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Integration conditions of III-V binary compound semiconductor materials and Si semiconductor material photovoltaic properties of silicon with the structure (Si)1-x(GaSb)x–Si

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Integration conditions of III-V binary compound semiconductor materials and Si semiconductor material, photovoltaic properties of silicon with the structure $(Si)_{1-x}(GaSb)_x$–Si

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Abstract. This work consists of two parts. In the first part, the integration level of III-V binary compound semiconductor materials and Si semiconductor materials and the difference in their lattice constants are discussed. In the second part, the research part, Ga as a group III element and Sb as a group V element are doped into the p-Si sample by diffusion method, and their photoelectric properties are studied. The research results show that the Ga and Sb elements are combined with each other, forming a new material with the structure (Si)1-x(GaSb)x in the Si crystal lattice.

INTRODUCTION

It is known that silicon is the main material of microelectronics, and it has been very well mastered and used in the field of optoelectronics. However, in the field of optoelectronics, the fundamental parameters of silicon, in particular the structure of energy bands, and the mobility of charge carriers, are limited compared to some compound semiconductors. Therefore, there is great interest in changing or controlling the fundamental parameters of silicon [1-3]. This can be done by combining silicon with other semiconductors, in particular III-V type compound semiconductors. There are several ways to form III-V compound semiconductors on the surface of silicon. However, during the direct growth of III-V group compounds on the Si surface, point dislocations, line dislocations (TD), antiphase boundaries (APB), micro twin crystals (MT) and micro cracks appear [4].

TABLE 1. Melting temperatures and charge carrier mobilities of Si [5-7], Ge [8,9] and some III-V [10-13] binary compound semiconductors

Semiconductors	Melting temperature (°C)	μ cm^2/(V·s)	
		electrons	holes
IV – elementary semiconductors			
Si	1414	1500	450
Ge	938.25	3900	1900
III-V binary compound semiconductors			
GaAs	1238	9400	491.5
InP	1062	5200	170
InSb	524	77000	850
GaP	1457	152	147
GaSb	712	3000	1000
InAs	942	34000	530

Various problems are encountered in the formation of III-V binary semiconductors on a silicon substrate. Examples of these include the increase in dislocation density due to the large difference in lattice constants and thermal expansion coefficients of the substrate and the growing layer [14], the problems of controlling the amount of group III and V elements in the layer formation, and the control of the thickness of the thin layer [15]. The table below shows the difference in lattice constants of silicon and III-V semiconductors (Table 2).

TABLE 2. Crystal lattice constants of III-V binary compound semiconductors

Binary compounds	$a_{III\leftrightarrow V}$, Å	$\Delta = \frac{a_{A^{III}B^{V}} - a_{Si}}{a_{Si}} \cdot 100\%$	Optimality levels
BN (Z)	3.6157	-33.41	3
BP (Z)	4.538	-16.43	2
BAs (Z)	4.777	-12.02	2
BSb (Z)	5.265	-3.04	1
AlN (Z)	3.2060	-18.86	2
AlP (Z)	5.5024	1.3	ideal
AlAs (Z)	5.717	5.28	1
AlSb (Z)	6.229	14.71	2
GaN (Z)	4.582	-15.62	2
GaP (Z)	5.451	0.38	ideal
GaAs (Z)	5.685	4.7	1
GaSb (Z)	6.0955	12.25	2
InN (W)	*a*=3.533; *c*=5.693	-34.93 4.84	3
InP (S)	5.86	7.92	1
InAs (Z)	6.0585	11.57	2
InSb (Z)	6.4788	19.31	2

where is Δ – the difference in lattice constants of the substrate (silicon) and the growing layer.

As can be seen from Table 2, AlP and GaP compound semiconductors are good candidates for growth on a silicon substrate.

In recent years, scientific interest in the formation of III-V compound semiconductor layers [16] and III-V binary compound clusters on silicon has been increasing [17-20]. This is due to the important aspects of materials science, such as obtaining materials with high purity, integrating semiconductors with each other and controlling their functional parameters.

The most common methods for forming III-V binary compounds on silicon are:

1 – epitaxial layer growth methods (such as MBE [21], VPE [22], LPE [23], SPE [24]);
2 – chemical vapor deposition methods (such as CVD [25], MOCVD [26]);
3 – diffusion method [27-31].

Thin layers on the substrate surface are usually formed in the following three main modes:

1 – islands (Volmer-Weber) [32];
2 – layer-by-layer (Frank-van der Merwe) [32];
3 – layer-plus-islands or SK (Stranski-Krastanov) [32].

The islands (Volmer-Weber) mode occurs when the molecules of the material being grown are more strongly attracted to each other than to the substrate, resulting in a 3D layer growth [32].

In the layer-by-layer (Frank-van der Merwe (FM)) regime, atoms are deposited primarily on the substrate surface, resulting in smooth, fully formed layers at the atomic level. This layer-by-layer growth is two-dimensional (2D), indicating that complete thin-film layers are formed before subsequent layers can grow [32].

Stranski-Krastanov growth is a two-step process characterized by both 2D layer and 3D island growth. The transition from layer-by-layer to island-based growth occurs at a critical layer thickness that is highly dependent on the chemical and physical properties of the substrate and film, such as surface energy and lattice parameters [32].

The relationship between the growth mode, the surface energy of the grown material, and the substrate can be expressed by equation (1):

$$\gamma_s = \gamma^* + \gamma_d \cos\theta \tag{1}$$

Here γ_s – is the surface energy of the substrate, γ^* – is the surface energy of the interface between the growing material and the substrate, γ_d – is the surface energy of the growing material, and θ – is the contact angle. In layer-by-layer growth, the grown material wets the substrate and $\theta \approx 0$, so However $\gamma_s \geq \gamma^* + \gamma_d \cdot$, the opposite is true for island growth and $\theta > 0$, so $\gamma_s < \gamma^* + \gamma_d \cdot$ SK growth combines the characteristics $\gamma_s > \gamma^* + \gamma_d$ of island and layer-by-layer growth that were initially present before the island was formed.

Besides epitaxial growth, the most practical method for controlling the type and concentration of impurities in specific regions of a semiconductor crystal is the diffusion method. The diffusion of impurities in semiconductors is a classic topic and has been extensively studied [15].

It is known that diffusion occurs when there is a difference in particle concentration [33]. The distribution of the impurity atoms in the crystal during diffusion can be determined by solving the diffusion equation based on Fick's laws. The first law of Fick is given by the following equation:

$$J = -D\frac{dN}{dx} \tag{2}$$

where, *J* is the concentration difference, $\frac{dN}{dx}$ the flux of impurity atoms crossing a unit surface in the *x* direction per unit time, *D* is the diffusion coefficient of the penetrating impurity atoms, *x* is the depth of penetration of the impurity atoms into the crystal, and *N* is the concentration of impurity atoms.

The concentration of the intervening atoms crossing at a given time and distance is calculated using the 2nd law of Fick:

$$\frac{dN}{dt} = D\frac{d^2N}{dx^2} \tag{3}$$

The diffusion of impurities into semiconductors occurs from the gas phase (if the vapor pressure is sufficient) or from a layer introduced into the surface of the material.

The main quantities of the diffusion process are *D*–diffusion coefficient, *N(x,t)*–distribution of the concentration of impurity atoms in the crystal, *x*–depth of penetration of impurity atoms into the crystal. The values of these quantities depend on the diffusion time and the diffusion temperature.

$$D = D_0 \cdot \exp\left(-\frac{Q}{kT}\right) \tag{4}$$

where *D* is the diffusion coefficient, D_0 is the value equal to the diffusion rate as the temperature approaches infinity, i.e. the diffusion constant (a constant that depends on the type of impurity and semiconductor), *k* is the Boltzmann constant, *T* is the diffusion temperature, *Q* is the activation energy required for the impurity atom to transition from one stationary state to another in the semiconductor crystal lattice (the value of *Q* varies over a wide range depending on the physical parameters of the impurity atom and the semiconductor material).

The solution of equation (3) gives the equation for the distribution of the impurity atom concentration in the crystal for diffusion from an infinite source:

$$N(x,t) = C_s \cdot erfc\left(\frac{x}{2 \cdot \sqrt{D \cdot t}}\right) \tag{5}$$

The concentration distribution of impurity atoms within a crystal during diffusion from a limited source is determined by the following equation (6):

$$N\left(x,t\right) = \frac{C_s}{\sqrt{\pi \cdot D \cdot t}} \cdot \exp\left(-\frac{x^2}{4 \cdot D \cdot t}\right) \tag{6}$$

where *t* is the diffusion time, *x* is the depth of penetration of the impurity atoms into the semiconductor material, and *D* is the diffusion coefficient at a given temperature [34].

The diffusion of impurity atoms in a crystal depends on many parameters, in addition to temperature, such as the material composition, the position of the Fermi level, or the concentration of point defects. To understand these relationships, it is necessary to look at the diffusion mechanisms microscopically. Although a combination of these diffusion pathways usually occurs in practice, we will consider some of the important mechanisms separately. Often, the dominant mechanism provides a reasonable description of the diffusion process, at least in some limited temperature range [35].

It is known that real crystals contain several types of defects.

There are 5 mechanisms for the movement of atoms in a crystal lattice:

- exchange mechanism—atoms located at lattice sites exchange their positions (for an ideal crystal);
- vacancy mechanism—one of the atoms located at the lattice sites moves to the site (vacancy) that has lost its atom;
- inter-site mechanism—an atom located at a site between the sites jumps to the site between the sites;
- incorrect inter-site mechanism—an atom located at a site between the sites knocks out an atom located at a site next to it and takes its place (at the site);
- inter-site exchange mechanism—an atom located at a site between the sites moves between the sites of the crystal lattice and in case 1 it occupies a vacancy in the site; in case 2 it knocks out another atom in the site and takes its place.

The formation of clusters with Mn dopants in Si crystals has been reported in several studies by the authors [36-41]. It was found that clusters of dopants formed in Si crystals improved the electrophysical, photoelectric, thermoelectric, and magnetic properties of silicon to some extent, and devices such as thermal sensors, magnetic sensors, and IR sensors were prepared and applied in practice from samples containing clusters.

The combination of silicon and III-V binary semiconductors on a Si substrate is of great interest due to the prospects for their application in various devices. For example, we can cite monolithic optoelectronic devices with Si-based control circuits or multi-cascade solar cells with an active Si layer.

In particular, due to the structures based on GaSb and Si, the small band gap energy of the GaSb binary compound semiconductor ($E_{g,GaSb}$=0.72 eV, $E_{g,Si}$=1.12 eV, at T=300 K), the large mobility of electrons and holes compared to silicon (μ_n=3000, μ_p=1000 cm^2/(V s) for GaSb; μ_n=1500, μ_p=500 cm^2/(V s) for Si), and the fact that GaSb is a semiconductor with a linear transition structure, while Si is a semiconductor with a nonlinear transition structure, the interest in the integration of Si and GaSb semiconductors is very high.

EXPERIMENTAL RESEARCH

For the experiment, a silicon wafer grown by the Chochral method, with a resistivity of ρ~0.5 Ω·cm, doped with boron dopants (n_p=5×10^{16} cm^{-3}), was selected. As is known, the requirements for the samples in studying the photoelectric properties of the samples are that the samples should have a p-n structure and the thickness of the samples should be uniform. Therefore, in order to create a *p-n* junction in the samples, Ga and Sb atoms were diffused. The diffusion process was carried out in two stages and the samples were divided into two groups.

Group 1 samples: in the first stage, the *p*-Si sample was heated at 1200 °C for 0.5 hours; in the second stage, Sb impurity atoms were diffused from the gas phase into this sample at 1200 °C for 0.5 hours;

Group 2 samples: in the first stage, Ga impurity atoms were diffused into the *p*-Si sample at 1200 °C for 0.5 hours; in the second stage, Sb impurity atoms were diffused from the gas phase into this sample at 1200 °C for 0.5 hours.

It is known that Ga dopants form an acceptor surface in silicon, and Sb dopants form a donor surface. In order to form a *p-n* junction in a silicon sample, Ga dopants were first diffused, and then Sb dopants. Since the diffusion process is carried out from the gas phase, dopants diffuse into the sample from all sides. After diffusion, ~100 µm was removed from one side and the sides of the sample surface (Fig. 1). Then, the thicknesses of both groups of samples were taken to be uniform w≈400 µm.

It is known that the bandgap energies of the GaSb binary compound and Si semiconductors are $E_{g,GaSb}$=0.726 eV and $E_{g,Si}$=1.12 eV, respectively. A silicon sample generates a photocurrent when the condition $h\nu \geq E_{g,Si}$ is met. That is, in cases where $h\nu < E_{g,Si}$, it does not perceive or transmits energies in the infrared region of the light beam. For this purpose, measurements were made by illuminating the sample with light on the side where the dopant atoms were not introduced.

a) *b*)

FIGURE 1. Principal schematic view of the samples after doping Ga and Sb impurity atoms into Si (*a*) Group I sample; (*b*) Group II sample.

After that, samples with p-n junctions were examined on an IKS-12 spectrophotometer to study their photoelectric properties (Figure 2).

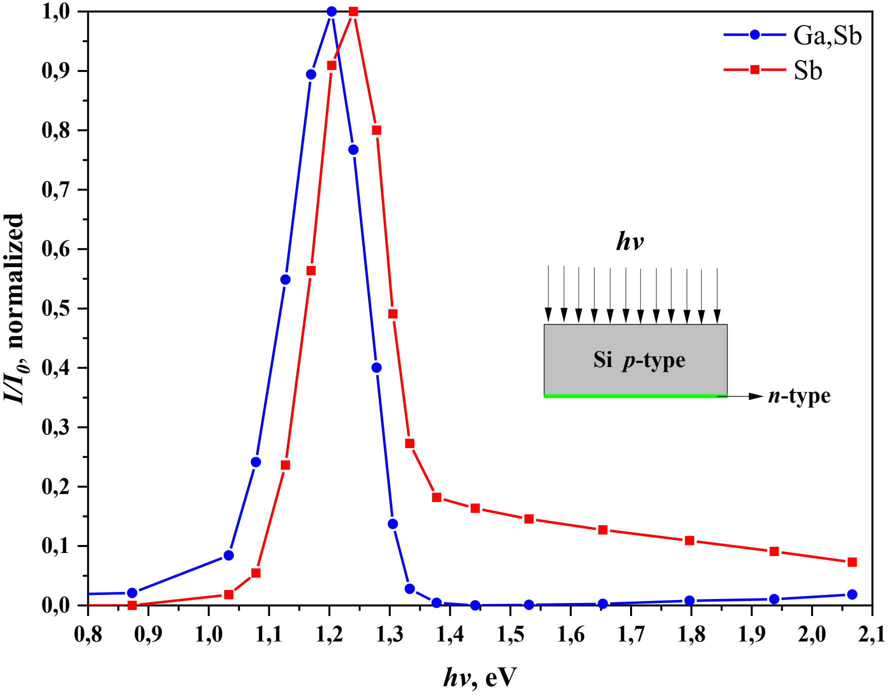

FIGURE 2. Graph of the dependence of the short-circuit current in the sample on the light energy.

CONCLUSIONS

In this case, the samples of groups 1 and 2 were additionally heated at a temperature of T=600 °C after diffusion, and the photoelectric properties of the samples after additional heating are studied in the graph in Figure 2. As can be seen from the graph in Figure 2, the photoelectric sensitivity of the sample of group 1 started from 1.0 eV and reached its maximum value at a photon energy of 1.24 eV. The photoelectric sensitivity of the sample of group 2 started from 0.87 eV and reached its maximum value at an energy of 1.2 eV. From this, it can be concluded that when the samples of group 2 were additionally heated at a temperature of 600 °C, the photoelectric sensitivity of silicon shifted towards the infrared region as a result of the mutual bonding of Ga and Sb impurity atoms.

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