Radiation-doped SiC*/Si heterostructure formation and defects evolution

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Abstract. The authors consider heterostructures of silicon carbide obtained during endotaxy on silicon substrates. The question is raised in connection with the description of the endotaxy process itself at the structural level. Authors focus on the technological aspects of the formation of a stable $\beta$-SiC/Si heterostructure by endotaxy in relation to the evolution of point defects of various nature and their probable association models with the participation of a radionuclide impurity at the micro-alloying level: 1) the growth of the SiC*/Si thin layer with C\textsuperscript{14} atoms in the doping process; 2) physical properties of defects formation; 3) some interface between properties and efficiency.

1. Introduction
Recent studies have focused on the conversion of beta electron energy into electrical energy within SiC*/Si heterostructures doped with carbon\textsuperscript{14} [1, 2], which act as the internal source of the spectrum of primary electrons – the "inner sun" type technology. The separate question is raised in connection with the description of the endotaxy process itself at the structural level. Analysis of the technological aspects of endotaxy formation high-temperature and radiationresistant heterostructure $\beta$-SiC/Si in relation to the distribution of the concentration of point defects of various nature, deep centers [3] and their probable models of associations with the participation of foreign impurities is the main way to improve the reliability of sensors of physical quantities based on them. In addition, the analysis of reversible associations processes [4] opens up ways to optimize the kinetics of diffusion mass transfer and microlegation in the phase transformation of the silicon substrate into a film of silicon carbide.

With the advisability of concentrations of neutral defects from the factors of supersaturation of the gas phase by the conditional atomic concentration of carbon (hypothetical pressure), from the concentration of impurities in the gas phase, as well as from its own defects of various nature [4], they have the potential for the formation of deep levels in the forbidden zone and the potential for association. We involve modern computer methods, such as DFT, in the analysis of defect formation.

2. Diffusion of carbon atoms inside the silicon substrate and influence factors
The question of diffusion of carbon atoms inside the silicon substrate in the process of endotaxy during doping with radionuclide is interesting. In our case, the SiCheterostructure on the Si substrate is a photo-beta converter. Si substrates are placed in a high-frequency heating reactor, and the SiC film is
epitaxially built up in the surface of Si, in a hydrogen environment by the CVD method, carbon-14 is introduced with carbon-12 as an alloying impurity (one C-14 atom per 100,000 C-12 atoms, 10^{18} \text{cm}^{-3}). The endotaxy process is important at the earliest stage of beta transducer manufacturing, when silicon carbide with C-14 molecules is formed on the silicon substrate and at the same time created by a p-n transition or in a simple version without a p-n transition, based on an isotypic heterostructure.

Silicon carbide film has a thickness of 50 nm to 5 \mu m, the structure of polytypes: hexagonal on the substrate of silicon carbide or cubic on the substrate of monocrystalline silicon. Quantitative composition of the compound: stoichiometric or superstehiometric in the direction of excess carbon, including carbon-14 due to its own point defect formation.

The energy of beta-electrons of C-14 decay is not sufficient to generate radiation defects, and the use of porous morphology of the surface of activated silicon carbide increases its radiation resistance due to the flow of defects onto the developed surface.

The structure of the transducer includes a built-in field separating secondary electrons and holes. The built-in field can be implemented (in addition to the p-n transition):

- Heterostructure (n-SiC/n-Si), since the formation of the structure is produced on the substrate of monocrystalline silicon, which is due to the feasibility study of its manufacture;

- If the embedded field combines the p-n junction in silicon carbide and the heterostructure as an integral part of the structure, then the heterostructure can be isotype or anisotypic. This can lead to a situation where the built-in fields are directed counter, and this is manifested in the efficiency of the converter, so the work considers the isotype heterostructure;

- Separation of non-equilibrium carriers can be realized using metallized contacts to the semiconductor - this is the Schottky model contact;

- If the built-in field is implemented by a combination of p-n junction in silicon carbide and a Schottky-type barrier, then there is a need for additional research, since the directions of the intensity of the electric built-in fields may not coincide, which will affect the efficiency of current generation due to the high resistance of the counter-included diode structures.

It is well known that a significant factor of efficiency is the difference between the lattice periods and the coefficients of thermal expansion of the mating materials. The stressed heterostructure changes the mobility of carriers by 2-4 times [5]. This circumstance causes the appearance of significant mechanical mismatch stresses, relaxing to residual ones by generating a dislocation grid, and the latter also performs the positive role of a hidden getter moving in front of the silicon carbide phase growth front as a buffer layer located in the Si phase. The difference in the physics-chemical properties of the mating materials is manifested in the asymmetric distribution of the dislocation grid and the spatial charge range between the mating phases (an asymmetric transition due to the method of its formation, for example, by rearranging the previous layer of the film) relative to the metallurgical boundary, in particular, this is experimentally confirmed by the distribution of the dislocation density of the mismatch between the phases.

In the case of endotaxy technology, there is a diffusion mechanism for the formation of the 3C-SiC phase, while there is a movement of the grid of dislocations of the mismatch of the lattice parameters, which are formed at the growth temperature and are located in the silicon phase. The theoretical description of this mechanism is of particular interest. In addition to the possibilities of solving the general problem of diffusion, the problem of how the phases of silicon carbide are formed on a silicon substrate from the point of view of energy benefits is singled out separately. This refers to the comparison of the energy of the formation of vacancies inside the structure with the formation energies of the silicon carbide cells themselves, which, to date, is available for research within the framework of the Density Functional Theory (DFT) [6]. The endotaxy technology also performs gettering - "cleaning" of the structure during doping from uncontrolled foreign impurities and point defects, where, when a new phase germinates inside the silicon, a moving grid of dislocations of mismatch of the lattice parameters in the Si-phase plays the role of a hidden getter, including for C-14. In this case, another additional mechanism of diffusion currents arises in the region of the electron concentration gradient from the region of the gettered C-14.
3. Investigation of influence factors and SiC*/Si structure description in DFT

Point defects find a good description within the DFT framework. Methods of Density Functional Theory (DFT) [7, 8] are considered one of the most accurate since the calculation results are in good agreement with experimental data, and at the same time, they do not require additional empirical parameters. The method is based on the calculation of the electronic structure, when instead of the wave function the electron density is used to define the main characteristics of the system. The form of the density functional can be considered in various approximations:

• local density approximation (LDA) [9]
• general gradient approximation (GGA) [10, 11]
• hybrid methods [12, 13]

These approaches can be produced both in the plane wave basis [14] and in the orbital basis [15]. The first one is well applicable to periodic structures, and, therefore, it is also suitable to our structure, i.e. we suppose that we are dealing with SiC crystals. The SiC cell has the form according to the Fig. 1. Point defects are created in the positions of carbon and silicon atoms by removing or replacing. This can be implemented automatically for all variants of point defects positions, for instance by SOD software [16].

Figure 1. The cubic silicon carbide 3C-SiC: a) initial crystal; b) the cell with points defects (black rounds)

In the first place the structure stability investigation of the substance requires a calculation of the formation energy for cell. However, value of the energy can makes sense only in comparison with other calculations of similar structures and compositions. In practice, there are many situations when a simple comparison of energy structures is not possible due to differences in stoichiometry and types of the structures. We can solve this problem estimating, so called, binding energy, i.e. the energy which is necessary to give one atom to extract it from the composition of the substance. The most stable structures have the lowest value $E_b$. The binding energy can be represented as it is shown in formula (1):

$$E_b = \frac{E - NE_{X_1} - ME_{X_2}}{N + M},$$

where $E_{X_1}, E_{X_2}$ - one atom energy of pure substance, $E$ - energy of total structure.

This approach allows us to consider doped structures. The calculation of structures with defects in the framework of the DFT implements in supercells to exclude the influence of defects on each other.

The comparison takes place into account the fact that the energy calculation is carried out for all cells with the same cutoff value of the energy of plane waves (cutoff parameters). Also, a large number
of partitions in the reciprocal space increases the calculation time, but improves the final result. This means that there is a need to repeat calculations many times with various of the cutoff values and different k-points in the reciprocal space.

These calculations were carried out by the authors in the work [6]. It should be noted that disordered structures (with interstitial atoms or amorphous states, as well as solid-phase solutions) cannot be described in approaches designed for periodic structures. Therefore, other types of defects can be considered either in some approximations or in other methods.

4. Example
The semiconductor structure of a single-crystal silicon carbide for a radioisotope energy source has the following sequence of layers: - the silicon substrate of n-type conductivity KDB-4.5 (100)orientation with a thick 0.5 microns layer of silicon oxide on the non-working side; - the silicon carbide film along the inner surface of the pores with a sequence of layers forming a structure with an n-p transition, and the n-layer of the film comes to the surface with an alloying admixture of phosphorus and carbon-14, respectively, with concentrations of $5 \times 10^{18}$ cm$^{-3}$ and $10^{20}$ cm$^{-3}$, the ratio of carbon-14 atoms to carbon-12 atoms in the silicon carbide film is one atom per $10^{-3}$-$10^{6}$ atoms. The interrelations of the components in the layers of the por-n-SiC/pSiC/p-Si/SiO2 heterostructure are manifested in the fact that the alloying admixture of atomic carbon-14, which is part of the silicon carbide (Si$^{14}$C) molecule of the semiconductor structure, emits beta electrons with energy sufficient to generate secondary electron-hole carrier pairs in the p-n region of the n-SiC/p-SiC junction, the latter are separated by the electrostatic internal field of the junction. A thick layer of SiO2 from the non-working side is intended to exclude the diffusion of carbon-14 into silicon and the formation of silicon carbide from the non-working side. A structure with a developed surface area with the same geometric volume dimensions increases the specific activity of the radioisotope and at the same time is an effective drain of radiation-induced structural defects, which increases radiation passivity and does not violate the functional properties of the separation of secondary electron-hole pairs. The properties of the structure of the substance are manifested by probe measurements of the structure prepared in a planar version. In the planar version, the measuring probes are installed on n-silicon carbide and the opened window area up to p-silicon carbide. For chips of a planar structure with geometric dimensions of the working side, respectively, 5x10 mm, the short-circuit current and the no-load voltage are on average 22 nA and 0.45 mV, respectively (the measuring camera prefix excludes electromagnetic interference and optical radiation, except for natural thermal). (activity of 1g C-14 is equivalent to 54 kCi ($2 \times 10^{15}$Bq) or 3g SiC. The average specific activity is 50-56 Ku/mol).

5. Conclusion
The analysis of the above dependencies is carried out and some recommendations are given for carrying out the technological process of forming complex heterostructures for various purposes. Approaches are considered from the point of view of the formation, influence and evolution of defects to the description of the developed and obtained the new substance – a material for a radioisotope energy source containing a single - crystal phase of the semiconductor structure of silicon carbide in the form of a film having n- and/or p-type conductivity for separating electron-hole pairs, including carbon-14 atoms in the molecular structure of silicon carbide for converting its radiation energy into electrical energy. Impurity atoms and vacancies can be considered as the main defects that manifest themselves in the endotaxy process and determine the formation of the silicon carbide structure. Thus, the problem is considered from the point of view of energetically favorable states of the system, which pass from one phase to another, changing the structure.

It should be noted that disordered structures can described only limited number of approaches. There are a few solutions in DFT for this, and this topic requires further development. Therefore, we can explain completely a point defects behavior only.
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