JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 12, December 2009, p. 2150 - 2154

Semiconductor detectors for high radiation fields: microscopic processes in materials and the control of device parameters

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The knowledge of the effects of radiation in semiconductor devices, in particular in detectors, represents an important and active field of research. The influence of isovalent impurities, carbon and germanium, on the radiation damage of silicon for detectors is investigated in the frame of a quantitative phenomenological model for defect kinetics, developed previously by the authors. The concentrations of defects induced by irradiation in materials with different doping levels are calculated, as well as the leakage current and effective carrier concentrations in p-n junction detectors made from these materials. The beneficial effect of Ge on the radiation damage of silicon is deduced.

(Received July 5, 2009; accepted November 12, 2009)

Keywords: Defects, Silicon detectors, Iisovalent impurities, Radiation field, Radiation damage

1. Introduction

Radiation damage studies in silicon have a long history, but there are still a lot of unanswered questions.

A remarkable progress has been realised in the last years in the clarification of different aspects related to the formation, evolution and characteristics of primary radiation defects in silicon. In the same time, the specific role of impurities in secondary defect formation, as well as their combined influence on the macroscopic characteristics of silicon devices operating in radiation fields is studied both as fundamental processes and for applications.

The main idea of this paper is to contribute with new steps in the understanding of the peculiarities of primary defects in semiconductors, especially in silicon, as structure and mechanisms of production and evolution, as well as to search new ways which could conduce to a decrease of the degradation. We discuss a method to diminish the concentration of defects with great impact on macroscopic characteristics of detectors by doping silicon crystals with isovalent impurities in the aim to reduce the generation rate of secondary radiation defects with deep energy levels.

C and *Ge* are completely miscible with *Si*, so that by this method, a gradual doping of the silicon crystal could be realised up to new materials as *SiC* or *SiGe*. The current explanation related to the influence of isovalent impurities is based on the role of internal local lattice strains caused by the difference in covalent radii between the matrix and the impurity atoms.

The understanding of the mechanism of primary and secondary defect production and annealing permits the control of macroscopic device parameters, essentially modified by irradiation [1].

2. Macroscopic characteristics of silicon detectors influenced by irradiation

Modelling the detector as a totally depleted p-n junction, the increase of the volume density of the leakage current, j, due to radiation damage could be approximately written (in agreement with Shockley Read Hall model), as:

$$j = q\langle v_{th}\rangle n_i[\sum_d [N_d]\sigma_d \cdot \exp\left(-\frac{|E_d - E_i|}{kT}\right) + \sum_a [N_a]\sigma_a \cdot \exp\left(-\frac{|E_a - E_i|}{kT}\right)] \quad (1)$$

The absolute value of the effective concentration in the space charge region is:

$$N_{eff} = |\sum_d [N_d]\left(\frac{N_C}{N_V}\right)\cdot\left(\frac{\sigma_n}{\sigma_p}\right)_d \cdot \exp\left(-\frac{2|E_d - E_i|}{kT}\right) - \sum_a [N_a]\left(\frac{N_V}{N_C}\right)\cdot\left(\frac{\sigma_p}{\sigma_n}\right)_a \cdot \exp\left(-\frac{2|E_a - E_i|}{kT}\right) + N_{sd} - N_{sa}| \quad (2)$$

and the effective trapping times for electrons and holes, τ_e and τ_h respectively are given by:

$$\frac{1}{\tau_e} = v_{th} \sum_d \sigma_d [N_d] f_d \quad (3)$$

$$\frac{1}{\tau_h} = v_{th} \sum_d \sigma_a [N_a] f_a \quad (4)$$

In the equations, index "*d*" is associated with deep donor defects "*a*" with deep acceptors, "*sd*" and "*sa*" with shallow donors and acceptors respectively. Here $\sigma_n(\sigma_p)$ are the cross sections for the capture of carriers, E_i is the intrinsic level, n_i the intrinsic concentration of carriers and $< v_{th} >$ is the average between electron and hole thermal velocities, q – the electric charge of the electron. N_C and N_V represent the effective densities of states in the conduction (valence) band, f_d and f_a are the occupation factors for the deep levels, and quantities in square brackets refers to concentrations of defects.

3. Primary defects

In silicon, the Si – Si bond length in the bulk is 2.35 Å and the bond angle is 109°.

The vacancy is the primary defect obtained after the interaction process between the incoming particle and a nucleus placed in a site of the lattice, when the recoil nucleus leaves its site. For the formation energy, values between 2.84 and 4.29 eV were reported in the literature, dependent on the charge state and on the calculation method [2, 3]

For interstitials the problem is more complicated because in the literature four distinct types were identified: the hexagonal interstitial is a sixfold coordinated defect with bonds of length 2.36 Å, joining it to six neighbours who are fivefold coordinated. The tetrahedral type it is fourfold coordinated defect; which has bonds of length 2.44 Å joining it to its four neighbours, which are therefore five coordinated. The <110> split interstitial: two atoms forming the defect are fourfold coordinated, and two of the surrounding atoms are fivefold coordinated. Interstitial of the 'caged' type contains two normal bonds, of length of 2.32 Å, five longer bonds in the range 2.55 and 2.82 Å and three unbounded neighbours at 3.10 and 3.35 Å [4].

The Frenkel pair (FP) is a bounded vacancy-interstitial pair, metastable, which evolves either toward annihilation, or toward dissociation. It has a formation energy of around 2.3 eV [5], and a recombination barrier of 1.1 – 1.2 eV [6]. FPs have been observed in silicon after electron irradiation at liquid helium temperature, using RX measurements [7].

The **f**our**f**olded **c**oordinated **s**ilicon **d**efect (FFCD) is obtained by moving atoms from the initial positions, but this displacement does keep the bonds with the neighbours, preserving the four-fold coordination. This defect could be produced if the transferred energy is above the threshold for its formation in a region which includes at least two neighbouring atoms. In this case the bound lengths are between 2.25 and 2.47 Å and angles vary in the 97-116° range. The formation energy is 2.45 eV (for p-type silicon), 2.42 eV (intrinsic), 2.39 eV (n-type), lower then for the well know vacancies and interstitials.

Its existence in the semiconductor (not yet completely accepted, because it has not directly evidenced experimentally), produces a new symmetry of the material. It is stable and non-mobile defect. In successive works [8, 9, 10] it was established that this defect has at least two acceptor levels in forbidden band, $Si_{FFCD}^{-/0}$ and $Si_{FFCD}^{2-/-}$, with energy levels: E_c – (0.46 ÷ 0.51) eV and E_c – 0.18 eV respectively, is produced in irradiation processes, as a fraction of about 10% of the total number of vacancies and interstitials, the deepest level having a capture cross section $(5 \div 10) \times 10^{-15}$ cm^2 and $\sigma_p/\sigma_n \cong 1 \div 5$.

Fedina and co-workers, using *in situ* HREM irradiation experiments at 400 keV at room temperature put in evidence a structure, located in the {113} plane and identified it with a chain of FFCDs, where interstitials and vacancies aggregated together [11].

In Figure 1, we present a compilation of the values reported in the literature for the energy levels of primary defects in the silicon band gap.

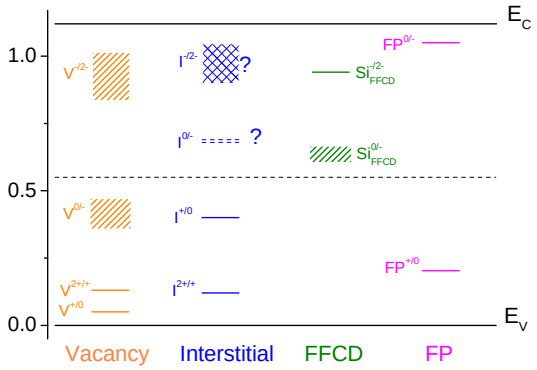

Fig. 1. Energy levels (in eV) of primary defects in silicon

4. Isovalent impurities as doping elements in silicon

For silicon, the isovalent elements are: carbon, germanium, tin and lead. They could be incorporated into Si in substitutional places, and are not active electrically. Doping with these elements gives rise to considerable local perturbation of the lattice, which affects defect-impurity interaction in Si and is studied in the hope to realise an enhancement of its radiation and thermal resistance [12]. The covalent radii of group IV elements are: 0.77 Å (carbon), 1.11 Å (silicon), 1.22 Å (germanium), 1.41 Å (tin) 1.47 Å (lead) [13].

Due to the relation between the covalent radii of *C*, on one side, and *Ge*, *Sn* and *Pb* on the other side, with the covalent radius of silicon, the vacancies and interstitials generated by irradiation move in the elastic-stress fields generated by C_s and Ge_s, (or Sn_s, Pb_s): the vacancy flux is directed toward Ge_s (or Sn_s, Pb_s) atoms, whereas the interstitial flux is directed to C_s ones [14].

The studies of possible effects of isovalent impurities are a very active field of research. It has been shown that *Sn* and *Pb* doping results in the decrease of divancancy concentration following irradiation [15, 16].

From these impurities, we chose to discuss here the influence of *C* and *Ge*: *C*, because its presence into *Si* crystals cannot be avoided, and *Ge* because the centre resulting from its interaction with primary defects has not deep energy levels in the gap.

Carbon, together with oxygen, is the most important impurity in silicon [17]. Both of them have a strong influence on defect kinetics in silicon [18]. *C* is added to the single crystal inadvertently, occupies substitutional sites in the lattice, and, e.g. in float zone (FZ) Si has typically concentrations of around 10^{16} cm^{-3} and in Czochralski (Cz) *Si* of the order of 5×10^{17} cm^{-3}.

The Watkins replacement mechanism [19] is the main mechanism responsible for interstitial disappearance after irradiation, especially in n-type silicon.

$$C + I \rightarrow C_i \tag{5}$$

Interstitial carbon anneals in at 160 – 180 K, and anneals out at 260 -280 K. C_i, mobile at RT is captured by a substitutional element to form stable defects:

$$C_i + X \rightarrow C_i X \tag{6}$$

where *X* could be *O, C, P*.

The presence of substitutional germanium atoms gives rise to compressive elastic strains in the *Si* lattice due to the difference in the covalent radii of *Ge* and *Si*. These strains can be relieved by the capture of vacancies and it is expected that *Ge* impurity atoms act as effective trapping sites for vacancies:

$$Ge + V \leftrightarrow GeV \tag{7}$$

The *GeV* complex in *Si* irradiated at low temperatures was reliably identified by EPR a long time ago [20]. It has a shallow energy level in the gap. There is some uncertainty related to its position, values of $E_c - 0.29$ eV [21], $E_c - (0.13 \div 0.17)$ eV [2], and $E_c - (0.05 \div 0.08)$ eV [22] being reported in the literature. In the present calculations, we used the intermediate value of $E_c - 0.17$ eV. Due to the fact that at room temperature the defect is unstable, in the equations of defect kinetics both its formation and dissociation were considered.

5. Results and discussion

The Si_{FFCD} defect gives a partial explanation of the degradation. In previous papers ([9, 23, 24]) we demonstrated that the main discrepancies observed between microscopic models for defects and measurements of change of device parameters after hadron (protons, neutrons positive and negative pions) and electron irradiation are solved considering the production of Si_{FFCD} defect for temperatures between 0^0C and 20^0C, different technologies (FZ and DOFZ) or crystal orientation.

We investigated the influence of *Ge* doping on *Si* containing *O* and *C* on its radiation resistance. In the model of defect kinetics developed previously [25], *Ge* addition conduces to the formation of the *VGe* centre by *V* capture. Consequently, the concentrations of all defects, solutions of the coupled system of differential equations, change.

Five different doping with *C* and *Ge* of the starting material (FZ Si, with 5×10^{11} *P*/cm^3, 10^{15} *O*/cm^3) were considered, characterised by different concentrations of *C* and *Ge*: **1**): 10^{15} *C*/cm^3, 0 *Ge*/cm^3; **2**): 5×10^{17} *C*/cm^3, 0 *Ge*/cm^3; **3**): 10^{15} *C*/cm^3, 10^{15} *Ge*/cm^3; **4**): 5×10^{17} *C*/cm^3, 5×10^{17} *Ge*/cm^3; **5**): 10^{15} *C*/cm^3, 5×10^{17} *Ge*/cm^3.

In Figures 2 and 3, the time dependencies of the concentrations of vacancies and divacancies are presented. These results are solutions of the system of coupled differential equations, supposing an irradiation with 24 GeV/c protons, with 10^{14} part/cm^2, at room temperature. It could be observed that the most rapid decrease of *V* concentration corresponds to the material characterised by a moderate content of *C* and high *Ge* doping. For this material, the lowest concentration of divacancies is obtained as well. The slowest decrease of vacancy concentration is predicted for a carbon rich material without *Ge*, and this case is also characterised by the greatest concentration of divacancies – see Figure 3.

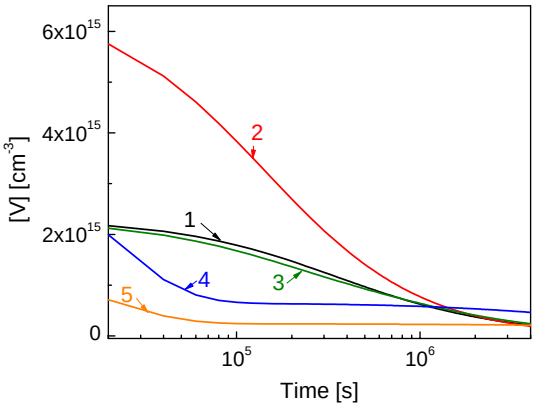

Fig. 2 Time dependence of the concentration of vacancies in 5 FZ Si crystals: ***1****: 10^{15} C/cm^3, 0 Ge/cm^3;* ***2****: 5×10^{17} C/cm^3, 0 Ge/cm^3;* ***3****: 10^{15} C/cm^3, 10^{15} Ge/cm^3;****4****: 5×10^{17} C/cm^3 , 5×10^{17} Ge/cm^3;* ***5*** *: 10^{15} C/cm^3, 5×10^{17} Ge/cm^3.*

A lower concentration of divacancies was obtained for *Ge* doped silicon. More, the concentration of divacancies decreases with the increase of *Ge* contents, in agreement with the experimental observations of Khirunenko et al. [26]., germanium atoms being centers of indirect recombination of primary radiation defects. Doping with *Ge*, by the formation of *VGe* defect, seems to represent a

possible solution to improve the effects of radiation due to secondary defect complexes, especially to diminish the concentration of divacancies.

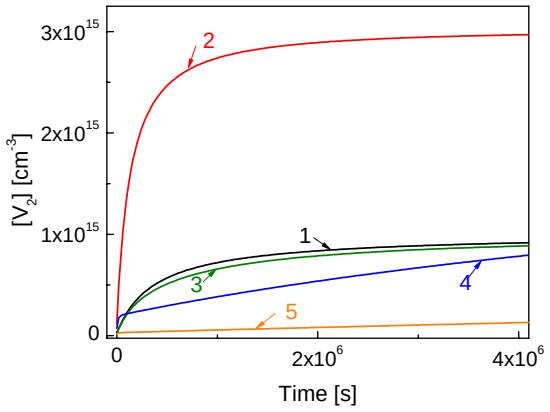

Fig. 3 Time dependence of the concentration of divacancies in the same starting materials as in Fig. 3, differently doped with C and Ge

In these cases, the concentration and time evolution of divacancies is a monitor for the parameters of macroscopic degradation of the device.

A high concentration of germanium assures a small time variation of the alpha degradation constant of the leakage current of the detector, and a relatively quick stabilization. The effective carrier concentration in the depleted region of the detector inverts a short time after irradiation, but is stabilised at relatively low values in Ge rich samples. All these results are presented in figures 4 and 5.

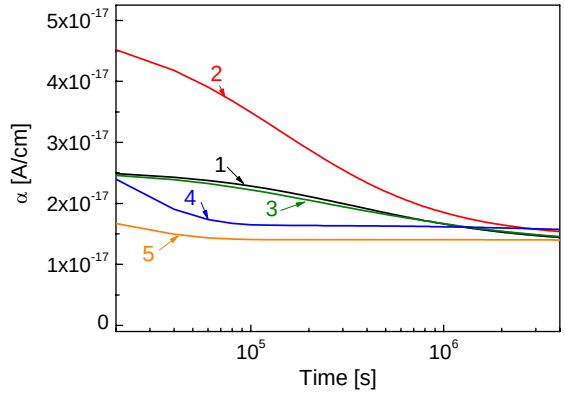

Fig. 4 Time dependence of the degradation constant of the leakage current in p-n junctions made from the Si crystals of Fig. 3, after proton irradiation at room temperature.

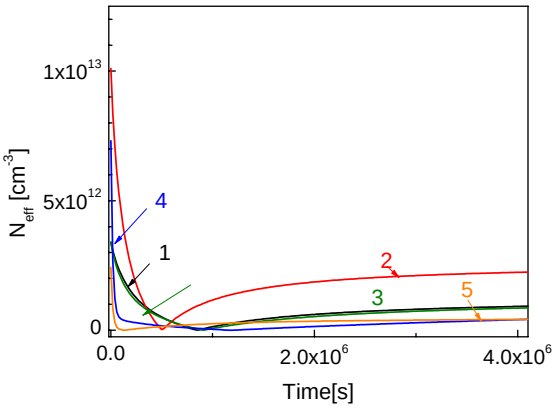

Fig. 5 Time dependence of the effective concentration in the depleted region of p-n junctions made from the Si crystals of Fig. 3, after proton irradiation at room temperature.

It was shown by Londos et al. [27] that the radiation damage of Ge-doped Cz Si subjected to fast electron irradiation and subsequent annealing presents a marked sensitivity to germanium, but the authors attributed the observed effects to the strains induced in the Si lattice by Ge impurity atoms rather than to the *VGe* defect.

Arivanandhan et al. [28].showed that Ge acts as a vacancy trapping centre in Ga/Ge codoped Cz-Si, resulting in a low defect density and high minority carrier lifetime.

6. Conclusions

In spite of more than 65 years of theoretical and experimental study, starting with Wigner's paper in '46, [29] and the remarkable technological results, degradation processes in silicon are not fully understood.

Models of defect kinetics explain relatively well different aspects of the degradation.

Isovalent impurities in silicon, especially germanium, represent a promising direction of study. Ge doped silicon appears radiation harder in respect to Si without Ge. Fundamental and applicative studies must be continued for the clarification of the properties and influence of some defects. *Ge* atoms are sinks for vacancies, forming the *VGe* centre which has a shallower level in the band gap in respect with, e.g. the divacancy. Aspects of *VGe* defect stability and of *Ge*-related defect kinetics in silicon must be experimentally clarified.

Acknowledgments

We acknowledge financial support of Romanian National University Research Council, under contract IDEI 499/2009.

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