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Detection of Hydrogen Impurity in Silicon Radiation Detectors

L. F. Makarenko*, F. P. Korshunov, S. B. Lastovskiĭ**, and N. I. Zamyatin*****

** Belarussian State University, Minsk, 220050 Belarus*

*** Institute of Solid-State and Semiconductor Physics, Belarussian Academy of Sciences, ul. Brovki 17, Minsk, 220072 Belarus*

**** Joint Institute for Nuclear Research, Dubna, Moscow oblast, 141980 Russia*

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Abstract—The behavior of silicon particle detectors irradiated with 2.5-MeV electrons during subsequent annealing is studied. Annealing at 100–250°C was found to result in the formation of two types of traps with the levels $E_c - 0.32$ eV and $E_v + 0.29$ eV. Increasing the annealing temperature to 300°C makes both traps disappear. On the basis of data obtained, it was concluded that these traps are related to hydrogen-containing complexes. The presence of hydrogen in a crystal results in a decrease in the annealing temperature for vacancy–oxygen (*V*O) complexes and complexes consisting of carbon and oxygen interstitials (C_iO_i). The reason for this phenomenon is the passivation of these complexes by hydrogen, which results in the formation of electrically active *V*OH centers {with the level $E_c - 0.32$ eV} in an intermediate stage of this process. It is assumed that hydrogen penetrates the structures under investigation in one of the stages of their fabrication. *© 2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Nowadays, in order to perform experiments in high-energy physics, one needs silicon particle detectors that retain their working capacity even if the content of compensating radiation defects (RDs) exceeds the content of shallow-level impurities in the base region of the detector by more than a factor of 100. The need for such detectors stimulated multiple investigations of the radiation damage in detector-grade silicon (see report [1] and references therein).

One of the principal purposes of these studies was to investigate the possibility of applying the defect-engineering technique for improving the radiation resistance of detectors. This method consists of the purposeful addition of impurities that affect the processes of formation of electrically active defects during irradiation and, thus, make it possible to control the macroscopic parameters of the detector structures.

Some models of defect formation, which served as a basis for using various processing procedures to improve the resistance of detectors with respect to a number of parameters, have been developed [1, 2]. In these models, oxygen and carbon were assumed to be those impurities that completely determine the formation of electrically active complexes in irradiated silicon. However, the available models cannot adequately describe the properties of real structures. Thus, the processes of interaction of RDs both with each other and with impurities are now being studied in more detail.

As recent investigations [3–6] show, hydrogen can penetrate silicon crystals even at room temperature. In this case, conventional processing operations in the fabrication of detector structures may be responsible for the appearance of hydrogen in them. For example, hydrogen penetrates Si structures during wet chemical etching [3–6]. These data make it possible to assume that hydrogen may also be present in silicon detectors. The purpose of this study is to verify the above hypothesis.

2. EXPERIMENTAL

In this study, we investigated detectors fabricated from silicon with a resistivity of 4 kΩ cm and a phosphorus concentration of $\sim 10^{12}$ cm^{-3} (Wacker Chemitronics, Germany). In fabricating the detector structures, we used conventional stages of planar technology: ion implantation, thermal oxidation, etching, and deposition of metals. In order to introduce radiation defects, we used irradiation with gamma-ray photons from a ^{60}Co source and with fast electrons with an energy of $E \approx 2.5$ MeV. After irradiation, isochronous annealing (30 min) was performed in air in the temperature range of 100–300°C to determine the thermal stability of RDs and study their interaction with the hydrogen impurity.

The defect content was determined by deep-level transient spectroscopy (DLTS). The measurements were carried out in the temperature range of 79–300 K. The bridge operating frequency amounted to 1 MHz.

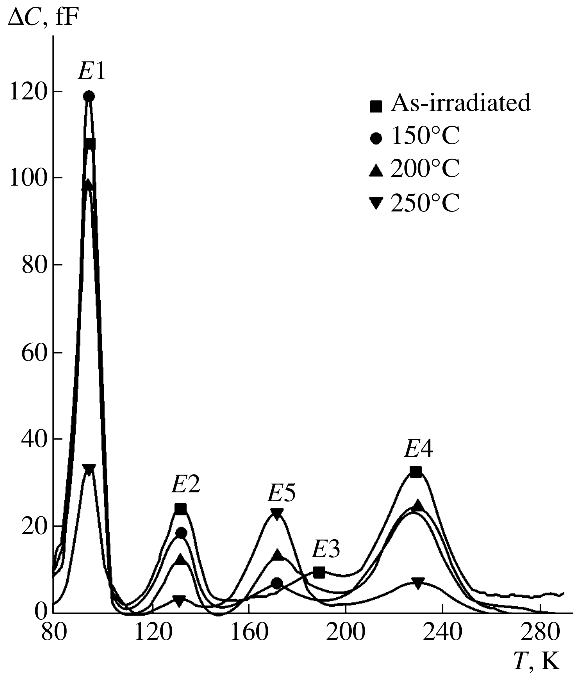

Fig. 1. Energy levels of the traps for majority charge carriers in the DLTS spectra of detectors, as-irradiated (with 2.5-MeV electrons) and isochronously annealed (for 30 min) after irradiation at temperatures T_{ann} indicated in the figure.

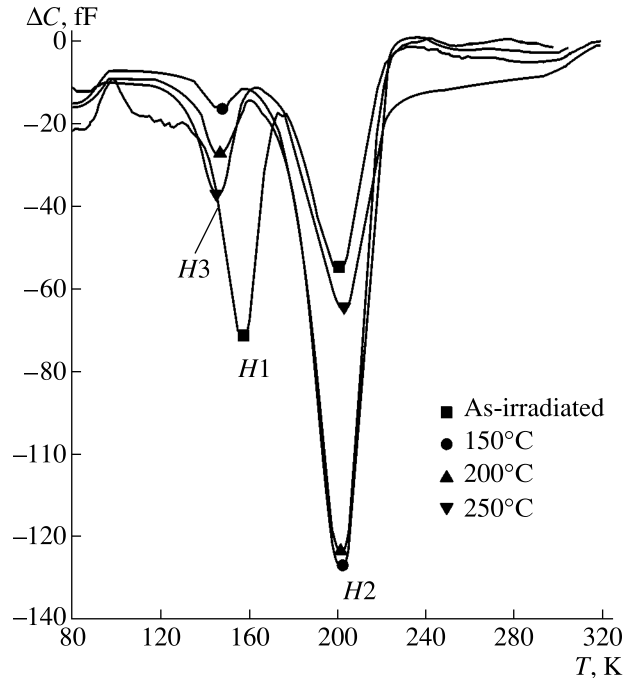

Fig. 2. Energy levels of the traps for minority charge carriers in the DLTS spectra of detectors, as-irradiated (with 2.5-MeV electrons) and isochronously annealed (for 30 min) after irradiation at temperatures T_{ann} indicated in the figure.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Detection of Hydrogen Centers

The temperature necessary for annealing RDs depends on the presence of hydrogen impurity. One might expect that, during annealing, passivation of vacancy-type defects should occur first [3, 7]. In order to study this effect, we performed isochronous annealing of detector structures irradiated with fast electrons. Figure 1 shows DLTS spectra measured immediately after irradiation and after isochronous annealing at various temperatures for 30 min. Immediately after irradiation, four trapping levels are observed: *E*1 at $\sim E_c$ – 0.17 eV, *E*2 at $\sim E_c$ – 0.25 eV, *E*3 at $\sim E_c$ – 0.37 eV, and *E*4 at $\sim E_c$ – 0.42 eV. The annealing at 150°C leads to an increase in the amplitude of the signal related to the *E*1 trap and to the appearance of a new trapping level *E*5 at (E_c – 0.32 eV). If the annealing temperature increases, the content of *E*5 centers increases, whereas the content of the *E*1 centers decreases. According to [3–6], the *E*5 trap may be related to a vacancy–oxygen–hydrogen complex (*V*OH).

Another center which, according to [8], may also be indicative of the presence of hydrogen is the trapping level at $E_v + 0.28 \pm 0.01$ eV. In order to detect this center, we studied the DLTS spectra related to the traps for minority charge carriers (Fig. 2). As can be seen Fig. 2, in the spectrum recorded immediately after irradiation, two traps are observed: *H*1 at E_v + 0.30 eV and *H*2 at E_v + 0.36 eV. After annealing at 150°C, the *H*1 trap disappears, while the content of *H*2 centers increases substantially. At higher temperatures, a new trap *H*3 (at E_v + 0.29 eV) appears. The content of these traps increases with an increase in the annealing temperature up to 250°C. The amplitudes of the peaks related to the traps under observation are shown in Fig. 3 as functions of the annealing temperature.

The data we observed may be interpreted as follows. The energy position and the temperature stability of the *H*1 trap indicate that it may be related to the carbon interstitial (C_i) [9]. At $T \approx$ 50–100°C, this atom becomes mobile and migrates through the crystal until it is captured either by an oxygen interstitial (O_i) or by a substitutional carbon atom (C_s) [9, 10]. In this case, either a complex consisting of a carbon interstitial and an oxygen interstitial (C_i–O_i) with a donor level at $\sim E_v$ + 0.35 eV or a complex consisting of a carbon interstitial and a substitutional carbon atom (C_i–C_s) with an acceptor level at $\sim E_c$ – 0.17 eV are formed [9, 10]. In the crystals under investigation, most defects C_i are involved in formation of C_i–O_i complexes, which is indicative of a relatively high content of oxygen impurity.

The centers with energy levels at E_c – 0.32 eV (*E*5) and E_v + 0.29 eV (*H*3) are related to the complexes containing hydrogen [3–6, 8]. In study [8], it was suggested that these two levels represent the acceptor and donor

levels of the complex consisting of an oxygen vacancy and a hydrogen atom (*V*OH). This suggestion is confirmed by our data. The *E*5 and *H*3 centers have similar contents, and both of these centers vanish simultaneously after annealing at 300°C (Fig. 3). Thus, the set of data we obtained makes it possible to conclude that the detector structures under study contain hydrogen impurity.

Presumably, hydrogen penetrated the structures during a certain processing stage. As our experiments showed, the relative content of the *V*O and *V*OH complexes is virtually invariable at distances in the range of 30–90 μm from the *p*–*n* junction. Hence, we can conclude that either hydrogen penetrated the structure during a high-temperature stage (for example, oxidation) or the structure was subjected to thermal treatment after hydrogen penetrated it.

Previously, the presence of hydrogen in detector structures was reported in [11]. It was observed in that study that a trapping level at $E_v - 0.32$ eV appeared after γ irradiation at 350°C. However, it is well known from the data in the literature [12, 13] that this trap is annealed at 300°C in the same way as in the structures we studied. Therefore, it is worth noting that the data from [11] cannot be unambiguously interpreted and, thus, cannot verify the presence of hydrogen in the silicon detectors.

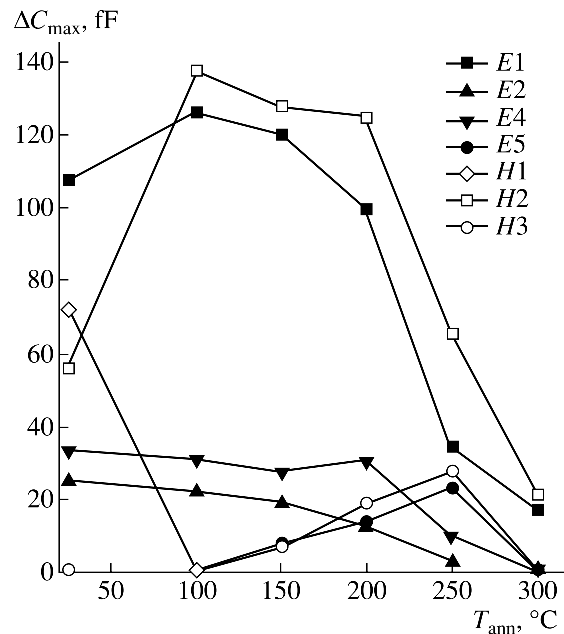

Fig. 3. Variations in the amplitudes of DLTS peaks related to the radiation defects *V*O + C_iC_s (*E*1), *V*OH (*E*5, *H*3?), *VV* (*E*2, *E*4), C_i (*H*1), and C_iC_i (*H*2) as a result of isochronous annealing (for 30 min) and as functions of the annealing temperature T_{ann}.

3.2. Behavior of Divacancies in Detector Structures with Hydrogen

One of the major defects determining the degradation of detectors used in projects in high-energy physics is the divacancy [1, 2]. Therefore, it is of interest, first of all, to investigate the possibility of passivating this defect. As follows from the data reported in [3], a divacancy may be efficiently passivated when doping surface layers with hydrogen during wet etching of silicon. However, in the structures we studied, total passivation of divacancies was not observed. Although our data cannot be interpreted as unambiguously as the data on the formation of the *V*OH complex, nevertheless, it may be concluded that the hydrogen atom and the divacancy interact with each other.

The divacancy is known to have two acceptor levels at $E \approx E_c - 0.24$ eV and $E \approx E_c - 0.42$ eV [14] in the upper half of the band gap of silicon. In the detectors we studied, these levels correspond to the *E*2 and *E*4 traps. However, the contents of these traps are not equal. The largest value of the signal related to the deeper *E*4 trap exceeds that for the *E*2 trap. This fact enables us to conclude that the *E*4 peak is related to at least two centers. As a rule, it is assumed that, in addition to the divacancy, the phosphorus–vacancy complex (*E* center) also contributes to the amplitude of the *E*4 peak. In order to verify this assumption, we irradiated

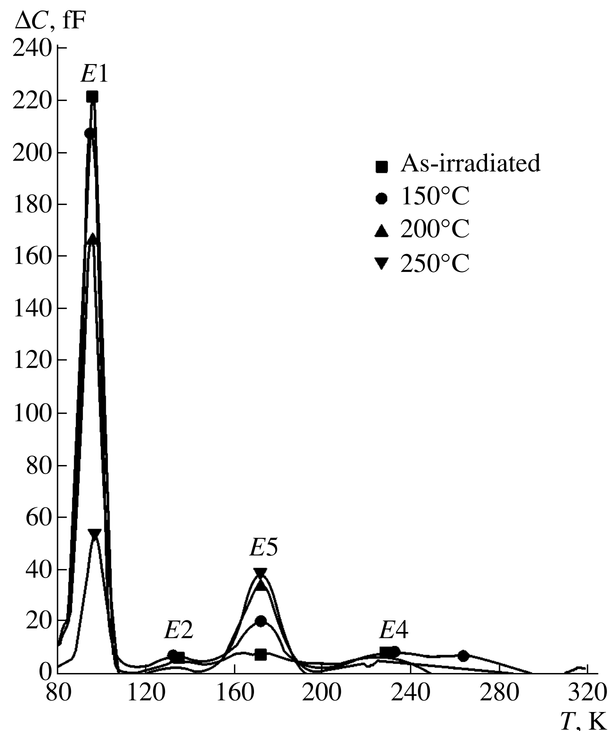

Fig. 4. Energy levels of the traps for majority charge carriers in the DLTS spectra of detectors, as-irradiated (with gamma-ray photons from a ^{60}Co source) and isochronously annealed (for 30 min) after irradiation, at temperatures T_{ann} indicated in the figure.

another detector structure from the same set with γ rays from a ^{60}Co source. The DLTS spectrum of this structure is shown in Fig. 4. It follows from this spectrum that virtually no *E* centers are formed in the structures under investigation due to the γ irradiation. This fact indicates that the oxygen concentration exceeds 10^{15} cm^{-3} in the crystals we studied, and [O]/[P] > 10^3. Thus, the nature of the center that additionally contributes to the amplitude of the *E*4 peak immediately after the electron irradiation is unclear.

The processes of annealing of the *E*2 and *E*4 traps are also somewhat different (Fig. 3). The content of *E*2 centers decreases steadily as the annealing temperature increases and becomes virtually zero at 250°C. The thermal stability of the *E*4 traps is higher. Such a behavior of the traps during annealing can also be explained by the presence of hydrogen in the crystals under investigation. The partial disappearance of divacancies at $T_{ann} < 250$°C, which manifests itself in a decrease in the content of *E*2 traps, can be explained by the interaction of divacancies with hydrogen, with the formation of divacancy–hydrogen complexes. According to [13], such a complex has an acceptor level at $\sim E_c - 0.43$ eV, which is close to the level of the divacancy *E*(0/–). Therefore, the peaks in the DLTS spectra related to the levels of the divacancy *E*(0/–) and the divacancy–hydrogen complex are virtually indistinguishable.

Consequently, we may suggest that it is the interaction between the divacancy and hydrogen atom (V_2 + H $\longrightarrow$ V_2H) that is responsible for the virtual constancy of the height of the *E*2 peak after annealing at $T = 200$°C. The content of divacancies decreases, which results in a decrease in the amplitude of the *E*2 peak. However, the content of V_2H complexes increases, and the total content [V_2] + [V_2H] remains invariable in this case (the amplitude of the *E*4 peak remains virtually constant). According to [13], the V_2H complex, as well as the divacancy, is stable up to 250°C, which agrees with our data. Thus, the interaction between hydrogen atoms and divacancies results in the formation of electrically active divacancy–hydrogen complexes in the structures under investigation. It is the *E*4 trap, which is as stable in our structures as in the crystals containing no hydrogen, that is related to this complex.

For practical purposes, it is important to estimate the influence of the observed transformations of the defect complexes on the detector characteristics. Evidently, the total passivation of the *V*O and C_iO_i complexes should result in a decrease in the full-depletion voltage (V_{FD}) in the irradiated detectors. When the passivation is incomplete, the characteristics may degrade due to an increase in V_{FD}. According to [15], the closer the defect level to the midgap, the stronger its influence on the value of V_{FD} in heavily irradiated detectors. Consequently, if most *A* centers (with a level at $E_c - 0.17$ eV) are incompletely passivated and convert to *V*OH complexes (with a deeper acceptor level at $E_c - 0.32$ eV), this may lead to increasing V_{FD}. If the interaction of hydrogen with divacancies results only in the formation of V_2H complexes, hydrogen also does not positively affect the detector characteristics, in particular, the value of V_{FD}.

No hydrogen was deliberately introduced into the structures investigated in this study. For this reason, its content appears to be not very high and only partial passivation of radiation defects was observed. One might expect that a larger fraction of radiation defects will be passivated if the hydrogen content is increased, and this will occur at lower temperatures than that at which it was observed in this study. However, additional investigations are necessary to find out whether hydrogen can improve the radiation resistance of radiation detectors operating at temperatures close to room temperature.

4. CONCLUSION

Thus, the results we have obtained indicate that hydrogen is present in silicon detectors and that it actively interacts with primary radiation defects. The presence of hydrogen in the crystal results in the decreasing of the annealing temperature for the *V*O and C_iO_i complexes, which are stable under conventional conditions up to 300°C. The decrease in the annealing temperature is explained by the interaction of these centers with hydrogen and by the formation of electrically active *V*OH centers in an intermediate stage of this process. The interaction between the radiation defects and hydrogen must be taken into account when developing an optimal technology for the fabrication of radiation-resistant silicon radiation detectors.

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