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Obtaining manganese silicide films on a silicon substrate by the diffusion method

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Investigation of auto-oscillation currents in compensated silicon doped with impurity atoms of manganese, zinc, sulphur or selenium can observe several types of current instabilities with different natures and excitation conditions. The boundary regions of auto-oscillation currents such as temperature instabilities, recombination waves and injection instabilities in temperature, electric field, intensity of illumination as well as in resistivity and conductivity type of compensated silicon samples were determined. From the analysis of the obtained results the possibility of using the detected auto-oscillation currents in compensated silicon for creating solid-state generators and sensors of physical quantities is shown. The mechanism of manganese diffusion into silicon leading to the formation of higher manganese silicides on the silicon surface was determined. The X-ray analysis data allowed to find that in the temperature range of thermal annealing T=800÷1100°C, polycrystalline films corresponding to the phases of higher manganese silicides are formed. The possibility of creating the efficient thermopiles based on the obtained structures of the MnxSi1-x – Si<Mn>-MnxSi1-x type based on silicon, the operating parameters of which are not inferior to existing thermopiles, and sometimes have certain advantages, is shown.

Keywords: auto-oscillation currents, electric field strength, illumination, temperature, compensated silicon, amplitude, frequency, heterogeneity, photon energy.
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1 Introduction

The study of the diffusion distribution of impurities in semiconductor materials, in particular, in silicon, is necessary to elucidate the mechanism of the diffusion process, as well as to determine the role of impurity atoms on the electrical and photoelectric parameters of the source material [1–4].

The process of diffusion of impurity atoms into silicon is carried out in a relatively wide range of high temperatures (T=800÷1300°C), which leads to the formation of additional thermal defects, which strongly affect the fundamental parameters of silicon. In addition, during diffusion, silicides and other metal and dielectric film layers are formed on the silicon surface. The surface state of silicon after diffusion doping with impurity atoms has not been studied in detail. Some authors, when studying the processes of diffusion of impurity atoms into a semiconductor, removed near-surface layers and did not pay attention to studying the surface properties of diffusion-doped silicon [5, 6].

This paper presents the results of a study of silicon doped with impurity manganese atoms, in which higher manganese silicides were formed on the surface. Films of manganese silicides on silicon were obtained in an evacuated quartz ampoule of evacuated high vacuum, about $P=10^{-5} \div 10^{-6}$ mm Hg. Art. [7]. Single-crystal silicon grades KDB-1 and KDB-10, $10 \times 10 \times 0.8$ mm^3 in size, with the [111] crystallographic axis orientation, were used as substrates. The surface of the substrates was cleaned mechanically and chemically before loading into ampoules. The amount of manganese diffusant in the quartz ampoule was based on the calculation of the evaporation time and is sufficient for complete deposition on the silicon substrate. The samples were cooled slowly in air to room temperature without violating the vacuum level in the ampoule. The results of the study showed that by controlling the modes (temperature, time) of the technological process, it is possible to obtain films of manganese silicides with different thicknesses and electrical parameters. These results made it possible to determine the optimal temperature and time for the formation of silicide with the desired parameters.

2 Technology for obtaining materials and research method

The electrical parameters of the obtained films were measured by the Van der Pauw method on the Ecopia HMS-3000 Hall Measurement System, and the electrical resistance and Hall coefficient were determined as a function of temperature. The Hall coefficient in all silicide layers of the obtained silicon samples, regardless of the diffusion temperature and additional thermal annealing, was positive, the concentration of current carriers was equal to $\rho \approx 10^{20}$см$^{-3}$. The dependence of the structure of the formed films on the substrate temperature was also studied. X-ray and electron microscopic methods were used to control the composition and structure of the obtained films. The phase analysis of manganese silicide films was carried out by taking X-ray reflection spectra on a DRON-1 instrument. The topology of the resulting films of manganese silicides and their elemental composition were evaluated using an X-ray microanalyzer in a Ukha-840 scanning electron microscope.

From the analysis of the obtained X-ray patterns, it was found that in the temperature range of thermal annealing T=800÷1100°C, polycrystalline films corresponding to the phases of higher manganese silicides (HSM) are formed. The composition of the films grown in the temperature range T=910÷1040°C, obtained using an X-ray microanalyzer, turned out to be close to the composition of bulk HSM (MnSi). It is established that the formed film microstructures depend on the substrate temperature ($T_{subs.}$). An amorphous film of manganese silicides formed at temperatures T≤880°C, with a subsequent increase in temperatures above T≥970°C, forms a single-crystal layer consisting of manganese monosilicide. The surface topology of the obtained films was studied using a scanning electron microscope. Grain sizes were determined from the surface images of manganese silicide films. For example, in the samples obtained at T=1070°C, the grain sizes are ~5÷20 μm. The electron diffraction patterns for reflection from the surface of the obtained films indicate that they mainly constitute the HSM phase, but, in addition, lines belonging to manganese monosilicide were detected.

It is known that a banded structure is observed in massive HSM crystals, this is due to the precipitation during the growth of interlayers of silicon-depleted manganese monosilicide. An analysis of the structural data suggests that the resulting films, at T≥970°C, the HCM film grows in the form of grains. Thus, in the process of diffusion of manganese atoms into silicon, a flow of atoms is formed, which are deposited on substrates and, as a result of diffusion, form compounds of the $MnxSi_{1-x}$ type. Structural studies, depending on the technological modes of manganese diffusion, made it possible to optimize the conditions for obtaining manganese silicide films with specified electrophysical parameters.

3 Experimental results and their discussion

An analysis of literature data [8-12] shows that the phase of higher manganese silicides Mn0.25Si1-0.25 (HSM) formed at a thermal annealing temperature in the range T=1050÷1150°C is the most promising material for thermoelectric generators (converters) in photoelectronics. A correlation between the phase composition of silicide films and the coefficient of anisotropic thermal EMF has been established, and the possibility of obtaining polycrystalline films approaching in electrical and kinetic parameters to a massive HSM single crystal has been shown. It was shown that technological factors such as vacuum level, substrate temperature, quartz ampoule volume, substrate surface treatment, and cooling conditions are important for the production of HCM films. Table – 1 shows the values of some physical parameters of the obtained films of higher manganese silicides in silicon, where you can see the systematic dependence of the parameters of the obtained films of manganese silicides on the substrate temperature.

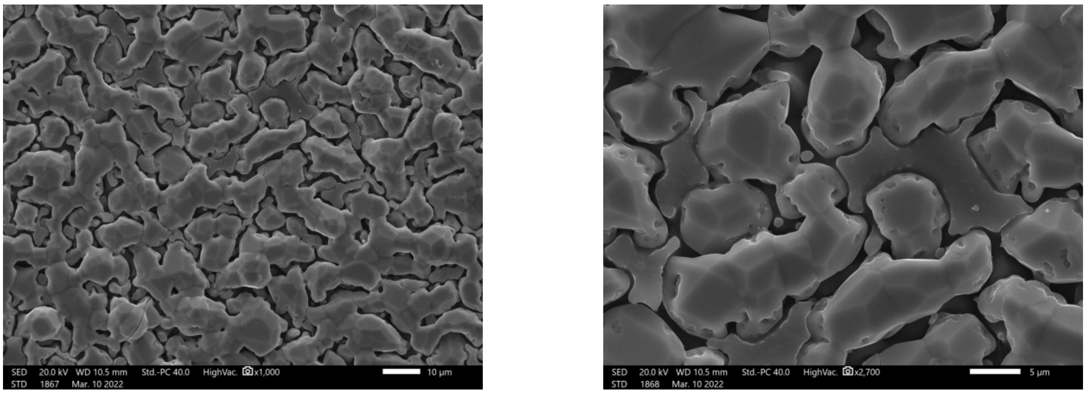
It has been established that the films grown on the basis of the initial KDB-1 and KDB-10 silicon in the temperature range T=1040÷1070°C contained predominantly the HSM polycrystalline phase; in the films grown in the temperature range T=1100÷1200°C, monosilicides were the dominant phase; at temperatures below T≤900°C, the films were amorphous.

Table 1 – Physical parameters of manganese silicide films (vacuum P~10^6 mm Hg, rapid cooling)

Diffusion temperature, °C	Surface resistance, R_r, Ом	Surface resistivity ρ, Ohm×cm	Conversion factor, Sv, μV/W	Hall coefficient, Rx,1/Ohm•cm^{-1}
1120	264	0,004	266	0,065
1110	180	0,012	310	0,059
1070	165	0,023	486	0,062
1040	115	0,026	1880	0,066

The study of the phase composition of the films over the thickness showed that during the evaporation of impurity Mn atoms in a quartz ampoule with a diameter of 10 – 12 mm in vacuum, P≈10^{-5} mm Hg. Art. in the temperature range T=1050÷1100°C with subsequent slow cooling of the samples, polycrystalline films were formed, which near the silicon surface consisted of a mixture of two phases – manganese monosilicide and higher manganese silicides with a predominance of monosilicide, in the upper layer there are mainly HSM phase layers. Interesting scientific results were obtained [13,14] when conducting diffusion in a quartz tube of evacuated vacuum P≈10^{-2} mm Hg. Art. during the entire process of diffusion of manganese atoms into silicon and subsequent slow cooling in air. Under these conditions, films were formed consisting of HSM grains up to 10 μm thick. Additional thermal annealing of the samples in the temperature range T=350÷800°C led to the enlargement of the formed HSM grains. It has been established that such films have a high conversion coefficient [15], and anisotropic properties of kinetic and thermoelectric parameters corresponding to the parameters of bulk HSM single crystals have been found in them.

When studying the topology of the silicon surface with films of higher manganese silicides, it was found that, on average, the grain size is 4–5 μm, although individual crystallites reach up to ≈10 μm. Micrographs of the HSM film grown by us are shown in Fig. 1.



a) at a resolution of 10 μm. b) at a resolution of 5 μm.

Figure 1 – Electron diffraction patterns "for reflection" from a polycrystalline film of manganese silicides on silicon

An analysis of the results of complex studies of the physical properties of higher manganese silicide on the silicon surface, carried out by various modern methods, shows that all numerous crystalline structures have a tetragonal syngony (Fig. 2) and exhibit a superperiodic structure in the direction of the c axis (c is the main crystal growth axis of silicon). The HSM crystal lattice is usually described on the basis of the concept of a "hard" manganese sublattice and a relatively "soft" silicon sublattice. In the manganese sublattice, for all detected HSM phases, one can single out a subcell or nanocluster containing four Mn atoms with a lattice constant parameter along the c axis, which is approximately equal to 4.36Å. Silicon atoms in adjacent layers, perpendicular to the c axis, are arranged in pairs in adjacent squares, which also makes it possible to isolate a subcell of four manganese atoms in the silicon sublattice (Fig. 2).

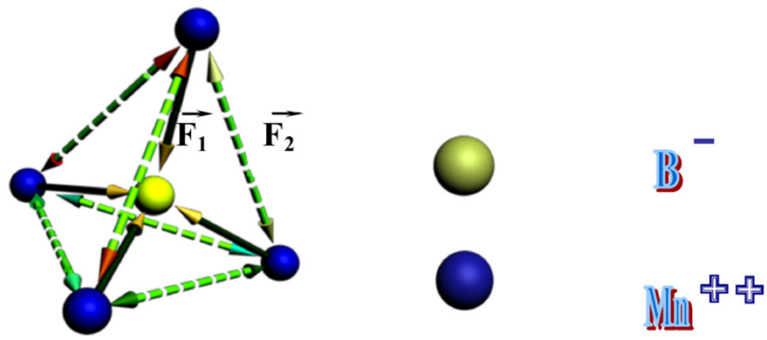


Figure 2 – Structure of a nanocluster of manganese atoms in a silicon lattice $[(Mn)_4^{+8}B^{-}]^{+7}$.

After analyzing the main regularities of the crystal structure of the studied phases, based on the results obtained, it was concluded that, in reality, the set of structures that can arise in the homogeneity region of HSM is much wider, since a change in the composition of HSM does not lead to the formation of structural defects, but only to a change in the ratios of characteristic sublattice parameters along the c axis. A universal method of description was proposed and all commensurate structures located in the domain of HSM existence were calculated.

4 Conclusions

The crystal axis with the orientation of the tetragonal cell of the manganese sublattice and the pitch of the helix along which the silicon atoms are arranged are incommensurable. It is known that the interaction of periodic subsystems with mutually incommensurable periods leads to the formation of incommensurate structures, which are something intermediate between crystalline and disordered structures. However, despite the absence of periodicity along the axis with any finite period, the diffraction patterns from such structures contain reflections with a small width.

Electron microscopic studies have confirmed the presence of incommensurate superstructures on the silicon surface of higher manganese silicides Mn_xSi_{1-x}. In [16], the authors analyzed the diffraction effects appearing in electron diffraction patterns from crystals with incommensurate modulated structures and orientational anomalies associated with them.

An analysis of the results obtained using a transmission electron microscope showed that, in the grown HSM films with grain sizes on the order of ~10 μm, manganese monosilicide can be present as a polycrystalline phase on the silicon surface as a crystallite.

As a result of the studies carried out, the mechanism of manganese diffusion into silicon was established, leading to the formation of higher manganese silicides on the silicon surface. It has been established that the films grown on the silicon surface consist of HSM grains with the predominant orientation of the c axis perpendicular to the substrate. On the surface of HSM crystallites, manganese monosilicide is present as a polycrystalline phase. Such films have a high conversion coefficient, anisotropic properties of kinetic and thermoelectric parameters are found in them, depending on the direction of the crystallization axis of the silicon substrate.

The possibility of creating efficient thermopiles based on the obtained structures of the type Mn_xSi_{1-x} – Si<Mn>-Mn_xSi_{1-x} based on silicon, the operating parameters of which are not inferior to existing thermopiles, and sometimes have certain advantages, is shown.

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