UDK 621.315.592.3

The influence of magnetic processing on properties and phase composition of alloyed semiconductor silicon

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Abstract
In the course of the research, we have noted the influence of weak constant magnetic field on the structure, phase composition, and properties of silicon, namely, significant increment of microhardness and considerable degradation of electrophysical properties, forming of polycrystalline structure in silicon specimens. The qualitative explanations of magneto-stimulated phenomena in studied specimens have been suggested. In the article the influence of alloying and magnetic processing (MP) at the structure and properties of Si specimens has been studied.
Keywords: MONOCRYSTALLINE SILICON, SILICON-GERMANIUM ALLOYS, MICROSTRUCTURE, MICROHARDNESS, ELECTROPHYSICAL PROPERTIES, MAGNETO-STIMULATED EFFECTS

Introduction

Relevance of the research was focused on the possibility of purposeful control of the structure and properties of semiconductor silicon by reducing defects density, improving the lifetime of minority carriers, and decreasing electrical resistivity due to highly efficient methods of external and complex effects.

It should be noted that the patterns of structure formation in semiconductor crystals at low doses of external influence, in particular, magnetic, X-ray radiation, remain little studied. There are only a few works which are devoted to the study of the problem.

In recent years, as a method that can cause structural relaxations processes and therefore influence the structure-sensitive properties of semiconductors, is being considered the magnetic treatment of various kinds of semiconductors in magnetic fields [1].

At the present time, special attention of scientific society in the world is drawn to issues related to research of structure and structural-sensitive properties of semiconductor materials and compounds at influence of external effects. Under these conditions devices, which are based on semiconductor materials, often operate.

Despite the scientific and practical significance of the studies of the complex effects on the structure and properties of semiconductors, they are absent in modern literature [2].

In this regard, the investigations of structure of silicon and its properties at the complex physical and chemical effects in liquid and solid states is very important and urgent task.

In the article the influence of alloying and magnetic processing (MP) at the structure and properties of Si specimens has been studied.

Materials and methods

As the initial materials, specimens of single-crystal semiconductor silicon were chosen; the were grown by Czochralski (Cz-Si), undoped and doped with Hf, Zr, Mg, Al, in an amount from 2 * 10-4 to 8.7 * 10-2% at.

Silicon specimens have been treated in a constant magnetic field with the induction of 0.07 Tesla. Exposure of samples was 240 and 720 hours. To identify the general structure of silicon specimens, in the work the solution HF: H_2O: CrO_3 in ratio 3:3:1 was used. Microstructure was studied using an optical microscope "Neophot-21". Microhardness was measured with the device PMT-3 with a load of 20 g. The resistivity measured by 4-probe method with an accuracy of 2.5%. Measurements of minority carrier lifetime were conducted by the photocurrent attenuation that occurred in the samples under GaAs light emission diode. The X-ray diffraction analysis and Ritveld method [3] have been used for identification of lattices type and phase composition of specimens after magnetic processing.

Table 1. Electrophysical properties of adopted Si specimens after MP

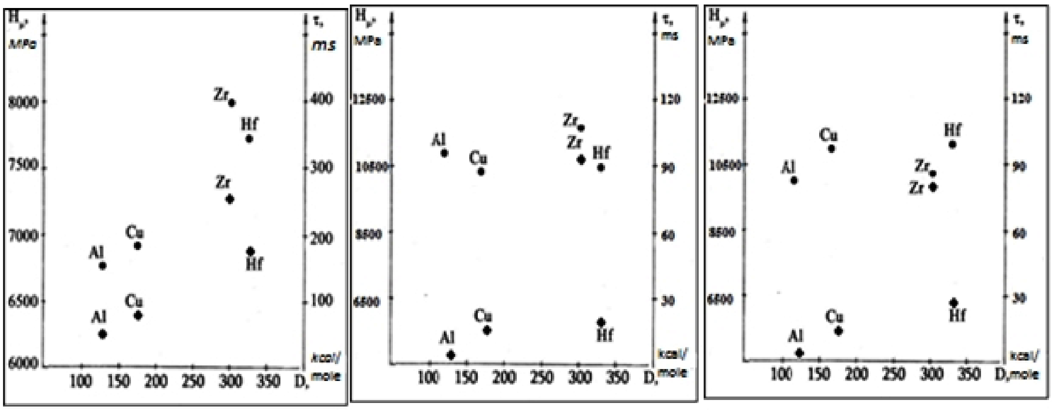
Specimen	Electrophysical parameters	Initial state	240 h of exposition	720 h of exposition
Cz-Si	ρ	80-100	46-49	83-92
	τ	574	0,65	0,63
	Conductivity type	p	p	p
Cz-Si-Al	ρ	200-210	55-65	60-65
	τ	12,1-12,5	0,40	0,32
	Conductivity type	p	p	p
Cz-Si-Hf	ρ	180-192	12,8-14,3	13,5-14,0
	τ	148	23,08	28,11
	Conductivity type	p	p	p
Cz-Si-Mg	ρ	170-190	44,8-46,2	43,7-50,0
	τ	134-138	16,32	14,55
	Conductivity type	p	p	p
Cz-Si-Zr	ρ	308-324	13,0-23,5	22,5-25,6
	τ	228	93,3	69,57
	Conductivity type	n	n	n

Table 1 shows the results of measurements of electrical resistivity and lifetime of minority carriers in silicon specimens before and after magnetic treatment. Analysis of the data shows the degradation of electrophysical parameters of all specimens. This is primarily due to the increase of microhardness and internal defects density.

Reducing the lifetime of minority carriers can also be linked to the oxygen content in the surface layers of silicon. As shown in [4] during magnetic treatment of silicon in the surface layers of the material, the content of oxygen and ions of alkali metals (K +, Na +) as well as hydroxyl groups and other radicals significantly increases, that associated with activation of the surface and enhancement of its adsorption capacity under the influence of a weak magnetic field. Oxygen in main (triplet) state and radical groups adsorbed on the surface of the silicon can capture carriers [5], and significantly reduce the time they exist in free form.

Doping silicon with elements that have a greater affinity for oxygen - Zr, Hf, Mg, Al - may reduce the impact of the latter on the lifetime of the current carriers through its binding (in the sequence to reduce). This is a possible reason why the specimens doped with the abovementioned elements at the high microhardness have relatively high values of lifetime of minority carriers (exception - Si (Al)).

The authors of [6], show dependence between H_{μ} and τ_{MCC} from the interaction energy of atoms in the crystal lattice of silicon doped with B, Al, Cu, Sn, Ge, Zr, Hf (figure 1a). With the above elements doped silicon while increasing the binding energy between the atoms of the Si-Si by alloying silicon with above elements has been noted increasing the matrix microhardness and lifetime of minority carriers. The elements Ge and Sn, referred to neutral, do not affect the value of microhardness and lifetime of minority carriers.



a) initial state; b) after 240 hours of exposition; c) after 720 hours of exposition

Figure 1. The dependence between Figure 1. The dependence between H_{μ} and τ_{MCC} from Si-Si binding energy after doping:

• - H_{μ} ,MPa;

♦ - τ_{MCC} ,μs

Apparently, in the initial state, there is correlation between mechanical and electrical properties of doped specimens which were annealed in the intervals of I, II, and III phase transformations: with increasing the interaction energy (by alloying) between the atoms of silicon was observed almost linear increasing in both microhardness and lifetime of minority charge carriers in silicon.

After magnetic treatment (0.07 T) over 240 (Fig. 1 b) and 720 hours (Fig. 1 c), there is a strong increase in microhardness and degradation of the electrical properties of the specimens. Dependency between the binding energy, microhardness and lifetime of minority charge carriers after processing, was not observed.

After MP in the structure of specimens formation of a large number of twins was observed, that is probably caused by formation of a certain amount of unknown silicon phase by shear mechanism [6]. The fact that the in undoped silicon low-temperature shear phase transition $Si_{FCC} \leftrightarrow Si_{ROMB}$ occurs at temperatures above 350º C (Tab. 2) says that in this case it was caused by the influence of the magnetic field.

Table 2. Temperatures of phase transformations in alloyed silicon

Cz-Si/ Alloying element	Temperature/coefficient of thermal expansion $^0C/\alpha \cdot 10^{-6} \cdot {}^0C^{-1}$		
	I $Si_{FCC} \leftrightarrow Si_{ROMB}$	II $Si_{ROMB} \leftrightarrow Si_{BCC}$	III Si_{BCC} $_{III} \leftrightarrow Si_{HCP}$
Cz-Si	350/4.3	700/4.4	900/5.3

Cz-Si+Al	450/5.0	750/4.5	900/6.0
Cz-Si+Zr	500/4.5	-	850/4.7
Cz-Si+Hf	380/4.5	-	850/4.7

After 720 hours of MP significant changes in the structure of the specimens was observed, and the measurements showed an increase of microhardness and electrical resistivity compared with ones of specimens that were exposed for 240 hours. This points out at further development of phase transformation and stabilization of structure under the influence of a magnetic field. No signs of phase transformations in the structure of the specimens doped with Al, Zr, Hf and Mg under the influence of a magnetic field were detected, but the density of defects in the crystal structure has been increased significantly.

Each of alloying elements that have been mentioned above, increases the critical temperature of I, II, and III phase transitions in silicon (Table 2), and may increase the thermodynamic stability of the phases to the magnetic field (magnetic field brings additional energy into the system). It is also likely that the alloying elements stabilize Si_{BCCIII} high-temperature phase, thereby excluding shear-diffusion phase transformation and formation of twins in the structure.

It is known that aluminum greatly reduces the interaction energy of silicon atoms and assists the implementation of the shear and shear-diffusion phase transformations in silicon. On the contrary - hafnium significantly increases the binding energy of silicon atoms that inhibits the phase transformation and stabilizes Si_{FCC} structure of silicon.

But, as defined in [4], structural changes in Cz-Si (Al) and Cz-Si (Hf) specimens under constant magnetic field are almost identical. This suggests that processing in a magnetic field inhibits the phase transformations.

To identify the phases in specimens which have been passed MP, was used the X-ray diffraction analysis. Figure 2 shows the X-ray diffraction pattern of Cz-Si in the initial state.

The X-ray diffraction patterns of specimens in the initial state show interference peaks corresponding to reflection from (111), (220), and (511) which are typical to Fd3m lattice. There have been some splitting peaks that correspond to (111) and (511). Splitting in diffraction peaks indicates the presence of distortion in the crystal lattice of Cz-Si in initial state, at this splitting the maximum (511) should be associated with the superposition of Si_{ROMBIC} interference peaks [6]. The X-ray diffraction pattern of Cz-Si, after magnetic treatment (720 hours) is shown in Figure 3.

Weak interference lines from (111), (220), (311), (511) correspond to Si_{FCC} phase. There are interference peaks which correspond to Si_{ROMBIC} phase formation of which in specimens has been suggested in previous studies [2].

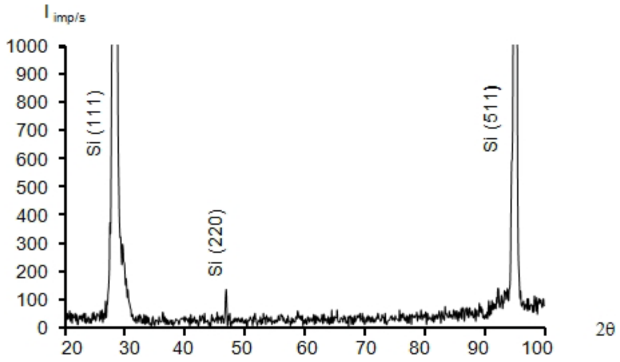


Figure 2. X-ray diffraction pattern of Cz-Si specimen in initial state

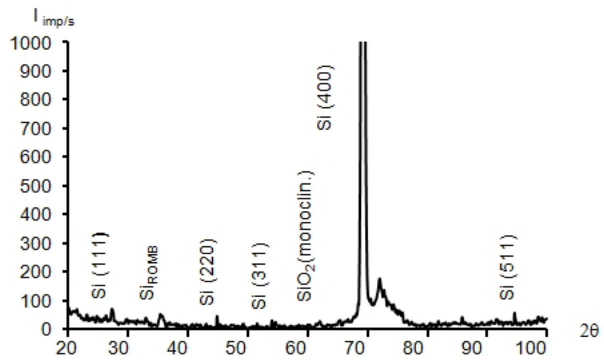


Figure 3. X-ray diffraction pattern of Cz-Si specimen after 720 hours of MP

The maximum intensity on the X-ray diffraction pattern has (400) peak, also significant splitting of it has been observed. The of high intensity and splitting of (400) may be caused by a strain and deformation of silicon lattice along one of the diagonals of the cube i.e. the formation of Si_{BCT} phase [6] as well the appearance of reflections from monoclinic silicon oxide (SiO_2) [7]. The latter assumption is confirmed by a significant increase of oxygen content in the surface layers of silicon after MP [8].

Registration of diffraction peaks, which occur as the result of distortion of SiIII BCC (SiBCT), and the emergence of Si_{ROMB} phase indicates a development of phase transformations in silicon after MP and relaxation.

Conclusions

Thus, the magnetic processing almost takes off the effect of elements that increase binding energy between Si atoms and the lifetime of minority carriers (Zr, Hf, Pb, Nb, Mo, REM, Au, W). This is caused by increasing of internal defects density and adsorption of oxygen in the surface layers of silicon that leads to scattering and recombination of minority charge carriers and consequently increasing the electrical resistivity. As well X-ray diffraction analysis shows that MP causes development of shear and shear-diffusion phase transitions and the increasing of SiO_2 content in the surface layers of silicon specimens.

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