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Primary defects in silicon: existence, characteristics, and their role after high fluence irradiation

S. LAZANU*, I. LAZANU[a], V. CIUPINA[b], G. PRODAN[b]
National Institute for Materials Physics, Bucharest-Magurele, POBox MG-7, Romania
[a]University of Bucharest, Bucharest-Magurele, POBox MG-11, Romania
[b]"Ovidius" University, Constantza, Romania

In this contribution, an extensive analysis of the primary defects in silicon: vacancy, interstitial and Si_{FFCD} is performed. Irradiation studies are a useful tool to study production, characteristics and annealing of defects. The experimental results obtained after high proton fluence irradiation of silicon detectors are used in this paper to understand aspects related to the existence and proprieties of primary defects. Investigations on possible differences induced by irradiation in the lattice of silicon, using transmission electron microscopy analysis, have been started and some first preliminary results are presented.

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1. Introduction

Silicon represents the most used semiconductor material and its technology has been improved very much in the last decades. Studies of intrinsic point defects in silicon have attracted a great deal of interest because of their technological importance. In contrast with other semiconductors, in Si a paradoxical situation exists: until now it is not completely established what are all primary defects and what are their properties.

In this contribution, an extensive analysis of the primary vacancy and interstitial defects is performed. A new perspective is brought by the consideration of the existence of the new type of primary defect, the fourfould coordinated defect, Si_{FFCD}, that is a configurational defect, having a different symmetry in respect to the diamond lattice structure. Irradiation studies in semiconductors are a useful tool to investigate the processes of defect production and their annealing in conditions of existence of different impurities in the material. The experimental results obtained after high proton fluence irradiation of silicon detectors are used in this paper to understand aspects related to the existence and proprieties of primary defects. Investigations on possible differences induced by irradiation in silicon lattice, using transmission electron microscopy analysis, have been started and preliminary results are presented.

2. Primary defects in silicon

2.1. Vacancy and self interstitial in silicon

The stability of crystalline silicon comes from the fact that each silicon atom can accommodate its four valence electrons in four covalent bonds with its four neighbours. The production of primary defects and the existence of impurities or lattice defects destroy the fourfold coordination.

The lattice vacancy and self interstitial are, by their nature, the simplest known defects, produced by the processes of energy transfer to the lattice, for example thermally or by irradiation with energetic particles. In thermal equilibrium the concentration of vacancies and self-interstitials is small because their formation energies are several eV.

It has been established that the structural characteristics of the "classical" vacancy are: the bond length in the bulk is 2.35Å and the bond angle – 109°. The formation energy is 3.01 eV (p-type silicon), 3.17 eV (intrinsic), and 3.14 eV (n-type).

For interstitials, different structural configurations are possible:

i) The hexagonal configuration, a sixfold coordinated defect with bonds of length 2.36 Å, joining it to six neighbours which are fivefold coordinated;

ii) The tetrahedral interstitial is fourfold coordinated; has bonds of length 2.44 Å joining it to its four neighbours, which are therefore fivefold coordinated;

iii) The split - <110> configuration: two atoms forming the defect are fourfold coordinated, and two of the surrounding atoms are fivefold coordinated;

iv) The 'caged' interstitial contains two normal bonds, of length of 2.32 Å, five longer bonds in the range 2.55÷2.82 Å and three unbounded neighbours at 3.10÷3.35 Å. The calculations [11], [12], [13] found that the tetrahedral interstitial and caged interstitial are metastable.

For interstitials, the lowest formation energies in eV are 2.80 (for p-type material), 2.98 (for n-type) and 3.31 in the intrinsic case, respectively.

In silicon the vacancy takes on five different charge states in the band gap: V^{2+}, V^{+}, V^{0}, V^{-}, and V^{2-} and the self-interstitial could exist in four charge states after some authors [1]: I^-, I^0, I^+ and I^{2+}, or in five states, after other authors [2, 3].

The charge states V^{2+}, V^+, V^0 form the so-called negative U system, caused when the energy gain of a Jahn-Teller distortion is larger than the repulsive energy of the electrons, case in which the (0/+) level is inverted in respect to (+/++) level, which is the striking consequence of the fact that the V^+ charge state is metastable.

In Tables 1a and 1b we present a compilation of experimental determinations and theoretical predictions of the energy levels in the band gap for these defects.

Table 1a: Energy levels of isolated vacancies in silicon.

Energy level [eV] / Reference		Assigned charge state
Experimental	Calculated	
$E_v + 0.05$ [4]		$V^{+/0}$
$E_v + 0.13$ [4]		$V^{2+/+}$
	$E_v + 0.36$ [5]	$V^{0/-}$
$E_v + 0.47$ [1]		Non attributed
	$E_v + 0.76$ [6]	Non attributed
$E_v + 0.84$ [1]		Non attributed
	$E_v + 0.84$ [5]	$V^{2-/-}$
$E_v + 1.01$ [7]		$V^{2-/-}$

Table 1b: Energy levels of isolated interstitials in silicon.

Energy level [eV] / Reference		Assigned charge state
Experimental	Calculated	
	$E_v + 0.12$ [6]	Non attributed
$E_v + 0.26$ [1]		Non attributed
	$E_v + 0.4$ [3]	$I^{2+/+}$
$E_v + 0.45$? [1]		Non attributed
	Ev + 0.52 [6]	Non attributed
$E_v + 0.68$ [1]		Non attributed
	$E_v + 0.7$ [3]	$I^{+/0}$ T-X cross
	$E_v + 0.76$ [2]	$I^{2+/-}$
	$E_v + 0.9$ [3]	$I^{+/0}$ T-T cross
	$E_v + 1.04$ [2]	$I^{-/2-}$

2.2. Fourfold silicon defect (Si_{FFCD})

This defect named and used in the following discussion as Si_{FFCD} (**F**our**f**olded **C**oordinated **si**licon **D**efect) was predicted theoretically by Goedecker and co-workers [8].

In the formation of Si_{FFCD} two neighbouring atoms are implied. The defect is obtained by moving atoms (rotating them) from the initial positions into others, which are more favourable energetically. For Si_{FFCD} the formation is easily understandable as a process in more steps - see Figure 1. The swinging movement of one atom excited due to thermal energy transfer, to the interaction with an irradiation field, to the interaction in the lattice with a mobile atom or defect or by another mechanism, could break only two bonds with the neighbours. If the considered atom is from the upper position in the elementary cell, it breaks only the bounds with the lower neighbours. A corresponding swing is needed for the lower atom implied. These atoms move from their initial positions, and in the final position two new bonds are formed so that in the end all atoms are again fourfold coordinated.

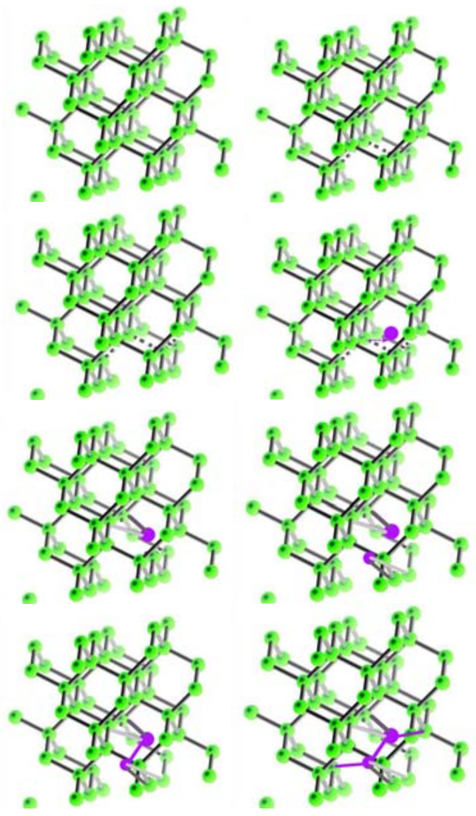

Fig. 1. Formation of the Si_{FFCD}. The process is presented as a sequence of elementary steps. Left top is the unmodified silicon lattice, and right bottom the new symmetry of the lattice after the formation of Si_{FFCD}.

The bound lengths are between 2.227 ÷ 2.47 Å and angles vary in the 97 ÷ 116° range. So, bound lengths and angles do not deviate significantly from their bulk values, but by its formation a new symmetry of the lattice is obtained. There is a pair of length 2.346 Å bonds and one of length 2.457 Å.

The formation energy is 2.45 eV (for p-type silicon), 2.42 eV (intrinsic), 2.39 eV (n-type), lower than the energy of formation of both vacancies and interstitials. Al-Mushadani and Needs [9] using *ab initio* density-functional methods investigated the energy of formation of various defects as a function of temperature. They obtained that at low temperatures the Si_{FFCD} is more stable than the vacancy and above 1049 K the stability is interchanged.

In principle this new type of defect could be characteristic for all semiconductors with diamond structure. Moreira, Miwa and Venezuela [10] found that the FFCD exists and is also stable in Ge, and the theoretical prediction is in agreement with the experimental data [11].

3. New contribution to the characterisation of primary defects in silicon

Irradiation studies in semiconductors are a useful tool to investigate defects in semiconductors, but this procedure is difficult to be used due the incomplete knowledge of the processes of defect production and of their annealing in conditions of existence of different impurities in the material.

In the irradiation processes, the concentration of primary defects per unit particle fluence (*CPD*) depends on the type of incident particle and on its kinetic energy E, and on the characteristics of the semiconductor : atomic density (N), atomic number (A), threshold energy for displacements (E_d) and details on the interaction mechanism: differential cross section of the interaction between the incident particle and the nucleus of the lattice for the process or mechanism i, responsible in defect production ($d\sigma/d\Omega$), recoil energy of the residual nucleus produced in interaction i (E_{Ri}.) and Lindhard factor that describes the partition of the recoil energy between ionisation and displacements ($L(E_{Ri})$). All these dependencies are expressed in the formula:

$$CPD(E) = \frac{N}{2E_d}\int\sum_i\left(\frac{d\sigma}{d\Omega}\right)_i L(E_{Ri})\,d\Omega$$

Time dependence of defect concentrations is obtained considering the subsequent interactions of primary defects between them or with other defects and with impurities in the lattice, with their reciprocal annihilation and with the formation of "stable" defects.

The Si_{FFCD} defect has not been yet detected experimentally. This fact is not unexpected because the search for defects is always guided by theoretical predictions.

In a recent paper, Ref. [12], the authors consider that this defect is produced more abundantly in irradiation processes at high fluences of particles. Using correlated experimental information at microscopic and macroscopic level, the characteristics of Si_{FFCD} have been established. From this analysis, it has been obtained that the Si_{FFCD} defect is produced with a concentration of about 10% from all vacancies per act of interaction and is stable in time. The defect has an energy level in the band gap between $E_c - (0.46 \div 0.48)$ eV, a capture cross section between $(5\cdot\div 10)\times 10^{-15}$ cm^2 and a ratio $\sigma_p/\sigma_n = 1 \div 5$.

Despite its stability and its low energy of formation, the concentration is low in respect to the vacancy and interstitial, because to obtain this new configurational structure it is necessary that two neighbouring atoms in the lattice are simultaneously excited and jump from their usual positions.

The production of primary defects by irradiation depends on crystal orientation, on the irradiation field, on the type of particles and on their energy.

The anisotropy of the effective threshold energy in silicon at irradiation after different crystal directions is clearly observed in FZ materials. Theoretical predictions of threshold energies in silicon are controversial – see the review in Ref. [13], in conditions of lack of systematic experimental studies. The anisotropy of the threshold energy for displacements conduces to the anisotropy of primary defect production. In the present calculations we used for threshold energy values of 21 eV on <111> and 30 eV on <100>. This characteristic could be correlated with atomic surface densities of 7.8 x 10^{14} atoms/cm^2 for <111> direction and 6.8 x 10^{14} atoms/cm^2 for <100> direction. These anisotropy aspects, which affect the concentration of primary defects and further the generation rate of primary defects have been investigated; they are observable in the experimental data and a good agreement of our calculations with these data have been obtained – see Figure 2. In this figure, the dependence of the effective carrier concentration in the space charge region of silicon detectors irradiated with pions (a) and protons on two crystal orientations (b) are presented: experimental data – points, and calculations – lines. Experimental data for pions are from Ref. [14], and for protons from Ref. [15]. In the same figures, the fluence dependence of the Si_{FFCD} is also presented. A tentative explanation of these results is that terminal recoils, with energies below threshold value cannot produce vacancies and interstitials, and lose their energy in the lattice and favour the swinging movement of atoms and favour the production of Si_{FFCD}. In accord with predictions, terminal recoils will produce more FFCD along the <100> direction in comparison with <111> and this result is validated by the data in the Figure 2.

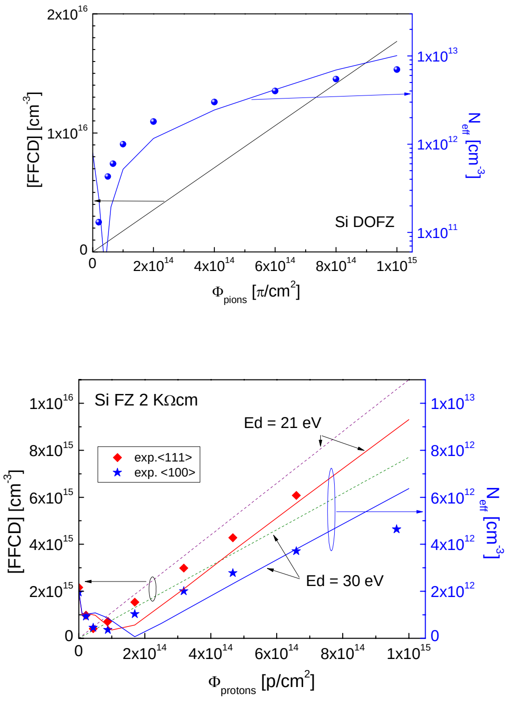

Fig. 2. Fluence dependence of the concentration of Si_{FFCD} (left axis, dotted line) and of N_{eff} (right axis) after pion (a) and proton (b) irradiation of silicon detectors

Experimental systematic studies of defect production in irradiated silicon were started, using the Transmission Electron Microscopy technique (using a Philips CM120ST electron microscope at Constantza University). In some preliminary HRTEM investigations in silicon irradiated with protons of 24 GeV/c at fluences of the order 10^{13} p/cm^2, a degradation of the monocrystalline state for spatial regions of the order of ten nm is suggested – see Figure 3. This result is in agreement with the simulations of Huhtinen [16] related to formation of clusters of vacancies after proton irradiation. These investigations are in progress.

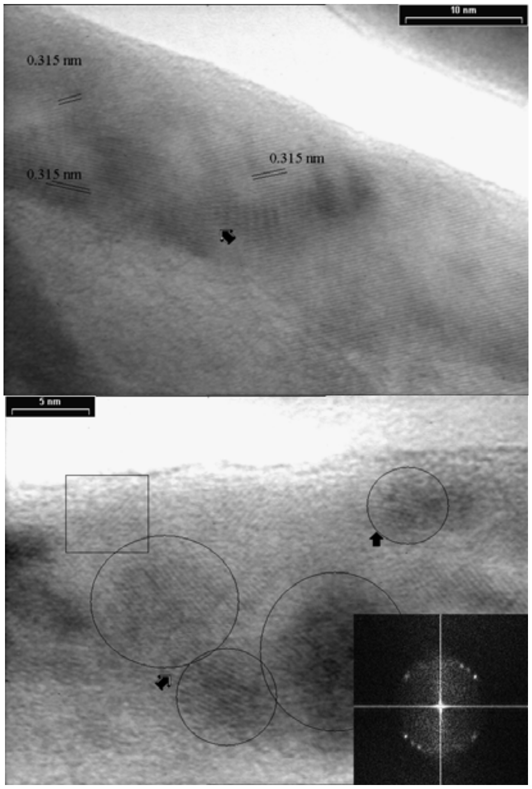

Fig. 3. HRTEM analysis on silicon irradiated with protons:of 24 GeV/c, at a fluence around 5 x 10^{13} p/cm^2. The regions with different crystalline directions are indicated. Fourier diagram suggests different orientations between the regions.

4. Summary

Starting from the fundamental role of primary defects induced by irradiation, a compilation of experimental determinations and theoretical predictions of the energy levels in the band gap has been presented. A new perspective is brought by the consideration of the existence of the new primary defect, the fourfould coordinated defect, the characteristics of which have been determined elsewhere. The influence of crystal orientation in respect to the irradiating beam is also analysed, using the anisotropy of the threshold energy.

Preliminary results on the high resolution transmission electron microscopy analysis of silicon irradiated at high fluences of protons have also been reported.

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[*] Corresponding author: lazanu@infim.ro