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Application of Watkins' Model of Phosphorus- and Arsenic-Vacancy Pairs to the Interstitialcy-Diffusion of Phosphorus and Arsenic in Silicon

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1. Introduction

Group V impurities in silicon are located at substitutional sites. Therefore, their diffusion is assisted by vacancies or self-interstitials located at the impurities' nearest neighbour sites. These are called the vacancy mechanism and the interstitialcy mechanism. In general, these two mechanisms are different. The purpose of this study is to apply the pair diffusion model of the vacancy mechanism to the interstitialcy mechanism of impurity diffusion.

2. Diffusion of Group V Impurities and Impurity-Vacancy Pairs

In 1964 and 1968, Watkins et al. [1,2] obtained the migration energy of group V impurity-vacancy pairs in Si, $E^{\mathrm{m}}_{\mathrm{pair}}$. In 1969, Hirata et al. [3] obtained the activation energy for annealing of the pairs, $E^{\mathrm{a}}_{\mathrm{pair}}$, which is nearly equal to $E^{\mathrm{m}}_{\mathrm{pair}}$. They also obtained the lower limit (LL) of the binding energy between the impurity and the vacancy, $E^{\mathrm{bLL}}_{\mathrm{pair}}$. In 1971, Ghoshtagore [4] obtained the activation energy for diffusion of impurities, $E^{\mathrm{D}}_{\mathrm{imp}}$. In 1973, Yoshida and Hasiguti [5] obtained the vacancy formation energy, $E^{\mathrm{f}}_{\mathrm{V}}$, from the study of dissociative diffusion of Ni in Si. These are shown in Table I.

3. Pair Diffusion Model of the Vacancy Mechanism

In 1973, by studying the diffusion of group V impurities via the vacancy mechanism, Yoshida and Hasiguti [5] obtained eq. (1) and proposed the pair diffusion model of the vacancy mechanism, namely the impurities diffuse only as impurity-vacancy pairs,

$$E^{\mathrm{D}}_{\mathrm{imp}} = E^{\mathrm{m}}_{\mathrm{pair}} + E^{\mathrm{f}}_{\mathrm{V}} - E^{\mathrm{b}}_{\mathrm{pair}} . \qquad (1)$$

The value of $E^{\mathrm{b}}_{\mathrm{pair}}$ of eq. (1) obtained from the values of $E^{\mathrm{D}}_{\mathrm{imp}}$, $E^{\mathrm{m}}_{\mathrm{pair}}$, and $E^{\mathrm{f}}_{\mathrm{V}}$ in Table I is also shown in Table I. In Table I, $E^{\mathrm{bLL}}_{\mathrm{pair}} < E^{\mathrm{b}}_{\mathrm{pair}}$ is satisfied and $E^{\mathrm{b}}_{\mathrm{pair}}$ does not depend on impurity. *Statement 1*: "The value of $E^{\mathrm{b}}_{\mathrm{pair}}$ shows that we can apply Watkins's model of P-V and As-V pairs to the pair diffusion model of the vacancy mechanism of P and As diffusion."

Table I. $E^{\mathrm{m}}_{\mathrm{pair}} \approx (E^{\mathrm{a}}_{\mathrm{pair}})$, $E^{\mathrm{bLL}}_{\mathrm{pair}}$, $E^{\mathrm{b}}_{\mathrm{pair}}$, and $E^{\mathrm{D}}_{\mathrm{imp}}$ in eV, and $f^{\mathrm{I}}_{\mathrm{imp}}$. $E^{\mathrm{f}}_{\mathrm{V}} = 4.24\,\mathrm{eV}$ [5]

Impurity-vacancy pair				Impurity diffusion		
	$E^{\mathrm{m}}_{\mathrm{pair}} \approx (E^{\mathrm{a}}_{\mathrm{pair}})$	$E^{\mathrm{bLL}}_{\mathrm{pair}}$	$E^{\mathrm{b}}_{\mathrm{pair}}$		$E^{\mathrm{D}}_{\mathrm{imp}}$	$f^{\mathrm{I}}_{\mathrm{imp}}$
(PV)	0.93[1] (0.94[3])	1.04[3]	1.87[5]	P	3.30[4]	0.6 – 0.8 [7] 0.86 – 0.96 [8,9]
(AsV)	1.07[2] (1.07[3])	1.23[3]	1.87[5]	As	3.44[4]	0.6 [7]
(SbV)	1.29[2] (1.28[3])	1.44[3]	1.88[5]	Sb	3.65[4]	0.015 [10]
(BiV)	(1.46[3])	1.64[3]	1.85[5]	Bi	3.85[4]	

4. Interstitialcy Mechanism of Impurity Diffusion

Extrinsic stacking faults are generated and the diffusion of P and As is enhanced by the oxidation of the Si specimen. Therefore, it has been proposed [6] that both P and As diffuse by the dual mechanism of vacancy and interstitialcy (I).

The fractions of the interstitialcy component in the diffusion of P ($f^{\mathrm{I}}_{\mathrm{P}}$) [7] [8,9], of As ($f^{\mathrm{I}}_{\mathrm{As}}$) [7], and of Sb ($f^{\mathrm{I}}_{\mathrm{Sb}}$) [10] are shown in Table I. *Statement 2:* "Based on these, it has been concluded [7-9] that the interstitialcy mechanism is dominant in P and As diffusion. "

5. Conclusion

Statement 1 in §3 and *Statement 2* in §4 are inconsistent. Currently, little is known about P-I and As-I pairs. Therefore, by applying Watkins' model to the interstitialcy mechanism, $E^{\mathrm{m}}_{(\mathrm{PV})^0} + E^{\mathrm{f}}_{\mathrm{V}} \approx E^{\mathrm{m}}_{(\mathrm{PI})^0} + E^{\mathrm{f}}_{\mathrm{I}}$ and $E^{\mathrm{m}}_{(\mathrm{AsV})^0} + E^{\mathrm{f}}_{\mathrm{V}} \approx E^{\mathrm{m}}_{(\mathrm{AsI})^0} + E^{\mathrm{f}}_{\mathrm{I}}$ can be obtained from eq. (1), where $E^{\mathrm{m}}_{(\mathrm{PI})^0}$ and $E^{\mathrm{m}}_{(\mathrm{AsI})^0}$ are the migration energies of P-I and As-I pairs, and $E^{\mathrm{f}}_{\mathrm{I}}$ is the formation energy of the self-interstitial.

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