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THE MECHANISM OF THE FORMATION OF BINARY COMPOUNDS BETWEEN Zn AND S IMPURITY ATOMS IN Si CRYSTAL LATTICE

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The paper presents the results of an experimental study of surface morphology, elemental composition, electrophysical and optical properties of Si samples earlier doped with impurity atoms of Zn and S. The results of the study revealed a sufficient concentration of Zn and S elements on Si surface after diffusion (3.1% and 2.6% by weight, respectively). After additional thermal treatment at different temperatures, i.e., at 850°C and 875°C, the samples of I group have regained their initial parameters. However, it's noteworthy that the mobility of charge carriers in group I samples was comparatively lower than that in group II samples allegedly under the influence of Zn and S binary molecules. After additional heat treatment of all samples at a temperature of 875°C, the authors have studied optical absorption coefficients. And their band gap energies were determined using the Tauc Plot method. According to the results of the study, the optical band gaps in group II and III samples were 1.12 eV, whereas the band gap energy in group I samples after additional thermal treatment at a temperature of 875 °C turned out to be 1.31 eV. Having theoretically calculated the band gap by applying Vegard's law, the authors suggested that the new structure must be of $Si_{0.92}ZnS_{0.08}$ - type.
Keywords: *Resistivity, Silicon, Impurity atoms, Binary compound, Diffusion, Mobility of charge carriers, Concentration of charge carriers*
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1. INTRODUCTION

Wide-bandgap semiconductor compounds have over recently become a new opportunity for perspective optical research and application development. An increased interest in ZnS-type semiconductor compounds in recent years was largely due to its application in optical electronic devices such as light-emitting diodes, flat panel displays, non-linear optical devices, sensors, lasers as well as photocatalysis [1-5]. Due to large band gap values, these materials are likely to be proper source for the production of LEDs [6,7]. However, engineering single crystalline samples of ZnS-type binary semiconductor compounds is both technologically and materially expensive. The authors in [8,10] are said to have engineered the islets of GaSb binary compounds on the surface of Si by using the diffusion technique, thus theoretically justifying and practically calculating the band gap energy and lattice parameters of the novel compound. Therefore, the proper technology is in place so that one can actually engineer ZnS binary compounds in single crystalline Si, thus allowing to obtain novel types of materials by applying the diffusion technique.

Therefore, it is of both scientific and practical importance to form ZnS semiconductor compounds in silicon crystal lattice and study its fundamental parameters. It is known that the ZnS semiconductor is mainly formed in one of cubic sphalerite (E_g=3,54 eV [1-7]) or hexagonal wurtzite (E_g=3,8÷3,91 eV [1-7]) structures.

2. MATERIALS AND METHODS

A single crystalline silicon wafer grown by the Chokhralskiy method, dopped with phosphorus impurity atoms, with a specific resistance of ~100 Ω·cm was chosen as a starting material (the concentration oxygen NO~10^{17} cm^{-3}). The silicon wafer was cut in geometry of 1×4×8 mm^3 and the surface of the samples was subjected to mechanical treatment and chemical cleansing. Afterwards, the Zn and S were diffused in into samples during the two-stage process. The samples were divided into three groups:

The group 1 samples: in the first stage, S atoms were diffused into silicon samples at a temperature of T=1250°C for t=10 hours, while in the second stage, Zn atoms were diffused at a temperature of T=1200 °C for t=1 hour;

The group 2 samples: in the first stage, S atoms were diffused into the silicon samples at a temperature of T=1250°C for a period of t=10 hours, while in the second stage, the samples were additional annealed at a temperature of T=1200°C for a period of t=1 hour;

The group 3 samples: in the first stage, pure silicon samples without inclusions were annealed at a temperature of T=1250 °C for t=10 hours, in the second stage, Zn impurity atoms were diffused at a temperature of T=1200°C for a period of t=1 hour.

After diffusion, the samples were repeatedly additionally subjected to mechanical treatment and chemically cleansed. The elemental analysis of the samples was done using an Energy-Dispersive X-ray spectrometer (EDS - Oxford Instrument) - Aztec Energy Advanced X-ray SDD scanning electron microscope (SEM) (Fig. 1), optical analysis was obtained on a Shimadzu UV-1900i spectrophotometer. After that, the samples were additional annealed step by step at temperatures of 600, 700, 800, 825, 850, 875, 900, 950 and 1000°C, and after each additional annealing, the

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electrophysical properties of the samples were measured on HLS-3000 Ecopia Hall Effect Measurement System. All measurements were made at 300°K, i.e., the room temperature.

3. RESULTS AND DISCUSSION

3.1. Element analysis

Elemental analysis of samples was done after two-stage diffusion.

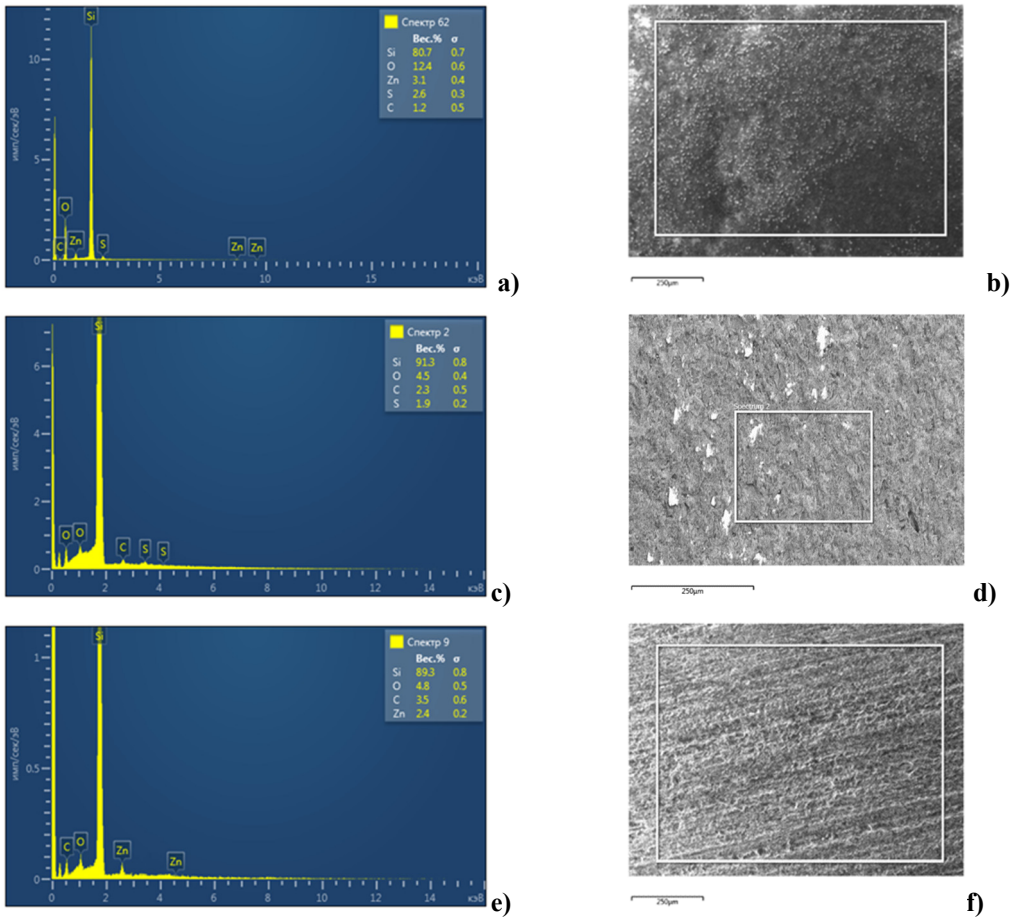

Figure 1. Elemental analysis and SEM images of the surface of the samples:
a), c), e) elemental composition of group I, II, III samples, respectively;
b), f), d) SEM images of the surface of samples of groups I, II, III, respectively

As can be seen from Figure 1-a), Si, O, C, Zn, and S were detected in 80.7, 12.4, 1.2, 3.1, and 2.6 mass fractions in the samples belonging to group I, respectively. In Figure 1-b), Si, O, C, S in the samples of group II were determined in 91.3, 4.5, 2.3, and 1.9 mass fractions, respectively. In Figure 1-c), in the samples of group III, Si, O, C, Zn were detected in 89.3, 4.8, 3.5 and 2.4 mass fractions, respectively. It is noteworthy, that the amount of oxygen detected in samples of group I and III are were almost equal to each other. However, the amount of oxygen detected in the samples belonging to group I appears to be significantly higher than the amount of oxygen detected in the samples of group II and III. The reason for this can be explained by the fact that Zn and S atoms on the surface of silicon must have attracted and bonded the oxygen previously contained in silicon.

3.2. Electrophysical analysis

Electrophysical properties [11-12] of the samples after two-stage diffusion were studied, and their results are presented in Table 1.

Table-1. Electrophysical parameters of the samples after the diffusion process

Samples	Conductivity type	Resistance ρ, Ω·cm	Mobility of charge carriers μ, $cm^2/(V·s)$	Concentration of charge carriers n or p, cm^{-3}
Starting silicon sample	*n*	108.71	1243	4.6×10^{13}
Group I samples, i.e., Si<S, Zn>	*p*	9.05	292	2.36×10^{15}
Group II samples, i.e., Si<S>	*n*	2.01	946	3.29×10^{15}
Group III samples, i.e., Si<Zn>	*p*	4.98	209	6.0×10^{15}

As can be seen from Table 1, the resistivity of the group I samples is 4.5 times greater than the resistivity of the Group II samples, and almost twice bigger than the resistivity of the group III samples. This can be explained by the mutual neutralization of Zn and S impurity atoms in the group I samples. It is known that in the silicon crystal lattice, S atoms form 2 donor energy levels (Ec – 0.26 eV and Ec – 0.48 eV) and they usually manifest themselves in three different states: 1–neutral (S^0), 2– one electron leaves, and the atom turns into a singly positively charged ion (S^+), 3 –two electrons leave, and the atom turns into a doubly positively charged ion (S^{++}).

In their turn, Zn impurity atoms create 2 acceptor energy levels (Ev + 0.26 eV and Ev + 0.55 eV, respectively) in the silicon crystal lattice, and they manifest themselves in three different states: 1–neutral (Zn^0), 2–accepts an electron, and the atom turns into a singly negatively charged ion (Zn^-), 3 - accepts two electrons, and the atom turns into a doubly negatively charged ion (Zn^{--}).

If the above two last mechanisms take place, the positive and negative ions of S and Zn impurity atoms in the silicon crystal lattice begin to attract each other. In this case, since the molar mass of Zn atom is 2 times larger than the molar mass of S atom, the attraction of a positively charged S ion to the negatively charged Zn ion is probably stronger. But one needs to create certain thermodynamic conditions to ensure that S and Zn ions migrate in the silicon crystal lattice subsequently forming a ZnS-molecule. For this purpose, the samples were additionally annealed at various temperatures for the same time duration. Afterwards, we have determined their electrophysical properties (Table 2).

Table 2. Electrophysical parameters (ρ,μ,n) of the samples after additional thermal treatment at various temperatures.

T, ^{0}C	samples	600	700	800	825	850	875	900	950	1000
t (hours)		1	1	1	1	1	1	1	1	1
ρ, Ω·cm	I-group	9,85	10	27,8	85,5	92,3	150	129	112	63
	II-group	2,1	2,06	2,04	2,05	2,1	2,2	2,4	2,5	2,7
	III group	5,15	5,21	5,32	5,33	5,41	5,61	5,71	6,2	7,2
μ, cm^2/(V·s)	I-group	285	240	443	324	783	810	57	276	335
	II-group	924	920	921	923	923	927	931	940	964
	III-group	198	196	194	197	195	198	202	207	211
n,p (cm^{-3})	I group	$2{,}2\cdot10^{15}$	$2{,}6\cdot10^{15}$	$5{,}7\cdot10^{14}$	$2{,}3\cdot10^{14}$	$8{,}6\cdot10^{13}$	$5{,}1\cdot10^{13}$	$8{,}5\cdot10^{14}$	$2\cdot10^{14}$	$2{,}9\cdot10^{14}$
	II group	$3{,}2\cdot10^{15}$	$3{,}3\cdot10^{15}$	$3{,}3\cdot10^{15}$	$3{,}3\cdot10^{15}$	$3{,}2\cdot10^{15}$	$3{,}1\cdot10^{15}$	$2{,}8\cdot10^{15}$	$2{,}7\cdot10^{15}$	$2{,}4\cdot10^{15}$
	III group	$6{,}1\cdot10^{15}$	$6{,}1\cdot10^{15}$	$6{,}0\cdot10^{15}$	$5{,}9\cdot10^{15}$	$5{,}9\cdot10^{15}$	$5{,}6\cdot10^{15}$	$5{,}4\cdot10^{15}$	$4{,}9\cdot10^{15}$	$4{,}1\cdot10^{15}$
Type of conductivity	I group	*p*	*p*	*p*	*p*	*n*	*n*	*p*	*p*	*p*
	II group	*n*	*n*	*n*	*n*	*n*	*n*	*n*	*n*	*n*
	III group	*p*	*p*	*p*	*p*	*p*	*p*	*p*	*p*	*p*

As can be seen from Table 2, the Group 3 samples were additional annealed step by step at temperatures of 600, 700, 800, 825, 850, 875, 900, 950 and 1000°C and their resistivity (ρ, Ω·cm), charge carriers mobility (μ, cm^2/(V·s)), charge carriers' concentrations (n,p, cm^{-3}), and the conductivity type were subsequently determined. As can be seen from Table-2, the results of electrophysical measurements in Group I samples annealed at temperatures T=850°C and T=875°C are rather anomalous. The rest of the results obey the known rules of physics due to which we will only discuss the results in the Group I sample annealed at temperatures T=850 °C and T=875 °C. The conductivity is n-type, the resistivity is 92.3 and 150 Ω·cm, respectively, the concentration of charge carriers is 8.6×10^{13} and 5.1×10^{13} cm^{-3}, respectively, the mobility of charge carriers is 783 and 810 cm^2/(V·s). From these results, one can conclude that the parameters in Group I samples regain their original values. When it comes to discussing the mobility of charge carriers, it can be seen that mobility parameters do not completely regain their initial value at these temperatures. Assuming that the mobility of charge carriers in n-type ZnS compound semiconductor is ~200 cm^2/(V·s), it can be said that the mobility of charge carriers of the initial silicon decreases due to forming of Zn and S compounds in the bulk of silicon. That is, the formation of the ZnS molecules in the silicon crystal lattice can be explained based on the results shown in Figure 2 below.

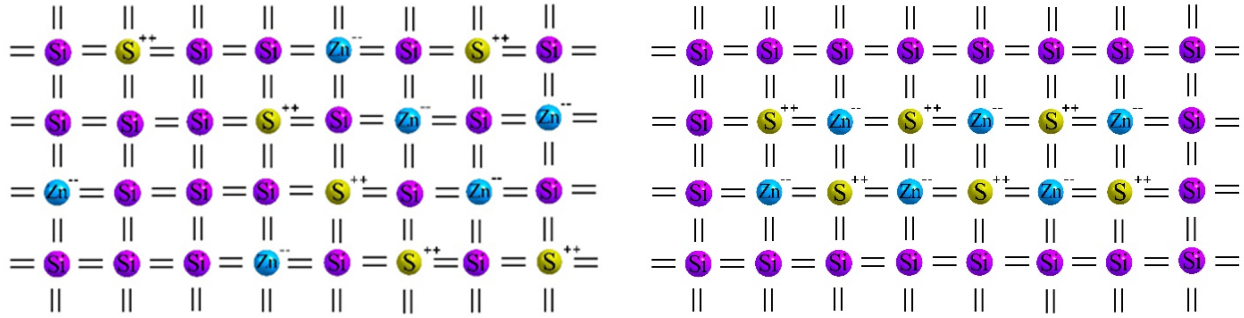

Figure 2. Zn and S atoms in the silicon monocrystal lattice:
a) before additional thermal treatment; b) after additional thermal treatment.

3.3. Optical analysis

One of the most preferred methods for determining the band gap of semiconductors is optical absorption method. There are no special requirements for the shape and geometry of samples under investigation, and the accuracy level of the measurement is sufficiently high.

The technique consists in the behavior of light whereby a certain portion of the monochromatic light beam directed at the surface of a semiconductor sample is reflected from the surface, a certain portion passes through the bulk of the sample, while the rest is absorbed in the bulk of a semiconductor material. As a result, the light intensity decreases. The relative change in the light intensity per unit volume is called the absorption coefficient. The value of the absorption coefficient depends on the wavelength (λ) of the incident radiation, and the function is called the absorption spectrum.

Absorption coefficient can be calculated based on the measurement of reflectance (R) and transmittance (T) using the following formula:

$$\alpha = \frac{1}{d}\ln\frac{(1-R)^2}{T} \tag{1}$$

where d is the sample thickness, R is the reflection coefficient, T is the light transmission coefficient. The Formula (1) is valid at T<10%. If T>10%, the relation (2) hereunder should be used to calculate the absorption coefficient:

$$T = \frac{(1-R)^2\exp(-\alpha d)}{1-R^2\exp(-2\alpha d)} \tag{2}$$

The absorption spectra of the samples were received using a Shimadzu UV-1900i -type spectrometer, and the optical band gaps of the samples were determined using the Tauc plot`s method [11] (Figure-3). Before the UV-1900i measurements, all samples were had a thickness of d~200 μm.

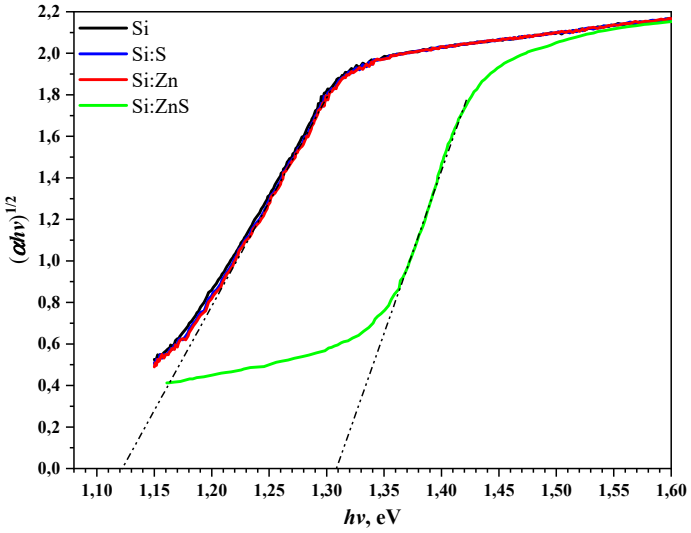

Figure 3. Optical band gaps of the samples

Figure 3 shows the measurement results of samples belonging to Group III, reference sample and Group I samples after additional thermal treatment at T=875 °C. As can be seen from Figure 3, optical band gaps of samples belonging to Group II and III and the reference sample are almost the same, that is ~1.12 eV. The optical band gap of Group I samples after additional thermal treatment at temperature T=875 °C was ~1.31 eV. Taking into account that the band gap energy of ZnS semiconductor at temperature T=300 °K is ~3.54 eV, the results are assumably indicative of the formation of ZnS binary molecules in the silicon crystal lattice.

Based on the measurement results and applying reciprocal calculation of Vegard's law [12] we will calculate the portion of each Si and ZnS in $Si_{1-x}ZnS_x$ compound.

$$E_{g,A_{1-x}B_x} = (1-x)\cdot E_{g,A} + x\cdot E_{g,B} \;\rightarrow\; E_{g,Si_{1-x}ZnS_x} = (1-x)\cdot E_{g,Si} + x\cdot E_{g,ZnS} \tag{3}$$

where x is the molar fraction of the substance, $E_{g,Si_{1-x}ZnS_x}$ is the band gap of the newly formed structure i.e., $E_{g,Si_{1-x}ZnS_x} = 1.31\ eV$, $E_{g,Si}$ - the band gap of silicon which is $E_{g,Si} = 1.12\ eV$ and $E_{g,ZnS}$ is the band gap of ZnS, equal to $E_{g,ZnS} = 3.54\ eV$ (the band gap of ZnS of cubic sphalerite structure). We will calculate the value of the unknown coefficient x in equation 3 based on the above information. According to the calculations, it was found that $x \approx 0.08$. Therefore, it can be said that the band gap energy of the newly engineered structure formed in silicon is equal to 1.31 eV.

4. CONCLUSION

The results of electrophysical and optical experiments showed that after two-stage diffusion of Zn and S into a monocrystalline silicon sample these elements incidentally do not form a compound in silicon due to the fact that both Zn and S are not deep-level creating impurities. To achieve that certain thermodynamic conditions are required to be in place in order to ensure forming bonds between these impurities in the silicon crystal lattice. The measured electrophysical results show that the formation of ZnS binary compounds was negatively affected by the low temperature when the samples of Group I were additional annealed in the temperature range of 600÷800°C, and the ZnS binary compounds began to form when additionally annealed in the temperature range of 800÷850°C. ZnS binary compounds are fully formed under additional thermal treatment in the temperature range of 850÷900°C, while in the temperature range of 900÷1000 °C, ZnS binary compounds must have dissociated into atoms again. This conclusion was confirmed by the surface morphological and elemental analysis of the samples, as well as the results of optical measurements.

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МЕХАНІЗМ УТВОРЕННЯ БІНАРНИХ СПОЛУК МІЖ ДОМІШКОВИМИ АТОМАМИ Zn ТА S У КРИСТАЛІЧНІЙ ГРАТЦІ Si

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У статті наведено результати експериментального дослідження морфології поверхні, елементного складу, електрофізичних і оптичних властивостей зразків Si, раніше легованих домішковими атомами Zn і S. Результати дослідження виявили достатню концентрацію елементів Zn і S на поверхні Si після дифузії (3,1% і 2,6% мас. відповідно). Після додаткової термічної обробки при різних температурах, тобто при 850°C і 875°C, зразки I групи відновили вихідні параметри. Проте варто відзначити, що рухливість носіїв заряду в зразках I групи була порівняно нижчою, ніж у зразках II групи нібито під впливом бінарних молекул Zn і S. Після додаткової термічної обробки всіх зразків при температурі 850°C автори досліджували коефіцієнти оптичного поглинання. Їхню енергію забороненої зони було визначено за допомогою методу Tauc Plot. За результатами дослідження встановлено, що ширина забороненої зони в зразках II та III групи становила 1,12 еВ, тоді як у зразках групи I після додаткової термічної обробки при температурі 850°C енергія забороненої зони виявилася 1,31 еВ. Теоретично розрахувавши ширину забороненої зони за допомогою закону Вегарда, автори припустили, що нова структура має бути типу $Si_{0,92}ZnS_{0,08}$.

Ключові слова: *питомий опір; кремній; домішкові атоми; бінарна сполука; дифузія, рухливість носіїв заряду; концентрація носіїв заряду*