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X-RAY DIFFRACTION STUDY OF THE PHASE STATE OF SILICON SINGLE CRYSTALS DOPED WITH MANGANESE

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Abstract. The phase states of manganese atoms in silicon have been studied using the X-ray diffraction method. It was found that the diffraction patterns of n-Si<Mn> and n-Si<Mn> samples with a SiO_2 film on the surface exhibit several selective structural reflections with different intensities. It is shown that the lattice parameter of Si<Mn> samples is slightly less than the lattice parameter of Si<Mn> samples with a SiO_2 film on the surface, and this leads to a shift of structural reflections in the Si<Mn> diffraction pattern towards smaller scattering angles.

Keywords: *silicon, manganese, film, silicon dioxide, x-ray diffraction, structure, lattice parameter.*

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1. Introduction

At present, solid-state electronic devices are used all over the world in almost all areas of science and technology (Zaynabidinov *et al.*, 2022; Utamuradova *et al.*, 2023; Utamuradova *et al.*, 2023; Askerov *et al.*, 2020). The field of application of solid-state devices is constantly expanding, fundamentally new devices are being created that stimulate the development of industry in new directions, which requires a significant increase in the perfection of the structure of Si, the main material of modern semiconductor solid-state electronics. In this regard, studies aimed at studying the processes of defect formation in Si doped with various impurities and establishing controlled methods for stabilizing the parameters of semiconductor devices are one of the important problems.

In Bahadyrkhanov et al. (2011) the electrophysical properties of manganese-doped silicon were studied by the low-temperature diffusion method. It has been established that the samples exhibit giant photoconductivity in the impurity region of the spectrum with λ = 3–1.5 μm, an anomalously high negative magnetoresistance, and a temperature dependence of the hole mobility, which are uncharacteristic of silicon. Based on the study of the state of manganese atoms by EPR and AFM methods, the structures of nanoclusters

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consisting of introduced manganese atoms and a method for controlling their charge state and magnetic moment are proposed.

As is known, silicon grown by the Czochralski method has an increased content of various background impurities - oxygen and carbon, up to $2 \cdot 10^{18}$ cm^{-3} and up to $5 \cdot 10^{16}$ cm^{-3}, respectively. Among the background impurities, the problem of oxygen in silicon for many years (more than 60 years) remains very relevant (Valikova *et al.,* 1982; Malyshchev *et al.,* 1974; Utamuradova *et al.,* 2019; Babich *et al.,* 1997; Abdurakhmanov *et al.,* 1998; Anfimov *et al.,* 2007).

Manganese atoms, which are a rapidly diffusing impurity in silicon, differ from other impurities not only in their high solubility and diffusion rate, but also in their ability to form various clusters, which affects the electrical parameters of microelectronic devices. However, the properties of only isolated manganese atoms in silicon have been sufficiently well studied so far, while there is no reliable identification for most of the various complexes of manganese with background and other dopants (Abdurakhmanov *et al.,* 1998; Utamuradova *et al.,* 2020).

The purpose of this work is to study the behavior of manganese atoms in the silicon crystal lattice using the X-ray diffraction method.

2. Experimental part

Doping of silicon with manganese atoms was carried out by diffusion from the gas phase in evacuated quartz ampoules at a temperature of 1100-1200ºC for 3 hours. We used n-Si crystals grown by the Czochralski method with resistivity ρ=40 Ω·cm. Some samples of n-Si were subjected to preliminary heat treatment at T=1200ºC, while a layer of silicon dioxide SiO_2 appeared on the surface of these samples. Diffusion of manganese was carried out into n-Si samples with and without a thin layer of SiO_2 on the surface.

Studies of the structural and phase states in silicon samples doped with manganese atoms were carried out on an Empyrean Malvern X-ray diffractometer. The OriginPro2019 program was used to determine the peak maximum. X-ray diffraction measurements were carried out in the Bragg-Brentano $2\theta_Б$ beam geometry in the range from 10° to 90° continuously at a scanning rate of 0.33 deg/min and an angular step of 0.0200 (deg).

3. Results and their discussion

The experimental results obtained using the X-ray diffraction method (Utamuradova *et al.,* 2022) for samples of n-Si<Mn> and n-Si<Mn> with a layer of SiO_2 and are shown in Fig.1-*a*. It can be seen from the diffraction pattern of the n-Si<Mn> sample with the SiO_2 layer that the diffraction pattern contains several selective structural reflections with different intensities.

An analysis of the results obtained showed that the surface of the sample corresponds to the crystallographic direction (111). This conclusion confirms the presence on the diffraction pattern of a series of selective structural reflections (HHH) (where H=1,2,3…), the structural data of which are given in Table 1. The observed diffraction reflection from Si<Mn> samples with a layer of SiO_2 with an intense reflection $(111)_\alpha$ at 2θ=28.46° and its next order $(333)_\alpha$ at 2θ=94.9°, their FWHM $(111)_\alpha \approx 1.2 \cdot 10^{-3}$ rad and FWHM $(333)_\alpha \simeq 1.74 \cdot 10^{-3}$ rad) testifies to the perfection of crystalline silicon with the value of the lattice parameter a_{Si}=0.5426 nm.

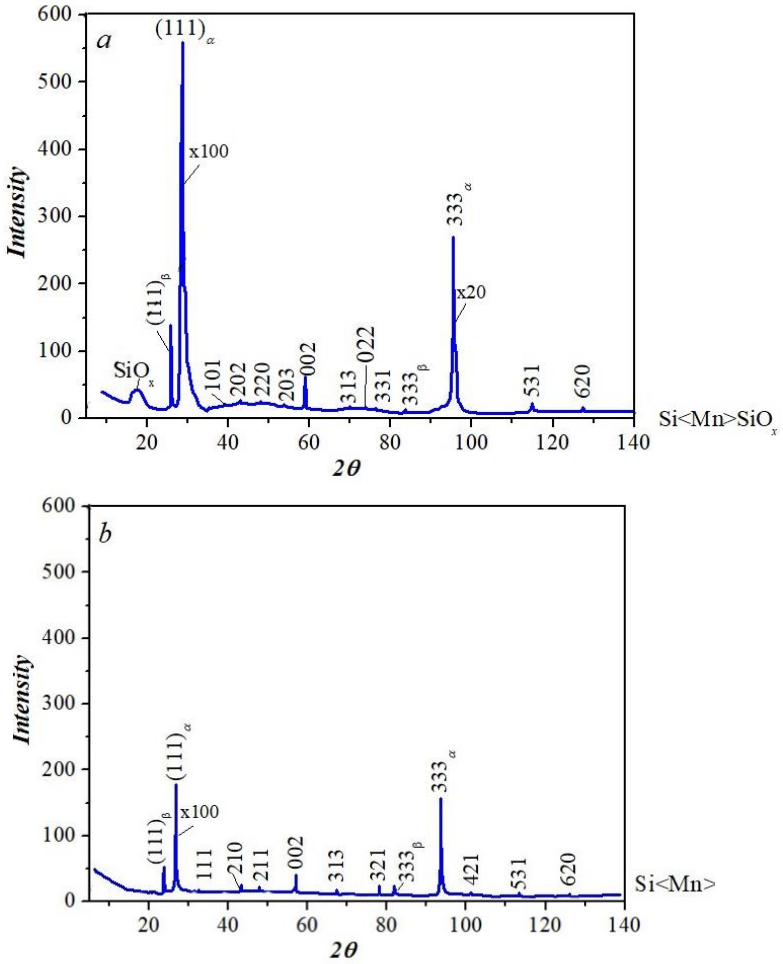

Fig. 1. Diffractograms of n-Si<Mn> single crystals with a SiO_2 film on the surface and n-Si<Mn>

An analysis of the experimental results shows that the n-Si<Mn> samples with a SiO_2 layer have a diamond-like structure and have a cubic Bravais lattice with the space group Fd3m. We have determined the sizes of crystallites for the n-Si<Mn>SiO_2 single crystal from the half-width of the (111) structural line, which was 67 nm.

On fig. 1-*b* shows the diffraction pattern of n-Si<Mn> samples. It differs from the diffraction pattern of n-Si<Mn> samples with a SiO_2 layer and there is no diffuse reflection at $2\theta \approx 17.4°$ on the X-ray diffraction pattern and a decrease in the intensity of structural reflection $(111)_\alpha$ by 2.5 times, the intensity of the third order $(333)_\alpha$ by 1.7 times, respectively, and the intensity of the structural reflection (002) is reduced, the intensities of the reflections, (313), (513) and (620) are also increased by several percent and they provide a diffraction shift in the spectra of the diffraction pattern of the n-Si<Mn> sample in side of smaller angles. The crystallite sizes and the lattice parameter determined from the half-width of the (111) structural line for n-Si<Mn> are 58 nm and a_{Si}=0.5419 nm, respectively, which is slightly less than the lattice parameter (a_{Si}=0.5426 nm) of sample n -Si<Mn> with SiO_2 layer. But this causes a shift of structural reflections in the n-Si<Mn> diffraction pattern towards smaller scattering angles.

Table 1. The positions of the diffraction patterns observed in the X-ray diffraction pattern of n-Si<Mn> single crystals with a layer of SiO_2 and n-Si<Mn> and their mutual difference Δ (°)

hkl	**Si<Mn>SiO_2**		**Si<Mn>**		Δ (°)
	d, Å	2*θ*, (°)	*d*, Å	2*θ*, (°)	
111_α	3,141	28,46	3,136	28,51	0,04
111	-	-	2,609	34,68	-
101	2,253	40,045	-	-	-
202	2,067	43,45	-	-	-
210	-	-	2,021	44,47	-
220	1,924	47,24	-	-	-
211	-	-	1,845	49,392	-
203	1,732	52,50	-	-	-
002	1,584	58,42	1,578	58,26	0,16
313	1,331	70,51	1,334	70,59	0,08
022	1,294	73,21	-	-	-
331	1,246	76,26	-	-	-
321	-	-	1,203	79,53	-
333_α	1,046	94,9°	*1,045*	95,12	0,03
421	-	-	0,986	102,48	-
531	0,9178	114,16	0,9171	114,11	0,05
620	0,8586	127,46	0,8578	127,38	0,08

On the diffraction pattern, in addition to the main reflections, there are also structural lines with a wide diffusion reflection at 2θ≈17.4° and a number of other structural lines with low intensity and a diffusion reflection band at scattering angles $2\theta_Б$ in the range from 34.1 to 93.3° (Fig. 2-*a*). The observed reflections at the indicated scattering angles on the surface layers of the studied samples indicate that they are caused by small structural fragments formed with the participation of an oxygen impurity during prolonged exposure at temperatures 400÷800ºC with subsequent cooling of the grown crystal (Chukinç 2008; Talanin *et al.* 2010). At the same time, during heat treatment at the indicated temperatures, the supersaturated solid solution of oxygen Si-O_n decomposes with the formation of simpler dissociative O_x complexes in the form of a quasi-molecule Si-O_i-Si, (bound in teratitial form), precipitates with different sizes, and silicon dioxide SiO_2 (Anfimov *et al.*, 2007; Gerasimenko *et al.*, 2007).

Some of the formed SiO_4 complexes at an annealing temperature of ≥450°C (consisting of four oxygen atoms) exhibit thermal donor properties with the formation of an energy level of E_c-0.02 eV (Chukin, 2008; Newman *et al.*, 1983) and thermal exposure at 780°C leads to a noticeable increase in the mobility of oxygen atoms and the formation of various inhomogeneities in the form of oxygen precipitates, the growth of which is due to a decrease in the free energy of the crystal, followed by a change in their size and the transition of the crystal to an equilibrium state with the formation of a stoichiometric amorphous SiO_2 layer both on the surface and at the boundaries of impurity-defect accumulations.

The difference in the ionic radius of oxygen (r_o^{2+} = 0.140 nm) compared to silicon (r_{Si}^{4+} =0.042 nm), the location of the impurity oxygen atom in the interstices on the Si-Si bonds in the silicon lattice, and a significant diffusion coefficient of oxygen in Si in the exposure temperature range ≥600ºC ($3\cdot10^{-12}$ cm^2/s) contributes to the effective formation of an association of oxygen with an admixture of defective accumulations.

In silicon dioxide, in the process of cooling when growing a crystal from a melt consisting of nanocrystallites and nanoclusters located in precipitates, an association of oxygen with these inhomogeneities occurs (see Fig. 2-*a*). These nanostructures have a low symmetry and are mainly located in the surface layers of a single crystal and at the Si-SiO_2 boundaries.

Sections of the structural lines of the diffraction pattern associated with the low-symmetry lattice of stoichiometric silicon dioxide in the inhomogeneous layers of a single crystal of Si are shown in Figs. 2-*a*. Fig. 2-*a* shows that there are several structural reflections on diffuse reflections, shown in Table 1.

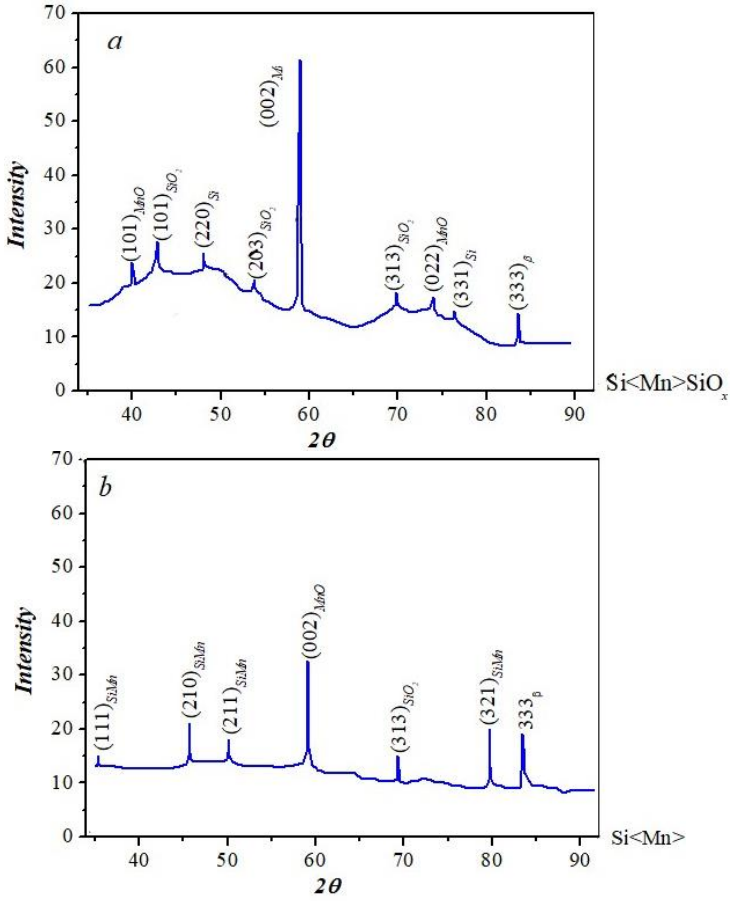

Fig. 2. Sections of the diffraction pattern of n-Si<Mn> single crystals with a layer of SiO_2 and n-Si<Mn>

These reflections with narrow widths indicate the crystalline state of the impurity phase of silicon dioxide SiO_2 at the boundaries of SiO_x (Terekhov *et al.,* 2012). The characteristic sizes of crystallites are in the range of 65÷72 nm. Processing and analysis of the experimental results of these reflections made it possible to determine the lattice parameter of nanocrystallites in SiO_2, with $a_{exp}=b_{exp}=$ 0.508428 nm and $c_{exp}=0.7098$ nm, which agrees quite well with the literature data (Terekhov *et al.,* 2012; Chukin, 2008).

Fig. 2-*b* shows sections of the diffraction pattern of a Si<Mn> single crystal and they show structural lines from lattices of the impurity phase of silicon dioxide (SiO_2) at 2θ=70.59°. In addition, the diffraction spectrum contains diffusion reflection at scattering angles $2\theta_Б$ in the range from 32.5 to 91.7°. Above the level of this diffuse reflection, four

more selective reflections with low intensity are clearly distinguished, having diffraction indices (111), (210), (211) and (321), which are shown in Table 1. They are caused by manganese-silicon nanocrystals in the form of SiMn, formed in sections of silicon subcrystallites, with an average characteristic size L_{SiMn}≈43 nm. These nanocrystals have cubic symmetry with the lattice parameter a_{exp}=0.4520 nm.

Diffraction lines (101), (002) and (022) (see Fig. 2-*a*), also (002) (see Fig. 2-*b*). The analysis showed that they are caused by manganese-oxygen precipitates in silicon, the sizes of these precipitates are in the range of 37÷51 nm. From the experimental results, MnO precipitates were determined, which have a face-centered orthorhombic Bravais lattice with lattice parameters a_{exp}=0.3201 nm, b_{exp}=0.4487 and c_{exp}=0.6332 nm.

4. Conclusion

Thus, based on the analysis of the results obtained and the studies carried out, the following conclusions can be drawn:

- high intensity and narrow half-width of the main reflection (111)α give information about the perfection of n-Si <Mn> samples with a layer of SiO_2 with a lattice parameter value a_{Si}=0.5426 nm and that it is a diamond-like structure with a cubic lattice (pr.gr.Fd3m);
- it is determined that the value of the lattice parameter of the sample n-Si<Mn> (a_{Si}=0.5419 nm) is slightly less than the value of the lattice parameter of the sample value n-Si<Mn> with a layer of SiO_2 (a_{Si}=0.5426 nm), but causes a shift structural reflections in the n-Si<Mn> diffraction pattern towards smaller scattering angles;
- self-formation of the SiO_2 impurity phase with lattice parameters a_{exp}=b_{exp}=0.508428 nm and c_{exp}=0.7098 nm and sizes from 65 nm to 72 nm was determined at the SiO_x boundaries;
- manganese-silicon nanocrystals with a size of ~43 nm are formed in the sections of silicon subcrystallites. These nanocrystals have cubic symmetry with the lattice parameter a_{exp}=0.4520 nm;
- manganese-oxygen precipitates were determined, which have a face-centered orthorhombic Bravais lattice with lattice parameters a_{exp}=0.3201 nm b_{exp}=0.4487 and c_{exp}=0.6332 nm with sizes ranging from 37÷51 nm.

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