

Model of High-Temperature Diffusion of Interstitial Silicon Atoms in Silicon

¹M. Jadan, ²A.R. Chelyadinskii and ²V. Yu. Yavid

¹Department of Applied Physics, Faculty of Science, Tafila Technical University,
P.O. Box 40, Al-Eys 66141, Tafila, Jordan; On Sabbatical Leave: Department of Physics,
Faculty of Science, Jazan University, P.O. Box 203, Abu Areesh, Jazan, KSA

²Department of Semiconductors Physics, Faculty of Physics, Byelorussian State University,
Pr. F. Skarina 4, 220050 Minsk, Belarus

Abstract: Problem statement: Correct description of the anomalous phenomena determined by self-point defects in implanted silicon desires knowledge of their properties. Interstitial Si atoms themselves display anomalies in their behavior and firstly in existence of two very different values of the diffusion coefficient. **Approach:** We analyzed experimental results and proposed the model of diffusion of interstitial Si atoms in silicon in two shapes. **Results:** At low saturation Si atoms diffuse as isolated atoms with a low diffusion coefficient ($\sim 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ at 900°C). At high supersaturation interstitial atoms diffused as Si-Si pairs, which had lower activation energy of migration and higher diffusion coefficients ($\sim 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$). **Conclusion:** The high diffusivity pairs were formed when two Si atoms hit in the same interstice. The atoms were not bound to one another by covalent bond. In a pair atoms were retained by a potential relief of the crystal.

Key words: Silicon, ion implantation, interstitial Si atoms, diffusion coefficient

INTRODUCTION

Point defects in silicon (vacancies and interstitials) play important role in electrical activation and diffusion of implanted impurities, in getter formation, in formation of the secondary damages. These defects substantially reduce the parameters of the devices and the device yield. The process of secondary defect formation is controlled by the diffusion of interstitial Si atoms. Nevertheless, during three decades there is not being resolved a problem on the high-temperature diffusion coefficient (D) of Si interstitial atoms in silicon single crystals. In a series of works D was defined to be $\sim 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ at 900°C ^[1-5]. In other data^[6-10] a diffusion constant was regarded to be about $10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ at this temperature. It was noted, that the large values of diffusion constants bound in experiments, where high levels of supersaturation by Si interstitial atoms had been created in a crystal. There was a suggestion, that the traps for Si atoms were responsible for the decrease of the diffusion coefficient^[10]. It was argued, that the peak D values were measured on epitaxial silicon layers, whereas in the Czochralski-grown crystals the diffusion constants had much smaller values. However, it was shown that in these most "dirty" crystals there could be large D values too^[11]. It was supposed^[11], that at high

supersaturation the traps were filled by Si atoms (saturated traps) and afterwards the diffusion constant became high. Such representation required, as the authors^[12] mentioned, the existence of time dependence of D. However, experiments^[12] have not confirmed such a dependence.

We propose a model explaining the existence of two set of values of Si interstitial atoms diffusivity in silicon lattice.

MATERIALS AND METHODS

The diffusivity of B or P in silicon is proportional to the self-interstitial concentration. This property is utilized to map the interstitial concentration as function of depth and determine the diffusion coefficient of interstitials. A source of interstitials were oxidation process or Ar^+ ion implantation^[2,9], using n- and p-type float zone <100> wafers with $\rho_0 = 10\text{-}20 \text{ Ohm.cm}$. Profiles were measured with a spreading resistance technique.

RESULTS

In Fig. 1 (curve 1) typical dependence of diffusion constant of Si atoms in silicon versus temperature D(T) in experiments with low saturation is shown^[9].

Corresponding Author: Muhanad Jadan, Department of Applied Physics, Faculty of Science, Tafila Technical University, P.O. Box 40, Al-Eys 66141, Tafila, Jordan; On Sabbatical Leave: Department of Physics, Faculty of Science, Jazan University, P.O. Box 203, Abu Areesh, Jazan, KSA Tel :+966551569536

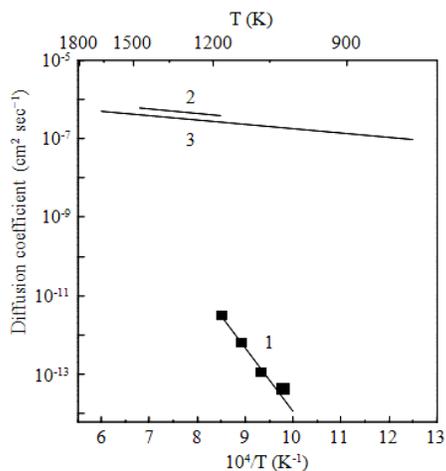


Fig. 1: Temperature dependencies of a diffusion constant of Si interstitial atoms in silicon. (1): Low saturation^[9]; (2 and 3): High supersaturation^[1,2]

In this case, the diffusion constants are not high and the steep dependence of diffusion constant on temperature is observed. At change of temperature on 200°C coefficient D varies on two orders of magnitude. Naturally, it is usual temperature dependence of diffusion constant for elements of medial atom masses in silicon^[13].

The curves 2 and 3 in Fig. 1 show dependence D(T) in silicon crystals with strong supersaturation by Si interstitial atoms^[1,2]. In this case D has high values (~10⁻⁷ cm² sec⁻¹) and very feebly depends on temperature. At change of temperature on 300°C the diffusion constant varies less, than twice. Determined from the curves D(T) activation energies of Si atoms diffusion for cases of weak and strong saturation differ practically on the order of magnitude.

DISCUSSION

The experimental results on a diffusion of Si interstitial atoms can be compared with results on a diffusion of implanted phosphorus. It was ascertained that implanted phosphorus in silicon had not only high diffusion constant, but with that the effective diffusion coefficient did not depend on temperature at rapid thermal annealing^[14]. These anomalies were explained with the help of a diffusion pair from P and Si atoms in the same interstice, which were not bound to one another by a covalent bond^[15].

By analogy with implanted phosphorus we believe that the accelerated diffusion of Si atoms is determined by diffusion of them, integrated in a pair Si-Si.

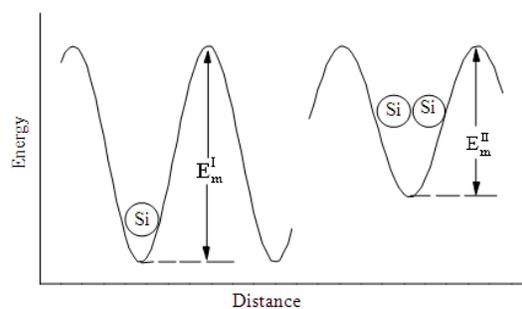


Fig. 2: An energy barrier for migration in silicon lattice of interstitial Si atoms E_m^I and Si-Si pair from interstitial silicon atoms E_m^{II}

This pair is formed at hit in the same interstice of two Si atoms at their high supersaturation. It is not difficult to estimate that at Si interstitial atoms concentration of 10²⁰ cm⁻³ concentration of randomly formed pairs is about 10¹⁸ cm⁻³. The interstitial atoms in the pair are not bound to one another by chemical covalent bond. The existence of the Si-Si pair is determined by a potential relief of the crystal (Fig. 2). In this scheme the quantity of a barrier for migration of an isolated Si atom is equal E_m^I , for the Si-Si pair- E_m^{II} . We believe that $E_m^{II} < E_m^I$.

But what is the reason of the lower barrier E_m^{II} for a pair in comparison with barrier E_m^I for alone Si atom? A series of interstitial centers (Si-P6^[16], Si-B3^[17], Si-A5^[18], Si-O2^[19], G-25^[20]) of a radiation origin is known in silicon. The interstitial Si atom is covalently bound to the lattice atoms in these centers. These centers have particular, referenced for each of them, temperature stability limit. But in the literature there are no data to believe that our interstitial Si atom, diffusing at high temperatures, is covalently bound to a lattice. Placed in an interstice the Si atom, elastically interacting with lattice atoms, locally distorts a potential relief of a crystal. This elastic interaction determines its standing in an interstice and quantity of the barrier E_m^I . If two Si atoms are located in the same interstice, the distortion of potential will be more considerable. The elastic interactions of two interstitial Si atoms with lattice atoms lower depth of the potential well in comparison with alone atom. It is schematically shown in Fig. 2.

When the Si-Si pair gains from lattice energy above the barrier E_m^{II} , it can jump into a neighboring interstice as a whole or the Si atoms can hop into different interstices (decomposition of the pair), i.e. for the pair the activation energy of migration and destruction has the same value.

It is easy to show that the temperature independence of experimentally observed diffusion constant of Si interstitial atoms in a pair follows from equality of activation energies of pair migration and annealing. Let speed of generation of Si-Si pairs is equal:

$$G = K \cdot C_1^2 \quad (1)$$

Where:

C_1 = Concentration of Si interstitial atoms

K = Speed of reaction

At temperature of a diffusion T_1 the number of pairs from interstitial atoms N is equal $G\tau_1$, where

$\tau_1 = \tau_0 \exp\left(\frac{E^{an}}{kT_1}\right)$ -lifetime of a pair. The diffusion flow of Si atoms J_1 in this case is equal:

$$J_1 = D_1 \frac{dN}{dx} = D_1 \frac{d}{dx} G\tau_1 \quad (2)$$

where, $D_1 = D_0 \exp\left(-\frac{E^{dif}}{kT_1}\right)$ is diffusion coefficient of a pair at temperature T_1 . For higher temperature T_2 the flow of particles J_2 will be:

$$J_2 = D_2 \frac{d}{dx} G\tau_2 = D_1 \exp\left(\frac{E^{dif} \Delta T}{kT_1 T_2}\right) \frac{d}{dx} G\tau_1 \exp\left(-\frac{E^{an} \Delta T}{kT_1 T_2}\right) \quad (3)$$

where, k is Boltzmann constant, $\Delta T = T_2 - T_1$. The flows J_1 and J_2 are equal at equality of activation energies of diffusion E^{dif} and annealing E^{an} and by virtue of feeble temperature dependence D_0 and τ_0 in comparison with temperature dependence of the exponential terms in D and τ ^[21]. As a result, the experimentally observed diffusion constants of Si atoms should be independent on temperature.

On experiment, nevertheless, dependence D on temperature, though feeble, exists (Fig. 1, curves 2 and 3). It is possible to explain such weak dependence D on temperatures if to take into account the contribution to a diffusion of Si isolated interstitial atoms. Their diffusion coefficient is much less than a diffusion coefficient of Si-Si pairs. But as the number of isolated interstitial atoms Si is much more than number of pairs, at high temperatures their contribution to diffusion flow becomes appreciable. Submitted on Fig. 1 (curve 3) the dependence of a diffusion constant on temperature experimentally was determined at temperatures above 1000°C and was extrapolated to

lower temperatures^[1]. Such extrapolation is not represented correct, as the contribution of isolated atoms Si in diffusion flow at low temperatures becomes inappreciable by virtue of low value of their diffusion constants.

It must be pointed out that as the Si atoms in a pair are not bound to one another by chemical covalent bond, the lifetime of this pair is not large and pairs do not make long-range migrations. But transiting small distances and collapsing, the pairs enrich this area of a crystal by Si atoms. At achievement of high concentration of interstitials the pairs are formed again. Thus at high supersaturation the excess concentration of interstitials is spread in depth of a crystal with a high effective diffusion coefficient.

At low saturation, when the quantity of pairs is not great, the transport is carried out only by isolated Si atoms, for which the diffusion constant is much below and has typical temperature dependence (Fig. 1, curve 1).

CONCLUSION

The apparent two groups of the data on coefficients of a high-temperature diffusion of Si atoms in silicon, distinguished on some orders of magnitude, are caused by a diffusion of silicon in two shapes. At low saturation Si atoms diffuse as isolated with a low diffusion constant (at 900°C coefficient D about 10^{-12} cm² sec⁻¹). At high supersaturation Si atoms form an Si-Si interstitial pair, having lower activation energy of a diffusion and accordingly higher diffusion coefficient ($D \approx 10^{-7}$ cm² sec⁻¹ at 900°C).

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