Electrodiffusion Method of Doping Silicon with Manganese

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Abstract. In this work, elemental analysis was performed, and electrophysical and photoelectric properties of silicon samples doped with Mn atoms by electrodiffusion were studied. The parameters and properties of samples obtained by introducing Mn atoms into silicon by electrodiffusion in the temperature range of 800-900 °C repeated the results obtained using traditional thermal diffusion technology in the temperature range of 1000÷1100 °C. It can be concluded that there is a possibility of increasing the solubility of Mn in silicon using the electrodiffusion method.

INTRODUCTION

In the works of the authors [1,2], the photoelectric properties of silicon samples with nanoclusters of manganese atoms were studied. Anomalous photoelectric phenomena were observed in these samples. The authors [3, 4] associate these phenomena with the presence of nanoclusters of impurity manganese atoms formed during the interaction with boron atoms in silicon. Moreover, with an increase in the boron concentration, the number of BMnn type nanoclusters increases and the influence of nanoclusters on the electrophysical and photoelectric properties of silicon samples increases [5, 6, 7]. Further development of this direction requires the development of new methods for increasing the solubility of manganese atoms in silicon.

The concentration of manganese atoms can be increased using ion alloying technology [8] and the electrodiffusion process, which, unlike thermal diffusion [9-14], involves a unidirectional rapid transfer of impurity atoms. Therefore, the study of the formation of nanoclusters and their influence on the photoelectric properties of silicon, when doping silicon [15-19] with impurity atoms of manganese under the influence of an external electric field, is both scientifically and practically relevant.

EXPERIMENTAL RESEARCH

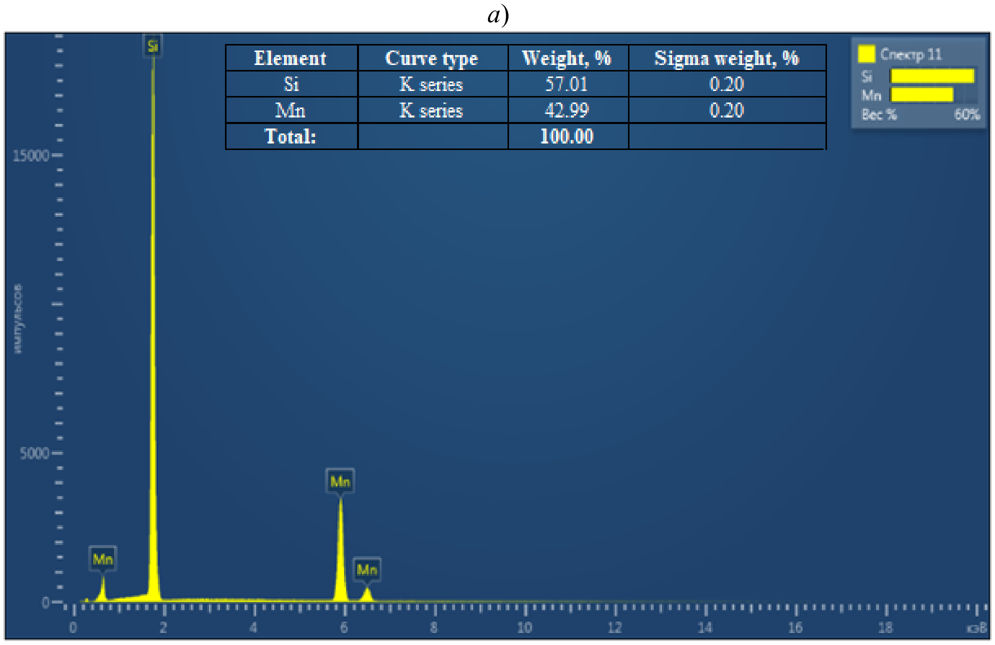
Single-crystal silicon of the *p*-Si brand ($N_B \approx 5\times10^{15}$ cm^{-3}) was used as the starting material. Samples were cut to dimensions of 5×10×1 mm^3 and, to clean the surface of the silicon samples, they were subjected to mechanical treatment and chemical etching in an acid etchant. After this, a thin layer of metallic manganese was formed on the surface of the samples using thermal evaporation in a VUP-4 vacuum unit.

Table 1. Specific resistance of samples

Samples	**ρ, Om·sm.**	
	«Positive»	«Negative»
Original	4-6	4-6
Control	4-6	4-6
batch 1 Si<B,Mn>	$1.50\cdot10^{2}$	$1.33\cdot10^{3}$
batch 2 Si<B,Mn>	$1.02\cdot10^{2}$	$1.21\cdot10^{3}$
batch 3 Si<B,Mn>	$7.82\cdot10^{1}$	$1.07\cdot10^{3}$
batch 4 Si<B,Mn>	$7.57\cdot10^{1}$	$8.91\cdot10^{2}$

Element	Curve type	Weight, %	Sigma weight, %
Si	K series	77.89	0.20
C	K series	18.95	0.20
Mn	K series	2.1	0.50
O	K series	1.06	0.50
Total:		**100.00**	

a)



Element	Curve type	Weight, %	Sigma weight, %
Si	K series	57.01	0.20
Mn	K series	42.99	0.20
Total:		**100.00**	

b)

Fig. 1. Elemental analysis of silicon samples obtained by electrodiffusion: a) - "positive" sample, b) - "negative" sample.

Two silicon samples were placed with the metallized surfaces facing each other and placed in an electrodiffusion setup. Electrodiffusion was carried out in a vacuum of no worse than 10^{-2} mm Hg. In this case, the positive pole of the electrodiffusion device was connected to one of the samples (the "positive" sample), and the negative pole to the other (the "negative" sample).

The electrodiffusion process was carried out for t=25-30 minutes with a direct current density of J=60-70 A/cm^2, during which the samples were heated to a temperature of T=800-900 °C. After completion of the electrodiffusion process, the samples were rapidly cooled by immersion in silicone oil and then chemically cleaned. The electrodiffusion process was repeated in 4 batches with identical electrodiffusion conditions and electrophysical parameters of the samples (a total of 8 samples were obtained).

The specific resistance of the samples (Table 1) was determined using the four-probe method on an RM 3000+ installation from Jandel.

From Table 1 it is evident that the specific resistance of the samples connected to the negative pole of the electrodiffusion device is greater than the specific resistance of the samples placed on the positive pole.

It is known that manganese in silicon at high temperatures diffuses (exists) predominantly in the form of interstitial positive ions, therefore, under the influence of an electric field, there is a preferential transfer of positive manganese ions into silicon connected to the negative pole of the electrodiffusion device. As a result, manganese atoms compensate for boron atoms, and their excess forms complexes (nanoclusters) of the BMn *n* type, where $n \leq 4$. From the analysis of the research results it was established that the specific resistance of the samples placed on the negative pole of the electrodiffusion device increased due to compensation. The specific resistance of the samples placed on the positive pole of the electrodiffusion device increased less as a result of thermal diffusion of impurity manganese atoms. The elemental composition of the obtained silicon samples was studied using a DJ-SEM 150D-ST scanning electron microscope (Fig. 1). Figures 1a and 1b show the results of elemental analysis of samples placed on the positive and negative poles, respectively. The tables below the EDS spectra provide numerical data from the elemental analysis. These results confirmed that the concentration of manganese impurity atoms was higher in the silicon sample placed at the negative pole of the electrodiffusion apparatus.

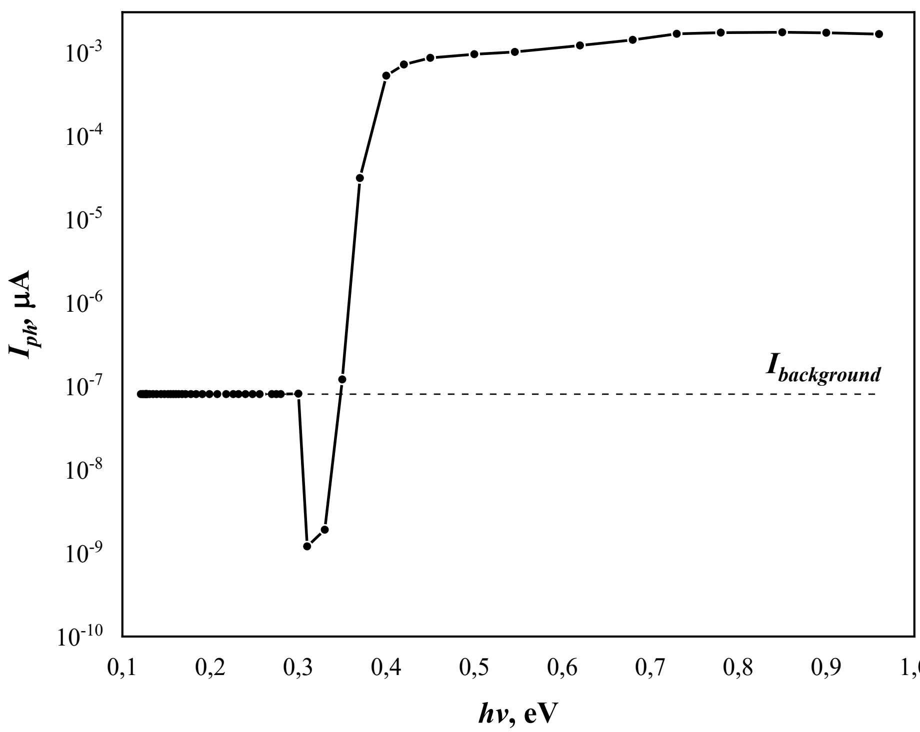


Fig.2. Infrared quenching of photoconductivity of silicon samples with manganese atom nanoclusters at T=100 K (ρ=1·10^3 Ohm·cm).

Calculations showed that in silicon samples placed at the negative pole of the electrodiffusion setup, the atomic fraction of manganese was ~75.4%, while in silicon samples placed at the positive pole, this figure was ~2.7%.

The photoelectric properties of silicon samples placed on the negative pole of an electrodiffusion device were studied using an IKS-21 spectrometer. Experiments were conducted at a temperature of T=100 K (Fig. 2). Figure 2 shows the spectral dependence of the photoconductivity of silicon samples doped with manganese impurity atoms, obtained with additional illumination by weak background integral light. The spectral photoresponse was calculated by subtracting the background light photocurrent. As can be seen from Fig. 1, photosensitivity begins at photon energies of *hν*~0.16 eV and increases continuously with incident photon energy. This process reaches a maximum at *hν*~0.3 eV.

A further increase in photon energy leads to a sharp decrease in photocurrent, i.e., IR quenching of the photocurrent is observed. This significantly reduces the photocurrent (by up to two orders of magnitude). Starting at $h\nu$=0.35 eV, the photocurrent increases sharply and reaches its maximum value already at $h\nu$=0.8 eV. Thus, in the spectral region of $h\nu$=0.4÷0.8 eV, these samples exhibit high-magnitude subband (possibly impurity) photoconductivity. This subband photoconductivity was observed even without background illumination. The phenomenon of infrared quenching was observed in all silicon samples located at the negative pole. According to the two-level model of IR quenching photoconductivity (IQPP) [20-24], photogeneration and carrier recombination, as well as the reorganization of sensitization centers, occur under the influence of integral background light. As a result, a sensitizing effect is observed. Additional illumination of the samples with IR light, with a photon energy equal to the ionization energy of the sensitization center, leads to the reverse process, resulting in a decrease in the photocurrent; that is, the IRCG effect occurs.

CONCLUSIONS

The parameters and properties of the samples obtained by introducing manganese atoms into silicon using the electrodiffusion method in the temperature range T= 800-900 °C repeated the results obtained by the authors in [25-28] using traditional thermal diffusion technology in the temperature range T=1000÷1100 °C. From this, it can be concluded that it is possible to increase the solubility of impurity manganese atoms in silicon using the electrodiffusion method.

Photoelectric properties of silicon samples with manganese atom nanoclusters demonstrate that the electrical and photoelectric properties [29-33] of the original material (silicon) can be significantly altered by the formation of manganese impurity atom nanoclusters. To elucidate the physical processes occurring in these materials, more detailed studies are needed, depending on the nature, structure, composition, and concentration of the resulting nanoclusters in silicon.

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