Solid Phase Epitaxy Formation of Silicon-GaSb Based Heterostructures

Dmitry L. Goroshko¹,², Evgeniy A. Chusovitin¹, Igor M. Chernev¹, Alexander V. Shevlyagin¹, Konstantin N. Galkin¹, and Nikolay G. Galkin¹,²

¹Institute of Automation and Control Processes FEB RAS, 5 Radio St., 690041 Vladivostok, Russia
²Far Eastern Federal University, 8 Sukhanova St., 690950 Vladivostok, Russia

E-mail: goroshko@iacp.dvo.ru

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A double-layer heterostructure with embedded single-crystalline silicon matrix nanocrystallites of gallium antimonide was grown. GaSb was formed by solid phase epitaxy method using Ga-Sb stoichiometric mixture of 2-nm-thick and a stepped annealing from 200 to 500 °C. The obtained nanocrystallites have a concentration of $7.1 \times 10^{10}$ cm$^{-2}$, a height of 4.6 nm and lateral dimensions of 16–20 nm. The GaSb nanocrystallites were covered with silicon layer using molecular beam epitaxy in two stage: 40-nm-thick at 300 °C followed by 60-nm-thick at 500 °C.

1. Introduction

High current level of development of silicon complementary metal-oxide-semiconductor technology, from one hand, and the promising physical properties of GaSb as a direct-gap semiconductor with high carrier mobility, on the other hand, will implement an integrated logical device along with discrete emitting and detecting devices operating in the spectral range corresponding to the transparency window of quartz fiber, which is currently still not realized within the silicon technology.

However, it is known that GaSb and Si have a large lattices mismatch, which leads to the formation of defects during epitaxial growth (microtwinning and misfit dislocations) [1,2]. In addition, according to the molecular beam epitaxy (MBE) results GaSb islands formed on Si have a low concentration of about $10^8$ cm$^{-2}$ due to high diffusivity of Ga atoms on the silicon surface [3]. Another disadvantage of MBE is connected with high desorption rate of Sb during growth process; to overcome the problem a deposition usually performed under supersaturated Sb flux condition with Sb/Ga ratio up to 5 [4]. In this case, after silicon overgrowth excess Sb atoms dope Si matrix resulting in type II band alignment of Si-GaSb heterojunction since usually GaSb has $p$-type conductivity, which results in very low efficiency of radiative recombination [5].

In this work we propose solid phase epitaxy (SPE) method for GaSb formation on Si(001) in the form of nanocrystallites (NCs) elastically embedded into the silicon matrix. Such approach allows to use Ga-Sb mixture with stoichiometric ratio 1:1 and eliminate harmful Sb doping of silicon which provides favorable type I band alignment.

2. Experiment

Substrates for all the samples were cut from silicon wafers with (001) surface orientation. Silicon, gallium and antimony were deposited from sublimation sources heated by a direct current. All the growth procedures were carried out in ultra-high vacuum (UHV) chamber with base pressure $2 \times 10^{-11}$ Torr equipped with a quartz microbalance, Auger electronic spectroscopy (AES) along with
electron energy loss spectroscopy (EELS) and low-energy electron diffraction (LEED) facilities.

The substrates were prepared using following procedure: after cleaning in chemical solvents, a degassing under UHV condition for 6–8 hours at a temperature of 600–700 °C was performed, and then, just before the growth procedure, a native oxide was removed by several high-temperature flashes \( (T_{\text{sub}} \approx 1160 \, ^\circ \text{C}, \, t = 30 \, \text{s}) \). According to AES the residual contaminations were below detection limit; LEED pattern show sharp two-domain 2×1 structure.

GaSb was formed by solid-phase epitaxy including room-temperature co-deposition of Ga and Sb in 1:1 ratio followed by annealing of the mixture at a temperature of 200–500 °C for 10–20 minutes. Gallium (99.999 %) and antimony (99.999 %) deposition rates were about 0.4 nm/min. The rates were calibrated using well known LEED pattern \[6\] and checked using atomic-force microscopy (AFM) measurement of effective thickness of the Ga or Sb islands deposited on clean silicon substrate. The thickness of a deposited mixture was varied from 2 to 23 nm for NCs and films formation, respectively. To embed NCs into the silicon matrix, 100 nm \( p^+ \)-Si \( (0.002 \, \Omega \times \text{cm}) \) layer was formed over NCs at a temperature of 300–500 °C. Silicon deposition rate was 1–2 nm/min and was calibrated using quartz microbalance.

### 3. Results and discussion

Usually, GaSb is grown by co-deposition on a heated silicon substrate. Such a method is likely to apply by analogy to homoepitaxial growth of GaSb \[7\]. In the case of homoepitaxy, supersaturation of Ga-Sb molecular beam with antimony is required due to high desorption coefficient of antimony at a growth temperature: at a GaSb substrate temperature over 200 °C only 1 monolayer (ML) of Sb is remained even if about 3–5 nm was deposited \[8\].

<table>
<thead>
<tr>
<th>Sample</th>
<th>GaSb mixture thickness, nm</th>
<th>SPE temper./time, °C/min</th>
<th>GaSb nanocrystallites on Si surface</th>
<th>Capping silicon layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>concentration, ( \times 10^{10} ) cm(^{-2} )</td>
<td>height, nm</td>
</tr>
<tr>
<td>X*</td>
<td>23</td>
<td>500/20</td>
<td>0.17</td>
<td>30</td>
</tr>
<tr>
<td>A</td>
<td>16</td>
<td>200-500/15</td>
<td>4.3</td>
<td>21</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>200-500/15</td>
<td>4.4</td>
<td>12.7</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
<td>200-500/15 + 600/20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>4</td>
<td>200, 350/15 500/90</td>
<td>2.3</td>
<td>17.6</td>
</tr>
<tr>
<td>E</td>
<td>4</td>
<td>200-500/15</td>
<td>2.5</td>
<td>17.5</td>
</tr>
<tr>
<td>F</td>
<td>4</td>
<td>200-500/15</td>
<td>4.6</td>
<td>10.1</td>
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<tr>
<td>G</td>
<td>2</td>
<td>200-500/10</td>
<td>7.1</td>
<td>4.6</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
<td>200-500/10</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Concentration, height and lateral size for sample X are related to Ga islands

As far as we know, there are no published studies on the GaSb formation by SPE, so we started our study from the growth of a thick GaSb film. At this stage it was necessary to find out the fundamental possibility of the GaSb formation by SPE.
It is known that the melting point of the bulk GaSb is 712 °C [9], and common GaSb homoepitaxy temperature is about 500 °C [10]. However, in the case of SPE the annealing of Ga-Sb mixture at a temperature of 500 °C was not allowed to form GaSb compound (sample X, Table I). Only Ga islands were observed on the substrate surface (image not shown). At the same time, 1×1 LEED pattern was observed that corresponds to ~ 1 ML of Sb [11]. This result is obviously connected with the above-mentioned property of antimony – easily desorbed from the Si surface if Sb coverage is more than 1 ML. The remaining monolayer of Sb strongly binds to the surface and desorbs at a temperature above 800 °C [8]. At the same time, Sb binding energy to the substrate is higher than that of Ga [8,12], which prevents GaSb formation from Ga islands and Sb ad-atoms.

The solution of the issue has been found in stepped annealing of Ga-Sb mixture at a temperature ranging from 200 to 500 °C with 50 °C increments and at annealing time of 15 min on each step (sample A). In Auger spectra at all stages of the sample formation after the deposition of Ga-Sb mixture there are peaks of both elements (Fig. 1(a)). Silicon peak disappears after room-temperature deposition Ga-Sb: thickness 16 nm is more than enough to completely cover the substrate surface. However, at a temperature of 300 °C weak silicon peak appears again indicating that the film is disrupted. LEED 1×1 pattern observed at 500 °C confirms that the film is disrupted because up to this point it has been shown only the background.

![AES and EELS spectra](Fig. 1)

According to electron energy loss spectroscopy (Fig. 1(b)), gallium antimonide begins to form immediately after the deposition of the mixture on an unheated surface. This is confirmed by EELS peak dynamics: the peaks at an energy of 15.3 and 7.0 eV appear, while the silicon plasmons 17.1 and 10.7 eV disappear. The first of these peaks (14.2–16.3 eV) corresponds to the bulk plasmon in GaSb. Its position is determined by the stoichiometry of the compound, and probably in the ideal case, it should be located at the energy of 14.7–14.8 eV [13]. In our experiment, the peak of 15.3 eV is shifted to lower energies during sample annealing and holds the position of 14.7 eV at 300 °C. Peak at an energy of 7.0 eV is a surface plasmon due to transitions from filled surface states to dangling bonds [13]. Upon annealing, and thus improving the crystal quality and the stoichiometry of the GaSb, it begins to resolve into two peaks at a temperature of 350 °C, and at 500 °C the peaks occupy the position of 6.0 and 9.3 eV, both of them corresponds to an interband transition in GaSb and surface plasmon due to transitions from filled surface states to dangling bonds, respectively [13].
As expected, a rough surface is observed in the AFM image of the sample A (Fig. 2(a)). The nanocrystallites concentration is $4.3 \times 10^{10}$ cm$^{-2}$, their average height is 21 nm and lateral size is 43–59 nm. Effective thickness estimated from the image was 13.76 nm, which is close enough to the nominal thickness of deposited mixture (16 nm). The small thickness deviation can be attributed to an deviation of calibration of the deposition rates. In the far-infrared region (FIR) transmittance spectrum (Fig. 2(b)) two intense peaks at 225 and 612 cm$^{-1}$ were observed, which correspond to GaSb (optical transition $\text{LO} (\Gamma_3)$) and Si, respectively [14].

Thus, SPE method with stepped annealing allows to form stoichiometric gallium antimonide compound on the surface of monocrystalline silicon.

The next stage of our work was devoted to study the formation of GaSb nanocrystallites with the highest concentration and minimum dimensions. To do this, we have reduced the thickness of the deposited Ga-Sb mixture down to 4 nm, while remain the stepped annealing: 200, 350 and 500 °C consecutively for 15 minutes at each step (sample B, Table I). At each growth stage, surface element composition and structure were controlled by AES, EELS and LEED. The position of the peaks in the Auger and EELS spectra corresponded to that described above for the thick GaSb film on sample A; 1×1 spots on LEED pattern originated from the silicon substrate have appeared after annealing at 350 °C, which is explained by much less initial GaSb film thickness and its disruption at a lower temperature. AFM image of the sample B surface is presented in the Fig. 3(a). The nanocrystallites concentration on the sample surface is $4.4 \times 10^{10}$ cm$^{-2}$, their height and lateral size are 12.7 nm and 35–46 nm, respectively (table I). In the FIR spectrum of the sample (and all the subsequent) peak at 225 cm$^{-1}$ were not found due to the limit of the spectrometer sensitivity. However, based on AES and EELS data we can argue that the observed nanocrystallites consist of GaSb.

Due to the nanocrystallites will be covered with silicon layer grown by MBE at a high temperature, it was necessary to study temperature stability of the formed GaSb nanocrystallites. Normally to obtain high crystallinity homoepitaxial silicon layer on Si (001) substrate must be heated up to 750 °C. Considering that this value is higher than the melting point of GaSb, it was decided to decrease the growth temperature down to 600 °C and anneal the sample with as-grown GaSb nanocrystallites at this temperature for 20 min (sample C, Table I). As a result, in EELS spectrum the GaSb bulk plasmon disappeared, while silicon bulk plasmon appeared (not shown), and LEED pattern 8×4 was registered (Fig. 3(b), insert). According to AFM data, there were no GaSb nanocrystallites (Fig. 3(b)); instead, there were holes with a concentration of $3 \times 10^9$ cm$^{-2}$, among them quite large and deep one could be found with a protruding rim around the hole perimeter. Analysis of the results has showed that annealing at 600 °C decomposes GaSb nanocrystallites. After the
decomposition, some antimony remains on the surface and forms 8×4 surface reconstruction, which is usually formed at a temperature of 600 °C and Sb coverage from 0.4 to 0.8 ML [11]; excess of the antimony is desorbed. Free gallium, in turn, coalesced (this is indicated by a lower concentration of holes on the sample surface compared to the concentration of nanocrystallites on the previous sample B as well as the presence of large holes) and etched silicon surface. Details of such phenomena are published elsewhere [15]. Thus, decomposition of GaSb nanocrystallites begins at a temperature about 600 °C.

![AFM image of uncovered samples](image)

**Fig. 3.** AFM image of uncovered samples: (a) – sample B (4 nm Ga-Sb annealed at 200-500 °C for 15 min), (b) - sample C (the same as B plus additional annealing at 600 °C for 20 min); insert is a LEED pattern registered from the sample C. (c) - sample D (the same as B plus additional annealing at 500 °C for 90 min).

Given the fact that the 600 °C was too high for the silicon epitaxy over GaSb nanocrystallites, it was decided to stay at 500 °C and check how long time annealing at this temperature affect the GaSb NCs. To this end, sample D was formed, and just after GaSb nanocrystallites formation it was annealed at 500 °C for 90 minutes (Fig. 3(c)). From AFM data one can see that 500 °C annealing lead to some coalescence of NCs: they are arranged in a short chain with 6–8 segments. Moreover, the size of each segment is preserved, and the total concentration also is almost unchanged (Table I).

Based on GaSb nanocrystallites temperature stability data, an attempt to cover the NCs with silicon layer at a temperature of 500 °C was made (sample E). The procedure of NCs formation completely repeated sample B; AES, EELS and LEED data have confirmed the formation of GaSb nanocrystallites on the surface. After the NCs were covered with 100-nm-thick silicon layer at 500 °C,
it has been found that Auger and EELS spectra have remained unchanged. Analysis of the AFM images (Fig. 4 (a)) of the surface showed that there are nanocrystallites on the surface with concentration and size vary by no more than 10% of those observed at uncovered sample D (Table I). Thus, under these conditions during the formation of the silicon epitaxial layer the GaSb nanocrystallites "emerge" on the epitaxial layer surface with its thickness increasing. The phenomenon of "emerging" previously observed by us during silicon coverage layer growth over NCs of semiconducting iron and chromium disilicide [16]. A possible mechanism of this phenomenon is diffusive motion of an nanocrystallite with different lattice parameter compared to matrix. At sufficient temperature and a low silicon growth rate, due to a high energy at interface nanocrystallite/matrix, the nanocrystallite extruded as a bubble on a surface. To solve the issue one can reduce the silicon growth temperature or increase the silicon growth rate. For technical reasons, the second option is currently not available to us, so for the next sample we set silicon growth temperature to 300 °C.

![Figure 4](image.png)

**Fig. 4.** AFM image of GaSb samples with silicon capping layer. (a) – sample E: silicon overgrowth was performed at 500 °C. (b) - sample F: low temperature Si overgrowth (80 nm at 300 °C).

GaSb NCs, obtained by deposition of a 4-nm-thick Ga-Sb mixture and subsequent stepped annealing, were covered with 80-nm-thick silicon layer at a temperature of 300 °C (sample F). As a result, on the Auger spectrum of Sb and Ga peaks became comparable with the noise level, and characteristic peaks of pure silicon appeared on EELS spectrum. According to AFM data (Fig. 4(b)) there are some nanocrystallites on the surface, but their size and concentration are quite different from those observed on the sample D (table I). Thus, temperature decreasing down to 300 °C preserves GaSb under the Si capping layer. In this case, low substrate temperature results in formation of rough silicon surface with high concentration of silicon nanocrystallites. The natural development of the procedure was to increase the overgrowth temperature for epitaxy of the next silicon layers along with control to prevent the emerging of GaSb nanocrystallites at this stage. According to this issue, the next sample was grown, in which we reduced the thickness of the GaSb mixture down to 2 nm for reducing a size and increasing a concentration of NCs. Silicon overgrowth was performed in two stages: first, we repeated 40 nm Si layer at 300 °C like for sample F and finally rise the temperature up to 500 °C and grew another 60 nm of Si. As a result, according to EELS and AES there was no evidence of emerged GaSb nanocrystallites on the surface.

Figure 5(a) shows result of the formation of the second layer of nanocrystallites on the capping silicon grown over the first GaSb array (sample G, Table I). One can see that concentration of the NCs on the surface is about 7.1×10^10 cm^-2, their height is 4.6 nm and lateral size is 16–20 nm. Consequently, decreasing of the thickness of Ga-Sb mixture does improve characteristic of the NCs.
array and results in about 2 times higher concentration compared with sample B (Table I). In comparison with literature data [17] where GaSb nanocrystallites with a density of $10^{11}$ cm$^{-2}$ achieved on Ga/Si(111)-$\sqrt{3}\times\sqrt{3}$, we have obtained a slightly lower concentration of NCs without implementation of any surface modification.

The final sample $H$ in the current set is composed of two arrays of GaSb nanocrystallites embedded into silicon. The procedure was as follows: after the deposition of 2 nm of Ga-Sb mixture on the substrate at room temperature it was heated at 200, 270 and 500 $^\circ$C for 10 min at each temperature. Capping silicon layer was grown at two stages: 40 nm Si at 300 $^\circ$C followed by 60 nm at 500 $^\circ$C. The procedure described was repeated twice resulted in formation of sample with smooth surface (root-mean square deviation is 2.2 nm) without any emerged nanocrystallites on the surface (Fig. 5(b)). The epitaxial relation with a substrate is proved by 1×1 LEED pattern with moderate background (Fig. 5(b), insert). Such procedure could be repeated as many times as required for the formation of desired volume of active region of device.

![Fig. 5](image)

**Fig. 5.** (a) - AFM image of the sample $G$ with second array of GaSb NCs grown over capping layer silicon capping layer. (b) – sample $H$ with two embedded layers of GaSb nanocrystallites; insert is a 1×1 LEED pattern registered from this surface.

### 4. Conclusion

As a result of the systematic investigations of SPE process of GaSb nanocrystallites formation and following embedding into single-crystalline silicon, it was shown that such approach has advantages in comparison with common molecular beam epitaxy of GaSb. We managed to obtain high concentration of GaSb nanocrystallites without Sb soaking or implementation of the surface modification. Consequently, formation of the silicon capping layer takes place without Sb doping that should guarantee formation of type I band alignment heterostructure.

The peculiarity of such approach is implementation of stepped annealing of GaSb mixture at the temperatures from 200 to 500 $^\circ$C. Despite of Ga-Sb mixture thickness (2-16 nm) a formation of GaSb NCs with stoichiometric composition occurs at 300–350 $^\circ$C. Failing to perform low temperature annealing at the first stage and heating as-deposited mixture of Ga-Sb at 500 $^\circ$C results it re-evaporation of Sb. Correspondingly, GaSb nanocrystallites are subjected to decomposition and re-evaporation from Si(001) after annealing at 600 $^\circ$C.

Investigations of the silicon epitaxial growth over GaSb NCs revealed that the temperature of about 500 $^\circ$C gives rise to the full emersion of GaSb to the surface. Decreasing of the overgrowth temperature at the first stage of Si MBE down to 300 $^\circ$C allows to stabilize GaSb NCs at the interface; next rising temperature up to 500 $^\circ$C supports Si epitaxy and leads to formation of a smooth surface. Repetition of GaSb nanocrystallites formation followed by silicon overgrowth results in embedding
of two layers of GaSb nanocrystallites.

Possible directions for optimization of the structure would be: i) further decreasing of the Ga-Sb mixture for formation of higher density of NCs; ii) improving the crystalline quality by increasing the growth temperature at the second stage of Si overgrowth or prolonged recrystallization; iii) decreasing the thickness of capping layers for increasing volume density of NCs. Further experiments are required for clarification of these issues, in particular a transmission electron microscopy with high resolution.

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References