Organometallic Vapor Phase Epitaxial Growth   of $AlAs_xSb_{1-x}$ Films Using Tertiarybutylarsine

Organometallic Vapor Phase Epitaxial Growth of AlAs$_x$Sb$_{1-x}$ Films Using Tertiarybutylarsine

Wei-Kuo CHEN, Jehn OU and Wei-I LEE

Department of Electrophysics, Chiao-Tung University, Hsin-Chu, Taiwan, R.O.C.

The deposition of AlAs$_x$Sb$_{1-x}$ films is studied systematically using an organometallic vapor phase epitaxy growth technique. It is found that the growth of AlAsSb films requires a low V/III ratio to enhance the incorporation of antimony into the solid. The composition of the alloy also depends strongly on the growth temperature. Experimental data shows that films grown at higher temperatures yield much higher AlSb contents in the AlAs$_x$Sb$_{1-x}$ alloys. This is contrary to the results reported for GaAsSb films. In our study, we are able to grow metastable AlAs$_x$Sb$_{1-x}$ epitaxial films throughout the entire range of the solid composition for temperatures above 550 °C.

KEYWORDS: MOVPE, AlAsSb, distribution coefficient, miscibility gap

The novel III–V ternary alloy AlAs$_{0.56}$Sb$_{0.44}$ is a potentially important material for InP-based optoelectronic devices. Due to the large Γ-bandgap of 2.6 eV.[1] and hence the lowest refractive index of value 3.0 in the InP material system, it has been demonstrated to have a very high reflectivity with a thin AlAs$_{0.56}$Sb$_{0.44}$/ GaInAs(P) quarter-wave stack, which is essential for improving the performance of the InP vertical cavity laser.[2-4] Besides, the high conduction-band edge discontinuity with In$_{0.47}$Ga$_{0.53}$As ($\Delta E_c = 0.67$ eV)[5,6] as well as the possibility of realizing Schottky contacts can also be advantageous for certain millimeter-wave devices, such as MESFET, HEMT, etc. In addition, the staggered line-up feature of AlAsSb/InP heterostructures[5,6] is also of particular interest. The large conduction and valence band offset differences can significantly reduced the multiplication noise in Avalanche photodetector.[7] In short, it is very desirable to study the growing of the AlAs$_x$Sb$_{1-x}$ ternary compounds in order to compete in the fabrication of the future optoelectronic devices.

At present, relatively little has been published on AlAs$_x$Sb$_{1-x}$ preparation and its physical information.[1,5,8] Tai and Inata have studied the optical and electrical properties using optical reflection and tunneling transport phenomena. All their samples were grown by the molecular beam epitaxy (MBE) technique. No other growth method has yet been reported. It may be associated with the difficulty in growing such a wide-miscibility-gap alloys. In addition, the growth of Al-containing compounds usually requires higher growth temperatures in order to minimize the H$_2$O and O$_2$ incorporation.[9] This makes the growth window of the AlAsSb film even narrower and thus defers the material exploitation. In this paper, we present the first organometallic epitaxial growth of the AlAs$_x$Sb$_{1-x}$ films. The dependence of the compositions on the growth temperatures, V/III ratios, and Sb partial pressures are investigated thoroughly in this work.

The films we studied were grown on InP(100) substrates by atmospheric pressure organometallic vapor phase epitaxy (OMVPE). Electronic-grade trimethylaluminum (TMAl), tertiarybutylarsine (TBAs) and trimethylantimony (TMSb) were used as

source reactants, and were thermostated at 17 °C, 1 °C, and −17 °C, respectively. Prior to the growth, the InP substrates were degreased in warm organic solvents, acid etched in 4:1:1 H$_2$SO$_4$:H$_2$O$_2$:H$_2$O chemical solution, and finally thermal cleaned in the reactor at 610 °C in a phosphine ambient to remove native oxide. The temperature was then adjusted to the desired growth temperatures (500 °C~675 °C) for the commencement of the epitaxial growth. The total H$_2$ carrier flow rate was 1.5 SLM during the growth, which yields a linear gas velocity of 10 cm/s immediately in front of susceptor. Typical film thickness in our experiment is around 1.5 μm.

The surface morphologies of the grown epilayers were characterized by a scanning electron microscope (SEM) and a Normarski optical microscope. The solid composition was determined using both the electron microprobe analysis and the X-ray diffractometer. They are in quite good agreements. Thickness was measured either by the surface profilometer or the cross-section of SEM.

In growing the Sb-containing compounds, including the AlAsSb compounds, it is seen to be inevitable to play the low V/III ratio trick in order to avoid the formation of any Sb droplets. Accordingly, we started our study with a V/III ratio of 1.2 and $X_{Sb}^v = 0.66$ to examine the growth temperature dependence, where X_{Sb}^v is defined as the ratio of the TMSb partial pressure to the total group V partial pressure. The growth efficiency is plotted against the reciprocal temperature in Fig. 1. At low temperatures, the growth is apparently controlled by surface kinetics. Arrhenius fit of this data gives the corresponding activation energy of 27.5 kcal/mol. For temperatures above 625 °C, mass transport dominates the reaction. The growth efficiency reaches a high value of approximately 8000 μm/mol, implying that no sever parasitic reaction occurs between TMAl, TMSb and TBAs in overall growth process.

In an attempt to understand the stoichiometric dependence of the epitaxial films on the Sb/As gas phase ratio, we grew a set of samples at 550 °C. The lower curve of Fig. 2, denoted by open circles, indicates that Sb atoms are unlikely to incorporate into the solid at a high value of V/III ratio, such as 1.7. As a matter of
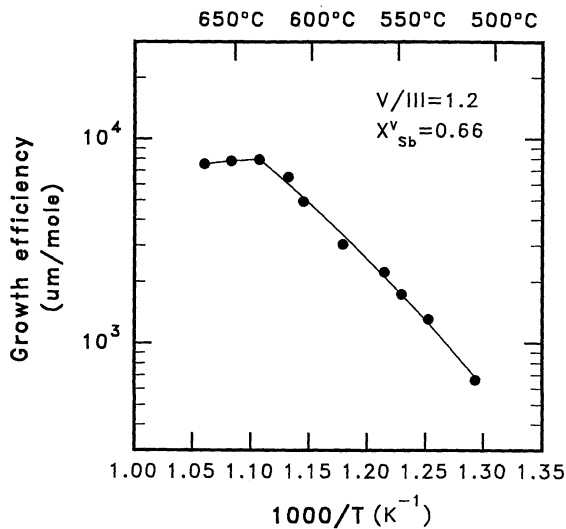
Fig. 1.   Growth efficiency for AlAsSb versus reciprocal growth temperature. The TMAl:TMSb:TBAs input partial pressure ratio was kept at 1:0.8:0.4.
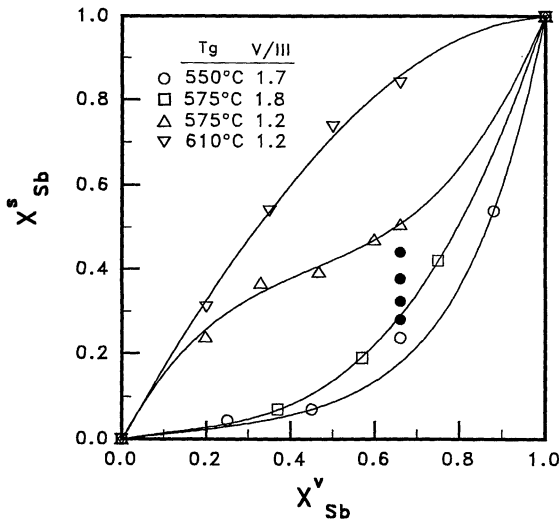

Fig. 2.   Mole fraction of AlSb in the solid as a function of the ratio TMSb/(TMSb+TBAs). A set of films grown at $X_{Sb}^{v}=0.66$ and 550°C for different V/III ratios are indicated as one open circle and four closed circles with ratios at 1.7, 1.5, 1.35, 1.2, ad 1.0, in an ascending order in the figure.

fact, V/III ratio has a large influence in controlling the composition of the AlAsSb films. When X_{Sb}^{v} is held at 0.66, it is found that as the V/III ratio decreases from 1.7 to 1, the AlSb solid mole fraction is increased from 0.24 to 0.44. Qualitatively, this trend is similar to the results of the OMVPE-grown $GaAs_x Sb_{1-x}$ films, reported by Stringfellow.[10] For the above immiscible materials, when the V/III ratio is lowered to unity, the binding of the group V with the group III atoms is less affected by their bonding energy, but is controlled primarily by the random distribution of the reactants in the growing surface. By following through the procedure, we are able to attain the InP-lattice matched film, $AlAs_{0.56}Sb_{0.44}$, and the surface morphology for sample grown at 600°C, for example, is virtually featureless at

a magnification of 400 using a Nomarski interference contrast microscope (Fig. 3).

In Fig. 4 we show the AlSb solid concentration as a function of the temperature for epilayers grown at constant values of V/III=1.2 and $X_{Sb}^{v}=0.66$. As can be seen in Fig. 4, the deposition of Sb and As has a strong dependence on the growth temperatures. A sharp increase of the Sb incorporation was noted as the growth temperature increased from 525°C to 610°C, in the span of less than 100°C. The corresponding Sb solid composition, the X_{Sb}^{s}, spreading from 0.17 to 0.83, is varied by nearly a factor of 5. When we define the solid-vapor distribution coefficient k_{Sb}, similar to the concept of "sticking coefficient" in molecular beam epitaxy, as

$$k_{Sb} = \frac{X_{Sb}^{s}}{1-X_{Sb}^{s}} \times \left\{ \frac{P_{TMSb}}{P_{TBAs}} \right\}^{-1},$$
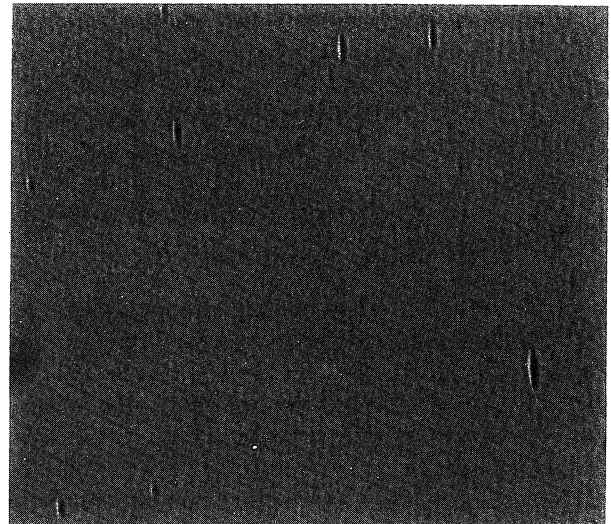

20 μ m

Fig. 3.   Interference contrast photomicrograph of $AlAs_{0.56}Sb_{0.44}$ epilayer grown at 600°C with V/III=1.1 and $X_{Sb}^{v}=0.44$.
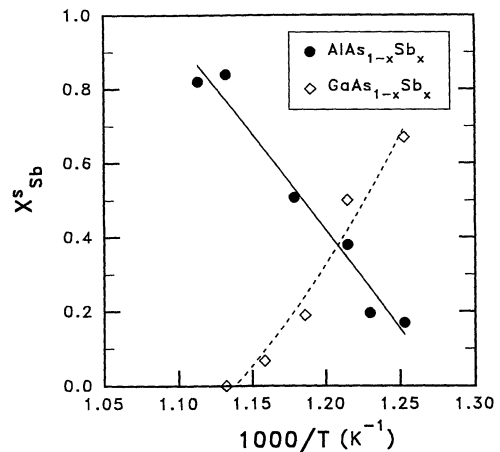

Fig. 4.   Compositions of AlSb content in AlAsSb ad GaSb content in GaAsSb as a function of growth temperatures with constant V/III=1.2 and $X_{Sb}^{v}=0.66$.

where P_{TMSb} and P_{TBAs} represent the input partial pressure of the TMSb and the TBAs, respectively, then the Sb distribution coefficient at 610°C has a value of 2.35, while at 525°C it is only 0.11. The calculated activation energy for the Sb distribution coefficient is 2.1 eV (48.6 kcal/mol). Ideally, the distribution coefficient should be equal to unity, as in the case of TMAl, and TMGa in the growth of the AlGaAs films. The fact that k_{Sb} has a value close to unity indicates that the control of the TMSb flow does not need to be so stringent for the growth of different AlAsSb ternary compounds at higher growth temperatures. Actually, we can obtain the $AlAs_xSb_{1-x}$ films over the entire range of compositions for temperatures ranging from 550°C to 600°C, regardless of the wide material immiscibility.

There are several factors that concern us regarding the distribution of the alloy constituents. Firstly, from simple kinetic arguments, the Sb atoms, which are less volatile than As atoms, incorporate preferentially into the solid. However, this can not account for such a large difference in the Sb distribution as the growth temperature is changed. The incorporation of the Sb for the growth of the AlAsSb films may also connect to the pyrolysis of the TMSb and its competitor, the arsenic precursor.[11] In our study TBAs is employed to replace the stable AsH_3, because its pyrolysis is almost 90% completed at 500°C,[12] well below our nominal growth temperatures. Therefore, it is expected that the effect due to the degree of decomposition of arsenic source, if any, can be reduced to a less extent. On the other hand, TMSb is decomposed incompletely below 600°C,[12] the likely explanation for Sb incorporation behavior seems to be related to the cracking of TMSb. For comparison, we made another series of GaAsSb samples, which is also a metastable alloy, in the temperature range from 525°C to 610°C with all precursors remaining the same except the replacement of the TMAl by the Ga source. It is interesting to note that almost no GaSb content can be found for those films grown at higher temperatures, as shown in Fig. 4. The tendency is just opposite to the results observed in AlAsSb. Thus, for the experimental condition used in our study, the pyrolysis of TMSb itself, although, will help the supply of active Sb reagent in the reaction at high temperatures, it can not be the decisive factor involved in the mixing of the Sb, As atoms on their group V sublattices. Stringfellow has alledged that for III-V semiconductor alloys AC_xD_{1-x}, where C, D are group V not involving the PH_3, their epitaxial growth can be characterized very well by simple thermodynamic calculation.[13] The AlAsSb may have the same growth manner as the cases in GaAsSb, InAsSb, and so on.[13-15]

In summary, we have carried out the first MOVPE-growth of $AlAs_xSb_{1-x}$ films using TMAl, TMSb and TBAs as source precursors. There is no sever parasitic reaction occurred between TMAl, TMSb and TBAs, since a considerably high growth efficiency, 8000 μm/mole, is obtained for the growth of the $AlAs_xSb_{1-x}$ films. The composition of the alloy is found to be very sensitive to the input V/III ratio. By reducing the V/III ratio from 1.7 to 1.0 at constant growth temperature of 550°C, the Sb solid concentration is found to be increased from 0.24 to 0.44 for a fixed $X^v_{Sb}=0.66$. More profoud effect is observed as the growth temperature changes. For films grown at V/III=1.2 and the conditions discussed above, we find that the AlSb mole fraction is varied remarkably by a factor of ~5, from 0.17 to 0.83 for temperatures between 525°C and 610°C. The associated activation energy of antimony distribution coefficient is 2.1 eV. For the system of the $AlAs_xSb_{1-x}$ films, although there appears a very wide immiscible region as predicted by thermodynamics at thermal equilibrium, we have shown that the entire composition of the $AlAs_xSb_{1-x}$ films can be synthesized using the MOVPE growth technique.

Acknowledgments

1) K. Tai, R. J. Fischer and A. Y. Cho: Electron. Lett. 25 (1989) 1159.
2) I. Watanabe, F. Koyama and K. Iga: Electron. Lett. 22 (1986) 1326.
3) D. G. Deppe, N. D. Gerrard, C. J. Pinzone, R. D. Dupuis and E. F. Schubert: Appl. Phys. Lett. 56 (1990) 315.
4) Y. Imajo, A. Kasukawa, S. Kashiwa and H. Okamoto: Jpn. J. Appl. Phys. 29 (1990) L1130.
5) T. Inata, S. Muto, Y. Nakata and T. Fujii: Jpn. J. Appl. Phys. 29 (1990) L1382.
6) S. Tiwari and D. J. Frank: Appl. Phys. Lett. 60 (1992) 630.
7) S. M. Sze: Physics of Semiconductor Devices (Wiley, New York, 1981) 2nd ed., Chap. 13, p. 768.
8) Bolognesi and H. Kromer: Phys. Rev. B 46 (1992) 16142.
9) G. B. Stringfellow: J. Cryst. Growth 55 (1981) 42.
10) G. B. Stringfellow and M. J. Cherng: J. Cryst. Growth 64 (1983) 413.
11) L. Samuelson, P. Omling and H. G. Grimmeiss: J. Cryst. Growth 61 (1983) 425.
12) M. J. Cherng, H. R. Jen, C. A. Larsen and G. B. Stringfellow: J. Cryst. Growth 77 (1986) 408.
13) G. B. Stringfellow: J. Cryst. Growth 62 (1983) 225.
14) R. M. Biefeld: J. Cryst. Growth 75 (1986) 255.
15) M. J. Cherng, H. R. Jen, C. A. Larson, G. B. Stringfellow, H. Lundt and P. C. Taylor: J. Cryst. Growth 77 (1986) 408.