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A SURFACE STUDY OF Si DOPED SIMULTANEOUSLY WITH Ga AND Sb†

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The paper is concerned with the study of silicon samples doped with gallium (Ga) and antimony (Sb) atoms. In particular, the elemental analysis, SEM imaging, and Raman spectrometry analysis of the samples are presented. The elemental analysis revealed that the relative concentrations of Ga (0.4) were almost equal to those of Sb (0.39) and both were formed on the surface of Si. The SEM imaging showed that GaSb microsized islands (diameter of 1 to 15 microns) and a density of ~10^6 cm^{-2} were being formed on the surface of Si in the course of the process of diffusion doping. Raman spectral analysis showed that a semiconductor with GaSb molecules self-assemble on Si surface.
Keywords: *Silicon; Gallium; Antimony; Doped; Diffusion; Microsized islands*
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INTRODUCTION

Presently, because of such fundamental parameters as high mobility, direct band-band transitions, relatively narrow band gap, the future of *III-Sb* type binary composite semiconductors seems to be promising in the years ahead [1-3]. In electronics and optoelectronics, of greater interest is the possibility to process new materials that are relatively inexpensive in terms of manufacture, and key physical parameters of which are in stark contrast to those of existing semiconductor materials [4–5]. As [6–7] evidenced, thin layers of *GaSb* on various substrates were obtained by using the modern method of molecular beam epitaxy (MBE), and their properties were studied using Raman spectroscopy [8]. The possibility of manufacturing high-frequency electronic devices [9-10] and the possibility of obtaining infrared sensors were shown in [11-13].

Meanwhile, the implementation of such complex technological processes requires the availability of modern and very expensive MBE devices [14]. The diffusion technology we are proposing herewith is comparatively cheap, optimally developed and mastered by our specialists in laboratory conditions. In the present experiment, the silicon (Si) samples diffusional doped with gallium (Ga) and antimony (Sb) atoms, were studied on SEM imaging (SEM EVO MA) and by Raman spectral analysis (Senterra II brand), all studies having been performed at room temperature (T =300 °K).

The lattice constants of silicon (Si) and gallium antimonide (GaSb) are 5.34 Å and 6.1 Å, respectively, and their lattice constant's mismatche accounts ~12%.

MATERIALS AND METHODS

Single-crystal *n*-type silicon samples ($\rho = 1\Omega\cdot cm$, $n\sim5\cdot10^{15}$ cm^{-3}) grown by the Czochralski method were chosen as objects for the study. Before launching the diffusion process, surfaces of the samples were kept in hydrofluoric acid (HF) for 1–2 min and degreased in the standard way. The diffusion process was carried out in a vacuum tube furnace for Laboratory Material Burning type *AOT-GLS-1750X*. The diffusion process was launched starting from room temperature T=30°C to temperature T=1200°C and continued for t=5 hours at this temperature in the gas-phase medium of impurity atoms. After diffusion, the samples were divided into two groups: the First Group (I): GaSb:Si; The Second Group (II): reference Si samples.

Group I - Ga and Sb atoms were doped into silicon samples simultaneously (Si sample, Ga and Sb impurities were all placed into one quartz ampoule).

Group II – reference Si samples without impurities were heated for comparative analysis under the same thermodynamic conditions.

RESULTS AND DISCUSSION

SEM- and EDS analysis

As can be seen from Fig. 1a, white spots of somewhat irregular shape must have formed on the surface of the sample (group I), while there are no such spots on the surface of the sample (group II) (see Fig. 1b). On Fig. 1 the analyzes of elemental compositions of 3 spectra (spectra 11, 12 and 13) are shown. Regarding the 11^{th} spectrum – the elemental analysis was obtained for the area outlined by white circumference transparent on Figure 1-a (Figure 1-c). The elements Si, Ga, Sb, O, and C were determined in the 11th spectrum and their conditional concentrations were calculated as 0.9, 0.08, 0.04, 0.03, and 0.02, respectively. The elemental composition of the spot where white islands are

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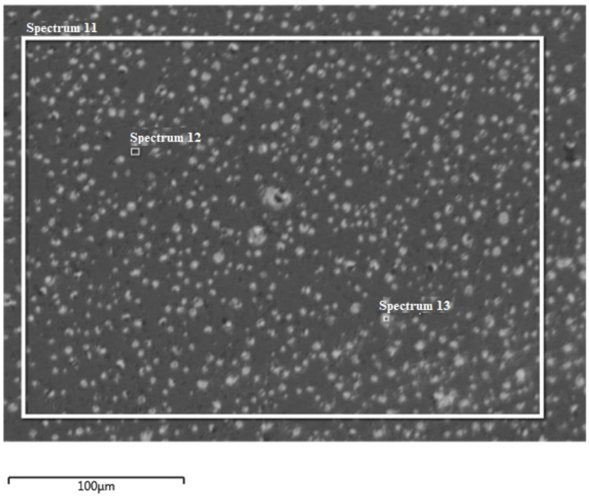
not being formed are represented on 12th-spectrum of Figure 1-a (Figure 2-a). In 12th spectrum, only the element Si was found, its conditional concentration was calculated as 1.16. The elemental composition of one of the white islands in the 13th spectrum (in Fig. 1-a) was determined (Fig. 2-b). The elements Si, Ga, Sb and O were identified on spectrum 13 and their conditional concentrations were calculated as 0.02, 0.4, 0.39 and 0.06 respectively.

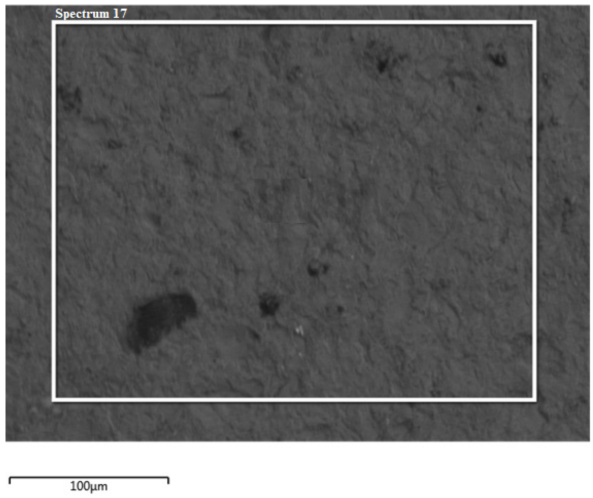
The elemental composition of the area circled by the white line on the surface of the sample of group II was determined (see Fig. 1b) (spectrum 17 in Fig. 1d). The elements Si, O and C were identified in spectrum 17 and their conditional concentrations were calculated as 0.97, 0.16 and 0.01 respectively.

Group I

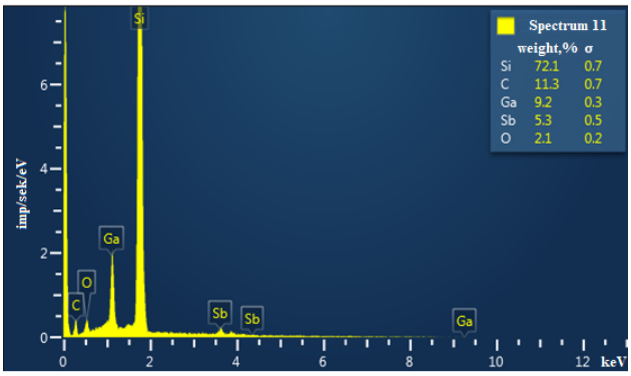


a)

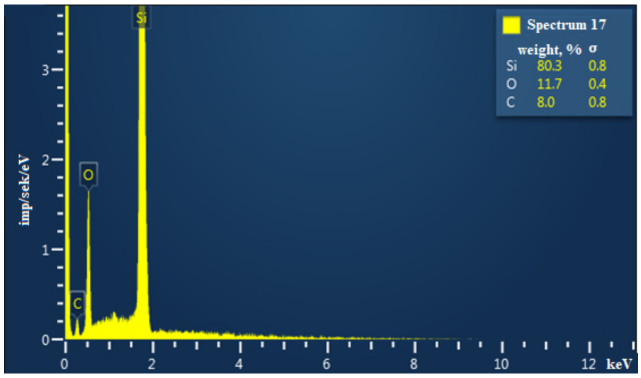
Group II



b)

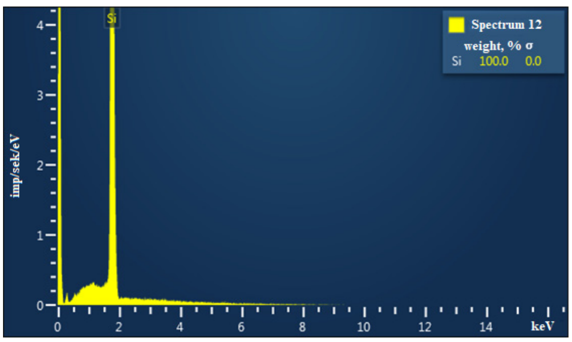


c)

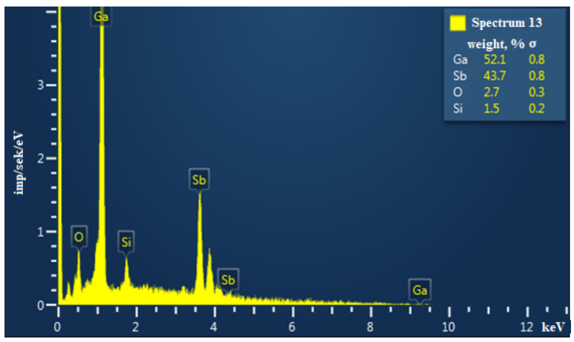


d)

Figure 1. SEM analysis of investigated samples after diffusion; a) SEM imaging of the surface of the I-group sample; b) SEM imaging of the surface of a sample of group II; c) elemental analysis of the surface of a sample of group I; d) elemental analysis of the surface of a sample of group II



a)



b)

Figure 2. Elemental analysis obtained at local spots on the surface of a group I sample; a) elemental analysis of spectrum 12 in Fig. 1-a); b) Elemental analysis of spectrum 13 in Fig. 1a)

The islands formed on the surface of a I-group sample contain the elements Ga, Sb, O, and Si, which is due to the fact that the conditional concentrations of the elements of Ga and Sb in the islands (0.4 and 0.39, respectively) are almost the same and significantly exceed the conditional concentrations of elements O and Si. These islands could be regarded as composite *GaSb* semiconductor islands. It can be assumed that O and Si elements found in the formed GaSb islands must have diffused from adjacent genuine Si material into the alien GaSb island (Fig. 2b, Table 1). In addition, it was revealed that the resulting GaSb semiconductor islands serve as attractors for O atoms on the Si surface (Table 1: spectra 11, 12, 13).

Table 1. Results of elemental analysis of samples of groups I and II

Element	Line type	Conditional concentration	Weight.%	Sigma Weight. %
		11-spectr		
C	K series	0.02	11.34	0.69
O	K series	0.03	2.12	0.24
Si	K series	0.90	72.12	0.74
Ga	L series	0.08	9.16	0.29
Sb	L series	0.04	5.26	0.50
Sum:			100.00	
		12-spectr		
Si	K series	1.16	100.00	0.00
Sum:			100.00	
		13-spectr		
O	K series	0.06	2.67	0.26
Si	K series	0.02	1.48	0.19
Ga	L series	0.40	52.14	0.82
Sb	L series	0.39	43.72	0.85
Sum:			100.00	
		17-spectr		
C	K series	0.01	7.97	0.79
O	K series	0.16	11.71	0.39
Si	K series	0.97	80.32	0.78
Sum:			**100.00**	

Figure 3 shows the SEM image of the surface of a sample from group I. The Figure shows that islands of GaSb semiconductor compound with a diameter of 1 µm to 15 µm are formed on the Si surface. The density of these microscopic islands, calculated judging from Fig. 3 is approximately 10^6 $см^{-2}$.

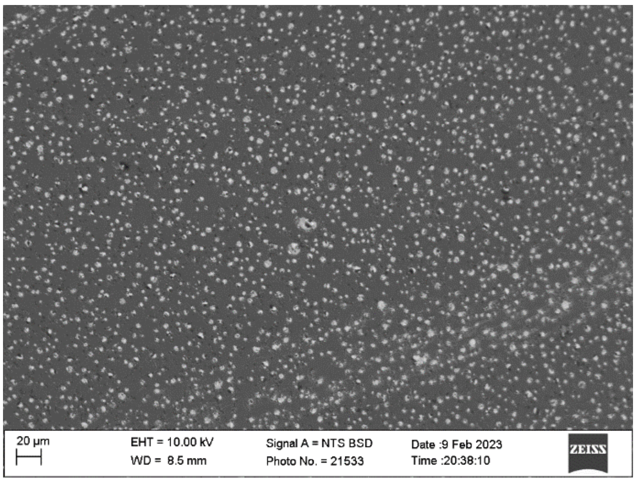


Figure 3. SEM imaging results of the surface of a sample of group I

Raman spectrometry

Raman spectroscopy is the standard method for studying lattice vibrations and their interaction with other induced oscillations. In Raman spectroscopy, only samples of group I were studied, i.e., Si samples doped with Ga and Sb atoms by the diffusion method (Fig. 4). It is known from the literature that the 520 cm^{-1} mode in the vibrational spectrum corresponds to the Si-Si bond [15], whereas 226 cm^{-1} and 220 cm^{-1} modes correspond to the Ga-Sb compounds, respectively, in the LO and TO modes [16].

On Fig. 4-a) one can see that the fundamental mode was observed at 519 cm^{-1}, which is confirmed by the literature [15] and corresponds to the vibration frequency of a Si-Si-type bond. As can be seen from Fig. 4b), the main peak was observed at vibration frequency of 224.5 cm^{-1}, which is confirmed by the literature data [16], that this peak belongs to the vibration frequency of LO mode of the Ga-Sb compound.

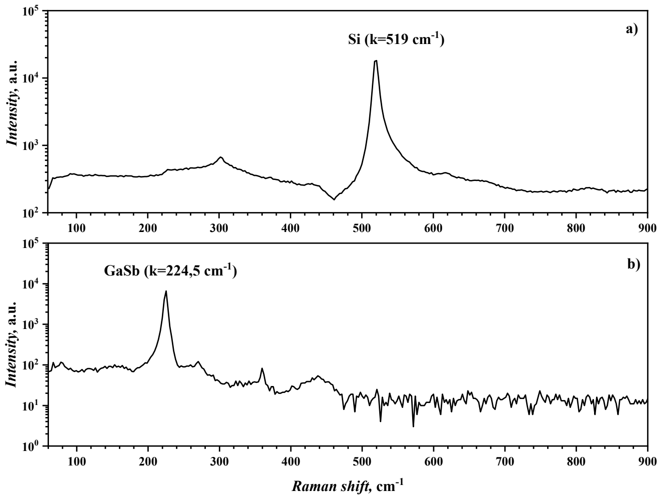


Figure 4. Spectral analysis of Raman spectra of the surface of samples of group I; a) spectral analysis of the Raman spectrum 12 in Figs. 1-a); b) Spectral analysis of Raman spectrum 13 in Figure 1a).

CONCLUSION

That the GaSb-type composite semiconductor probably forms on the surface of a Si sample doped with Ga and Sb atoms by diffusion doping, was confirmed by elemental analysis, SEM imaging, and Raman spectral analysis. The results of the experiment showed the possibility of engineering a novel crystal containing GaSb on the Si surface using a comparatively cheap and conventional diffusion technology. The obtained experimental results show that Si containing GaSb islands can be used as the main material in the development of infrared detectors, infrared lasers, infrared LEDs, high-speed electronic devices (for example: transistors) and high-efficiency solar panels.

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ДОСЛІДЖЕННЯ ПОВЕРХНІ Si, ЛЕГОВАНОГО ОДНОЧАСНО Ga ТА Sb

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Стаття присвячена дослідженню зразків кремнію, легованих атомами галію (Ga) і сурми (Sb). Зокрема, представлено елементний аналіз, SEM зображення та спектрометричний аналіз зразків за допомогою комбінаційного розсіювання. Елементний аналіз показав, що відносні концентрації Ga (0,4) майже дорівнюють концентраціям Sb (0,39), і обидва утворилися на поверхні Si. SEM-зображення показало, що в процесі дифузійного легування на поверхні кремнію утворюються острівці мікророзміру GaSb (діаметром від 1 до 15 мікрон) і щільністю ~106 см$^{-2}$. Раманівський спектральний аналіз показав, що напівпровідник із молекулами GaSb самозбирається на поверхні Si.

Ключові слова: *кремній; галій; сурма; легування; дифузія; острови мікророзміру*