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2016 IOP Conf. Ser.: Mater. Sci. Eng. 128 012021

(http://iopscience.iop.org/1757-899X/128/1/012021)

IOP Conf. Series: Materials Science and Engineering **128** (2016) 012021 doi:10.1088/1757-899X/128/1/012021

Growth mechanism of GaAs1-xSbx ternary alloy thin film on MOCVD reactor using TMGa, TDMAAs and TDMASb

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Abstract. . Metal Organic Chemical Vapor Deposition (MOCVD) is a method for growing a solid material (in the form of thin films, especially for semiconductor materials) using vapor phase metal organic sources. Studies on the growth mechanism of GaAs1-xSbx ternary alloy thin solid film in the range of miscibility-gap using metal organic sources trimethylgallium (TMGa), trisdimethylaminoarsenic (TDMAAs), and trisdimethylaminoantimony (TDMASb) on MOCVD reactor has been done to understand the physical and chemical processes involved. Knowledge of the processes that occur during alloy formation is very important to determine the couple of growth condition and growth parameters are appropriate for yield high quality GaAs1-xSbx alloy. The mechanism has been studied include decomposition of metal organic sources and chemical reactions that may occur, the incorporation of the alloy elements forming and the contaminants element that are formed in the gown thin film. In this paper presented the results of experimental data on the growth of GaAs1-xSbx alloy using Vertical-MOCVD reactor to demonstrate its potential in growing GaAs1-xSbx alloy in the range of its miscibility gap.

1. Introduction

Recently the ternary alloy GaAsSb has been studied intensively as the candidates for long-wavelength infrared laser diode. This material has a range of values of the energy gap (Eg) between 0.72 to 1.42 eV depends on the content of Sb elements. This energy gap range corresponding with wavelength range required in the optical fiber communication systems [1,2,3,4].

In growing GaAsSb epitaxial layers, there are several major challenges to obtain high-quality and high-performance epitaxially grown layers. One of all is the wide alloy composition range of the GaAsSb miscibility gap when mixing GaAs and GaSb. If two binary semiconductor materials that have large difference in lattice parameters, for example GaAs and GaSb, are mixed together to form an alloy, it is hard to avoid the phase separation of two binary materials below the critical temperature (Tc). Thermodynamics can be used to predict the occurrence of spinodal decomposition or phase separation. By using a straightforward regular-solution model can be calculated the excess-free energy curves as a function of Sb composition x at various temperatures for GaAs1-xSbx as shown in Figure 1 [5]. The large positive mixing enthalpy with a large difference in lattice constant can overwhelm the negative mixing entropy, resulting in mixing Gibb's free energy with an upward curve in the center of the composition region, below the critical temperature (in Figure 1, Tc is around 760ºC). This means that at equilibrium, the mixing composition within the upward curved region is not stable and the alloy decomposes into a mixture of two phases. Therefore, it is theoretically impossible to grow an alloy within the miscibility gap by any equilibrium growth technique e.g., liquid phase epitaxy (LPE), at temperatures below Tc. However, under certain conditions, the alloys in the miscibility gap can be successfully grown even at lower temperatures than Tc by non-equilibrium growth techniques such as MBE or MOCVD. In the MBE and MOCVD growth processes, there are two components of physical processes that occur they are thermodynamics and kinetics. The thermodynamic determine the driving force for overall process of the film growth, while the kinetics describe the rate at which various processes occur. Controlling the kinetic parameters can disturb the equilibrium thermodynamics, so that fluctuations in the composition due to the phase separation can occur at temperatures around Tc, consequently the composition of the mixture can be in a metastable state [6]. Therefore, with using both modern growth techniques it is possible to grow a ternary alloy GaAs1-xSbx in the range composition of its miscibility gap.

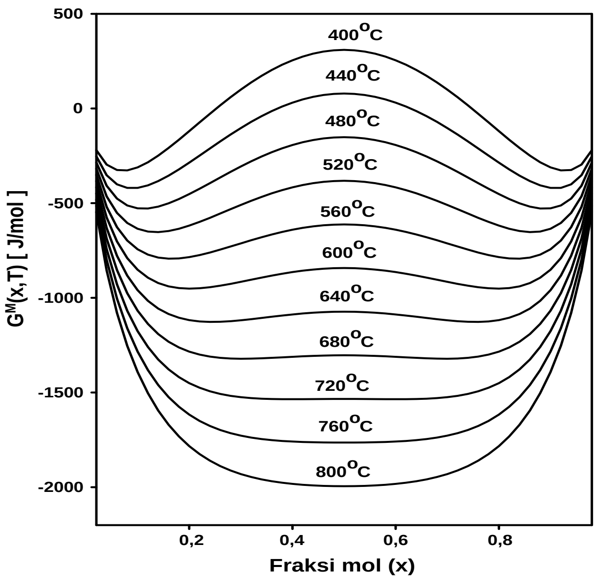

Figure 1. Calculated excess-free energy as a function of *x* at different temperatures for $GaAs_{1-x}Sb_x$.

This paper describes the results of a study on the mechanisms of physical and chemical in the growing process of ternary alloy GaAs1-xSbx by MOCVD technique using metalorganic sources TMGa, TDMAAs, and TDMASb, and the characterization of GaAs1-xSbx thin film grown by MOCVD technique.

2. Methods

To probe the feasibility of growing a $GaAs_{1-x}Sb_x$ thin film by MOCVD technique, a series of experiments about growth of GaAsSb thin films has been conducted. The MOCVD reactor system used in this experiment is vertical type-MOCVD reactor which available in Laboratory for Electronic Material Physics, Prodi Fisika FMIPA ITB. Semi-insulating GaAs crystal (100) was used as the

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substrate. Schematically, MOCVD reactor system that is used, is shown in Figure 2. The conditions and parameters of growth of $GaAs_{1-x}Sb_x$ films are shown in Table 1.

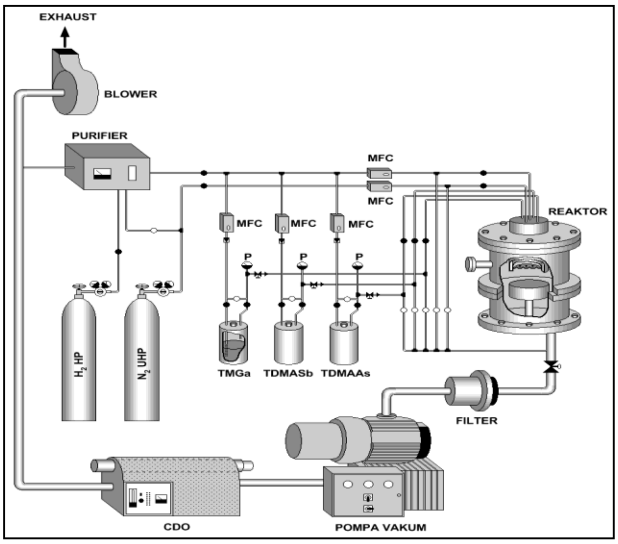

Figure 2. Schematic of Vertical Type MOCVD reactor

Table 1. The conditions and parameters for growing $GaAs_{1-x}Sb_x$ thin films

No	Parameter penumbuhan	Kondisi
1	Tekanan *chamber* reaktor	~ 50 Torr
2	Laju aliran gas Nitrogen pengencer	300 Sccm
3	Laju aliran gas Hidrogen pengencer	300 Sccm
4	Temperatur *bubbler* TMGa	-10°C
5	Tekanan *bubbler* TMGa	10 psi
6	Temperatur *bubbler* TDMAAs	24°C
7	Tekanan *bubbler* TDMAAs	0,5 bar
8	Temperatur *bubbler* TDMASb	26°C
9	Tekanan *bubbler* TDMASb	0,5 bar
10	Rasio V/III	1,2 – 4,8
11	Temperatur penumbuhan	520 – 600°C
12	Fraksi mol masukan uap sumber TDMASb (x_v)	0 - 1

Structural properties of the films were characterized by X-ray diffraction (XRD), the element composition of the films were examined using energy dispersive spectroscopy (EDS), and the electrical properties of the $GaAs_{1-x}Sb_x$ films were investigated using the room-temperature semi-automated Van der Pauw Hall-effect measurement to determine the type of semiconductors, carrier mobility, and carrier concentration.

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3. Results and Discussion

Figure 3 shows the X-ray diffraction pattern of a several $GaAs_{1-x}Sb_x$ films grown at growth temperature of about 580ºC and the V/III ratio of about 4.8 with the inputs composition of the Sb vapor source (xv) is varied. The orientation of the crystal plane were observed represented by (400) plane, because the whole grown films have a single crystal orientation.

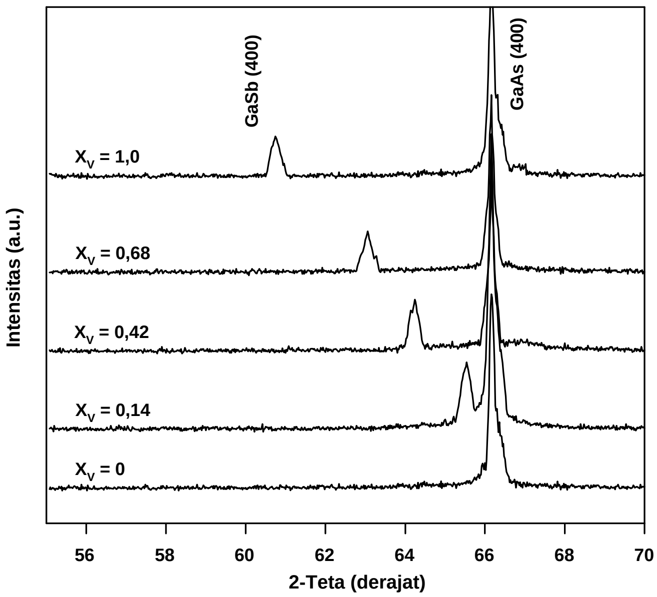

Figure 3. XRD pattern for (400) plane from several $GaAs_{1-x}Sb_x$ films samples growth at growth temperature of about 580ºC and V/III ratio of about 4,8 with varied x_v

It appears that a shift in the peak angle of the (400) plane towards smaller 2θ when the composition of the Sb vapor source inputs increase. This shift indicates changes in the value of the lattice constant of the material towards a greater, that is from the lattice constant of GaAs to the lattice constant of GaSb. According to the Vegard equation, a shift toward smaller diffraction angle indicating incorporation Sb atoms into binary GaAs form a ternary $GaAs_{1-x}Sb_x$.

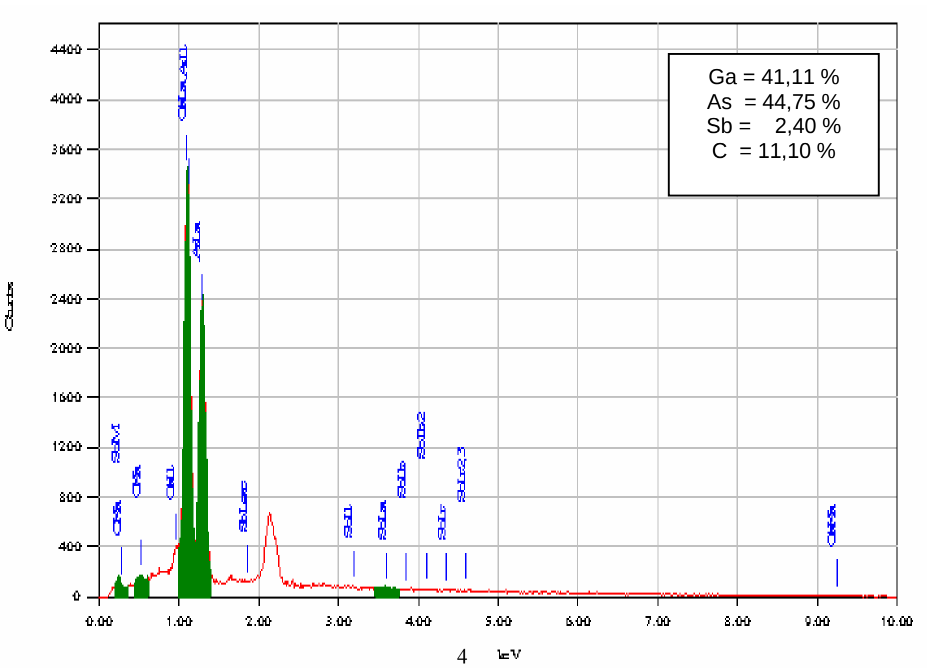

Figure 4. Results of EDS characterization of GaAsSb film

Figure 4 shows the percent composition of the elements attached to the $GaAs_{1-x}Sb_x$ thin film sample grown at a temperature of 580ºC and the V/III ratio of about 4.8 with mole fraction of Sb source vapour input (xv) of about 0.14, resulting from EDS (energy dispersive spectroscopy) measurement. The EDS data showed that the three elements of the alloy that is Ga, As, and Sb has been incorporated in the film. In addition there are a number of the carbon (C) elements in the film. The results of this characterization has shown that the $GaAs_{1-x}Sb_x$ thin films have been successfully grown by MOCVD on the range of its miscibility-gap.

Growing process of $GaAs_{1-x}Sb_x$ films by MOCVD method can be described as shown in Figure 5 [7]. Because of heat gradient vertically upwards due to heating at the bottom, then the metalorganic precursors are introduce into the reaction chamber will undergo pyrolytic decomposition at the top. Reactants of decomposition will move across the boundary layer to the substrate surface. Getting closer to the substrate, the decomposition will be complete, and when it reaches the substrate will occur heterogeneous vapor /solid phase reaction form a thin film of solid material. There are several parameters that control the film formation reaction in the MOCVD reactor, such as growth temperature, reaction pressure, and flow rate V/III ratio [8]. So to obtain good quality films, it is necessary to optimization of the three parameters of this growth. By using concepts of physics and chemistry, MOCVD growth mechanism can be studied. Good knowledge of this mechanism is very useful in determining the fit growth conditions and parameters for growing process.

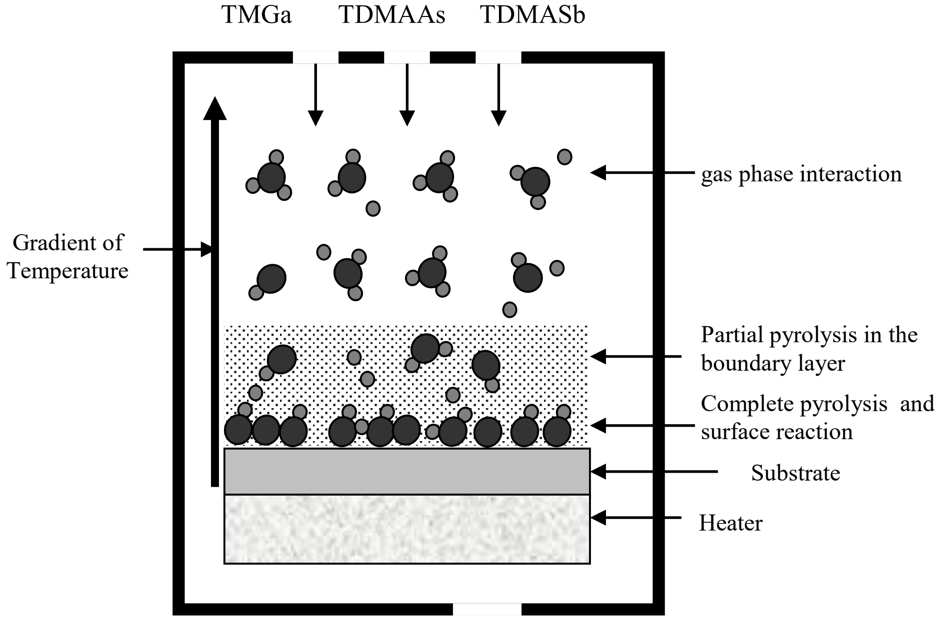

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Figure 5. Schematic process of growing $GaAs_{1-x}Sb_x$ films in the Vertical-MOCVD reactor

Pyrolytic decomposition of TMGa will produce Ga atoms and methyl radicals [6], while the pyrolytic decomposition of TDMAAs (or TDMASb) will produce As (or Sb) atoms, reactive aminos such as $N(CH_3)_2$ and aziridin ($HN(CH_2)_2$), and H atoms [9]. Decomposition mechanism of each metalorganic sources are shown in Figure 6a to 6c.

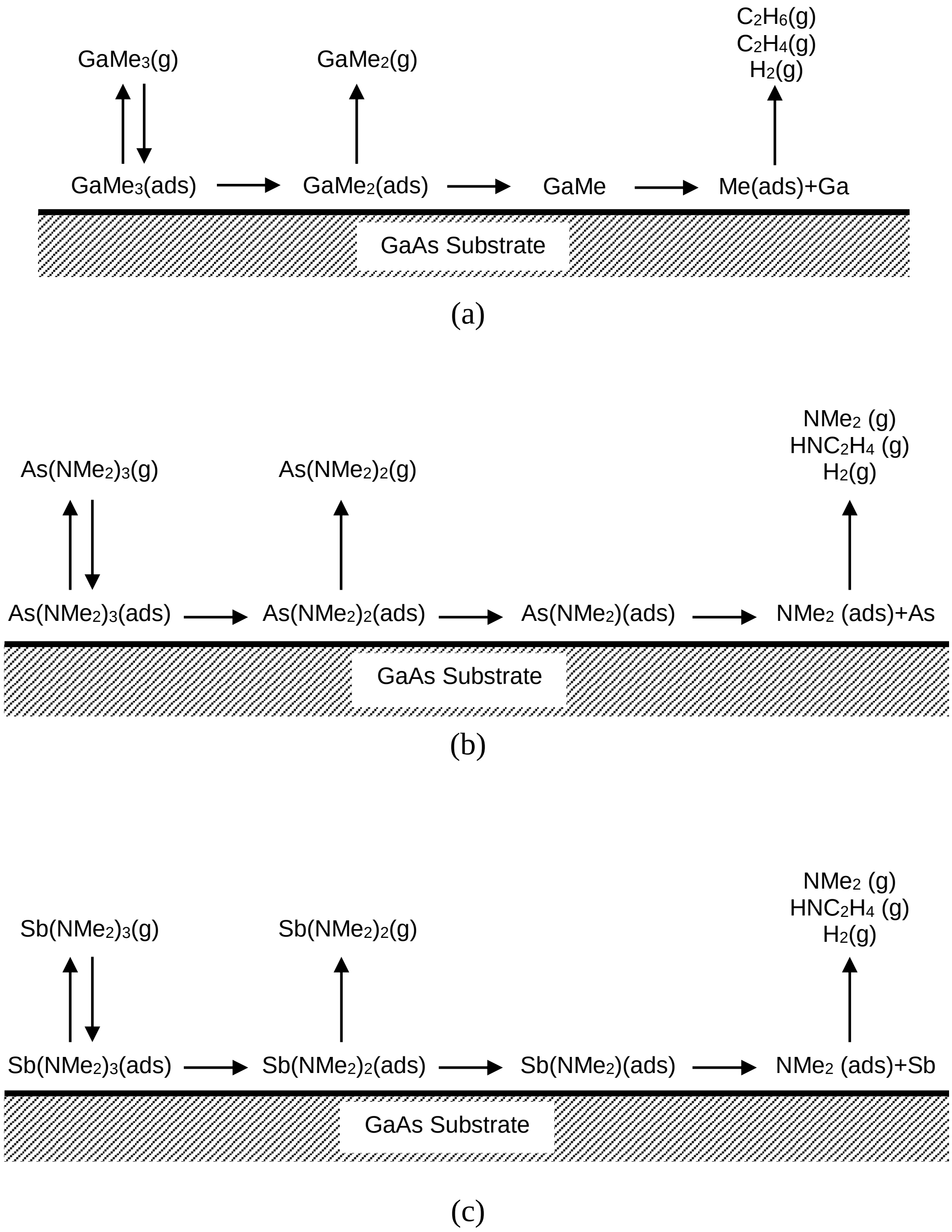

Figure 6. Schematic pyrolitic decomposition for each precursor on the GaAs substrate; (a) TMGa, (b) TDMAAs, (c) TDMASb

Based on the decomposition mechanism, the chemical reactions that occur in the growth of of GaAs, GaSb, and $GaAs_{1-x}Sb_x$ thin film by using TMGa, TDMAAs, and TDMASb on the the MOCVD reactor is predicted as follows:

$$Ga(CH_3)_{3(V)} + xSb[N(CH_3)_2]_{3(V)} + (1-x)As[N(CH_3)_2]_{3(V)} \Rightarrow GaAs_{(1-x)}Sb_{(x)(S)} + 2N(CH_3)_{3(V)} + HN(CH_2)_{2(V)} + CH_{4(V)} \quad (1)$$

Based on the results of measurements of the charge carrier concentration using Hall Van der Pauw method showed that the charge carrier concentration of the order of 10^{17} cm^{-3}, with the majority carrier is hole. The formation of holes as the dominant type of charge carrier in the $GaAs_{1-x}Sb_x$ is due to the contamination of carbon (C) derived from metalorganic sources used. In TMGa chemical structure, there is a direct bond between Ga atoms and carbon atoms (C). Due to the dehydrogenation the species surface [Ga = CH_3], then it is possible to form gallium carbene species [Ga = CH_2] who has a strong bond with the substrate surface. This species [Ga = CH_2] can be react with free Ga atoms, which results in displaced of As atoms and its position occupied by carbon atoms [8]. Carbon is a group IV atom that has four valence electrons. When this atom is bonded with Ga atoms and occupies a position of As or Sb atoms which is pentavalent atoms, there will be generate a hole in the film due to vacancy of electrons in this bond. Hole is a positive charge carrier, so from this process will form a p-type semiconductor. The mechanism of incorpotion of carbon atoms into the grown films are shown in Figure 7.

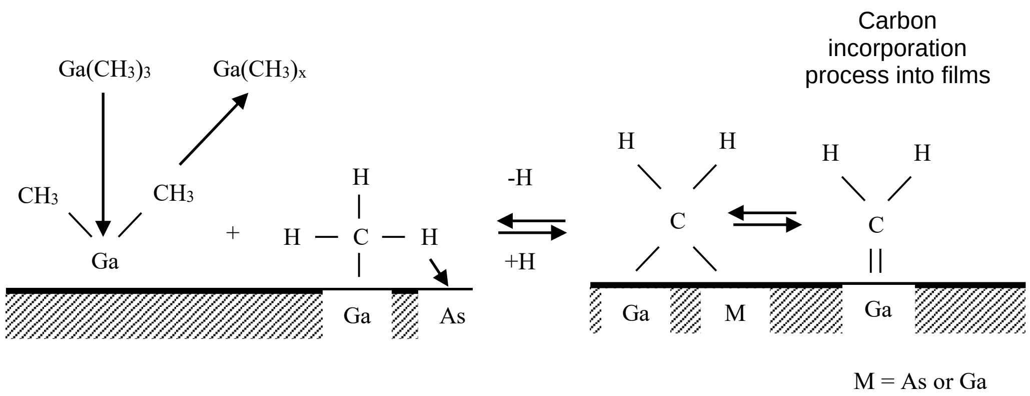

Figure 7. The mechanism of carbon incorporation into the film $GaAs_{1-x}Sb_x$

Order of the charge carrier concentration (hole) is lower than that obtained by Fink, et. al [10]. They get a charge carrier concentration (hole) of the order of 10^{18} to 10^{19} cm^{-3} when using metalorganic sources TMGa, TBAs (Tetrabuthyl Arsine), TMSb (Trimethyl Antimony), and AsH_3 (Arsine) to grow $GaAs_{1-x}Sb_x$ films. This shows that the use of new metalorganic sources TDMAAs and TDMASb can reduce contamination of carbon (C) in the $GaAs_{1-x}Sb_x$ Film. On the metalorganic sources TDMAAs {As [$N(CH_3)_2]_3$} and TDMASb{Sb [$N(CH_3)_2]_3$} there are no direct bonding between As or Sb atoms with C atoms, but is buffered by N atom. So the probability of incorporation of carbon atoms that are in both these sources into grown $GaAs_{1-x}Sb_x$ thin films is relativelly small [9].

4. Conclusion

Metalorganic Chemical Vapor Deposition (MOCVD) technique as a semiconductor thin film deposition techniques that its process conditions are not in thermodynamic equilibrium, have a good potential to be used as a growth technique for $GaAs_{1-x}Sb_x$ ternary alloy thin film. The existence of this

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potential demonstrated by the success of grow $GaAs_{1-x}Sb_x$ films by MOCVD technique in the range of its miscibility gap. The XRD and EDS characterization results showed that the grown thin films was in the form of $GaAs_{1-x}Sb_x$ ternary alloy. Use TDMAAs and TDMASb combine with TMGa as a metalorganic sources produce carbon (C) contamination in the $GaAs_{1-x}Sb_x$ film fairly low, of the order of 10^{17} cm^{-3}, one to two order lower than that resulting from the use of conventional metalorganic sources in form methyl compounds such as TMSb, TMAS, and TBAs or Arsine.

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