Influence of structural defects in silicon on formation of photosensitive heterostructures Mn_4Si_7-Si<Mn>-Mn_4Si_7 and Mn_4Si_7-Si<Mn>-M

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The paper considers the influence of a transition amorphous layer at the interface between the higher manganese silicide (HMS) Mn_4Si_7 and silicon doped with manganese (Si <Mn>) on the photoelectric properties of heterostructures. The role of the initial structural defects in the near-surface layers of the single-crystal silicon on the penetration of manganese atoms into Si upon doping from the gas phase is shown.It has been established that at high temperatures (T>1050 $^\circ$ C) Mn atoms deposited on the silicon surface group together (due to surface diffusion), forming droplets of liquid manganese, which dissolve the near-surface silicon layer, forming a liquid solution – a melt of Mnand Si. When Mn atoms transfer from the vapor phase into the liquid solution-melt and Si atoms diffuse into it from the boundary regions, including the amorphous bulk Si layer, the solution-melt increases in size and solidifies. During solidification, higher manganese silicide (HMS) Mn_4Si_7 is formed, and under silicide, due to intense diffusion of Si atoms, the Si-Si bonds break, and an amorphous and elastically deformed Si region is formed, which predetermines the evolution of photoelectric phenomena in heterostructures Mn_4Si_7-Si<Mn>-Mn_4Si_7 and Mn_4Si_7-Si<Mn>-M.

Keywords: metal matrix composite, scanning probe microscope, atomic force microscopy, electric wire explosion, magnetic pulse compaction, dynamic plastic deformation.

Introduction

In earlier published works, in Si samples with deep Mn levels obtained by diffusion doping, a considerable difference in electrophysical properties was often observed. For example, in some heterostructures Mn_4Si_7-Si<Mn>-Mn_4Si_7 and Mn_4Si_7-Si<Mn>-M there were no such unique photoelectric phenomena as infrared quenching (IRQ), temperature quenching of photoconductivity (TPQ), long-term relaxation (LTR), residual photoconductivity, etc.This enables us to suppose that the observed phenomena may depend on the perfection of the original Si crystal.

The purpose of this work is to study the influence of structural defects in the single-crystal silicon on the formation of photosensitive heterophase structures Mn_4Si_7-Si<Mn>-Mn_4Si_7 and Mn_4Si_7-Si<Mn>-M in the process of diffusion doping with manganese.

Fabrication of heterostructures and research methods

To solve this problem, sample parties from KDB − 10 silicon ingots with a diameter of 76 mm and a plate thickness of 2 mm were made. Silicon ingots were cut into plates using two methods: 1) cutting with a diamond disc with an outer cutting edge (a is the first party of samples); 2) cutting with a disk with an inner cutting edge reinforced with diamond powder (b is the second party of samples).These methods of cutting crystals are used to determine the interaction of the cutting edge (inner or outer) of the disk and the ingot material, and to assess the degree of formation of damaged layers on the surface of the plates and their influence on the process of diffusion doping.

According to [1], the thickness of the layer disturbed during cutting can reach 50 μm, and consists of several sections, namely: a rough section with a thickness of the order of (1-3) μm, which is a highly disordered layer from a mixture of individual particles of the material of various sizes, is formed at the surface of the plate. It is followed by a defective layer with a thickness of about (10–30) μm, consisting of crystalline blocks, cracks, and dislocation nets of various configurations. An elastic deformation zone with a thickness of up to 5 μm is formed on the boundary between this region and the undisturbed single crystal. In the process of plate polishing, it is not possible to completely remove the damaged layers formed during crystal cutting from the surface; moreover, the polishing itself leads to the formation of damaged layers with smaller defects in depth [1]. From such plates rectangular specimens with dimensions $(18 \times 4 \times 2)$ mm^3 and $(10 \times 3 \times 2)$ mm^3 were cut. All parties of samples had p-type conductivity with a free hole concentration at 300 K equal to ($1 \approx 1.5 \cdot 10^{15}$ cm^{-3}) and mobility 400 cm^2 V^{-1} s^{-1}.

p-Si samples from the first and second party were loaded into a quartz ampoule in pairs with a sample of twice-sublimated manganese in the form of a powder with a grain size of not more than 50 microns. Diffusion of manganese into silicon proceeded from the gas phase at a temperature of (1040-1070) ° C for (40-60) min

in a vacuum created in a quartz ampoule. As manganese is a sublimating metal, as a result of heating in a furnace, it transfers from a solid to a gaseous state. The pressure of elastic vapors depends on the temperature and at the specified temperature was ≈ 0.7 Pa [2]. The doped samples were quenched by dropping ampoules into water.

The profiles of the conductivity distribution over the sample thickness were determined by successive layer removal and measurement of surface resistance Rs using the four probe method [3]. At the same time, the Hall effect was measured. The obtained profiles of the distribution of carrier concentration in Si<Mn> had two sections:

1) a near-surface layer with p-type conductivity with a carrier density of $\approx$ (1019–1020) cm $^{-3}$ and Hall mobility μp = (10–17) cm ^{2} B $^{-1}$ s $^{-1}$;

2) a bulk layer having a carrier concentration $\approx$ (1011–1012) cm $^{-3}$ close to the intrinsic one and Hall mobility μn=(600–700) cm ^{2} B $^{-1}$ s $^{-1}$ [4].

In accordance with the technique described in [4] (removing of surface layers not less than 20 μm thick from the sample surface, except one end and opposite to it), a blocking contact (M) was created by spraying Al or depositing alloys NiGa or AlGa.Thus, a model heterostructure of the HMS-Si<Mn>-HMS was created. The HMS-Si<Mn>-M structure was made by preserving the HMS layers at both ends and removing them from the other four faces. The areas of current contacts of HMS and the metal were $2 \cdot 10^{-2}$ cm ^{2}, and the length of the base regions was chosen from 0.3 to 1 cm.

Electrical and photoelectric characteristics of the structures were taken in a special cryostat, where the specified temperatures were maintained by electronic control of the heater (KT808A transistor was used as the heater) with an accuracy of 0.01 K. As a light source, a gallium arsenide LED was used, the radiation of which was regulated and supplied to the base region of the diode using a light fiber.

The morphology, microstructure and chemical composition of the doped Si<Mn> samples were examined by scanning electron microscopy (SEM) and X-ray energy dispersive spectrometry (EMF) on a Quanta 200 3D microscope (FEI, Holland) with accelerating voltages from 5 to 30 kV in secondary and reverse modes of scattered electrons [5].

To study the structure of cross sections of the HMS films, samples were etched with three beams of Ar $^+$ ions at an accelerating voltage of (1-5) keV through a protective mask into LeicaTIC.

The structure of the HMS and Si<Mn> and their boundaries at the nanoscale level were determined using the Fourier transform of the local HREM regions of images (a detailed structural analysis of the interface between the HMS and silicon is given in [5, 6]).

Experimental results and discussion

Based on our many-year studies, it was established that the first characteristic of high photosensitivity of the heterostructure is: when cooled in the dark to

a temperature of 80 K, the current flowing through the structure decreased, approaching the leakage current $I_t \leq 10^{-12}$ A (see Figure 1, curve 1). If, on cooling, the structure was illuminated with white light, the process was of a different nature, namely: when the temperature of the structure decreased to (170-250) K, the current flow initially decreased by several orders of magnitude relative to the values of current determined at room temperature, after further cooling to 80 K, a sharp increase in the photocurrent values was observed (by 2-3 orders of magnitude higher than the values of the photocurrent taken at room temperature, see Figure 1, curve 4).
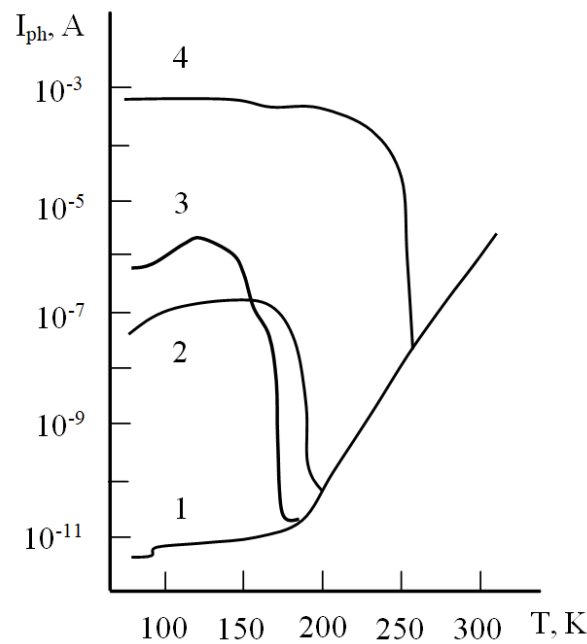

Figure 1. Temperature dependences of the photocurrent $I_{ph} = f(T)$ in the HMS-Si <Mn>-HMS heterostructure, taken at a constant applied voltage U=60 V: curve 1 is taken after cooling in the dark; curve 2 is taken after illumination with a radiation density of $1 \cdot 10^{-2}$ W cm^{-2}; curves 3 and 4 are taken at radiation densities of $2 \cdot 10^{-5}$ W cm^{-2} and $1 \cdot 10^{-2}$ W cm^{-2}.

The photovoltaic-ampere characteristic (PVAC) of the heterostructure had a linear section, a quadratic section and a section of a sharp current increase [7, 8]. Such heterostructures were characterized by such photoelectric phenomena as infrared damping, temperature quenching, long-term relaxation of residual conductivity, enhancement of phase transitions, and temperature-electric instabilities [8-10]. It is the heterostructures of the first party of samples (a) doped with manganese that possessed such photoelectric properties. In the second party (b), the above-listed photoelectric phenomena were absent, although their basic region (Si<Mn>) had high resistance.

In order to find out the reason for the manifestation or absence of the above-mentioned photoelectric phenomena, structural studies of the interface between the HMS and Si <Mn> were carried out for heterostructures from samples (a) and (b) parties.

Electron microscopic studies of samples (a) showed that the thickness of the transition region between the HMS and Si <Mn> is $\leq$ 20 nm (Figure 2), and it is a layer of amorphous silicon. The experimental data we obtained allow us to propose the following scheme for the formation of a film. The manganese atoms,

precipitating from the vapor – gas phase onto the substrate, interact with the silicon atoms and form nuclei and small islands of manganese silicide. Further, small islands grow due to the migration of molecules on the substrate and form larger islands. As a result of the diffusive mass transfer of silicon and Mn_4Si_7 molecules to the forming islands, stepped craters appear in some places of the substrate. Growing, the islands form a continuous film Mn4Si7.
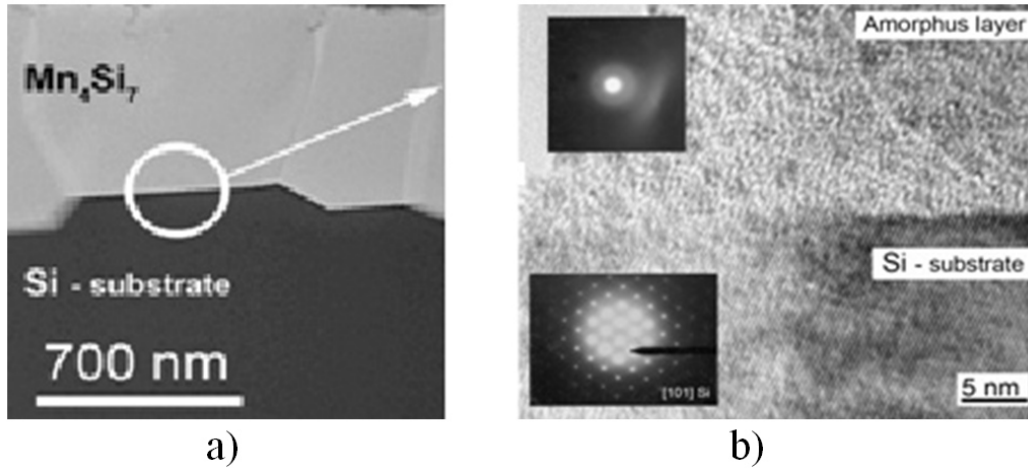

Figure 2. Electron microscopic images: a) between the film of higher manganese silicide and silicon substrate, b) between silicon substrate and amorphous layer.

For the second (b) party of manganese-doped Si samples, no amorphous layer was found at the interface. A detailed structural analysis of the HMS film/substrate interface (Si <Mn>) for samples of series (b) was carried out in [5, 6].
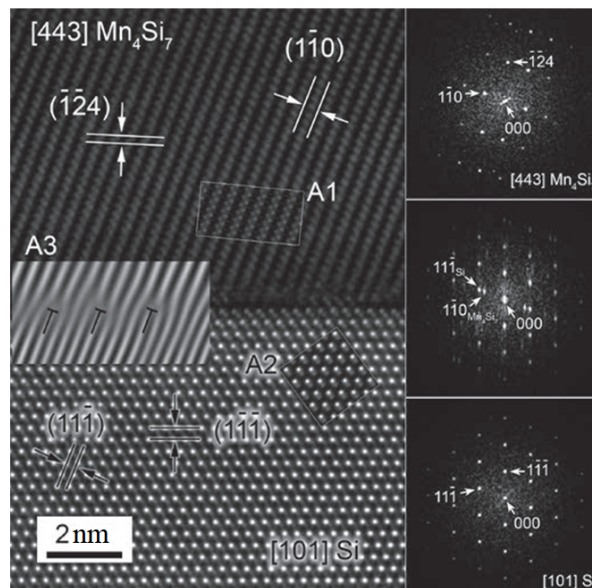

Figure 3. High-resolution transmission electron microscopic image of the interface between the HMS film and the Si substrate (left). Diffractograms obtained by the Fourier transform of selected regions of the HREM image – HMS films, the interface and the silicon substrate (right). Inserts A1 and A2 are simulated HREM images with orientation of [443] Mn_4Si_7 and [101] Si directions parallel to the incident electron beam. Insert A3 is HREM image filtered by reflexes $11\bar{1}$ Si and $1\bar{1}0$ Mn_4Si_7, identifying a grid of dislocation mismatches at the interface.

The high-resolution transmission electron microscopic image of the interface is shown in Figure 3. From Figure 3 it follows that the interface is semi-coherent,

and a regular net of unfit dislocations is formed in it.

As noted above, an HMS (Mn_4Si_7) film is formed in the surface layer, and under it, an amorphous transition layer with an insignificant concentration of electrically active atoms of manganese and boron is formed. And only below this transition layer, a uniformly doped volume of Si <Mn> is located. In general, this distribution of impurities is, on the one hand, caused by the reverse movement of the impurity to the surface during sample cooling to room temperature. On the other hand, silicides formed on the crystal surface and acting as a getter for impurities contribute to the reverse output process [4]. An important role in diffusion processes is played by the complex structure of the damaged layer on the surface of the Si crystal [1]. The depth of the distorted layer in Si may increase the depth of penetration of manganese atoms and thereby increases its solubility in the surface layer and further entry into the Si crystal lattice with subsequent diffusion distribution throughout the volume. However, the reactive nature of the mutual diffusion of manganese and silicon atoms is a complex process. In addition to the penetration of manganese atoms into Si from the gas phase, the Mn atoms deposited on the silicon surface can be grouped (due to surface diffusion) and form liquid manganese droplets on the Si surface dissolving the near-surface silicon layer, which leads to the formation of a liquid Mn-Si solution.

In the process of the entry of Mn atoms from the vapor phase into the liquid solution-melt and the diffusion entry of Si atoms from the boundary regions, including the amorphous bulk Si layer, the volume of the solution-melt increases and it solidifies. During solidification, the highest manganese silicide (HMS) Mn_4Si_7 is formed [4, 11, 12]. Under silicide, due to intense diffusion of Si atoms, Si-Si bonds break and an amorphous and elastically deformed Si region is formed [13].

Conclusion

Thus, it can be concluded that during the diffusion doping of silicon with manganese, the disturbed layers on the surface of the crystals deepen penetration of manganese atoms, facilitate the adsorption, dissolution and diffusion of Mn into the Si volume, and also contribute to the formation of an amorphous layer at the interface of the HMS and Si <Mn>. The presence of such an amorphous transition layer (in samples of party a) contributes to the rapid ionization of the current carriers under application of the external voltage, as well as formation of photoelectric phenomena: infrared damping, temperature quenching, high photosensitivity, long-term relaxation of residual conductivity, etc.

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