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Formation of Submicron n^+-Layers in Silicon Implanted with H^+-Ions

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Formation of submicron n^+-layers in commercial Pd–Si Schottky diodes with the active base region fabricated on epitaxial phosphorus-doped silicon, implanted with 300 keV hydrogen ions and thermally treated in the temperature range 20–450 °C, is studied. Standard C–V measurements and deep level transient spectroscopy were used. It is shown that formation of n^+-layers at the end of projective range of ions was caused by producing of hydrogen-related donors of two types, one of them is bistable. The kinetics of their accumulation is described by the first-order reaction with the following values of parameters for bistable and not transforming H-donors: the activation energy $\Delta E_1 = 2.3$ eV, the pre-exponential factor $\tau_{01} = 9.1 \times 10^{-17}$ s, the ultimate concentration $N_{01} = (1 \pm 0.1) \times 10^{16}$ cm^{-3}; $\Delta E_2 = 1.4$ eV, $\tau_{02} = 4.2 \times 10^{-9}$ s, $N_{02} = (3 \pm 0.1) \times 10^{16}$ cm^{-3}. Correlation between processes of transformation of post-implantation radiation defects and hydrogen-related donors formation was identified.

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1. Introduction

Proton-beam irradiation is a potentially attractive approach for modifying the electrical properties of silicon crystals [1]. One of the most interesting properties of implanted hydrogen is that its interaction with radiation-induced and native defects during heat treatment leads to the formation of high concentrations (up to 10^{17} cm^{-3}) of shallow hydrogen-related donors (H-donors) [2–4]. It is also important to note that H-donors do not contain oxygen atoms in our case [5]. Most of the donor formation investigations were made for ≈ 100 μm thick floating zone grown Si layers produced using multi-energy H^+ ion implantation [3, 4]. However, it was shown previously [6] that significant features in H-donors formation were observed in the submicron layers with high density of the introduced hydrogen. The purpose of this work was to study the formation and properties of submicron n^+-layers in epitaxial silicon.

2. Experimental

In our studies, we used commercial Pd–Si Schottky diodes with the active base region made of epitaxial phosphorus-doped silicon 5 μm in thickness, with a resistivity $\rho = 1.05$ Ω cm. The diodes were implanted with 300 keV H^+ ions at room temperature from the planar side through a Pd contact. The fluence varied in the range $F = (1\times10^{13}$–$1\times10^{15})$ cm^{-2}. The electron concentration profiles were obtained by standard C–V measurements at a bridge frequency of 1.2 MHz. For prevention of influence of deep traps, in some cases C–V measurements were made at liquid nitrogen temperature when the electron emission rate from the traps was smaller than frequency of measurement. Implanted hydrogen concentration profiles were calculated by means of TRIM software. The parameters of radiation-induced defects were determined by deep level transient spectroscopy (DLTS) at 1 MHz and a gating time ratio $t_2/t_1 = 5$. The bias was varied in the range 0–5 V, which corresponded to a probing depth in the base region from 0.2 to 2.1 μm.

3. Results and discussion

Changes of the depletion region width (reverse bias $U = -5$ V, temperature $T = 86$ K) and dependence of radiation-induced defects concentration from isochronal (20 min) annealing temperature are presented in Fig. 1. The DLTS spectra are shown in Fig. 2. Values of parameters of post-implantation radiation defects (curve 1) are found using the Arrhenius plots. These parameters and identification of defects (according to data [1]) are given in Table.

The depletion region width before implantation was $d = 3.6$ μm. According to the comparative analysis of the obtained data (Fig. 1), increasing of d up to 4 μm is generally caused by formation of E-center (curve 1) because concentration of A-center and VOH defect (curves 2, 3) are negligible (E-center — donor–vacancy defect, A-center — oxygen–vacancy defect, VOH

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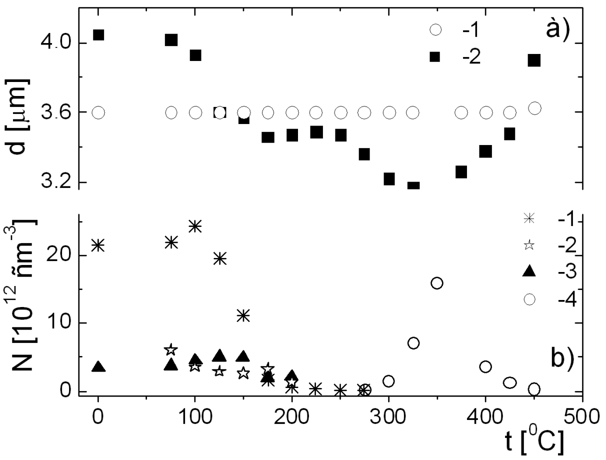

Fig. 1. Depletion region width (a) ($U = -5$ V, $T_{\mathrm{meas}} =$ 86 K) and radiation defects concentration (b) changing with the increasing of annealing temperature for the Schottky diode. Irradiation fluence $F = 1 \times 10^{13}$ cm^{-2}. (a) 1 — control, 2 — after irradiation, (b) 1 — E-center, 2 — A-center, 3 — VOH, 4 — $E_{\mathrm{c}} - 0.21$ eV.

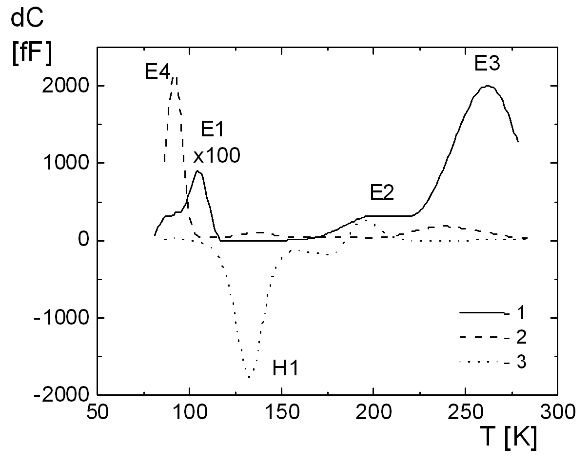

Fig. 2. DLTS spectra (gate-off time, 2.6 μs) of Pd–Si Schottky diodes implanted with hydrogen ions to $F = 1 \times 10^{14}$ cm^{-2} at different thermal treatment: 1 — after implantation, 2 — 350 ℃, 3 — 450 ℃.

— vacancy–oxygen–hydrogen defect). After E-center annealing at $t = 200$ ℃ d restores to the initial value. With further rise of annealing temperature, quantity d becomes below the initial value. This fact indicates formation of donors. Their maximum concentration is reached at $t = 350$ ℃ and coincides with the concentration of undefined defect E4 (energy level $E_{\mathrm{c}} - 0.21$ eV and the capture cross-section $\sigma = 2 \times 10^{-11}$ cm^2) in Fig. 2 (curve 2). At the temperature 450 ℃ the depletion region width exceeds the initial value, and anomalous peak (a minority carriers trap in the absence of hole injection) appears in the DLTS spectrum (curve 3). This peak corresponds to acceptor center H1 (energy level $E_{\mathrm{v}} + 0.31$ eV), and their concentration is approximately equal to the concentration of E4 defect. Therefore, sufficiently clear correlation between the process of H-donors formation and the radiation defects transformation is observed.

TABLE

Main parameters of post-implantation radiation defects in H$^+$ ion-irradiated silicon.

Peak number	Activation energy [eV]	Capture cross-section [10^{-15} cm^2]	Annealing temperature [℃]	Identification
E1	$E_{\mathrm{c}} - (0.165 \pm 0.05)$	5 ± 2	350	(V–O)$^{0/-}$, A-center
E2	$E_{\mathrm{c}} - 0.31$	1.6	250	VOH-center
E3	$E_{\mathrm{c}} - (0.42 \pm 0.01)$	1 ± 0.3	150	(P–V)$^{-/0}$, E-center

Distribution of the electron concentration in the base of diodes, which was implanted by H$^+$ ions, at different temperatures of the treatment is presented in Fig. 3. Also calculated, subject to energy losses in the metal contact electrode, profile of implanted hydrogen is shown here. It is obvious that the experimental (curve 2) and calculated (curve 5) profiles agree, and their half-width is approximately equal to 0.4 μm. As a result we can conclude that submicron n^+-layer formation is determined by generation of hydrogen-related donors (H-donors). It is known that at least two types of H-donors are produced [6]. One of them is the donor with a negative effective correlation energy (bistable donor); the transformation between two equilibrium configurations of bistable donor proceeds with the Fermi level position $E_{\mathrm{F}} = E_{\mathrm{C}} - 0.30$ eV [7]. Actually, storing of the samples at $t = 100$ ℃ reduces approximately twice the concentration of H-donors, and the subsequent quenching from 200 ℃ in water recovers their initial concentration (Fig. 3). This procedure can be repeated over and over again.

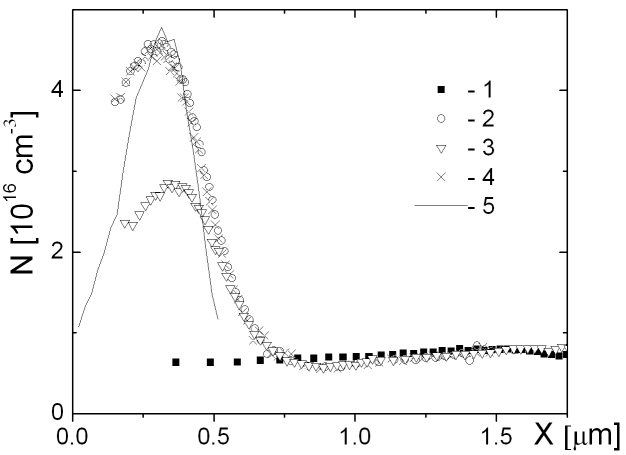

Fig. 3. Electron concentration profiles across the base region of Pd–Si Schottky diodes implanted with hydrogen ions to $F = 10^{15}$ cm^{-2} and following treatment: 2 — 350 ℃, 20 min; 3 — 100 ℃, 7 h; 4 — 200 ℃, 20 min and quenching to water; 1 — initial; 5 — calculated profile of implanted hydrogen (normalized to maximum of electron concentration).

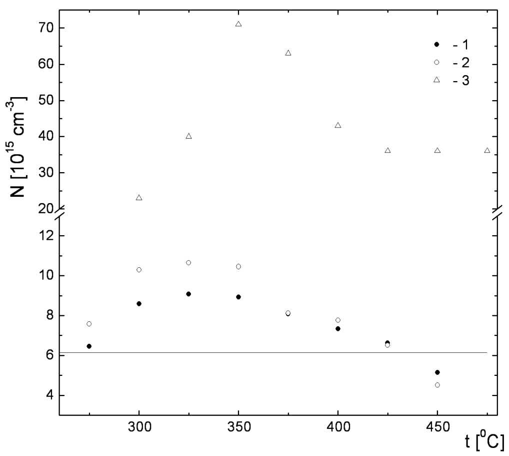

Fig. 4. Effect of isochronal (20 min) annealing on conductivity electron concentration in the maximum of their distribution in the base of the Schottky diode, implanted with different fluences of hydrogen ions. F [cm^{-2}]: 1 — 1×10^{13}; 2 — 1×10^{14}; 3 — 1×10^{15}. Concentration of dopant (phosphorus) is marked by solid line.

The results of isochronal annealing of excess conduction electrons are given in Fig. 4. Concentration of excess conduction electrons N corresponds to their maximum profile in the base of the Schottky diodes, implanted with different hydrogen ion fluences. The initial level ($\approx 6.2 \times 10^{15}$ cm^{-3}) of base layer doping is marked in Fig. 4 by the horizontal line. We can see that type of accumulation and the first stage of H-donors annealing is approximately equal for all implanted fluences. However, behavior of isochronal annealing curves considerably depends on implantation fluence in the case of the second stage of annealing ($t > 425$ ℃). In the case of $F = 1 \times 10^{15}$ cm^{-2} H-donors concentration in the temperature range (425–475) ℃ is higher than dopant concentration and is equal to 3.5×10^{16} cm^{-3}. But in the case of $F \leq 1\times10^{14}$ cm^{-2} H-donors completely anneal after $t > 425$ ℃ and compensating defects appear, because conductivity electron concentration becomes below initial. The presence of two stages of annealing is related to the existence of two types of the H-donors, one of which is bistable (Fig. 3) and anneals with increasing temperature to 475 ℃.

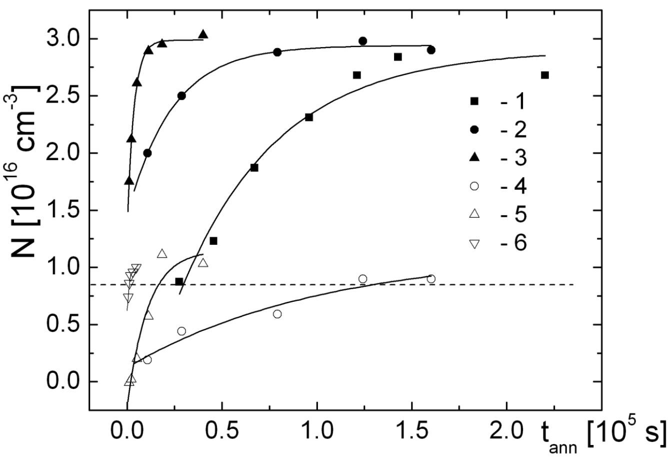

Fig. 5. Dependences of concentration of bistable (1, 2, 3) and not transforming (4, 5, 6) hydrogen-related donors on thermal treatment time for different temperatures. T [℃]: 1 — 250; 2 — 300; 3 — 350; 4 — 250; 5 — 275; 6 — 300.

The kinetics of donor accumulation of both types — bistable (1, 2, 3) and not transforming (4, 5, 6) — in the temperature range 250–350 ℃ is presented in Fig. 5. As we can see, there is a limit concentration for each type of H-donors. The kinetics of accumulation described by the first-order reaction (continuous lines) is in conformity with the expression

$$N = N_0 \left[1 - \exp\left(-\frac{t_{\rm ann}}{\tau}\right)\right], \tag{3.1}$$

where

$$\tau = \tau_0 \exp\left(\frac{\Delta E}{kT}\right), \tag{3.2}$$

τ — time constant, $t_{\rm ann}$ — annealing time, N_0 — concentration limit of H-donors; τ_0 — pre-exponential factor, ΔE — activation energy, k — the Boltzmann constant, T — temperature. From Fig. 5 we took the values of parameters for the bistable and not transforming H-donors respectively: $\Delta E_1 = 2.3$ eV, $\tau_{01} = 9.1 \times 10^{-17}$ s, $N_{01} = (1 \pm 0.1) \times 10^{16}$ cm^{-3}, $\Delta E_2 = 1.4$ eV, $\tau_{02} = 4.2 \times 10^{-9}$ s, $N_{02} = (3 \pm 0.1) \times 10^{16}$ cm^{-3}.

4. Conclusions

Submicron n^+-layers are formed in silicon after implantation with H^+ ions and thermal treatment. These layers are produced at the end of projective range of ions at the expense of simultaneous formation of hydrogen-related donors of two types; one of them has bistable property. H-donors formation starts after annealing of post-implantation radiation vacancy defects. Also H-donors formation correlates with introduction of new deep level defects. The kinetics of H-donors accumulation of both types is described by the first-order reaction.

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