



QUASI-CHEMICAL REACTIONS IN IRRADIATED SILICON

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There are described the quasi-chemical reactions that take place between radiation defects and impurities in irradiated silicon. It has been experimentally investigated single-crystalline n- and p-type silicon doped, respectively, with phosphorus or boron, irradiated with high-energy electrons or protons and subjected to the high-temperature isochronous annealing. Rates of quasi-chemical reactions are found to be dependent on the charge-states of reactants and then controllable by varying the irradiation conditions – beam-intensity, irradiation temperature and IR light exposure during the irradiation, as well as temperature of annealing of the previously irradiated samples. It is shown that the quasi-chemical reactions can serve as effective tools for tuning the electronic properties of silicon, the basic material of micro- and nanoelectronics.

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Introduction

As is known, structural imperfections and chemical impurities presented in a crystalline lattice can react quasi-chemically with each other resulting in new defect-complexes. In particular, some of quasi-chemical reactions in semiconductors lead the formation of electrically active defects those are thermally stable and, therefore, significantly affect electronic properties of the material. For this reason, the control utilizing quasi-chemical reactions should be considered as an important tool to obtain new crystalline semiconductor materials with predetermined set of desired electronic properties.

A series of our previous studies (see, e.g., papers¹⁻¹⁰) devoted to single-crystalline silicon, basic material of modern ICs, irradiated with high-energy particles has revealed a number of quasi-chemical reactions involving radiation-induced defects, which significantly affect semiconducting properties of this material. Here our purpose is to describe and systemize quasi-chemical reactions that take place in irradiated silicon, as well as identify their potential applications. The paper is organized as follows.

After present Introduction we give the Experimental part describing the samples studied and the measuring methods applied. Following section characterizes the quasi-chemical reactions, which occur with primary radiation defects in silicon at low (room) temperature and low intensity of irradiation.

Rate and even possibility of a quasi-chemical reaction are essentially determined by the charge-states of reactants as the strength of electrostatic attraction between oppositely charged defects and/or impurities and repulsion between like-charged ones, respectively, favors or hampers the reaction. But, charge-states of radiation-defects depend on the conditions of irradiation. It is a reason why special sections are devoted to the influence on quasi-chemical reactions in crystalline silicon of factors such as irradiation intensity and lightening or heating in process of irradiation.

It should be borne in mind that the quasi-chemical reactions take place not only during the irradiation but also the aging of an irradiated sample in ambient conditions or its isochronous annealing at elevated temperatures. For this reason, the influence of annealing on the quasi-chemical reactions in irradiated silicon is presented by the special section as well.

At the end of the paper we summarize obtained results and briefly outline their Prospects for practical applications.

Experimental

We have mainly investigated single-crystalline zone-melted silicon (Si) containing background impurity oxygen (O) in concentration of $\sim 10^{16} \text{cm}^{-3}$ as it was determined from the IR absorption spectrum. The density of growth dislocations in test samples estimated from the etching pits does not exceed $4 \cdot 10^4 \text{cm}^{-2}$. In addition, it has been studied several samples grown by Czochralski method, i.e. with significantly higher oxygen content: $\sim 10^{18} \text{cm}^{-3}$. Samples of both origins contain $\sim 10^{16} \text{cm}^{-3}$ of background impurity carbon (C). It has been investigated samples of n- and p-type conduction doped with phosphorus (P) or boron (B) at concentrations of $\sim 10^{13}$ – 10^{14} and $\sim 10^{14} \text{cm}^{-3}$, respectively. The samples were prepared in form of bars of sizes of $1 \text{mm} \times 3 \text{mm} \times 10 \text{mm}$.

These samples were irradiated with 2 and 8 MeV electrons or 25 MeV protons. Irradiation carried out in the direction perpendicular to the samples largest faces (111). Irradiation doses, $1.0 \cdot 10^{14}$ – $5.0 \cdot 10^{15}$ for electrons, and $2.7 \cdot 10^{12}$ and $8.1 \cdot 10^{12} \text{cm}^{-2}$ for protons, were adjusted so that at nitrogen boiling point (77K) the concentration of majority charge carriers trapped by radiation defects did not exceed the dopants concentration. Used intensities of electron- and proton-beams were of $\sim 10^{12}$ – 10^{13} and $\sim 10^{11} \text{cm}^{-2} \cdot \text{s}^{-1}$, respectively. Irradiations were carried out both at room (300K) and elevated temperatures during heating in the range 20–400°C. It has been also studied the effect of IR-lightening during irradiation on the kinetics of defects formation. From levels corresponding the different radiation defects, electrons were excited into the conduction band by the IR monochromatic light with photons energy of $h\nu = 0.2$ – 0.5eV . The samples were annealed isochronously in the temperature range of 80–600°C with steps of 10°C for 10 min at a fixed temperature.

To identify the nature of electrically active defects resulting from quasi-chemical reactions accompanying irradiation and heat treatment, from Hall-measurements it was determined their ionization energies and thermal stabilities, i.e., annealing temperatures. Ohmic contacts necessary in such measurements were prepared by rubbing aluminum (Al) on surfaces of test samples. Temperature-curves of majority carriers' Hall-concentration $N-T$ were taken from 77 to 300K. In order to illustrate, some of these characteristics are shown in Figure 1. Methodology of determining the concentration of defects in irradiated silicon from the curves $N-T$ and $N-T_{\text{ann}}$, where T_{ann} is the annealing temperature, had been described in details in above cited papers.

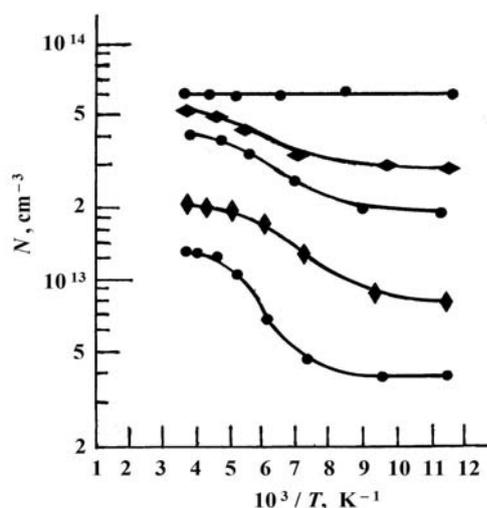


Figure 1. Temperature-dependence of electron concentration in n-Si crystals 1 – before irradiation, 2 – after electron-irradiation with dose of $1.5 \cdot 10^{14} \text{ cm}^{-2}$ at 300K, and 3–5 – after annealing at temperatures 100, 150 and 300°C

Effectiveness of introduction of various radiation-induced defects $\eta = \partial N_{\text{RD}} / \partial \Phi$, where N_{RD} is the concentration of defects of given type and Φ is the irradiation dose, measured after cycles of irradiation accompanied with IR lightening or isochronous annealing. For this purpose, we used the method of local irradiation followed by the measuring the bulk photo-emf U_{ph} along the irradiated part of the sample. These measurements were carried out at a fixed dose and, therefore, photo-emf was proportional of the effectiveness of introduction of radiation defects: $U_{\text{ph}} \sim \eta$. The relative errors of all these measurements do not exceed $\sim 10\%$.

Results and Discussion

Charge-states of vacancies and interstitials at their formation in process of low-intensity irradiation at room temperature

As is known,¹¹ the irradiation of silicon with beams of elementary particles forms primary radiation defects – vacancies and interstitials, so-called Frenkel pairs. Some of them experience mutual annihilation or recombination at crystal surfaces. The remaining nonequilibrium Si-interstitials are more mobile than vacancies and, therefore, rapidly form complexes with background impurity O and/or

C. Although, concentrations of these complexes are extremely low. The majority of interstitials tend to form clusters¹² which substantially do not interact with other structural defects or impurity atoms. As for the non-equilibrium (radiation) vacancies remaining in the bulk, they are also quite mobile and participate in different quasi-chemical reactions forming radiation defects of high-orders. Many of these vacancy-complexes are electrically active and hence largely determine electrical parameters of the semiconducting material.

In the quasi-chemical reactions occurring in irradiated n-Si crystals, it can be formed following electrically active vacancy-complexes: A-center (background impurity oxygen + vacancy: OV), E-center (dopant atom, usually, phosphorus + vacancy: PV), divacancy V_2 (or complex VV), etc. In p-Si crystals, there are formed complexes BV (dopant atom, usually, boron + vacancy), B/OV (interstitial boron atom + background oxygen + vacancy), OCV_2 (background oxygen and carbon + divacancy), etc.

In order to determine the sign of electric charge of vacancies in n-Si crystals, we irradiated them with 25MeV protons at 300K. It turned out that in initial samples in almost the entire temperature range of measurements, $N-T$ dependence corresponds to ionization of shallow donors associated with P: $N \approx 6 \cdot 10^{13} \text{ cm}^{-3} \approx \text{const}$ (Figure 2, Curve 1). The temperature-dependence of the electron concentration measured after proton irradiation with the dose of $2.7 \cdot 10^{12} \text{ cm}^{-2}$ corresponds to depletion of centers with electron energy level at $E_C - 0.17 \text{ eV}$ (Figure 2, Curve 6).

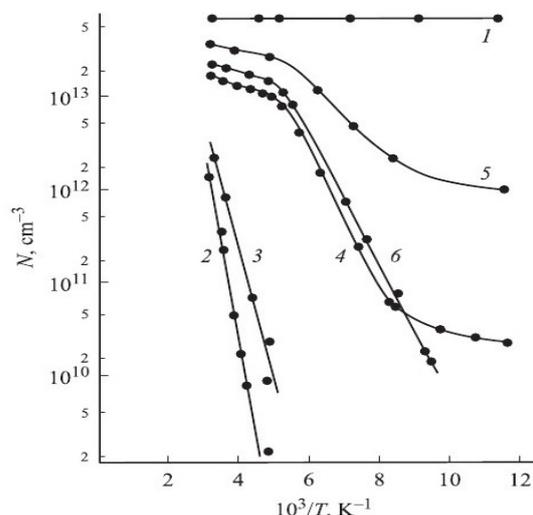
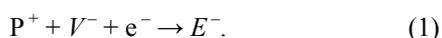


Figure 2. Temperature-dependence of electron concentration in n-Si crystals 1 – before irradiation, after irradiation at 300K by 25MeV protons with doses of 2–5 – $8.1 \cdot 10^{12}$ and 6 – $2.7 \cdot 10^{12} \text{ cm}^{-2}$, and annealed at temperatures 4 – 150 and 5 – 300°C

As a result of irradiation with dose of $8.1 \cdot 10^{12} \text{ cm}^{-2}$, $N-T$ curves reveal straight-line sections those correspond to depletion of centers at $E_C - 0.42 \text{ eV}$ (Figure 2, Curve 3) or are associated with centers with energy levels placed at $E_C - 0.54 \text{ eV}$ (Figure 2, Curve 2). As is known,¹² the level $E_C - 0.17 \text{ eV}$ is attributed with A-centers, the level $E_C - 0.42 \text{ eV}$ with E-centers and divacancies V_2 (or reveals their superposition), and, finally, the level $E_C - 0.54 \text{ eV}$ with

centers whose nature remains uncertain (the assumption¹² that it belongs to divacancies has been questioned). Curves 4 and 5 in Figure 2 correspond to depletion of *A*-centers and are obtained by measuring the samples irradiated with the dose of $8.1 \cdot 10^{12} \text{cm}^{-2}$ followed by annealing at 150 and 300°C.

Usually, in n-Si crystals irradiated with ~2MeV electrons at room temperature, formation efficiency of *E*-centers is somewhat higher than that for *A*-centers, notwithstanding the fact that the concentration of background O is about 3 orders of magnitude higher compared to that of dopant P. The high efficiency of introduction of *E*-centers must be due to the negative charge-state of vacancies, namely, their Coulomb attraction by ionized donors P^+ . Thus, the quasi-chemical reaction of formation of *E*-centers should be accompanied by the capture of an electron from the conduction band:



At room temperature *A*-centers with level at $E_C - 0.17 \text{eV}$ are not filled and, therefore, are in electrically neutral state. On the other hand, as noted above in silicon background oxygen is electrically inactive as well. From this we conclude that formation of an *A*-center from the negatively charged vacancy should be accompanied by excitation of an electron:



However, note that electron formed in this reaction, probably, does not move freely in the conduction band, but is captured by a deep center. As for the formed electrically neutral *A*-center, it can join with another (negatively charged) vacancy:



At room temperature, this oxygen–divacancy complex with deeper level at $E_C - 0.50 \text{eV}$ is negatively charged and due to the electrostatic repulsion further joining with negatively charged vacancies highly unlikely. Since at room temperature the *E*-centers with electron level at $E_C - 0.44 \text{eV}$ are negatively charged, the formation of similar divacancy-complexes is impossible as well. Joining of negatively charged vacancy V^- directly with the divacancy is hampered because its level $E_C - 0.39 \text{eV}$ is too deep enough and, therefore, at room temperature divacancy is negatively charged: V_2^- . It should be noted that the formation of divacancies V_2 by diffusion mechanism during the irradiation at room temperature from pairs of negatively charged monovacancies is unlikely. It is assumed that divacancies are formed as primary radiation defects (along with Frenkel pairs).

The reality of above listed quasi-chemical reactions is proved by the Figure 2, which shows that in n-Si during the irradiation at room temperature there are formed *A*- and *E*-centers, divacancies and OV_2^- -complexes. Note that the level $E_C - 0.50 \text{eV}$ corresponding to the complex OV_2^- we could not detect directly.

However, the existence of such a defect can be argued indirectly, by the increase in electrons concentration in process of isochronous annealing in the temperature range $\geq 500^\circ\text{C}$.

Since impurity B-atom in silicon crystals creates the shallow acceptor level, then at room temperature B-atoms are ionized by capturing of electrons from the valence band: B^- . Therefore, the dopant atoms in p-Si could not join with vacancies if they are negatively charged (like n-Si). On the other hand, in p-Si crystals produced by doping with boron and irradiated with electrons at room temperature there are found secondary radiation defects BV^+ with the energy level at $E_V + 0.45 \text{eV}$. This is a deep level capable to capture a hole from the valence band, what will lead to a positively charged defect-complex. Thus, $(\text{BV})^+$ complex should be formed by the following reaction:



Applying the method of local irradiation followed by the bulk photovoltage measurements, we have experimentally demonstrated¹⁵ that at room temperature and absence of any external influences the charges of primary radiation defects in n-Si crystals are of different sign of charge carriers, while in p-Si are of same sign. Therefore, we conclude that interstitials at the time of formation at room temperature both in n-Si and a p-Si should be charged positively.

Influence of irradiation intensity on efficiency of introduction of radiation defects

Influence of irradiation intensity φ on the efficiency of introduction of radiation defects η in n-Si has been studied for the series of three zone-melted samples doped to levels of $1 \cdot 10^{13}$, $6 \cdot 10^{13}$ and $2 \cdot 10^{14} \text{cm}^{-3}$ irradiated with 2MeV electrons at the dose of $5 \cdot 10^{15} \text{cm}^{-2}$. Measurements performed at room temperature, i.e. in the region of depletion of *A*-centers. Hence, the potential barrier between irradiated and non-irradiated parts of a sample was determined by changes in concentrations of radiation defects with deeper levels: *E*-centers and divacancies V_2 . It has been found that in certain interval the efficiency of introduction of radiation defects versus electron-beam intensity $\eta(\varphi)$ achieves the maximum that with increasing in electron concentration N moves towards higher values of φ . In crystals with above levels of doping, the critical values of intensity, respectively, are $2 \cdot 10^{12}$, $5 \cdot 10^{12}$ and $1 \cdot 10^{13} \text{cm}^{-2} \cdot \text{s}^{-1}$ (see Figure 3).

The $\eta(\varphi)$ curve having the maximum, position of which on φ -axis depends on N , suggest that there is satisfied an optimal relation between rate of creation of primary radiation defects, on the one hand, and changes in free charge carriers concentration, on the other hand. For small values of φ , all nonequilibrium vacancies become negatively charged and creation of divacancies by diffusion mechanism is unlikely because of strong electrostatic repulsion between vacancies. Under these conditions, high efficiency of formation of monovacancy defects, i.e. *E*-centers, according to the reaction (1) is expected. With increasing in the irradiation intensity not all the formed vacancies have a time to become negatively charged before joining with each other.

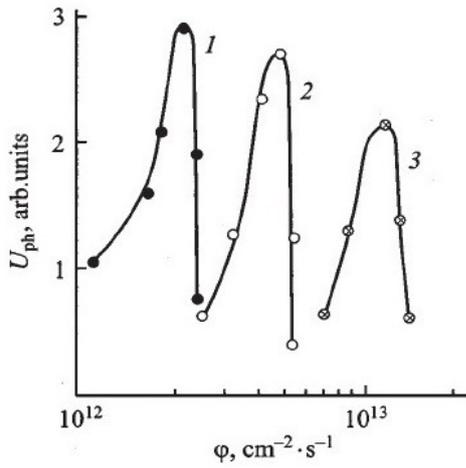
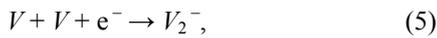


Figure 3. Bulk photo-emf versus electron-beam intensity in locally irradiated n-Si crystals. Energy of incident electrons is 2MeV and dose is $5 \cdot 10^{15} \text{cm}^{-2}$. Concentration of electrons is: 1 – $1 \cdot 10^{13}$, 2 – $6 \cdot 10^{13}$ and 3 – $2 \cdot 10^{14} \text{cm}^{-3}$

Accordingly, it increases the efficiency of formation of divacancies in the reaction,



which leads to the increase in share of divacancy complexes in the total concentration of radiation-induced defects.

But, this also reduces the total concentration of defects. Accordingly, photovoltage U_{ph} decreases and $U_{ph}(\eta)$ curve reveals a maximum. In crystals with different electron concentrations, the recharging of non-equilibrium vacancies occurs at different irradiation intensities that cause the different displacements of the maximum along the ϕ -axis.

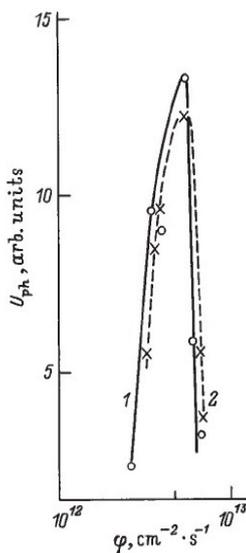


Figure 4. Bulk photo-emf versus electron-beam intensity in locally irradiated p-Si crystals. Energy of incident electrons equals to 2MeV and dose is $5 \cdot 10^{15} \text{cm}^{-2}$. 1 – without electric field and 2 – with biasing electric field of strength of 110V cm^{-1} .

Influence of the intensity of irradiation with 2MeV electrons on the defects formation in silicon has been also investigated for p-type material. It has been found that the

shape and position of the maximum is not changed substantially upon application of a constant electric field to the sample during its irradiation (Figure 4). Consequently, a part of reagents would be unchanged. This result is consistent with above interpretation that in such conditions there are mainly formed charged complexes $(BV)^+$. It is clear that such a product cannot be obtained via quasi-chemical reaction between oppositely charged reagents. Complex $(BV)^+$ is formed from the neutral complex of ionized dopant plus current carrier, $B^- + e^+$, and charged vacancy V^+ .

Influence of IR illumination in process of irradiation on defects formation

To study the effect of IR illumination on the kinetics of defects formation in silicon during 2MeV electron irradiation at room temperature, it has been studied n-Si samples, in which electrons from different levels of radiation defects are excited into the conduction band by monochromatic IR illumination with appropriate photon energies.

Isochronous annealing of irradiated crystals were performed at 200, 300 and 600°C, which are sufficient for complete annealing, respectively, E-centers, divacancies and complex-defects with high thermal stability – PV_2 , O_2V_2 , etc.¹²

As can be seen from Figure 5, the $\eta_E(h\nu)$ dependence has two minima at $h\nu_1=0.28\text{eV}$ and $h\nu_2=0.44\text{eV}$ (Curve 1); $\eta_A(h\nu)$ has the sharp maximum at $h\nu_1$ and it passes through the minimum at $h\nu_2$ (Curve 2); the $\eta_{TSC}(h\nu)$ has two maxima at $h\nu_1$ and $h\nu_2$ (Curve 3). As for the $\eta_{V2}(h\nu)$ dependence, it has the single maximum at $h\nu_1$ (Curve 4).

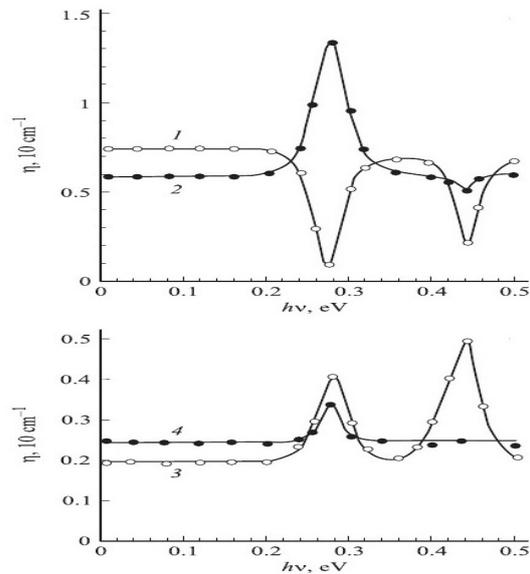
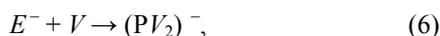


Figure 5. Efficiency of introduction of radiation-induced defects in n-Si versus energy of quantum of IR illumination in process of electron-irradiation: 1 – E-centers, 2 – A-centers, 3 – defects with high thermal stability, 4 – divacancies

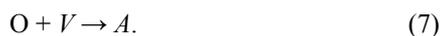
As noted above, at 300 K in n-Si crystals primary radiation defects – interstitial atom and vacancy – are charged oppositely: I^+ and V^- . Therefore, in dark the rate of

their recombination should be too high. On the other hand, it is known¹³ that monovacancy in the charge state V^- corresponds to the energy level located at $E_C-0.28\text{eV}$. When samples during irradiation are exposed by monochromatic IR light with quanta energy of $h\nu_1=0.28\text{eV}$, the vacancies are transferred into the neutral charge state and, accordingly, the rate of self-recombination of positively charged interstitials and neutral vacancies decreases. It takes also the place the increase in the concentration of non-equilibrium neutral vacancies, what leads to an increase in the efficiency of introduction of majority of secondary radiation defects. Although, in view of reducing in electrostatic attraction between ionized, i.e. positively charged, P atom and neutral vacancy the efficiency of introduction of E -centers decreases. In addition, some of the generated E -centers participating in quasi-chemical reactions with neutral vacancies are rebuilt in form of divacancy-defects,

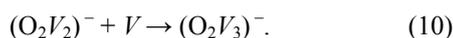
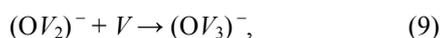
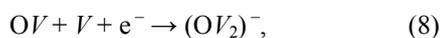


It leads to an additional decrease in η_E and the deep minimum on $\eta_E(h\nu)$ curve (Figure 5).

Non-equilibrium neutral vacancies that were not captured by positively charged P atoms are trapped by neutral O-atoms, the concentration of which is almost 3 orders of magnitude greater:



As a result, $\eta_A(h\nu)$ curve reveals the sharp peak at $h\nu_1=0.28\text{eV}$. For a neutral vacancy it will also be easier to interact with other deep and, therefore, negatively charged at room temperature complexes, what makes it possible the following series of conversions:¹²



Defect-complexes formed in reactions (6–10) are characterized by high thermal stability and lead to an increase in η_{TSC} (Figure 5, Curve 3). It should be noted that complexes OV_2 and O_2V_2 exist in low concentrations and, therefore, complexes OV_3 and O_2V_3 formed at their basis can be found in negligible concentrations. Hence, in the vicinity of $h\nu_1$ the value of η_{TSC} is mainly determined by the concentration of complexes PV_2 .

The cascade mechanism of formation of divacancies prevails over the diffusion mechanism, i.e. divacancies are mostly formed as primary radiation defects. The small increase in η_{V_2} at $h\nu_1$ (Figure 5, Curve 4) can be attributed to the increased probability of formation of divacancies from a pair of neutral monovacancies by diffusion mechanism:



As a result of all these processes in n-Si crystals irradiated with electrons under the IR illumination with photon energy of $h\nu_1=0.28\text{eV}$, the total concentration of radiation-induced defects, and, hence, the efficiency of their introduction remains essentially unchanged: it increases only ~ 1.2 -times.

Note for comparison that the doping with germanium (Ge) perhaps more than 7-fold increases the radiation resistance of silicon due to practically complete eliminating the formation of A -centers even in crystals with elevated concentration of oxygen.¹⁴⁻¹⁷

When n-Si crystal in process of irradiation is exposed to the light with energy of quanta of $h\nu_2=0.44\text{eV}$, negative E -centers become neutral. And due to the weakening in the electrostatic interaction between a neutral E -center and a negative vacancy the probability of formation of PV_2 complexes increases:



If we assume that the irradiation produces only monovacancy defects, then the concentrations of radiation-induced defects N_{RD} and primary vacancies N_V are the same: $N_{\text{RD}}=N_V$. But, if in parallel with monovacancies there are formed divacancies then $N_{\text{RD}}<N_V$. This inequality explains the observed decrease in η_E and η_A (Figure 5, Curves 1 and 2), appearance of the peak on $\eta_{V_2}(h\nu)$ curve (Figure 5, Curve 3) and the slight (~ 1.2 -fold) decrease in the number of radiation-induced defects in n-Si crystals irradiated under the IR illumination with photon energies of $h\nu_2=0.44\text{eV}$.

Thus, our studies have shown that IR illumination with suitable photon energy can significantly alter the efficiency of introduction of various radiation-induced defects in crystalline silicon, but the total efficiency will remain almost unchanged.

Influence of irradiation temperature on efficiency of defects introduction

The change in the charge-state of radiation defects occurs not only under the IR illumination, but also due to changes in irradiation temperature T_{irr} . Effect of the T_{irr} on the defects kinetics in silicon we have investigated for n-type crystals doped with phosphorus. Namely, we used zone-melted single crystals with electrons concentration of $6 \cdot 10^{13}\text{cm}^{-3}$. Figure 6 shows the efficiency of defects introduction versus the irradiation temperature. As one can see, at 150°C $\eta_E=0$, and $\eta_A(T_{\text{irr}})$ and $\eta_{\text{TSC}}(T_{\text{irr}})$ pass through maxima (Curves 1 and 4). In the region $100\text{--}150^\circ\text{C}$, Curve 2 passes through the minimum and in the region $170\text{--}440^\circ\text{C}$ efficiency decreases monotonically. This means that $\eta_{\text{TSC}} \approx \eta_{PV_2} + \eta_{OV_2} + \eta_{O_2V_2} + \eta_{OV_3}$.

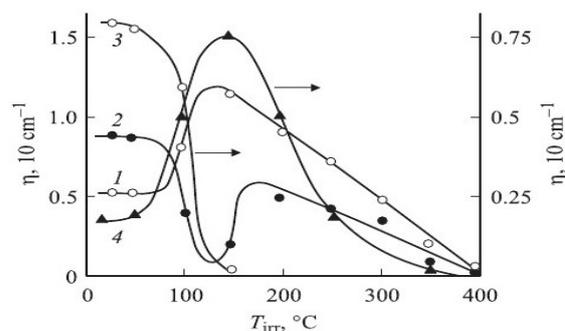
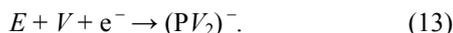


Figure 6 of defects introduction versus irradiation temperature in n-Si crystals irradiated by 2MeV electrons: 1 – A -centers, 2 – divacancies, 3 – E -centers, 4 – defects with high thermal stability

The η_E decreases with increasing T_{irr} up to 100–150°C, apparently, due to two processes: dissociation of a PV complex into P and V and transformation of a neutral E-center into more complex and more stable defect PV_2 :



Certain part of the non-equilibrium vacancies that have not been captured by neutral E-centers can be used for the formation of A-centers, on the basis of which the OV_2 complexes are formed in subsequent reaction



Within the band gap, OV_2 complexes correspond to the level of $E_C - 0.50\text{eV}$.¹² Consequently at room temperature these complexes are negatively charged like the monovacancies and the electrostatic repulsion hampers extension of the reaction (14) to form the complex OV_3 .

Non-monotonic $\eta_{V_2}(T_{\text{irr}})$ curve can be explained by changes in the charge-state of monovacancies. At low irradiation temperatures (20–80°C), with the accumulation of E-centers and the removal of electrons from the conduction band, up to the temperature of deionization of E-centers, the deal of neutral vacancies increases and crystal saturation by the vacancies is avoided by forming the divacancies V_2 . Dissociation of E-centers increases the deal of negative vacancies. In corresponding region, dependence of the efficiency of introduction of negative divacancies on irradiation temperature passes through the minimum (Figure 6, Curve 2), probably, due to electrostatic repulsion of charged vacancies those in more extent are spent on the formation of A-centers. Further increase in T_{irr} shifts the Fermi level to the middle of band gap and it starts recharging of vacancies: $V^- \rightarrow V + e^-$. The deal of neutral vacancies and η_{V_2} again increase. These processes can explain the existence of peaks in the vicinity of 150°C in the Figure 6 (Curves 1 and 4). At higher temperatures, $T_{\text{irr}} \geq 150$ –300°C, the dissociation of A-centers dominates and V_2 and OV_2 form more stable defect-complexes:



and



which are annealed at 410 and 470°C, respectively.¹²

When $T_{\text{irr}} = 400^\circ\text{C}$, there is satisfied the approximate equations: $\eta_E = \eta_A = \eta_{\text{TSC}} \approx 0$ (Figure 4, Curves 1 and 2), despite the fact that the annealing temperature for these complexes $\geq 400^\circ\text{C}$. This fact indicates that they are formed on the basis of the E- and A-centers according to reactions (13–16). In the range 20–150°C, efficiency of introduction of radiation defects with high thermal stability η_{TSC} increases due to the formation of PV_2 complexes on the basis of neutral E-centers, while in the range of 150–400°C it reduces what can be attributed to the decrease in η_E and η_A , i.e. rates of formation of E- and A-centers, which are formed on the basis of thermal-stable complexes PV_2 , OV_2 , O_2V and OV_3 . Last is annealed at $\geq 400^\circ\text{C}$.

Summarizing the results we can conclude that the increase in the irradiation temperature of silicon doped with phosphorus leads to the increase in efficiency of introduction multi-vacancy phosphorus- or oxygen-containing radiation defects.

Quasi-chemical reactions in irradiated silicon in process of isochronous annealing

When the annealing temperature increases, products of dissociation of relatively less stable defect complexes increasingly come into quasi-chemical reactions with impurity atoms or structural imperfections of the structure. The result is the formation of new more stable complexes, the increase in the concentration of some existing defects or their conversion into different type defects. In electron-irradiated zone-melted n-Si crystals with relatively low content of oxygen, $9 \cdot 10^{15}\text{cm}^{-3}$, formed complexes mainly are A- and E-centers and divacancies V_2 .

For test samples irradiated with 2MeV electrons at room temperature and annealed in the range of 80–400°C, it has been shown that E-centers are annealed in the range 100–150°C, V_2 – 250–300°C, and A-centers – around 300°C (Figure 7, Curves 1, 2 and 3). As can be seen from Figure 7, during the annealing of E-centers the concentration of A-centers increases (Curves 1 and 2). Presumably, one of the decay products of E-centers – monovacancy – participates into quasi-chemical reaction with impurity atom of oxygen that results in the effect observed at 150°C:

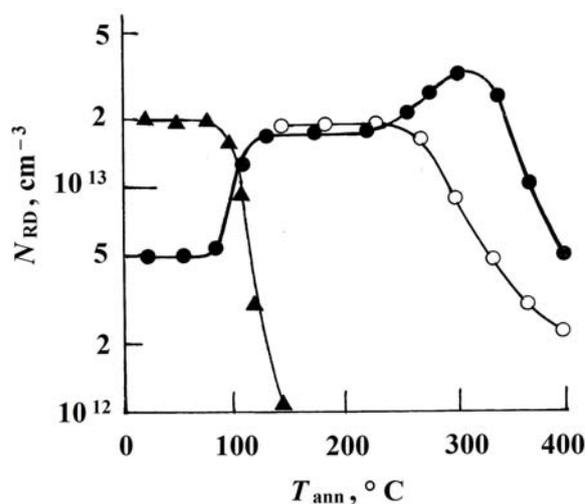


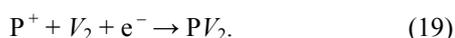
Figure 7. Changes in concentrations of 1 – E-centers, 2 – A-centers (2) and 3 – divacancies in electron-irradiated zone-melted n-Si versus isochronous annealing temperature

The increase in the concentration of A-centers is also observed due to conversion of V_2 in the range 250–300°C:



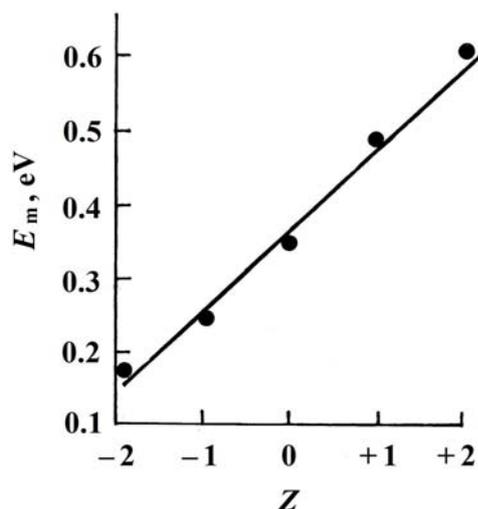
As can be seen from Figure 7, after the conversion of divacancies with concentration of $2 \cdot 10^{13}\text{cm}^{-3}$ there are formed A-centers with concentration of $1 \cdot 10^{13}\text{cm}^{-3}$ (Curves 2 and 3). The decay of V_2 means the formation of a

pair of vacancies. And for the formation of a single A -center it is sufficient only single vacancy. It turns out that the formation of A -centers consumed about a quarter of the annealed V_2 . Apparently, other divacancies are annealed by conversion into other defects such as complexes OV_2 , which in the silicon crystalline lattice are situated near the Si–O–Si bonds. At the first stage, it forms A -center via reaction $O + V \rightarrow A$ (formation mechanism of such a center is easy to analyze for the structure of silicon dioxide¹⁸). And after that, a second vacancy is added: $A + V \rightarrow OV_2$. The OV_2 complexes correspond to the energy level at $E_C-0.50\text{eV}$ and they are annealed at 350°C . It is possible that annealing of V_2 occurs by partially converting them into phosphorus-containing complexes PV_2 . These complexes in n-Si crystals are formed during a long exposure or isochronous annealing of irradiated samples.¹⁹ Under these conditions divacancies are transferred into the neutral charge-state and PV_2 complexes are formed by the reaction:



It is known¹⁴ that in silicon crystals grown by Czochralski method, i.e. with high oxygen content, the dominant radiation defect is A -center – OV complex. If isochronous annealing is conducted at $\geq 300^\circ\text{C}$, a significant part of these centers is transformed into O_2V . With increasing annealing temperature O_2V transforms into O_3V (450°C), then O_3V into O_4V ($450-485^\circ\text{C}$), etc. The O_2V complexes are formed via capturing diffusing A -centers by interstitial oxygen, while the centers with higher content of oxygen are formed via capturing of diffusing oxygen by the complexes O_2V , O_3V , O_4V , etc.¹⁴

Figure 8. Activation energy of vacancy migration in silicon versus its charge-state



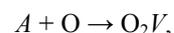
For p-Si crystals obtained by the Czochralski method and irradiated with 8MeV electrons at the dose of $5.0 \cdot 10^{15}\text{cm}^{-2}$, we identified (see the characteristics below) the values of the activation energy of migration E_m for vacancies in the charge-states of 0 and +2 as 0.35 and 0.60eV, respectively. These results, together with available data²⁰ are shown in Figure 8. As one can see, the activation energy of vacancy migration is linearly increasing function of the charge number Z of the defect. Therefore, it seems natural to

assume the same behavior for O_nV complexes ($n=1,2,3,\dots$). With increasing in the annealing temperature it changes their charge state: they lose electrons and become positively charged. Consequently, the activation energy of migration of O_nV complexes increases. When this value exceeds the activation energy of migration of interstitial oxygen atoms (2.54eV^{12}), complexes of higher order are formed mainly in the process of capture of diffusing background oxygen by the already existing oxygen–vacancy complexes.

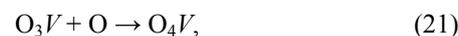
A minority of A -centers has to be annealed at 300°C by the dissociation reaction:



and rest of these centers is annealed by conversion. Produces are higher order radiation defects,

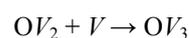
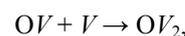


and



respectively, at 300, 450 and 485°C .

Simultaneously with the formation of O_nV complexes, there are also formed OV_n complexes ($n=1,2,3,\dots$). As noted above, in n-Si the level $E_C-0.28\text{eV}$ corresponds to nonequilibrium vacancy and, therefore, at room temperature they are charged negatively. In these conditions, reactions (2) and (3) form only A -centers and OV_2 . However, annealing at $\geq 500^\circ\text{C}$ transforms negative vacancies to the neutral state and then it starts the formation of radiation-induced defects in the high-order reactions:

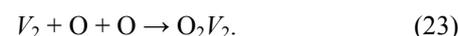


and

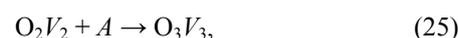


respectively, at 20, 300 and 450°C .

Annealing of A -centers at 350°C makes it possible the conversion



The concentration of O_2V_2 complexes should be very low because most of oxygen atoms return to interstitials, the normal position for this impurity in silicon lattice. At 400°C , the capture of vacancy or A -center by O_2V_2 complex transforms it, respectively, into complexes O_2V_3 or O_3V_3 :



Figures 9 and 10 show the changes in the concentration of major carriers depending on the measurement temperature and annealing temperature; and concentrations of major carriers and various radiation defects depending on the temperature of isochronous annealing in p-Si crystals doped up to level of $6 \cdot 10^{13} \text{ cm}^{-3}$ and irradiated with 8MeV electrons. The sharp increase in the hole concentration in the range of $T_{\text{ann}}=170\text{--}200^\circ\text{C}$ is due to the annealing of defects with the level at $E_V+0.45\text{eV}$ and concentration of $5 \cdot 10^{12} \text{ cm}^{-3}$. This level belongs to the complex of dopant impurity B with a vacancy, i.e. BV .¹²

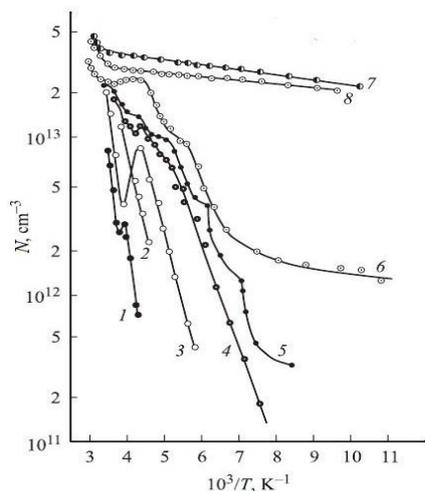


Figure 9. Temperature-dependence of hole concentration in p-Si crystals irradiated with 8MeV electrons at the dose of $5.0 \cdot 10^{15} \text{ cm}^{-2}$: 1 – before annealing and after annealing at 2 – 100, 3 – 170, 4 – 240, 5 – 270, 6 – 300, 7 – 400 and 8 – 500°C

In the range $T_{\text{ann}}=260\text{--}300^\circ\text{C}$, there are annealed defects with the energy level at $E_V+0.28\text{eV}$ and concentration of about $8 \cdot 10^{12} \text{ cm}^{-3}$ (Figure 9, Curve 3). Judging from annealing temperature and the energy level, these centers are divacancies.¹² Annealing of divacancies lead to a sharp increase in the concentration of defects with the energy level at $E_V+0.22\text{eV}$, so-called *H*-centers (Figure 9, Curve 4). Concentrations of divacancies broken by thermal treatment in the range $270\text{--}290^\circ\text{C}$, on the one hand, and formed centers with level at $E_V+0.22\text{eV}$, on the second hand, are equal within the measurements error limits. From this we can conclude that *H*-centers contain divacancies. On the stepped Curve 5 of Figure 9, third step corresponds to the transition of electrons from the valence band to the level at $E_V+0.22\text{eV}$, what leads to the increase in the hole concentration. As seen from Figure 9, the process ends at temperature of about 220K. Naturally, at higher (e.g., room) temperature electrons cannot return to the valence band causing compensation of holes.

Like a P-atom in n-Si, which forming *E*-center together with a vacancy, takes its fifth valence electron from the conduction band, in p-Si divacancy forming the level at $E_V+0.22\text{eV}$ takes an electron from the valence band. Therefore, annealing should increase the hole concentration. Although, in the range of $T_{\text{ann}}=270\text{--}290^\circ\text{C}$ the hole concentration remains almost unchanged (Figure 10, Curve 1). The explanation lies in the fact that the complexes formed during annealing of divacancies should contain

dopant B-atoms. Concentrations of boron atoms blocked by the formation of *H*-centers and major carriers formed during the annealing of divacancies are equal. Therefore, in the range $270\text{--}290^\circ\text{C}$ there are no changes in concentration of holes. These results confirm the previously expressed view on the existence in irradiated p-Si crystals complexes of boron dopants with divacancies, BV_2 , which are annealed at higher temperatures, in the range of $350\text{--}400^\circ\text{C}$.

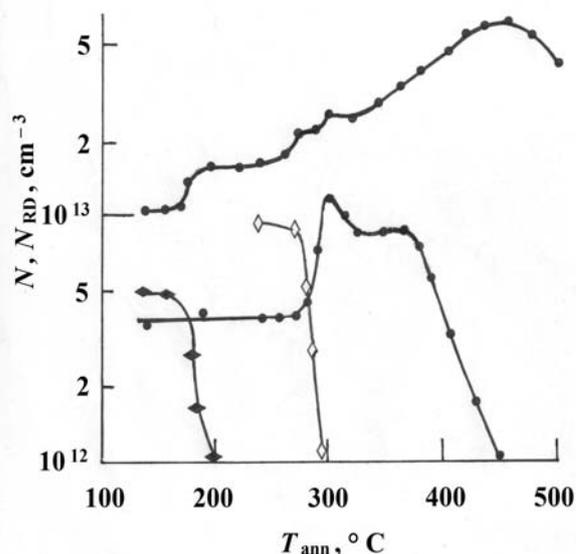


Figure 10. Concentrations of 1 – holes and 2–4 – some of radiation defects in p-Si crystals irradiated with 8MeV electrons at dose $5.0 \cdot 10^{15} \text{ cm}^{-2}$ versus isochronous annealing temperature

The activation energy of the migration of divacancies is about 1.30eV, while the binding energy of this defect is higher: 1.47eV.^{12,21} Therefore, in the crystal divacancies can migrate without dissociation. It is also known that the BV complexes are annealed at 180°C (Figure 10, Curve 2) and thus they cannot participate in the formation of BV_2 complexes in higher temperature range of $270\text{--}290^\circ\text{C}$. From the above it can be assumed that BV_2 complexes are formed by conversion of divacancies,



rather than sequential capture by B-atoms of vacancies *V* generated by irradiation, as it had been assumed previously.

As seen from Figure 10, *H*-centers are annealed in two stages: at $300\text{--}320$ and $360\text{--}440^\circ\text{C}$. The initial concentration of *H*-centers is $3.5 \cdot 10^{12} \text{ cm}^{-3}$ and the same concentration of centers is annealed at the first stage. The concentration of decayed centers at second stage coincides with the concentration of divacancies formed during annealing of complexes BV_2 ($3.5 \cdot 10^{12} \text{ cm}^{-3}$). These results suggest that the so-called *H*-center with the energy level at $E_V+0.22\text{eV}$ actually is the superposition of two defects, H_1 - and H_2 -centers, of different types with different annealing temperature intervals: $300\text{--}320$ and $360\text{--}440^\circ\text{C}$, respectively. At the first stage, there is annealed a center of currently unknown nature, and at the second stage – BV_2 complexes, which are formed during conversion of divacancies at $270\text{--}290^\circ\text{C}$ by joining with substituting B-atoms. After annealing at 300°C the change in the hole concentration may be due to

dissociation or formation of O_2V_2 complexes, so-called K -centers ($O + C + V_2$),²² and other deep and thermally stable centers.

Conclusion - Prospects for practical applications

Conducted investigation has shown that the variation in the parameters of irradiation by beams of elementary particles – temperature, intensity, IR illumination of crystals during irradiation – affects the quasi-chemical reactions that occur in silicon during irradiation and isochronous annealing of the irradiated material.

Control over quasi-chemical reactions allows obtaining of crystals with different sets of radiation-induced defects, i.e. crystals with certain electrical, optical or recombination properties. It is also possible to change the type of the dominant defect. In this regard, we note that most of the oxygen-containing complexes formed with high-temperature annealing of irradiated silicon are optically and electrically active and can significantly affect the characteristics of the silicon-based electronic devices.

Another example of this type is associated with changes in the charge-state of nonequilibrium vacancies formed in the process of irradiation, which react quasi-chemically with already existing defects. With this process it is possible to stimulate the formation of defects, such as multi-vacancy complexes OV_n , PV_n , etc ($n=1,2,3,\dots$). But, the more primary radiation defects, in particular, vacancies are spending per complex defect, the higher is the radiation resistance of the material. If, for example, instead of PV complexes (E -centers) there are formed PV_4 complexes it is possible to expect the 4-fold increase in the radiation resistance of crystalline silicon doped with phosphorus in regard to the concentration of majority charge carriers, i.e. electrons.

Quasi-chemical reactions also can control formation of “dielectric” and “metallic” nano-inclusions in the irradiated silicon and, hence, the electronic properties of this material.

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