Research of Isotopic Effect on Surface of Silicon After Thermal Annealing and Electronic Irradiation

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Abstract – The investigations of changes of the isotopic composition in surface layers of single crystal silicon samples were made after thermal annealing at different temperatures and at time of annealing about 1 hour, in present article. Those changes were compared. Experimental results on isotopic effect by electronic beam irradiation of single crystal silicon surface were shown here. Theoretical estimations of isotopic effect on the basis of sublimation principle are given and compared with experimental results in this report. The researches were made by the secondary ion mass spectrometry method (SIMS) on the device MC-7201M.

1. Introduction

It is well known that most of chemical elements have more than one stable isotope. The meaning isotope introduced by Soddy [3] is an atomic nucleus of the same chemical element with different amount of neutrons. Thus, the isotopes of the same chemical element only differ in mass and form of a nucleus, and therefore frequency of limited optical and zero-point vibrations, which in turn cause rather high reorganization of energy spectrum of electronic excitations [4]. It results in changes: energy values of interzonal transitions E_g, lattice dynamics of solid, thermal conductivity, heat of sublimation electronic conductivity, temperature of superconductivity of solid, isotopic substitution [5]. The review [2] contains in particular the following information that thermal conductivity of single isotopic sample ^{28}Si increases in comparison with natural silicon by 60 % at room temperature (T=300 K). At the same time, at about T=20 K, the thermal conductivity of single isotopic sample is 6 times larger than the size of natural sample.

All the mentioned facts allow us to hope, that changing surface isotopic composition without reorganization of material volume, it is possible to create structures with exotic and very useful practical properties. Surface isotopic effects have been observed earlier [1] in the processes of ion sputtering, ion implantation, hydrogen electronic charging and termodiffussion from outer source during the influence of electronic beam on "metal+hydrogen". Essential changes in the natural isotopic composition are observed in all the mentioned processes, both in surface layers, and in composition of secondary (emitted, scattered) particles. The purpose of the present article was to research the influence of thermal annealing at T=300, 600 and 900 °C, time of annealing about 1 hour, on changing of isotopic composition in surface layers of silicon single crystal samples and to compare experimental results with each other; to present experimental results on isotopic effect by electronic beam irradiation the silicon single crystal surface. The irradiation of plates of silicon single crystal surface by electronic beam was carried out through a polymeric film and without it at the pressure ~10^{-4} Pa, with current density of beam ~40 mcA/cm^2, time the irradiation ~20 min.

2. Experimental technique

The profiles of hydrogen isotopes in surface layers before and after thermal annealing of samples were studied by the method SIMS on the installation MC-7201M. Ion beam Ar$^+$ with energy of 4.5 keV, current density of 0.1 mA/cm^2, and section area with surface of 2.5 mm^2 was used as sounding. Remained vacuum was ~10^{-5} Pa, working vacuum ~10^{-4} Pa.

The analysis of samples was at the continuous recording of signals of secondary ion currents. Isotopic concentrations C were calculated by division the intensity of line of I isotope of this element by sum of intensities of all the lines of the same element. The relative error of measuring of spectral lines intensity did not exceed 5 %.

3. Results and discussion

The experimental results obtained on annealed samples and irradiated with electronic beam samples were given in Table 1 and compared with the initial. As we can see, that the change of isotope composition after irradiating with electronic beam without polymeric film is not observed.

The thermal annealed samples don't have the isotopic composition deviation from the initial one. There is an enrichment of surface with the lightest isotope ^{28}Si. This deviation, probably, is connected to the processes of the surface ionization, the sublimation and thermal stimulated desorption.

Table 1. Comparison of concentrations of silicon isotopes in a secondary ion flow at sputtering of silicon plates surfaces, after thermal annealing and electronic irradiation

A. m. u. of isotope ^{28}Si	Concentrations of silicon isotopes, %		
	Initial	irradiated	Annealed
28	78	78	81
29	19	19	16
30	3	3	3

Experimental results of silicon isotopic concentration on the surface after thermal annealing are shown in Table 2. Thermal annealing was made in vacuum ~10^{-4} Pa, at temperatures ~300, 600 and 900 °C and time of annealing ~60 minutes. In all three cases the enrichment of surface with light isotope ^{28}Si takes places. Obvious dependence of deviation of isotopic composition from natural one in surface area from temperature is not observed. This effect, probably, has connection with the processes of sublimation and thermal stimulated desorption.

Fig. 1 shows the change of isotopic composition on isotope ^{28}Si of silicon samples irradiated with electrons through polymeric film and without it from time of sputtering with ionic beam of sample surface. The basic regularity, in case of sample irradiated electronic beam through polymeric film, is observed in these processes and relevant to the change of isotopic composition, to the enrichment of surface with connected heavy isotopes of silicon. The reasons of such enrichment, probably, are the features of diffusion processes of hydrogen isotopes and electronic stimulated desorption processes. An ideal correct structure is usually attributed to crystal solids, representing space lattice which has equal atoms (or molecules) in its units.

As the result of thermal movement vibrations of atoms near their equilibrium positions appear keeping, however, this ideal correct position. Obviously, at rather high temperatures some atoms in volume and on the surface of crystal completely tear off from their equilibrium position and fly into the environmental space. Process of sublimation of solid results from this.

To calculate isotopic composition of gas phase and therefore to learn as isotopic composition of sample surface changes, we can use equation [6] given by the authors to find the density of atomic flow J evaporating from the unit of surface at the unit of time.

$$J = n \cdot \sqrt{\frac{kT}{2\pi m}} \cdot e^{-U_0/kT}, \tag{1}$$

where n – atomic concentration in sample, T – temperature of the sample, m – mass of the atom, k – Boltzmann constant, U_0 – surface energy of atom connection with surface.

The number of atoms evaporating for time t from the surface with area S is:

$$N = J \cdot S \cdot t, \tag{2}$$

where N – amount of evaporated atoms, S – area of surface, where evaporation takes place from, t – time of evaporation.

Table 2. Comparison concentrations of silicon isotopes in flow of secondary ions Si$^+$ during sputtering surfaces of silicon plates, after thermal annealing at temperature 300, 600 and 900 °C during 1 hour

A. m. u. of isotope ^{28}Si	Concentrations of silicon isotopes, %			
	Initial	300 °C	600 °C	900 °C
28	76	79	79	78
29	2	18	18	19
30	4	3	3	3

Let's consider the evaporation from the surface of samples of silicon isotopes and count coefficient of isotopic division at temperatures T=300, 600 and 900 °C and discuss the result.

Let's write down flows for each isotope taking into account (1):

$$J_{1,2,3} = n_{1,2,3} \cdot \sqrt{\frac{kT}{2 \cdot \pi \cdot m_{1,2,3}}} \cdot e^{-U_{10,20,30}/kT}, \tag{3}$$

where indexes 1, 2 and 3 show that parameter relates to ^{28}Si, ^{29}Si и ^{30}Si, respectively.

We know the natural isotopic composition of silicon as follows: P_{01}=92.23 % for isotope ^{28}Si; P_{02}=4.67 % for isotope ^{29}Si; P_{03}=3.1 % for isotope ^{30}Si. Let's find percentage of isotope ^{28}Si during sublimation in gas phase. You may find to using (3):

$$P_1 = \frac{N_1}{N_1 + N_2 + N_3}, \tag{4}$$

where N_1, N_2, N_3 – the amount of evaporated atoms of isotopes ^{28}Si, ^{29}Si и ^{30}Si, respectively. The equation (4) for shows that

$$P_1 = \frac{J_1}{J_1 + J_2 + J_3}, \tag{5}$$

when we use the equation (3), substituting it in (5) then we shall obtain

$$P_1 = \frac{1}{1 + \frac{n_2}{n_1} \cdot \sqrt{\frac{m_1}{m_2}} \cdot e^{-\Delta U_{21}/kT} + \frac{n_3}{n_1} \cdot \sqrt{\frac{m_1}{m_3}} \cdot e^{-\Delta U_{31}/kT}}, \tag{6}$$

where $\Delta U_{21} = U_{20} - U_{10}$ and $\Delta U_{31} = U_{30} - U_{10}$.

We calculated P1 at temperatures 300, 600 and 900 °C. ΔU_{21} и ΔU_{31} were taken equal 10^{-3} eV and $2 \cdot 10^{-3}$ eV, respectively, taking the account the data [7] for isotopic shift. Relations n_2/n_1 and n_3/n_1 were replaced by P_{02}/P_{01} and P_{03}/P_{01}, respectively, as they are equal. The results are shown in table 3.

From table 3 we can see that during the sublimation gas phase enrichment with isotope ^{28}Si is observed therefore surface layer of the sample must lack this isotope.

The converse effect is observed in experimental results. The surface is enriched with isotope ^{28}Si. It can be explained that the process of sublimation is

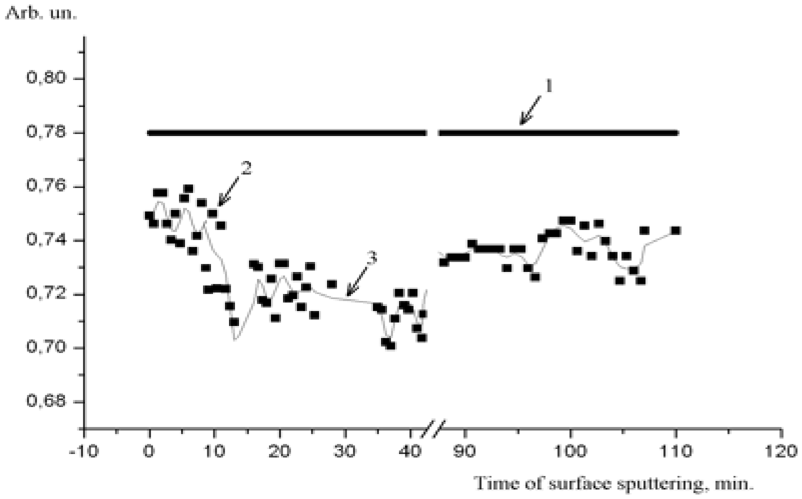

Fig. 1. Dependence of change of isotopic composition in surface area of silicon samples irradiated with electronic beam through polymeric film and without it on time of sputtering by ionic beam. 1 — irradiated silicon without polymeric film; 2 — the experimental points of irradiated silicon through polymeric film; 3 — flattening curve of irradiated silicon through polymeric film

not prevailing, it is quite possible that, change of isotopic composition occurs mainly due to thermal stimulated desorption and surface ionization.

Table 3. Calculated percentage composition of silicon isotopes in gas phase after sublimation and coefficient of isotopic division

	P_1	P_2+P_3	q
300 °C	92.6%	7.4%	1.054
600 °C	92.53%	7.47%	1.043
900 °C	92.5%	7.5%	1.039

4. Conclusion

In conclusion we can notice that during thermal annealing the isotopic composition of silicon surface changes with its enrichment with isotope ^{28}Si, and during the irradiation by electronic beam the surface of silicon samples through polymeric film the enrichment of surface area with heavy isotopes ^{29}Si and ^{30}Si takes place. The opportunity of changing silicon isotopic composition of surface makes the researches in this direction interesting enough to use of these processes in the technological purposes.

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