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PROPERTIES OF “HIGHER MANGANESE SILICIDE-SILICON” HETEROSTRUCTURE[†]

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Based on the diffusion technology, many scientists and specialists have conducted research on obtaining materials that are fundamentally different in electrical and photo-thermal parameters from the original material by introducing various input atoms into semiconductor materials and creating deep energy levels in their band gap. The electrical, photoelectric, optical, and magnetic properties of these semiconductor materials have been extensively studied with metal group elements, isovalent elements and rare earth elements added to silicon through the process of growth, ion implantation, or diffusion from the gaseous state. The technology of introducing impurity atoms into silicon by the diffusion method is distinguished from other methods in its simplicity, energy efficiency, and low cost. Up-to-date the technology of changing the resistivity and conductivity of the initial sample by diffusion of manganese atoms into single-crystal silicon is studied insufficiently.In the article, it was determined that when manganese atoms diffuse into silicon, a high-manganese silicide is formed on its surface and in the near-surface layer. Based on the analysis of the experimental results, the thermal EMF (electromotive force) in $Mn_4Si_7 - Si < Mn > - Mn_4Si_7$ structures in a certain temperature range and under illumination (with monochromatic or integrated light) is explained by the fact that it based on the Pelte effect, observed in semiconductors.The volt-ampere characteristics (VAC) of the obtained structures were measured at various temperatures, in the dark and in the light. Formation of a boundary layer with high resistivity at the boundary of the higher manganese-silicon transition, the transition from higher manganese silicide to the base of the structure due to the effect of ionization of pores during illumination of structures and external influence. The applied field was clarified based on VAC results. The manganese high silicide layer formed on the silicon surface has the properties of a semiconductor, and the formation of a heterojunction upon transition to silicon is shown on the basis of the sphere diagram.

Keywords: *Higher; Manganese; Silicide; Forbidden gap; Properties; Structure*
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INTRODUCTION

Nowadays, the requirements for thermal batteries created on the basis of higher manganese silicides (HMS) are almost the same as the requirements for bulk thermoelements, which implies that their operational performances must be tuned to be perfect [1]-[5]. While heat transfer in bulk thermoelectric materials is carried out on the basis of metal electrodes embedded into the semiconductor, in thin-layer thermoelectric materials and thermal batteries, heat transfer is carried out on the basis of a substrate on which the layer is grown [6],[7]. Since thermal batteries created on the basis of higher manganese silicides (HMS) are ususlally grown on the surface of silicon in the form of a thin layer, thus heat exchange occurs fast. Revealing practical application areas of thermal batteries, photodetectors and photodiodes assembled on the basis of the “HMS – silicon” structure is one of the most urgent problems of current scientific research [8]-[10].

Differences in two phases adjacent to “higher manganese silicide – silicon” transition boundary are not only due to the fact that their electrophysical parameters do differ, but also by varying value of the forbidden gap of materials in these phases [11], [12].

Study and analysis of experimental data on “higher manganese silicide – silicon” structures have shown that higher manganese silicide on the basis of Mn_4Si_7 compound, manifests semiconductor properties and its forbidden gap was determined by experimental study of temperature dependence of electric conductivity and Hall factor on HMS-3000 Van-der-Pau equipment.

It was reveald that the value E_g of the forbidden gap of higher manganese silicide was $E_g \approx 0.67 \div 0.8\, eV$ judging by the fact that charge carriers in the sample were holes. Thus, it was shown that in the “higher manganese silicide-silicon” boundary layer, a heterostructure was being formed.

TECHNIQUE AND EXPERIMENTAL

Boron-doped monocrystalline silicon wafer with resistivity of $10\ \Omega \cdot cm$, was used as a reference sample for forming HMS layer on silicon substrate. The authors have utilized the diffusion technique to form HMS layer on sample’s two-dimensional large surface. The thickness d of the HMS layer formed on the silicon surface was approximately $\approx 5 \div 7\ \mu m$. The conductivity of the resulting HMS layer was p-type (charge carriers holes), and their concentration $p \approx 10^{19} \div 10^{20}\ cm^{-3}$. Such a layer formed on the surface could be viewed as a heavily doped degenerate semiconductor. The

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value of relative resistance of the base region in the resulting structure was equal to $\rho \approx 10^5 \Omega \cdot cm$, and the concentration of charge carriers in it was approximately close to that in intrinsic silicon.

The resulting $Mn_4Si_7 - Si < Mn > - Mn_4Si_7$ structure in written form was shortly abbreviated as $p^+ - Si < Mn > -p^+$. The electrophysical and photoelectric properties of such structures were studied in a wide temperature range of $80 \div 300\ K$. For experiments, a task-specific cryostat was engineered that was designed to operate in the temperature range from $80K$ to room temperature and with specific glass window for exposure of a sample to integral and monochromatic light.

As a light source, the arsenide galium (GaAs) light emitting diode was used, as well as the IKS-21-type infrared spectrometer. While measuring the volt-ampere characteristics (VAC) of the structures at room temperature, the athors have observed two sections on current-voltage curve. At low temperatures ($T = 80K$), the value of the current would sharply (almost $6 \div 8$ times) decrease whereas relative resistance of the base region of the structure would starkly increase. At forward bias mode, the value of the current in the dark would decrease down to $J_d \approx 10^{-12}A$ whereas after the structures have been exposed to light, the value of photocurrent would increase to $\approx 10^{-3} \div 10^{-2}A$ (Fig.1).

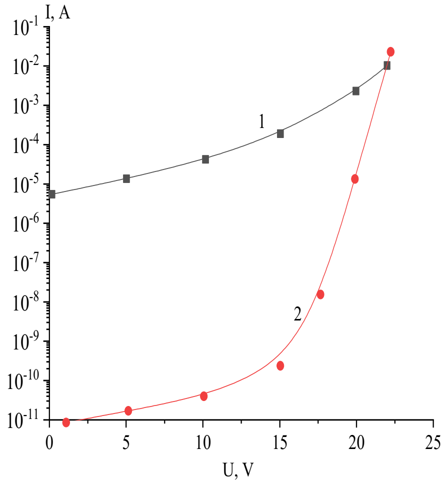

Figure 1. Volt-ampere curve of $\mathrm{p^+ - Si < Mn > -p^+}$ structure at $\mathrm{T = 300K}$ (1) and $\mathrm{T = 80K}$ (2) illuminated by photons with energy $\mathrm{h\nu \geq E_g}$

At a low temperatures (T=80K), the value of ΔU_K (voltage falling on boundary transition cross section of the pre-contact surface layer of the structure) have tended to increase due to decrease in relative resistance of the base region of the structure in times of its exposure to light. It is well known that, resistance at boundary area could be deterermined as follows $R_K = S\frac{\Delta U_K}{J}$. Here S – area of the opposite contact side of the structure. Theoretical calculations have revealed that the relative resistance of the base region of resulting structures at room temperature was equal to $\rho_\delta \approx 6 \cdot 10^4 \Omega \cdot cm$. The results of experiments aimed at determining the resistance of the base region of structures by two probe technique ($\rho = S\frac{U}{Jl}$, where l is the distance between probes) have revealed that the relative resistance of manganese high silicides grown on silicon substrate was equal to $\rho_\delta \approx 6{,}2 \cdot 10^4 \Omega \cdot sm$, which was close to the data of theoretical calculations.

To determine the concentration and mobility of charge carriers at the base region of the structure, the authors have applied the Hall factor technique at various temperatures. Also the authors have studied the photovolt-ampere characteristic at various values of monochromatic illumination at ($h\nu \geq E_g$).

Having known the value of R_x (Hall factor), the concentration of holes, as well as the the mobility of charge carriers (using the formula $\frac{R_x}{\rho} = \mu_p$) were subsequently calculated. At $J_p = 1mA$ (photocurrent), the concentration of charge carriers (holes) was equal to $p = 2{,}4 \cdot 10^{14}\ cm^{-3}$ while at $J_p = 2{,}5mA$, it was respectively $p = 2{,}5 \cdot 10^{15}\ cm^{-3}$. In both cases, Hall mobility μ_p was in the range $200 \div 300\ sm^2/V \cdot s$. At the same parameters of illumination of $M - Si < Mn > -M$ structure and at external source voltage U=10 V, the current J_p, was $8 \cdot 10^{-5}A$ and the concentration of holes was $p \leq 2.4 \cdot 10^{13}\ cm^{-3}$.

We have observed two section in VAC curve when the distance between the electrodes was negligent (9÷10mm), and when the structures were illuminated by monochromatic light. In this case, there was virtually no difference in parameters of the curves both in dark and exposed modes under voltage of $U \leq 1\ V$. After the voltage U have passed ≥ 2 V, the difference between VAC in dark and exposed modes rather increased, and the difference was stark almost 10^4 times (Fig. 2, 1 and 2 lines).

When the photocurrent value was $J_p \geq 4 \cdot 10^{-3}mA$, at HMS – silicon junction point excess heat was detected. When the photocurrent value reaches $J_p \geq 10^{-2}A$ excess heating at the transition bondary of $Mn_4Si_7 - Si < Mn >$ was significantly greater. When the pole of the constant current source connected to the structure was versed, heating field has moved to the opposite right side of the $Si < Mn > - Mn_4Si_7$ structure.

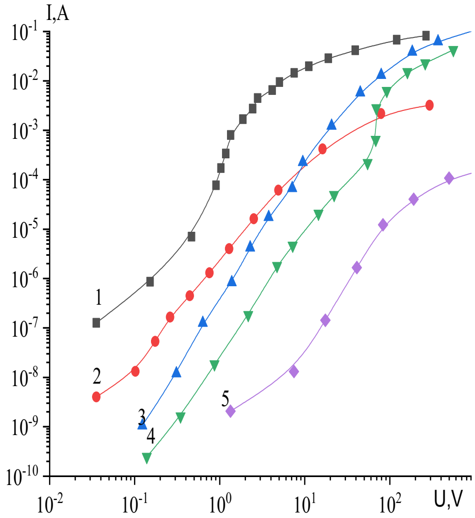

Figure 2. Volt-ampere characteristics of silicide structures at T=80K:
1 – while exposed to illumination when the width of the base section of $p^+ - Si < Mn > -p^+$ structure is 70÷75 μm
2 – $p^+ - Si < Mn > -p^+$ in dark conditions,
3 – $p^+ - Si < Mn > -M$ the width of the base section of the structure is 1.5 mm while forward bias voltage is applied,
4 – $p^+ - Si < Mn > -M$ width of the base section of the structure is 5 mm and while forward bias voltage is applied
5 – $p^+ - Si < Mn > -M$ is 5mm, and when the reverse voltage is connected, the base width of the structure

When the distribution of $U(L)$ (voltage drop on contacts from external voltage source connected to the structure in the base section of the structure) was studied, it was found that the majority of voltage appears to drop at the “*silicide-silicon”* transition boundary. In this case, it was found that primarily voltage drops on boundary section of the photoconductive border, where the resistance of the HMS structure is negligent (Fig. 3).

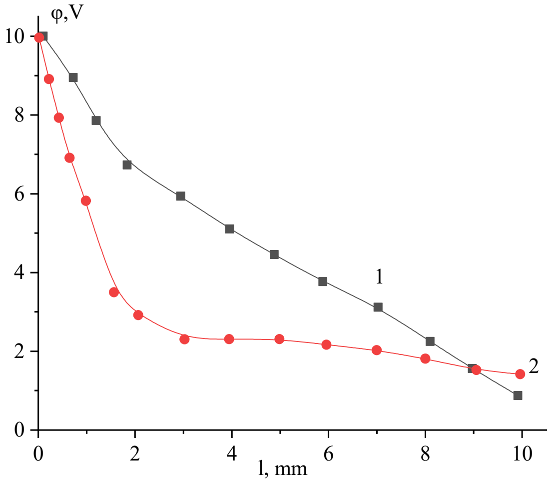

Figure 3. $p^+ - Si < Mn > - p^+$ external voltage drop distribution
1 - T=300K, 2-80K, when illuminated with monochromatic radiation ($h\nu \geq E_g$).

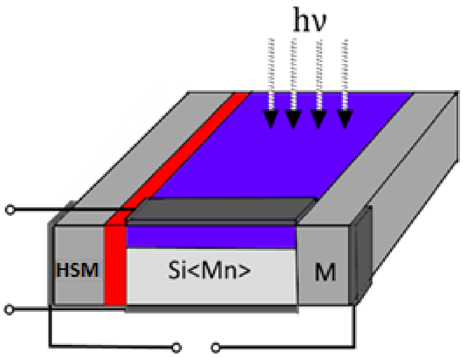

Figure 4. Connection of the structure to an external source at low temperatures and while illuminated by monochromatic light ($h\nu \geq E_g$).
HMS - higher manganese silicides

On Fig. 4 it is shown the structure of the $Mn_4Si_7 - Si < Mn > - Mn_4Si_7$ structure, its connection to an external power supply, the incidence of monochromatic radiation, and the measurement circuit of the generated thermal EMF (electromotive force).

DISCUSSION OF EXPERIMENTAL RESULTS

Tradionally, in times of exposure of the base region of the structure to light the phenomena of photoconductivity occurs due to which, non-equilibrium charge carriers such as electrons and holes are generated. Subsequently, the Fermi level moves towards the valence and the conduction bands, each leading to the formation of quasi Fermi levels. When the structure was illuminated with infrared light with a wavelength λ = 0.9 ÷ 1 μm (the depth of absorption of falling photons was up to ~100 μm), the thickness of the holes conductive layer with a small resistivity $\rho \approx 5 \div 10\ \Omega \cdot cm$

was equal to the depth of absorption of falling photons. In silicon doped with manganese atoms, such physical phenomena due to holes leading to massive photoconductivity were previously reported by several authors [13].

The resistivity value formed when the resulting structures are illuminated by low intensity infrared light happen to be small $\rho \approx 5 \div 10\ \Omega \cdot cm$, and the formation of a conductive layer with with hole conductivity was similar to the formation of non-equilibrium charge carriers (holes) at the base of the structure. At specific resistance of p-type sample (resistivity $\rho \approx\ 5 \div 10\ \Omega \cdot cm$) the concentration of holes was estimated at $\sim 10^{15} cm^{-3}$.

A similar situation was observed when the silicon samples doped with manganese atoms appeared to have completely compensated boron atoms after the samples were illuminated with photonic energy corresponding to a wavelength of $\lambda\ \approx 1$ µm [14],[15]. Such a precedent was not observed in the $p^{+} - Si < Mn > -p^{+}$ structures because the physical phenomena at the contact layers of such structures allegedly happen by injection of charge carriers in the heterojunction layer. Based on the analysis of the obtained experimental results, it was possible to explain the physical mechanism of contact phenomena observed in heterojunction structures.

A layer with a high resistance was formed at the transition boundary of the silicon (*HMS-Si<Mn>)* system doped with HMS and manganese impurity atoms, while the external voltage source was applied, a potential barrier was created due to electric displacement. Thus, the probability that charge carriers (holes) would heat up and migrate to the base region of the structure will increase. This in turn led to the occurrence of a mechanism of shock ionization due to photogeneration by boosting injection of holes heated from the HMS layer into the structure's base region (Si<Mn>).

It was determined that the following preconditions must be met in the heterojunction of the resulting structures in order to generate additional charge carriers:

1. Creation of conditions for the injection of holes into silicon from a layer of higher manganese silicides.
2. The thickness of higher manganese silicides-silicon transition layer shall be enough to induce injection phenomenon of charge carriers through the base region.

In other words, it is necessary that the length of free running path of the holes be greater than the thickness of the transition layer. In this case, the heated holes pass like they go through a tunnel crossing to the base of the structure. In this case, holes carry a certain energy and form an additional electron – hole pair based on the heating of the base region. This increases the value of the photocurrent several times and has led to a decrease in the resistance of the base region. The increase in the concentration of charge carriers at the base region of the the concerned structure in the irradiated position can be reduced by the following mechanism. That the value of photocurrent in $M - Si < Mn > -M$ structures appears to be several degrees higher than that in silicon samples, which are doped solely by manganese atoms in the normal state, was explained by the shock ionization of the charge carriers.

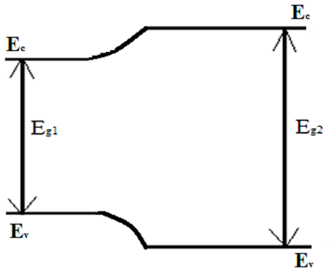

Figure 5. Band diagram of a heterojunction formed at the boundary of higher manganese silicide-silicon $E_{g1} \approx 0{,}67 \div 0{,}8$ eV, $E_{g2} = 1{,}12$ eV

When there are two types of charge carriers in semiconductors, and if a thermal gradient is created in them, the transfer of heat due to the concentration gradient of current carriers is observed (Pelte effect). It was found that the thermal EMF formed in the structure of manganese high silicide - silicon is almost not observed in the structures of the metal-silicon Si<Mn> system.

It was observed that in the resulting HMS – Si<Mn> – HMS structures we have witnessed symmetrical disposition in volt-ampere characteristics in the initial state (at low voltage and low current values) while samples were exposed to light. When replacing one of HMS layers in the structure with a metal contact, that is, in *HMS - Si<Mn> - M* structures, the value of the photocurrent- J_p in cases when the voltage is forward biased and inversed, proved to differ greatly from each other, and the difference is at least $\sim 10^{4}$. If the voltage supplied from an external source is U≥15 V, this difference is relatively lower ($10^{1} - 10^{2}$ times), but an increase in temperature was observed at the HMS -silicon contact, that is, the structure started to heat up. This, in turn, caused the current to step down under the influence of temperature [15]-[17].

Structures in the first and second regime ($p^{+}\ - S\ i < Mn >$–p^{+} and $M - Si < Mn > -M$, respectively) in the illuminated state, based on the analysis of the results obtained in VAC and the distribution of applied external voltage, manganese high silicide - silicon heterojunction diagram of the structure was proposed (Fig. 5).

CONCLUSION

Based on the scientific analysis of VAC of the resulting higher manganese silicide-silicon and metal-manganese doped silicon structures and the proposed heterojunction diagram, we assume the following:

1. The manganese high silicide formed on the silicon surface when the manganese atoms diffuse into the silicon (from the gas state or from the manganese metal layer on the silicon surface) has a monopolar injection contact feature that leads to injection of holes into the silicon bulk.
2. In $Mn_4Si_7 - S\ i < Mn > -Mn_4Si_7$ or $Mn_4Si_7 - S\ i < Mn > -$M structures with high resistance at relatively low temperatures (T = 80 ÷ 200K) and when illuminated with photons energy $h\nu \geq E_g$, the value of their resistance is believed to decrease sharply and it switched to a photoconductive state.

3. It was determined that the photosensitivity of the base region of the resulting structures increased at low temperatures, and the resistance decreased under the influence of light, due to avalanche ionization of charge carriers formed in higher manganese silicide, as well as the injection of certain additional energy into the transition layer.
4. It was shown that the formation of a heterojunction at the transition boundary of the higher manganese silicide-silicon structure and its VAC change under the influence of infrared radiation.

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ВЛАСТИВОСТІ ГЕТЕРОСТРУКТУРИ "СИЛІЦИД ВИЩОГО МАРГАНЦЮ-КРЕМНІЮ"

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На основі дифузійної технології багато вчених і фахівців проводили дослідження з отримання матеріалів, принципово відмінних за електричними і фототермічними параметрами від вихідного матеріалу, шляхом введення в напівпровідникові матеріали різних вхідних атомів і створення глибоких енергетичних рівнів в їх забороненій зоні. Електричні, фотоелектричні, оптичні та магнітні властивості цих напівпровідникових матеріалів були ретельно вивчені з елементами групи металів, ізовалентними елементами та рідкоземельними елементами, доданими до кремнію в процесі росту, іонної імплантації або дифузії з газоподібного стану. Технологія введення домішкових атомів у кремній дифузійним методом відрізняється від інших простотою, енергоефективністю та дешевизною. Сучасна технологія зміни питомого опору та електропровідності вихідного зразка шляхом дифузії атомів марганцю в монокристалічний кремній вивчена недостатньо. У статті встановлено, що при дифузії атомів марганцю в кремній утворюється високомарганцевий на його поверхні і в приповерхневому шарі утворюється силіцид. На основі аналізу експериментальних результатів встановлено термоЕРС (електрорушійна сила) в структурах $Mn_4Si_7\text{-}Si < Mn > - Mn_4Si_7$ в певному інтервалі температур і при освітленні (з монохроматичне або інтегроване світло) пояснюється тим, що він заснований на ефекті Пельтьє, який спостерігається в напівпровідниках. Вольт-амперні характеристики (VAC) отриманих структур були виміряні при різних температурах, у темряві та на світлі. Утворення прикордонного шару з високим питомим опором на межі вищого переходу марганець-кремній, переходу від вищого силіциду марганцю до основи структури за рахунок ефекту іонізації пор при освітленні структур і зовнішньому впливі. Область застосування була уточнена на основі результатів VAC. Шар вищого силіциду марганцю, утворений на поверхні кремнію, має властивості напівпровідника, а утворення гетеропереходу при переході на кремній показано на основі сферічної діаграми.

Ключові слова: *вищий; марганець; силіцид; заборонена зона; властивості; структура*