Semiconductors, 2024, Vol. 58, No. 10

Study of the incorporation of group V atoms into arsenide-phosphide solid solutions grown by vapor-phase epitaxy using $(CH_3)_3As$ as an arsenic source

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Received May 3, 2024
Revised July 2, 2024
Accepted October 30, 2024

In this paper, we consider the prospects of using trimethylarsine as an alternative source of arsenic atoms in metal-organic vapor-phase epitaxy of arsenide-phosphide solid solutions. Using $InAs_yP_{1-y}$ as an example, we show that when using trimethylarsine, the arsenic concentration in the solid phase is less affected by fluctuations in the growth parameters (composition of the gas mixture) than when using a standard arsenic source — arsine.

Keywords: MOVPE, trimethylarsine, TMAs, solid solutions, epitaxy.

DOI: 10.61011/SC.2024.10.59940.6592A

Efficiency of any energy source is its basic characteristic. It is known that efficiency of cascade photovoltaic converter directly depends on band gaps E_g of semiconductors comprising its sub-elements [1]. For the most efficient conversion of sun radiation spectrum E_g of one of sub-elements shall be ~ 1 eV [2]. To obtain such band gap the solid solution GaAsSbN grown on substrate GaAs can be used [3,4]. However, the technology of gas-phase epitaxial growth of nitride solid solutions is incompatible by hardware with the technology of semiconductor materials in arsenide and phosphorus systems. The alternative materials ensuring $E_g \sim 1$ eV include arsenide-phosphide solid solutions (GaInAsP, InAsP, AlInAsP, etc.). So, their growth is actual task for structures improvement of multi-junction solar cells. Moreover, these materials can be used to create photovoltaic converters of powerful laser radiation [5], e.g., at wavelength: 1064 nm (solid-state Nd:YAG-laser) and 1070 nm (ytterbium optical fiber laser).

One of the most modern, developed and industrially applicable methods of the epitaxial layers growth is metal-organic vapor-phase epitaxy (MOVPE) [6]. In MOVPE the metal-organic compounds are used as element sources of III group, and as sources of V group — hydrides subjected to pyrolytic decomposition in a reactor (typical growth temperatures 600−700°C) and adsorbed on substrate. Both ternary, and triple III−III−V phosphide and arsenide compounds are rather simply formed under conditions of excessive stream of atoms of V group in relation to atoms of III group in gaseous phase.

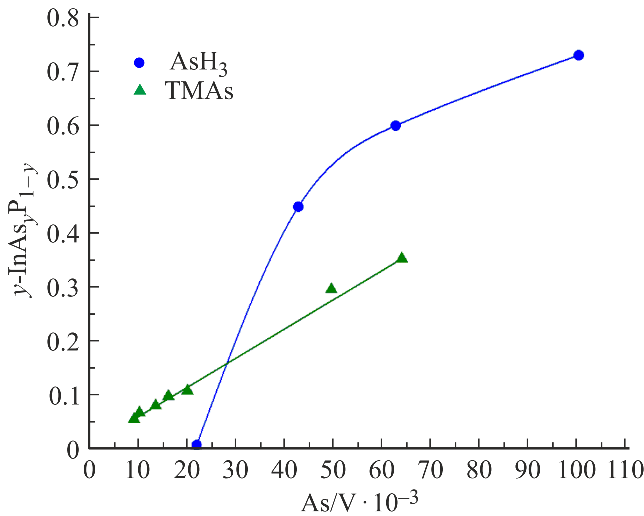
But in case of compounds of type III−V−V there is known problem — competition of atoms V group for places in anion sublattice [7], which is explained by difference in degree of pyrolytic decomposition of arsine (AsH_3) and phosphine (PH_3). If hybrid sources of V group are used the molar fractions of arsenic and phosphorus in solid phase highly depend on small changes of parameters of growth process (heterogeneity of temperature field of the reactor, fluctuation of gaseous phase composition etc.), this complicates growth of epitaxial layers of multicomponent semiconductor solutions with several elements of V group [8,9].

To solve this problem this paper recommends arsine, the hydride source of arsenic, by organic one — trimethylarsine ($(CH_3)_3As$). The idea of transition from technology of growth from arsine to alkylarsines (TMAs, TEAs etc.) was formulated previously in papers [10,11]. High toxicity of hydrides, necessity to store them at high pressures (this is associated with leak risk), and explosion danger are indicated as reason of such transition. In turn alkylarsines are less toxical [10], and are liquids easy for storage. In our paper we focus on the technological advantage of TMAs use, namely simplification of control of stoichiometric composition of solid phase during epitaxial growth.

Graph of arsenic content in solid phase $InAs_yP_{1-y}$ depending on fracture of arsenic-containing component in gaseous phase (ratio of mole stream of As-containing component to total mole stream of atoms of V group (As/V)), plotted as per experimental data, is presented in Figure.

To obtain this dependence two series of growth experiments were performed at temperature in the reactor 700°C. In one series the arsine was used as arsenic source, in another one — trimethylarsine. Samples InAsP/InP were grown at different ratios As/V. The photoluminescence spectra were measured, by them band gaps E_g of samples were determined. As dependence E_g in composition $InAs_yP_{1-y}$ is well known [12], this ensures unambiguous determination of stoichiometric coefficients of elements of V group in $InAs_yP_{1-y}$.

So, two functions are obtained: $f_{AsH_3}(As/V)$ and $f_{TMAs}(As/V)$, connecting arsenic content in gaseous and solid phases depending on selected source of arsenic atoms.



Graph of mole fraction of As in $InAs_yP_{1-y}$ depending on fraction of arsenic-containing component in gaseous mixture (dots — experimental data, solid lines — approximation).

At that change rate of these functions ϵ_j is

$$\epsilon_j(x) = \frac{df_j(x)}{dx},$$

where $x = As/V$, j — source of arsenic atoms.

Then, to change As content in solid phase Δf_j depending on composition fluctuation of gaseous mixture Δx relative to arbitrary point x_0 the following is true:

$$\Delta f_j = \int_{x_0-\Delta x}^{x_0+\Delta x} \epsilon_j(x)dx = 2c_j\Delta x,$$

where Δx — value of fluctuation, c_j — value meaning „average line" of function $\epsilon_j(x)$.

To compare changes in functions $f_{AsH_3}(x)$ and $f_{TMAs}(x)$ at same fluctuation Δx relative arbitrary point x_0 it is possible to introduce measure of sensitivity of solid phase composition as

$$\xi = \frac{\Delta f_{AsH_3}}{\Delta f_{TMAs}} = \frac{c_{AsH_3}}{c_{TMAs}}.$$

Value ξ shows by how times change in stoichiometry of V group in solid phase under effect of Δx during growth using AsH_3 is higher than when using TMAs.

Based on data shown in Figure the accessible for comparison region $f_{AsH_3}(x)$ and $f_{TMAs}(x)$ is in range $0.01 \le x \le 0.065$. At that we can conclude that in region $0.02 \le x \le 0.05$ of dependence $f_{AsH_3}(x)$ and $f_{TMAs}(x)$ are subjected to linear approximation and have coefficients: $c_{AsH_3} \approx 19.94$, $c_{TMAs} \approx 5.4$, from here it follows that $\Delta f_{AsH_3} \approx 3.7\Delta f_{TMAs}$. So, use of AsH_3 as source of arsenic atoms increase the sensitivity of epitaxial growth to composition fluctuations as compared to TMAs. In other words, small change in ratio As/V of gaseous mixture in case of AsH_3 results in significant change in arsenic content in $InAs_yP_{1-y}$, and gaseous mixture with TMAs at same change of As/V gives lower by 3.7 times change in composition $InAs_yP_{1-y}$.

From this we can conclude that the use of TMAs as source of As atoms allows improvement of the reproducibility of the growth process, reducing the influence of uncontrolled fluctuations of growth parameters, which entail change in the ratio As/V in the reactor, which ensures possibility of accurate control of stoichiometric composition of solid phase.

The transition from arsine to trimethylarsine, in addition to the advantages described above, will entail increase in the concentration of carbon impurity [10] in the epitaxial layers, which is a common feature during MOVPE. Based on results of papers [13,14] we can suppose that carbon will act as fine acceptor impurity. At that in case of epitaxy from sources of V group of high pure, if conditions $V/III \gg 1$ and As/$V \ll 1$ are met we can expect, that level of impurity with carbon will be $\sim 10^{15}\,cm^{-3}$ [15]. Hence, the necessity of semiconductor overcorrection to obtain of n-type of conductivity will lead to increase in concentration of defects, which will decrease mobility of charge carriers. So, if the manufactured device is not subjected to requirement of high response, which depends on mobility of charge carriers, then use of TMAs instead of AsH_3 can be effective technological solution.

Funding

This study was supported by the Russian Science Foundation, grant No. 22-19-00158, https://rscf.ru/project/22-19-00158/

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov