intermediate Si concentrations (extrinsic regime between $8\times10^{17}cm^{-3}$ and $5\times10^{18}cm^{-3}$), D_{Si} is approximately proportional to n ; and for low Si concentration(intrinsic rigime below $8\times10^{17}cm^{-3}$), D_{Si} is constant with n the intrinsic value. A $Si_{Ga}{}^{+}V_{Ga}{}^{-}$ complex is proposed as the species responsible for donor Si diffusion. A Ga-rich source incorporates Si as a net acceptor and the diffusion profiles result in concentration independent diffusion coefficients. A neutal As vacancy model is proposed for acceptor Si diffusion. A Si-GaAs tie line source develops profiles that may be represented with two branches ; near the surface, profiles are similar to Ga-rich source diffusion ; and deeper, profiles are similar to As-rich source diffusion.

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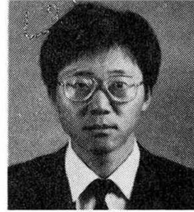

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