$E.L.\ Zhavzharov\ ^{\scriptscriptstyle{(1)}}\text{, associate professor, c.t.s.}$

T.V. Kritskaya (2), professor, d.t.s.

V.M. Matyushin (1), professor, d.t.s.

Yu.M. Chatshinov (3), senior researcher, c.t.s.

SOME FEATURES FOR CONDUCT OF HYDROGEN IN CRYSTALLINE SILICON

(1) Zaporozhe national technical university, Ukraine, (2) Zaporozhe state engineering academy, Ukraine, (3) Saint Petersburg state electrical engineering university V.I. Ul'yanov-Lenin «LETI», Russia

Content of hydrogen is investigational in crystalline silicon, got by different methods. There is a tendency for towards increasing of concentration of hydrogen with the height of process temperature. In single-crystals crystallization of which takes place at the temperature ~of 1412 °C, content of hydrogen is noticeable higher, than in the polycrystalline bars of silicon, got by besieging from a gas phase on padding at the temperatures of 850-1150 °C. Instability and rapid slump in time of high values of $\tau_{\text{n-e.ch.ca}}$ in the single-crystals of CZ-Si, grown at the atmosphere of Ar+SiH₄, can be related to the delocalization of hydrogen atoms from distributions and their subsequent diffusion from the volume of single-crystal of silicon. Slow degradation of $\tau_{\text{n-e.ch.ca}}$ in single-crystals, grown from the charge of the mixed composition, allows to count migration of atoms of hydrogen as one of reasons for decline of this parameter, along with disintegration of supersaturated solid solution of oxygen in the single-crystals of CZ-Si.

Key words: crystalline silicon, method of Chokhralsky, diffusion of hydrogen, time of life of non-equilibrium charge carriers, oxidizing defects of packing

A study of action for hydrogen is of interest both for understanding of processes of imperfectly-admixture co-operation in the volume of crystalline silicon and for creation of complex for technological operations at the receipt of semiconductor devices and integrated schemes.

Presently for explanation of physical and chemical processes, being at the basis of technological operations of alloying, measuring of electrophysics and structural parameters of single-crystals, influence of the hydrogen contained in silicon practically is not examined. By our researches [1], it was set that in the different types of crystalline silicon hydrogen is at very high concentrations, exceeding content of alloying elements, oxygen and carbon.

Taking into account that level of satiation by hydrogen higher in single-crystals, as compared to polycrystalline silicon, at identical terms the processes of growing were executed on the method of Chochralsky from loading of polycrystalline silicon-raw, circulating single-crystals, and also mixtures of circulating materials and raw. It is set that the highest values of $\tau_{n-e.ch.ca}$ were got on single-crystals from the mixed loading.

Also at the process of growing it war investigated possibility of receipt of silicon single-crystals with the closeness of distributions of $N_D \ge 10^3$ sm⁻² and by the

values of time of life of non-equilibrium charge ($\tau_{n\text{-}e\text{.}ch\text{.}ca} \ge 205 \text{ mcs}$) carriers. Coming from pre-condition about the possible tempering of centres of recombination at the conditions of intensification for speed of cooling of single-crystal [2], at the process of growing used the environments of inert gases with different heat conductivity, in particular, genius, argon and mixture argon + SiH_4 . As is generally known [3], silicomethane at temperatures more than 400 °C decomposes with atomic hydrogen formation which possesses highsolubility in the grate of silicon and does not result in formation of pores. The total concentration of admixtures in the used silicomethane did not exceed $2 \cdot 10^{-8}$ %.

The presented results show possibility of increase of $\tau_{n\text{-}e\text{.}ch\text{.}ca}$ in single-crystals, grown in mixture of $Ar+SiH_4$, as compared with processes, realized in an argon or helium. The most substantial increase for $\tau_{n\text{-}e\text{.}ch\text{.}ca}$ (to 750-800 mcs) was looked in single-crystals, grown in this mixture at pressure in the chamber of 133 $\kappa\Pi a$ (without the channel of gas), however the receipt of single-crystals of the required length was laboured. Control of oxygen concentration showed at the grown single-crystals, that her size had been on 30-35 % below, than in grown in the atmosphere of argon or helium, that it can be caused by more intensive evaporation of oxygen from fusion, and also additional cleaning of argon from moisture at presence a silicomethane.

Researches with using of Spectroscopes method, did not find out formations of hydrides. It is possible to suppose that hydrogen, contained in single-crystals (CZ-Si ~3.2·10¹⁸ sm⁻³, FZ-Si ~3.84·10¹⁸ sm⁻³), and also in a silicon-raw is in a cut-in kind (node-to-node position is at the grate of silicon) and free state (in micropores). In a silicon-raw, receipted by thermal decomposition of silicomethane, it is discovered that hydrogen forms monohydride connections (stripe of absorption in area of 2000 sm⁻¹) appearance of which can be related with education several of amorphous phase of silicon in the process of thermal dissociation of silicomethane.

Enhanceable content of hydrogen is in single-crystals, alloyed germanium, CZ-Si<Ge,P>, presumably, confirms set for the silicon-raw of tendency growth of content of this gas with the increase of closeness of crystalline phase. Closeness of single-crystals of CZ-Si<P> makes a 2.3280-2.3290 g/sm³, and CZ-Si<Ge,P> - 2.336-2.3464 (according to the concentration of phosphorus ~1.0·10¹⁵ and ~7.8·10¹⁵ sm⁻³, germanium - N_{Ge} ~8.5·10¹⁹ sm⁻³ and N_{Ge} ~2.2·10²⁰ sm⁻³).

Thus, single-crystals, got from fusion, are most saturated by hydrogen, the least are bars of polycrystalline silicon, grown by the method of thermal decomposition of silicomethane, at a temperature ~850 °C. Greater content of hydrogen is usually observed at less dense, more porous samples, and also at growth of surface of merithalluss borders (with diminishing of area for section of grains). It is also possible to talk about a tendency towards increasing of concentration of hydrogen with the height of temperature: in single-crystals crystallization of which takes place at a temperature ~ 1412 °C, content of hydrogen is noticeable higher, than in the polycrystalline bars of silicon, got besieging from a gas phase on padding at temperatures 850-1150 °C.

In the case of growing from fusion enhanceable content of hydrogen can be conditioned by entering of him to crystal due to dissociation of remaining vapors of water, being in the atmosphere of stove, or capture of hydroxy-groups content of which in quartz crucible can arrive 60 ppmw.

Enhanceable sizes of $\tau_{n\text{-}e.ch.ca}$ are in the single-crystals of CZ-Si, grown from the mixed loading (raw and turns), can testify to behalf of possible passivation of centres of recombination hydrogen, being in single-crystals.

Hydrogen in silicon is mainly in the atomic state in merithalluss, however at presence of potential pits, created by distributions, can be localized in them. Energy of connection for hydrogen atom with distribution is small, and in time (at default of additional signup by hydrogen) the atoms of hydrogen leave from the single-crystal of silicon in an atmosphere.

Consequently, diminishing of $\tau_{n\text{-}e.ch.ca}$ single-crystals of silicon it is possible with the sufficient high degree of validity to bind to the delocalization of hydrogen atoms from distributions and their subsequent diffusion to the volume of silicon.

Diminishing of hydrogen concentration in the volume of single-crystal of silicon takes place actively enough, because of diffusion in an atmosphere (at the conditions of experiment of $D = 2.94 \cdot 10^{-3} \text{ sm}^2 \text{ s}^{-1}$) through layer of natural oxide of SiO_2 on the surface of the grown single-crystal as a result of his self-control at normal terms (atmospheric pressure, room temperature).

Conclusions. Instability and rapid slump in time of high values of $\tau_{n\text{-}e\text{-}ch\text{-}ca}$ at the single-crystals of CZ-Si, grown at the atmosphere of $Ar+SiH_4$, can be related to the delocalization of hydrogen atoms from distributions and their subsequent diffusion from the volume of single-crystal of silicon. Enhanceable sizes of $\tau_{n\text{-}e\text{-}ch\text{-}ca}$ are at the single-crystals of CZ-Si, grown from the mixed loading (raw and turns), can testify to possible passivation of centres of recombination being in single-crystals hydrogen. However slow degradation of $\tau_{n\text{-}e\text{-}ch\text{-}ca}$ in this case allows to count migration of atoms of hydrogen as one of reasons for decline of this parameter, along with disintegration of supersaturated sosoloid of oxygen in the single-crystals of CZ-Si.

LIST OF LITERATURE

- 1. Богомаз, А. В. Особенности свойств кристаллического кремния, содержащего водовод [Текст] / А. В. Богомаз, Т. В. Критская, А. Н. Рябец // Известия вузов. Материалы электронной техники. 2009. № 3. С. 17-20.
- 2. Пат. 2927008. США МКИ. В01j 17/00, МКИ 23-273. Оборудование для выращивания монокристаллов кремния [Текст] / Shockly W., опубл. 01.03.1960.
- 3. Шварцман, Л. Я. Применение летучих неорганических гидридов при получении эпитаксиальных структур [Текст] / Л. Я. Шварцман, А. Г. Петрик // Научные труды Гиредмета. М.: Гиредмет, 1974. Т. 51.