InAsSb on GaAs (001): influence of the arsenic molecules form on composition and crystalline properties of MBE layers

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Abstract. The influence of As molecular form on the composition and crystalline properties of InAs$_x$Sb$_{1-x}$ solid solutions with MBE has been experimentally investigated. A series of samples has been grown at different growth temperatures. The grown samples were studied with the HRXRD and TEM methods. The incorporation coefficient of As$_4$ and As$_2$ molecules were determined at different growth temperatures. It has been found that the incorporation coefficient of As$_4$ much more dependent on growth temperature compared to As$_2$. It has been found that at a low growth temperature a step-like increase of Sb fraction in an InAs$_x$Sb$_{1-x}$ film leads to a decrease of threading dislocations density in a layer with a smaller $x$.

1. Introduction
The InAs$_x$Sb$_{1-x}$ solid solutions get much attention because of a possibility of creating IR-sensitive optoelectron devices on their base with a wavelength to 12.4 µm [1-5]. However, there are a number of problems concerned with obtaining high-quality epitaxial InAs$_x$Sb$_{1-x}$ layers.

One of them is the absence of a substrate material for the whole range of InAs$_x$Sb$_{1-x}$ compositions [6]. This leads to a degradation of the grown structures quality caused by the introduction of defects conditioned by mismatch film and substrate lattice constants.

Moreover, the formation of layers with a specific composition in the group V sublattice is a nontrivial problem too. The composition of the solid solution depends on both the value of Sb and As molecule fluxes ($J_{Sb}$ and $J_{As}$) and their incorporation coefficient $S_{Sb}$ и $S_{As}$. Incorporation coefficient is understood as a ratio of the atoms built in a crystal to their number arrived with the corresponding molecular flux for a time unit per surface unit. According to the definition of incorporation coefficients, arsenic composition $x$ in a InAs$_x$Sb$_{1-x}$ solid solution is connected with the density of group V molecular fluxes by the ratio:

$$ x = \frac{1}{1 + \frac{J_{Sb}}{J_{As}} \times \frac{S_{Sb}}{S_{As}}} $$

Relation $J_{As}/J_{Sb}$ is easily set and controlled during MBE, whereas relation $S_{Sb}/S_{As}$ is a complex function of growth conditions. The ratio of incorporation coefficients depends on substrate temperature ($T_S$), value and ration of group III and V elements molecular fluxes, molecular form of
group V elements in a flux [7]. These parameters allow immediate control of the surface state and the growing $\text{A}^{\text{III}}\text{B}^{\text{V}}$ film properties. Therefore, studying their influence on the $S_{\text{Sb}}/S_{\text{As}}$ ratio at MBE of solid $\text{InAs}_x\text{Sb}_{1-x}$ solutions is of interest.

The purpose of this work is experimental investigation of the influence of As molecular form and growth temperature on the composition and crystalline properties of $\text{InAs}_x\text{Sb}_{1-x}$ solid solutions grown on GaAs (001) substrate with the MBE method.

2. Experimental methods
The work has been carried out on the handmade MBE-machine "Shtat"-type equipped by a valve-type As source with a cracking zone to obtain As$_2$ and As$_4$ fluxes. The In and Sb$_4$ fluxes were formed by crucible sources with shutters. The density of atom and molecular fluxes coming up to the surface was determined by the indications of vacuum controller Granville Phillips 307 whose sensor was placed onto the substrate position [8] during the measurement. Substrate temperature control was realized by the indications of the thermocouple placed in the heating element. The flux sensor and the thermocouple indications were calibrated using the phase diagrams of GaAs (001) [9] surfaces on the methods formulated in [10].

A series of samples was grown at 320°C, 330°C, 355°C and 370°C. Each sample consisted of two layers. The first layer was grown using the As$_2$ molecular flux. After the end of the first layer growth, the growth manipulator with the substrate was turned to the molecular fluxes measurement position. The cracking zone temperature of the arsenic source was decreased from 950°C to 400°C for As$_4$ flux generation. The second solid solution layer was grown using the As$_4$ molecular flux equivalent to the As$_2$ in the atomic expression.

The In flux was equal to $5.45 \times 10^{14}$ atom/cm$^2$·s, which corresponds to the growth rate of one monolayer per second. The fluxes of group V, in the atom expression, was $\sim 8.6 \times 10^{14}$ atom/cm$^2$·s for Sb$_4$, for As$_2$ and As$_4$ $\sim 1.0 \times 10^{15}$ atom/cm$^2$·s. The thickness of epitaxial layers was 500 nm when using the As$_2$ and 350 nm when using the As$_4$.

3. Investigation methods
The grown samples were investigated by HRXRD and TEM.

3.1. Investigated by HRXRD
The grown samples were investigated by HRXRD. Registration of the X-Ray rocking curves was made on a two-crystal diffractometer using the crystal Ge (004) monochromator for line Cu K$_{al}$. The data on the dependence of the composition of $\text{InAs}_x\text{Sb}_{1-x}$ solid solution on $T$, are presented in Figure 1.
Figure 1. The arsenic fraction in the InAs$_x$Sb$_{1-x}$ solid solution as a function of $T_s$. The data for the films grown with As$_2$ are designated with asterisks, the data for the films grown with As$_4$ are designated with a diamond.

The data of FWHM for X-Ray rocking curve (W), which are given in Table 1, were obtained depending on the InAs$_x$Sb$_{1-x}$ film growth temperature. Here $h_1$ and $h_2$ are the first and second film thicknesses, respectively, R – relaxation degree, %.

Table 1. HRXRD data.

| Sample | $T_s$ °C | $h_1$ nm (As$_2$) | $h_2$ nm (As$_4$) | W $h_1$ | W $h_2$ | R $h_1$% | R $h_2$% |
|--------|---------|-------------------|-------------------|---------|---------|----------|----------|
| st 1468 | 320     | 500               | 350               | 2486    | 1690    | 96.65    | 99.75    |
| st 1469 | 330     | 500               | 350               | 2313    | 1678    | 95       | 100      |
| st 1470 | 355     | 500               | 350               | 2237    | 1629    | 95       | 97       |
| st 1471 | 370     | 500               | 350               | 2486    | 1690    | 91       | 100      |

It follows from the data of Table 1 that, in case of using As$_2$, a decrease of InAs$_x$Sb$_{1-x}$ film relaxation degree is observed with an increase of growth temperature.

Assisted with expression 1, the values of $S_{Sb4}/S_{As2}$ and $S_{Sb4}/S_{As4}$ ratios were calculated for arsenic and antimony molecules. The data about the composition of solid solution layers obtained with the HRXRD method and the $J_{As2}$, $J_{As4}$ and $J_{Sb4}$ values measured during the samples growth (see black squares in Figure 2 and Figure 3) were used for the calculation. The linear approximation of experimental data was carried out for dependence of the As fraction in the solid solution on the growth temperature (see Figure 1). This procedure allowed building the model dependences of $S_{Sb4}/S_{As2}$ and $S_{Sb4}/S_{As4}$ ratios on $T_s$.

The Figure 2 and 3 show that both $S_{Sb4}/S_{As2}$ and $S_{Sb4}/S_{As4}$ values decrease with increasing of $T_s$ in temperature range 320 – 370°C, but decreasing of $S_{Sb4}/S_{As4}$ about 5 times more. Such a difference in the behavior of these ratios is explained by the thing that As$_2$ molecules interact with a surface predominantly by the exchange mechanism, and As$_4$ molecules – by the vacancy mechanism [11].
Figure 2. $S_{Sb4}/S_{As2}$ as a function of $T_s$.

Figure 3. $S_{Sb4}/S_{As4}$ as a function of $T_s$.

The data of Figure 3 are in good qualitatively agreement with the results of Lee G S et al. [12]. It is important to note that although temperature ranges of our and G. S. Lee et al. investigations are analogous, the beam equivalent pressure ratios for group V elements $BEP(Sb_4)/BEP(As_4)$ is essentially different (from 0.08 to 0.38 – for ref. [12] and 0.72 – for our work).

3.2. Investigated by TEM

The structure of grown samples investigations were performed by a JEOL-4000EX electron microscope operated at 400 kV. The (110) cross sections for TEM studies were prepared in a standard manner by etching with argon ions. Bright-field / dark-field TEM and HRTEM were used.

It was found that a transition layer, that forms at the interface of InAs$_x$Sb$_{1-x}$ films with different compositions at low $T_s$, decrease the threading dislocations density to the 5-6 times (see Figure 4).
Figure 4. (a) – The (110) cross-sectional TEM image of the sample with two InAs\(_x\)Sb\(_{1-x}\) epilayers. The lower layer was grown with As\(_2\), top – with As\(_4\) (\(T_s = 320^\circ\text{C}\)); (b) – HRTEM image of the film/film interface; (c) – HRTEM image of the substrate/film interface. The arrays of misfit dislocations are shown on insets (derived by Fast Fourier Transform analysis of HRTEM images).

Such effect was not observed at high growth temperatures (see Figure 5).

Figure 5. The same as Figure 4, but for the case of \(T_s = 370^\circ\text{C}\).

4. Conclusion
It was clarified that, during InAs\(_x\)Sb\(_{1-x}\) MBE, the efficiency of As\(_2\) molecules incorporation, at other equal conditions, is considerably higher than that of As\(_4\) molecules. It was found that the As\(_4\) efficiency incorporation is more temperature sensitive compared to As\(_2\). It was found that a decrease of threading dislocations density occurs in the layer with a smaller \(x\) value at a low growth temperature in case of a step-like increase of the Sb fraction in a InAs\(_x\)Sb\(_{1-x}\) film. This phenomenon can be used in the creation of dislocation filters which will provide growing high-perfection InAs\(_x\)Sb\(_{1-x}\) solid solution layers on various A\(^{III}\)B\(^{V}\) semiconductor substrates.

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References
[1] Rogalski A 1989 Prog. Quant. Electr. 13 191
[2] Bethea C G, Yen M Y, Levine B F, Choi K K and Cho A Y 1987 Appl. Phys. Lett. 51 1431
[3] Dobbelaeere W, De Boeck J, Heremans P, Mertens R, Borghs G, Luyten W and Van Landuyt J 1992 Appl. Phys. Lett. 60 3256
[4] Besikci C, Ozer S, Van Hoof C, Zimmermann L, John J and Merken P 2001 Semicond. Sci. Tech. 16 992
[5] Gao Y Z, Gong X Y, Fang W Z, Wu G H and Feng Y B 2009 Japn. J. Appl. Phys. 48 080202
[6] Gao H, Wang W, Jiang Z, Liu L, Zhou J and Chen H 2007 J. Cryst. Growth. 308 406
[7] Semenov A N, Sorokin V S, Solovyev V A, Meltser B Ya and Ivanov S V 2004 Semiconductors 38 266
[8] Preobrazhenskii V V, Putyato M A, Pchelyakov O P and Semyagin B R 1999 J. Cryst. Growth. 201/202 170
[9] Preobrazhenskii V V, Putyato M A, Pchelyakov O P and Semyagin B R 1999 J. Cryst. Growth. 201/202 166
[10] Preobrazhenskii V V, Putyato M A and Semyagin B R 2002 Semiconductors 36 837
[11] Emelyanov E A, Feklin D F, Vasev A V, Putyato M A, Semyagin B R, Vasilenko A P, Pchelyakov O P and Preobrazhenskii V V 2011 Optoelectronics, Instrumentation and Data Processing (Avtometriya) 47 452.
[12] Lee G S, Lo Y, Lin Y F, Bedair S M and Laidig W D 1986 Appl. Phys. Lett. 47 1219