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Photovoltaic Properties of Silicon Doped with Manganese and Germanium

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It has been found that silicon samples doped with manganese and germanium atoms form binary compounds of Si_2<GeMn> type, which heavily impact to the electrophysical and optical properties of silicon. It was determined that effect of manganese atoms after diffusing into the silicon pre-doped with germanium atoms leads to 10 % decrease of optically active oxygen concentration. It has been experimentally proven that silicon doped with germanium and manganese atoms can be used for the development of infrared photodetectors operating in the wavelength range 1-8 μm and allow for more sensitive detection of infrared radiation and temperature. It was established that during the growth there is an interaction between Ge and Mn atoms. This is confirmed by the disappearance of the energy level of manganese in silicon, which is responsible for quenching photoconductivity in silicon doped with manganese atoms.

Keywords: Diffusion, Germanium, Manganese, Silicon, Solubility, Concentration, Binary complexes.

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1. INTRODUCTION

The doping of silicon by unary impurity atoms has been quite well studied and led to the rapid development of microelectronics [1-5]. Nowadays it is possible to obtain nanoclusters of impurity atoms of the same kind in the silicon lattice, i.e. a bulk nanostructured material has been obtained [6, 7]. This led to new opportunities for the development of sensitive sensors and devices based on silicon [8, 9]. It is to bring of interest to study silicon doped with two types of impurity atoms in terms of formation of molecular complexes between them in the silicon lattice. This paper presents the results of the study of photovoltaic properties of silicon doped with manganese and germanium atoms.

Diffusion and electrical properties of manganese atoms in silicon have been studied by many authors [10-13]. It was found that the diffusion coefficient of manganese in silicon varies depending on temperature according to the equation $D = 0.26\exp\left(-\frac{1.3}{kT}\right)$ cm^2/s, and so-lubility at $T = 1250$ °C is $N = 2.1\cdot10^{16}$ cm^{-3} and varies with temperature by the relation $N = 2.5\cdot10^{22}\exp\left(-\frac{2.1}{kT}\right)$ cm^{-3}. The authors point out that manganese atoms in silicon mainly diffuse along the interstitial-site states and can also be entrance via the lattice node sites, at relatively high temperatures $T > 1200$ °C.

According to classical theory the manganese atoms if located in the interstitial states, they create two donor levels into band gap of silicon with energies $E_{d1} = E_c - 0,27$ ($Mn^+ - 3d^5\,4s^1$) eV and $E_{d2} = E_c - 0,5$ ($Mn^{++} - 3d^5\,4s^0$) eV, if they takes place on nodes, then they act as acceptors $E_{a1} = E_V + 0,45$ ($Mn^{-1} - 3d^5\,4s^2\,4p^1$) and $E_{a2} = E_V + 0,45$ ($Mn^{-2} - 3d^5\,4s^2\,4p^2$) [13, 14]. But under certain technological conditions, the manganese atoms themselves form nanoclusters in the silicon lattice. The authors [15] found that during low-temperature doping of silicon with manganese atoms, were formed nanoclusters consisting of four manganese atoms. Thus strongly act magnetic properties of silicon [16].

In the case of germanium it becomes as an isovalent impurity atom for the silicon, due to donor and acceptor energy levels cannot be obtain in band gap of silicon. However germanium atoms during low-pressure chemical vapor deposition (LPCVD) formed self-assembled Ge pyramidal islands [15] with size ≈ 250 nm. Authors [9], consider self-assembled germanium islands grows on silicon at high temperatures. It has been shown that islands size is in the order of 150 nm wide.

Accordingly, it is of great scientific and practical interest to study the formation of clusters in the silicon lattice with the participation of both manganese and germanium atoms.

2. METHODOLOGY

The germanium atoms in silicon are isovalent impurities and have a very small diffusion coefficient. Therefore it is not possible to obtain bulk doped silicon with impurity germanium atoms via diffusion technology. In this regard, we choose a material pre-doped during grows of silicon with germanium atoms with concentration $N_{Ge} = 9\cdot10^{19}$ cm^{-3}. Samples were sawed from Si<Ge> wafers with size of $8\times4\times2$ mm^3, and then they were prepared in exactly the same conditions for two-step low-temperature diffusion of manganese atoms [17].

The low temperature diffusion process was carried out as follows. A quartz ampoule with silicon pre-doped with germanium atoms and dopant (manganese) was placed into “MAGNATIC” high temperature diffusion tube furnace. The air was previously evacuated from the quartz ampoule until the pressure were $P = 10^{-5}$ mmHg.

The temperature in the diffusion furnace was slowly raised from room temperature to $T_{min} = 630$ °C and then held at this temperature for $t = 30$ minutes. Then the temperature was raised to the final diffusion temperature $T_{max} = 1010$ °C at which the samples were held for $t = 30$ minutes. This diffusion process was carried out several times with changing of final diffusion temperature T_{max} respectively 1015 °C, 1025 °C, 1035 °C and 1040 °C with the same diffusion time $t = 30$ min.

As initial material were chosen two groups of materials. First group were made from *p*-type monocrystalline silicon with resistivity 10 Ω·cm Si<B>. For the second group were used *p*-type monocrystalline silicon with resistivity 10 Ω·cm contained Ge atoms, which has been added during crystal growth Si<B,Ge>. Diffusion of manganese atoms into samples carried out in identical conditions. After diffusion the samples were subjected to appropriate mechanical and chemical treatment to remove the manganese silicide layer from the surface.

3. RESULTS AND ITS DISCUSSION

After the diffusion process, second group materials had resistivity of $\rho = 10^2$ Ω·cm to $\rho = 10^5$ Ω·cm. The electrical parameters determined both two types of samples by the Hall Effect method (ECOPIA HMS-3000). The results are given in Table 1, and also given results of first group of materials for the comparison.

Table 1 – Electrical parameters of samples after the doping with manganese atoms

Samples	Diffusion temperature °C	Conductivity type	Specific resistance ρ, Ω·cm	Concentration of carriers p, n cm^{-3}	Mobility of carriers μ, cm/(V·s)
Si<B,Ge,Mn>a	1010	*p*	$4.3 \cdot 10^2$	$1.4 \cdot 10^{14}$	188
Si<B,Ge,Mn>b	1015	*p*	$8.9 \cdot 10^3$	$1.7 \cdot 10^{13}$	220
Si<B,Ge,Mn>c	1025	*p*	$5.7 \cdot 10^4$	$3.2 \cdot 10^{12}$	362
Si<B,Ge,Mn>d	1035	*p*	$7.5 \cdot 10^4$	$1.2 \cdot 10^{12}$	412
Si<B,Ge,Mn>f	1040	*p*	$1.5 \cdot 10^5$	$1{,}2 \cdot 10^{11}$	528
Si<B,Mn>a´	1010	*p*	$2.5 \cdot 10^2$	$3.7 \cdot 10^{14}$	175
Si<B,Mn>b´	1025	*p*	$4.1 \cdot 10^4$	$4.9 \cdot 10^{12}$	350
Si<B>		*p*	10.12	$1.6 \cdot 10^{15}$	301
Si<B,Ge>		*p*	17.04	$1.05 \cdot 10^{15}$	380

The study of spectral dependence of photoconductivity of the obtained samples was performed in the temperature range $T = 77 \div 350$ K in a wide range of IR radiation spectrum on spectrometer IKS-21 equipped with a special cryostat. While studying spectral dependence of photoconductivity, the intensity of monochromatic radiation was kept constant at the level of $J = 10^{-5}$ W/cm^2. Variation of the IR radiation intensity was carried out by means of calibration metal gauze installed between the input window of the IKS-21 and the globar.

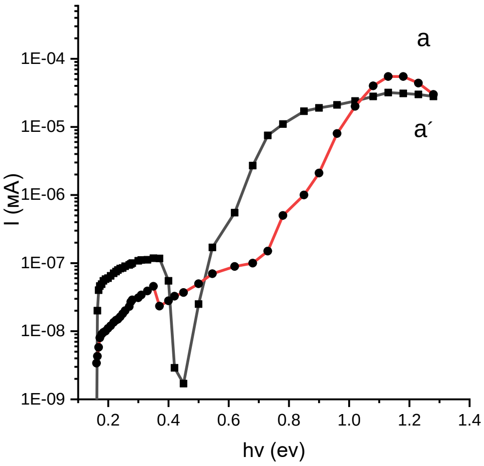

Fig. 1 – Spectral dependence of photoconductivity of samples $T = 100$ K (a) Si<Mn>, $\rho = 2.5 \cdot 10^2$ Ohm·cm, (b) Si<GeMn>, $\rho = 4.3 \cdot 10^2$ Ohm·cm

In order to prevent to ingress on the sample of scattered light and background radiation during the experiments, filters made of double-sided polished silicon wafers $d \sim 380$ μm thick were used, which were placed directly in front of the cryostat window.

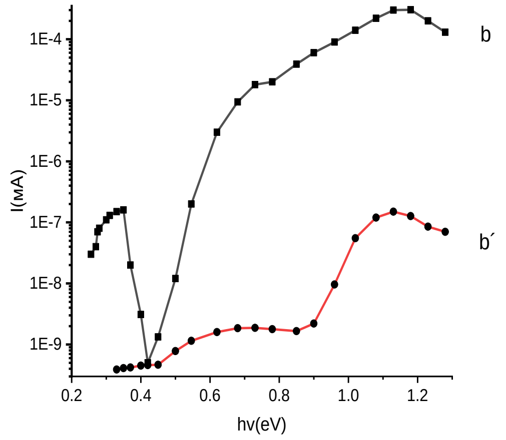

Fig. 2 – Spectral dependence of photoconductivity of samples $T = 100$ K b) Si<Mn>, b′) $\rho = 4.1 \cdot 10^4$ Om·cm, (b) Si<GeMn>, $\rho = 5.7 \cdot 10^4$ Om·m

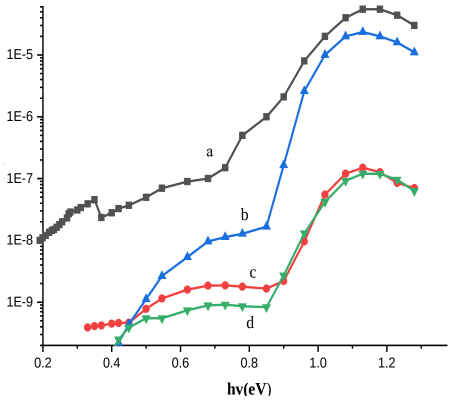

Fig. 3 – Spectral dependence of photoconductivity of samples $E = 6.5$ V/cm, $T = 100$ K, Si<GeMn>: a) $\rho = 4.3 \cdot 10^2$ Ohm·cm, b) $\rho = 5.7 \cdot 10^4$ Ohm·cm, c) $\rho = 7.5 \cdot 10^4$ Ohm·cm, d) $\rho = 1.5 \cdot 10^5$ Ohm·cm

Fig. 1, 2 and 3 shown the spectral dependence of photoconductivity of silicon doped with manganese atoms.

The oxygen content (concentration of optically active interstitial oxygen atoms No) was estimated from infrared transmission spectra at 1106 cm $^{-1}$ (9 μm) modified on an FSM-1200 infra-red spectrometer at room temperature (Fig. 4).

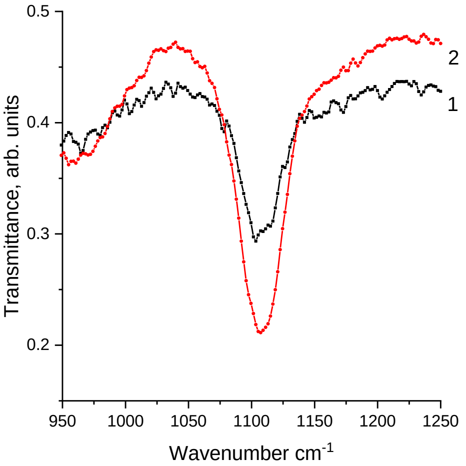

Fig. 4 – Dependence of light transmission of samples doped with manganese atoms on incident wavelength 1) Si<GeMn>, 2) control sample Si<Ge>

The concentration of optically active oxygen, after diffusion of manganese atoms, was calculated on the basis of the following formulae:

For silicon samples with an admixture of germanium additionally doped with manganese atoms – Si<GeMn>

$$N^{OPT} = 3.03\cdot10^{17}\cdot\frac{1}{d}\cdot\ln\frac{I}{I_0} = 2.5\cdot10^{18}\,\text{cm}^{-3}$$

For control samples – Si<Ge>

$$N^{OPT} = 3.143\cdot10^{17}\cdot\frac{1}{d}\cdot\ln\frac{I}{I_0} = 2.25\cdot10^{18}\,\text{cm}^{-3}$$

$$N_o^{OPT(control)} - \frac{N_o^{OPTSiGe\langle Mn\rangle}}{N_o^{OPT(control)}} = \frac{\left(2.5\cdot10^{18} - 2.25\cdot10^{18}\right)}{2.5\cdot10^{18}} = 0.1\text{cm}^{-3}$$

Thus, doping of silicon with manganese atoms leads to 10 % decrease of optically active oxygen concentration. It is found that the reduction of uncontrolled oxygen atoms concentration leads to the reduction of thermal and radiation defects in silicon, as the concentration of residual oxygen in silicon determines the change in the electrophysical parameters of the initial silicon. Control of residual oxygen concentration and uncontrolled impurity atoms by formed complexes of manganese and germanium atoms allows to obtain material with thermostable and radiation-resistant parameters that is necessary for devices operating in extreme conditions [18, 19].

It was found that in silicon samples doped with impurity manganese and germanium atoms binary compounds of Si_2<GeMn> type are formed, which strongly affect the electrophysical and optical properties of silicon. These binary compounds form clusters with ion-covalent bonding that lead to changes in the lattice constant and the crystal structure of silicon itself [20].

4. CONCLUSIONS

It was found that the diffusion of manganese atoms in silicon pre-doped with germanium atoms during growing occurs the interaction between Ge and Mn atoms. This is confirmed by the disappearance of the manganese energy level in silicon, which is responsible for quenching photoconductivity in control silicon samples doped with manganese atoms.

The experimental results show that silicon doped with germanium and manganese atoms can be used to create highly sensitive infrared photodetectors operating in the wavelength range of $\lambda = 1\text{-}8$ μm as a new class of sensors enabling more sensitive detection of infrared radiation and temperature.

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Фотоелектричні властивості кремнію, легованого марганцем і германієм

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Установлено, що зразки кремнію, леговані атомами марганцю та германію, утворюють бінарні сполуки типу Si_2<GeMn>, які сильно впливають на електрофізичні та оптичні властивості кремнію. Показано, що вплив атомів марганцю після дифузії в кремній призводить до 10 % зниження концентрації оптично активного кисню. Експериментально доведено, що кремній, легований атомами германію та марганцю, може бути використаний для розробки інфрачервоних фотодетекторів, що працюють в діапазоні довжин хвиль 1-8 мкм і дозволяють більш чутливо детектувати інфрачервоне випромінювання та температуру. Установлено, що під час росту відбувається взаємодія між атомами Ge і Mn. Це підтверджується зникненням рівня енергії марганцю в кремнії, який відповідає за гасіння фотопровідності в кремнії, легованому атомами марганцю.

Ключові слова: Дифузія, Германій, Марганець, Кремній, Розчинність, Концентрація, Бінарні комплекси.