

Growth of GaAsSb Thin Film by Vertical-MOCVD and their Characterization

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Abstract: The $\text{GaAs}_{1-x}\text{Sb}_x$ (GaAsSb) ternary alloy has been studied intensively as the candidates for long-wavelength optoelectronic devices such as infrared laser diode and photo detector. The immiscible compositional range in forming GaAsSb ternary alloy through substitution process is very wide. To grow a ternary alloy that have a wide range of compositional miscibility like GaAsSb needed the thermally non-equilibrium growth methods. Metalorganic Chemical Vapor Deposition (MOCVD) is one of the semiconductor thin film growth technique can be use to meet those requirements. One problem faced in growing GaAsSb thin films by MOCVD is the high carbon contamination in the grown films derived from metalorganic sources in the form of methyl compound. The high carbon contamination will degrade the electrical properties of grown films. On the metalorganic sources in the form of Trisdimethylamino compound such as Trisdimethyl Amino Arsenic (TDMAAs) and Trisdimethyl Amino Antimony (TDMASb), the bond between As/Sb atom and C atom in their chemical bonding structure buffered by N atom, so that incorporation of C atom into grown films can be reduced. In addition, these metalorganic sources has a low decomposition temperature, approximately 340°C and convenient vapor pressure for MOCVD growth. Generally semiconductor thin films grown on a relatively low temperature will have a good quality of morphology and physical properties. In this research, the MOCVD growth of metastable GaAsSb ternary alloy thin films using TMGa, TDMAAs and TDMASb has been done. This study describes the crystal structure, surface morphology and optical properties of GaAsSb thin films grown by Vertical-MOCVD.

Key words: GaAsSb, Vertical-MOCVD, TDMAAs, TDMASb, growth

INTRODUCTION

The application of long wavelength optoelectronic devices has recently become more and more extensively (Wang *et al.*, 2008). The GaAsSb ternary alloy has been studied intensively as the candidates for long-wavelength optoelectronic devices such as infrared laser diode and photodiode. By adjusting content of Sb elements in the GaAsSb ternary, the values of bandgap Energy (E_g) for this material can be ajusted in the range of 0.72-1.42 eV. This bandgap energy range corresponding with wavelength range required in the optical fiber communication systems (Sun *et al.*, 2002; Yeh *et al.*, 2006; Sadofyev and Samal, 2010; Kawamura and Sahashi, 2014; Park, 2011). For the future demands of high-speed optical communication systems, however, parallel processing data transmission using 1 or 2D array laser structures is required. The most promising structure for this purpose is Vertical Cavity Surface Emitting Laser (VCSELs) (Wilsen *et al.*, 1999). In the typical VCSEL structure, the vertical resonant-cavity geometry is formed by the upper and lower Distributed Bragg Reflectors (DBRs) that act as mirror. Until now, the DBR pairs who have highest

performance for VCSEL is AlGaAs/GaAs heterojunction. In order to use high-performance Al(Ga)As/GaAs DBR pairs, many researcher has been explored a novel material system that can be grown on GaAs substrates. Moreover, GaAs substrates are currently much cheaper and have a larger area than other commercially available substrates and the processing for GaAs is well establish.

The immiscible compositional range in forming $\text{GaAs}_{1-x}\text{Sb}_x$ ternary alloy through substitution process is very wide (ranging from $x = 0.2$ fo $x = 0.8$). To grow a ternary alloy that have a wide range of compositional miscibility like GaAsSb needed the thermally non-equilibrium growth methods. Metalorganic Chemical Vapor Deposition (MOCVD) is one of the semiconductor thin film growth technique can be use to meet those requirements. There have been continuous effort to obtain alloy composition inside the miscibility gap since the first Organometalic Vapor-Phase Epitaxy (OMVPE) growth of GaAsSb was reported by Manasevit. Many researcher have been demonstrated the succesful growth of GaAsSb films with compositions throughout the miscibility gap including (Shin *et al.*, 1997; Nooh, 2003).

One problem faced in growing GaAsSb thin films by MOCVD is the high carbon contamination in the grown films derived from metalorganic sources in the form of methyl compound due to the CH_3 radicals produced. The high carbon contamination will degrade the electrical properties of grown thin films. On the metalorganic sources in the form of Trisdimethyl amino compound such as Trisdimethyl Amino Arsenic (TDMAAs) and Trisdimethyl-amino Antimony (TDMASb), the bond between As/Sb atom and C atom in their chemical bonding structure buffered by N atom, so that incorporation of C atom into grown films can be reduced (Marx *et al.*, 1995). In addition, these metalorganic sources has a low decomposition temperature, approximately 340°C and convenient vapor pressure for MOCVD growth (Jones and Brien, 1997). Generally, semiconductor thin films grown on a relatively low temperature will have a good quality of morphology and physical properties. Two precursors, Trisdimethyl Amino Antimony (TDMASb) (Shin *et al.*, 1995) and Tertiary Butyl Dimethyl Amino Antimony (TBDMASb) (Chen *et al.*, 1992) have been used for the growth of Sb-containing compound by MOCVD in the temperature ranges $275\text{--}600$ and $325\text{--}650^\circ\text{C}$, respectively. The films grown using these precursors showed good crystalline quality with no serious impurity contamination.

In this research, the MOCVD growth of metastable GaAsSb ternary alloy thin films using TDMAAs and TDMASb has been done. This study describes the crystal structure, surface morphology and physical properties of GaAsSb thin films grown by Vertical-MOCVD.

MATERIALS AND METHODS

Experimental: The GaAsSb thin films were grown on SI-GaAs substrate by low-pressure Vertical-MOCVD. The use of the low pressure MOCVD lead to an increase of the growth rate and a decrease of impurity incorporation into the grown layer. TDMAAs and TDMASb were chosen because in their chemical bonding structure no direct bonding between As/Sb atom with C atom, it has a low decomposition temperature and convenient vapor pressure for MOCVD growth. Suhandi have been reported that GaAsSb thin film growing with using metalorganic sources TMGa, TDMAAs dan TDMASb have order of the charge carrier concentration (hole) is lower than that growing with using metalorganic sources TMGa, TBAs (Tetrabutyl Arsine), TMSb (Trimethylantimony) and AsH_3 (Arsine).

In this research, diagnostic studies have been conducted on the influences of growth temperature and 5/3 ratio on the crystal structur and the physical characteristic of the grown GaAsSb films. Temperature is an important factor in pyrolytic decomposition of the sources, molecule formation and crystal nucleation. The 5/3 ratio of the metalorganic sources determines the rate of incorporation of group V and group III elements to form 3-5 materials. Schematically, MOCVD reactor system used in this research is shown in Fig. 1. The typical growth parameters and conditions are shown in Table 1.

Crystal structure of the grown films were characterized by X-Ray Diffraction (XRD) to determine sb solid compotition incorporated into GaAsSb ternary, the

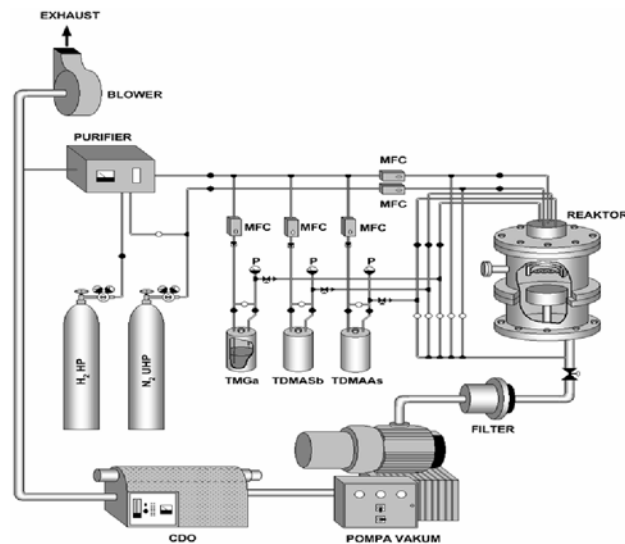


Fig. 1: Schematic diagram of Vertical-MOCVD reactor system

Table 1: Typical Growth parameters and condition for GaAsSb thin films

Growth parameters	Conditions
Reaction pressure	50 Torr
Growth temperature	520-590°C
5/3 ratio	1.2, 3.0, 4.8
Mol fraction of TDMASb input	0-1
Gas flow rate	
Nitrogen	300 Sccm
Hydrogen	300 Sccm

surface morphology and the thickness of the grown films were investigated using Scanning Electron Microscopy (SEM) to determine growth rate of films and the optical properties of the grown films were investigated by room temperature Photoluminescence (PL) spectroscopy.

RESULTS AND DISCUSSION

Figure 2 shows the X-ray diffraction pattern of a several GaAsSb films grown at growth temperature of about 580°C and the 5/3 ratio of about 4.8 with the input composition of the Sb vapor source (x_v) is varied. The orientation of the crystal plane were observed represented by (400) plane because the whole grown films have a single crystal orientation.

It appears that a shift in the peak angle of the (400) plane towards smaller 2θ when the composition of the Sb vapor source input increase. This shift indicates changes in the value of the lattice constant (a) of the material towards 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 GaAsSb.

To determine the sb solid composition in the GaAsSb ternary was used Vegard law based on the shift of the X-ray diffraction peak, when its composition changed. Vegard law states that for a ternary alloy formed by substitution, the lattice constant of solid materials will vary linearly to changes in its composition. Thus for $A_{III}B_{V(1-x)}C_{V(x)}$ ternary system can be formulated the linear relationship between the elemental composition of C in the ternary (x) with the lattice constants of materials (a) as follows:

$$x_{C(solid)} = \frac{a(A_{III}B_{V(1-x)}C_{V(x)}) - a(A_{III}B_V)}{a(A_{III}C_V) - a(A_{III}B_V)} \quad (1)$$

Therefore, the Vegard equation for GaAsSb ternary can be formulated as follows:

$$x_{Sb(solid)} = \frac{a(GaAsSb) - a(GaAs)}{a(GaSb) - a(GaAs)} \quad (2)$$

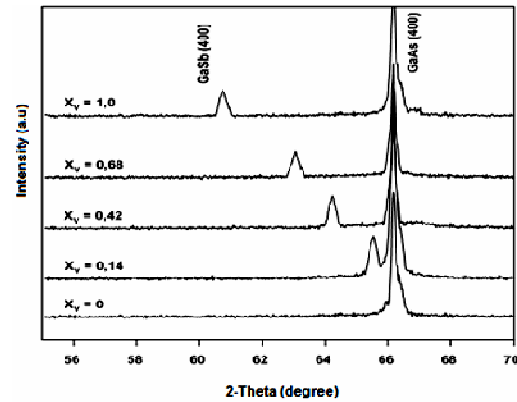


Fig. 2: XRD pattern for (400) plane from several GaAsSb films samples growth at temperature of about 580°C and 5/3 ratio of about 4.8 with varied x_v

For a cubic crystal system, the value of the lattice constant (a) can be obtained through the following equation (Suryanarayana and Norton, 1998):

$$a = \frac{\lambda}{2\sin\theta} \sqrt{h^2 + k^2 + l^2}$$

λ is the wavelength of X-ray radiation. By using Eq. 2 and 3, Sb solid composition in GaAsSb film can be determined if there is information about changes the angle of diffraction peaks for a certain crystal plane when the composition was varied. The use of Vegard law would be more accurate if the samples are characterized have a single crystal orientation. The main purpose of this characterization is to get a depiction of influence the growth parameter on the Sb solid composition in the GaAsSb film.

Based on the shift of the angle of X-ray diffraction peak when the mole fraction of Sb source vapor input enhanced, we can determine the elemental composition of Sb on the GaAsSb film using Vegard law (Eq. 1). The results are shown in Fig. 3. From the figure it can be observed that for the samples were grown by the 5/3 ratio approximately one the relationship between the mole fraction of Sb source vapor input (15) with the composition of Sb incorporated to the GaAsSb film (x_s) almost linear. When the 5/3 ratio increased, the Sb solid composition (x_s) incorporated in the GaAsSb ternary tend to be much smaller than the mole fraction of Sb source vapor input (x_v).

This occurs due to the driving force for the formation of GaAs greater than for the formation of GaSb. On the use of the 5/3 ratio approximately one, then it could hardly be competition between As and Sb atoms for the

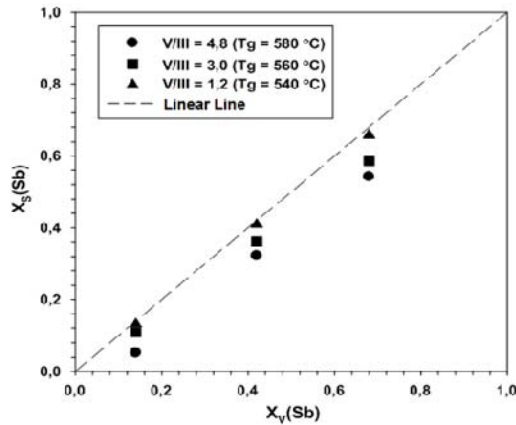


Fig. 3: The relationship of Sb solid composition in the GaAsSb with the molar fraction of Sb source vapor input for different 5/3 ratio

entire group V atom has an atomic pair Ga. But the use of the 5/3 ratio much larger than one which means the group V atoms are much larger than Ga atom, there will be competition between the group V atoms (As and Sb) for binding to Ga atom. Because of the driving force for the GaAs formation larger than the incorporation of Sb atoms in ternary will be difficult. As a result the fraction of Sb in the GaAsSb ternary will tend to smaller when the 5/3 ratio continuously improved.

The similar results were also obtained by Cherng *et al.* (1984). As described above, the decrease in the Sb composition that incorporated in the GaAsSb film at the use of the large 5/3 ratio, occurs due to the larger thermodynamic driving force for GaAs crystal formation at the use of the V/ III ratio is quite high, so that some Sb atoms rejected from GaAsSb crystal.

Figure 4 shows the surface morphology and cross-sectional of the GaAsSb thin film deposited on the SI-GaAs at a temperature of 700°C. It appears that the surface morphology GaAsSb contain small granules and porous character. From the cross-sectional image looks fairly evenly film thickness of about 1 μm .

Figure 5 shows the dependence of the growth rate of GaAsSb thin films on the growth temperature. In a low growth temperature range, up to 560°C, the process of growing controlled by the kinetics mechanism of decomposition of alkyls on the surface of the substrate. This condition is known as the kinetically controlled regime, where the growth rate is highly dependent on the growth temperature (degrees of pyrolysis) and virtually unaffected by changes in reaction pressure. It can be seen that in this temperature range, there is an exponential relationship between the growth rate with the growth

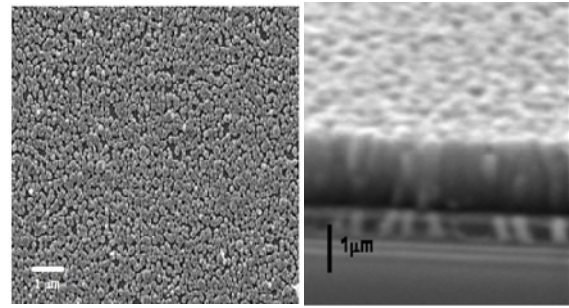


Fig. 4: The surface morphology and cross section of the GaAsSb grown at a temperature of 560°C and 5/3 ratio of about 3.0 with x_v of about 0.42

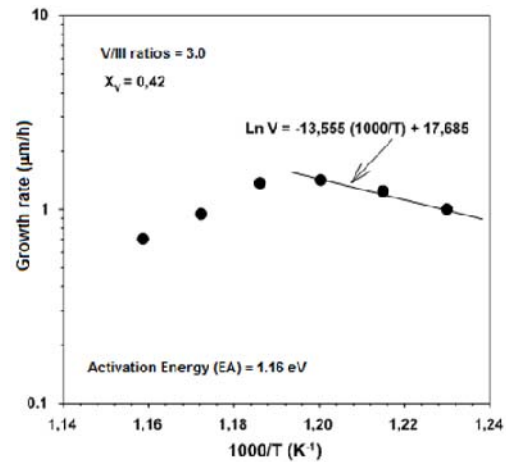


Fig. 5: Graph the growth rate of the GaAsSb as a function of the growth temperature

temperature. From this relationship can be determined the magnitude of the activation energy for the formation of GaAsSb film with using Arrhenius equation which is about 1.16 eV.

For a higher growth temperature, which is in the range of 560-570°C, the growth rate is relatively constant. Because in this temperature range, pyrolysis of molecules TMGa, TDMAs and TDMASb was complete, then the growth rate is more dominant is controlled by the concentration of precursor. This situation is known as mass transport limited. When the growth temperature increased again, the growth rate actually decreased. This occurs due to the desorption of gallium, arsenic and antimonat from the surface of substrate. The growth rate is not only as a function of the presence of atomic species and the rate of incorporation of precursor fragments on the surface of the growth but it also depends on the flow rate of carrier and the partial pressure of metalorganic sources (Koljonen *et al.*, 1995).

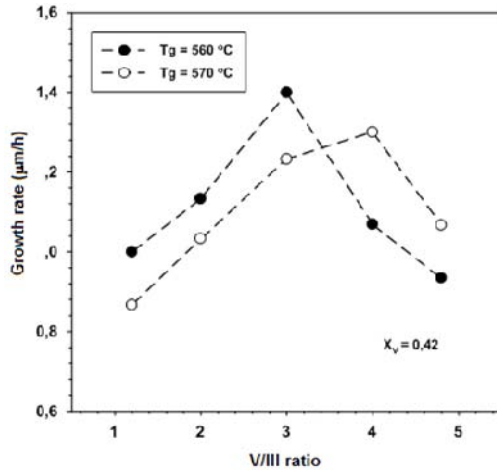


Fig. 6: Graph the growth rate of the GaAsSb films as a function of the 5/3 ratio

The 5/3 ratio is a parameter that also influences the growth rate, due to either deficiency or excess of 5 group elements on a semiconductor material will greatly reduce its quality. Figure 6 shows the growth rate of GaAsSb thin films as a function of the 5/3 ratio for $x_v = 0.42$. For the 5/3 ratio < 2 , the growth rate is relatively low, i.e., below $1.13 \mu\text{m h}^{-1}$. When the ratio 5/3 increased, the growth rate actually increased up to $1.4 \mu\text{m h}^{-1}$ at a 5/3 ratio of about 3. In this range of 5/3 ratio, it appears that the presence of the V group species is a key factor that controls the growth rate. But when the 5/3 ratio increased again, the growth rate actually decreased.

The decrease in growth rate when the 8 ratio to be increased is due to the presence excess of V group molecules (due to the low vapor pressure of TDMASb and TDMAAs) on the surface of the substrate which causes the appearance of circumstances surface for adsorption of Ga and resulted in a significant decrease in the adatom Ga. Blocking Ga adatom by V group atoms that excessive amount will result in a decrease in the growth rate. When the growth temperature increased (up to 570°C) position of the maximum growth rate shifted to the higher 5/3 ratio, however, the value of the maximum growth rate is still lower than that grown at temperature of 560°C . This indicate that there are 5/3 ratio and growth temperature pairs that produces optimum growth rate.

Figure 7 shows the PL spectrum for GaAs films ($x = 0$) and $\text{GaAs}_{1-x}\text{Sb}_x$ ($x = 0.06$) grown at the same growth temperature and the 5/3 ratio, i.e., 580°C and 4.8. It appears that there is a shift of the PL spectrum wavelength peak towards greater when the Sb atoms are substituted to a GaAs material forming GaAsSb ternary. The PL spectrum peaks at room temperature (300K) for the

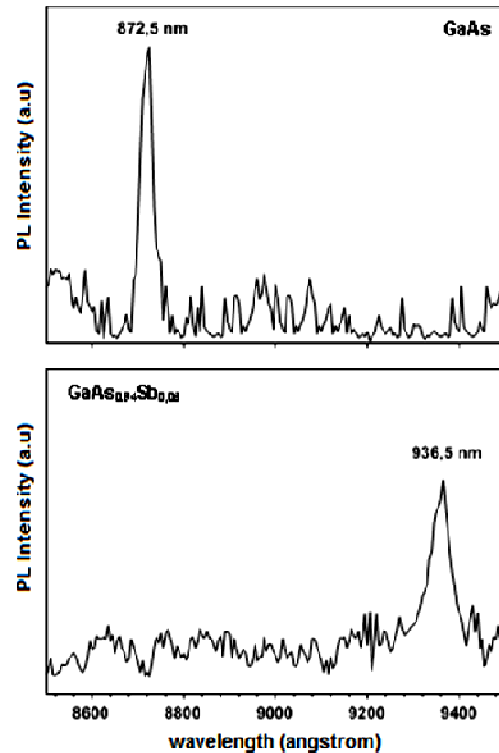


Fig. 7: PL spectra of GaAs and $\text{GaAs}_{0.94}\text{Sb}_{0.06}$ grown at temperature of 580°C and the 5/3 of about 4.8

GaAs material occurs at a wavelength of 872.5 nm, corresponds to the band gap Energy (E_g) of about 1.42 eV whereas the PL spectrum peaks for $\text{GaAs}_{0.94}\text{Sb}_{0.06}$ material occurs at a wavelength of 936.5 nm, corresponds to the band gap Energy (E_g) of about 1.33 eV.

CONCLUSION

A GaAsSb thin films which is a promising for long-wavelength optoelectronic devices material is grown by vertical MOCVD on SI-GaAs substrate using TDMAAs and TDMASb. The grown thin films were confirmed for Sb solid composition in the grown film using XRD analysis. The surface morphology, the thickness and the growth rate of the grown film were confirmed using SEM image analysis. The band gap energy of grown films were confirmed using PL spectrum analysis.

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