Extended Abstracts of the 18th (1986 International) Conference on Solid State Devices and Materials, Tokyo, 1986, pp. 435-438

Vapor Phase Epitaxial Growth of AlAs by Chloride Transport Method

Fumio HASEGAWA, Tadashi YAMAMOTO, Koji KATAYAMA and Yasuo NANNICHI

Institute of Materials Science, University of Tsukuba, Tsukuba Science City, Japan 305

AlAs epitaxial layer was successfully grown by chloride VPE method for the first time. Al was supplied as a Metal Organic compound, i.e. DMAC $--Al(CH_3)_2Cl--$ or TMA $--Al(CH_3)_3$ -- with a carrier gas of He, and As was supplied by $AsCl_3/(Hef1%H_2)$ instead of AsH_3 . DMAC or TMA is mixed with $AsCl_3$ at the source zone to produce aluminum chloride , and $(AlCl+AlCl_3)$ and As_4 are conveyed to the deposition zone. AlAs was deposited by introducing H₂ into the deposition zone, whose temperature is the same as that of the source zone²(700°C - 800°C). Only when the $AsCl_3/(DMAC$ or TMA) ratio was in a proper range (0.3-1.0), the AlAs was deposited. The growth rate of about 3um/hr was obtained for $AsCl_3/TMA=0.65$.

\$1. Introduction

AlGaAs layers for production of LED or LD(laser diodes) are generally grown by LPE-(Liquid Phase Epitaxy). But surface morphology and productivity are not necessarily good in LPE. Recently more sophisticated growth methods such as MOCVD(Metal Organic Chemical Vapor Deposition) or MBE(Molecular Beam Epitaxy) are being extensively developed. However, for practical applications, MOCVD and MBE have some disadvantages such as poor productivity, high running cost, and usage of highly poisonous gas.

On the other hand, for production of GaAs epitaxial layers for microwave GaAs FETs, chloride VPE (vapor phase epitaxy) is widely used. However, the biggest drawback of chloride VPE method was the fact that compound semiconductors containing Al could not be grown. Hydride VPE of AlAs has been tried by several people. Ettenberg et al. demonstrated the growth of AlAs by chloride VPE^{1,2)}, but the growth temperature was about 1000°C, and AsH₃ was used as a source of As.

Bachem and Heyen showed that AlGaAs layers could be grown by the hydride VPE method at lower temperatures such as 700°C- 800°C, which are comparable to the growth temperature of GaAs^{3,4)}.

*)Present Adress: Sony Central Research Lab. Fujitsuka-cho, Hodogaya-ku, Yokohama 305 AlGa metal alloy was used as a source and was placed in an Alumina crucible. In order to get a fresh AlGa melt surface, the $HC1/H_2$ gas was bubbled through the AlGa melt. Their results are significant, but poisonous AsH_3 gas had to be used as the As source, and composition of Al could not be controlled well.

The purpose of this work is to investigate the possibility of growing AlAs or AlGaAs by chloride VPE method in a similar way to GaAs growth. A Metal Organic compound was adopted as the Al source and $AsCl_3$ as the As source. The single flat temperature zone method, which has been developed by Seki et al.^{5,6)} was used for the growth of AlAs.

Prior to the experiments, thermodynamic analysis was performed to find the possibility of AlAs chloride VPE by the flat temperature zone method. It was confirmed that AlAs can be deposited in the all temperature range calculated $(700^{\circ}C-800^{\circ}C)$.

It was experimentally shown that AlAs can be grown by chloride VPE method similar to that of GaAs growth system, by selecting growth parameters and adopting a carbon coated quartz reactor. In this method, we do not need to use the poisonous AsH_3 . The V/III ratio was less than unity whereas it is 10 - 30 for MOCVD. The gas flow rate is also about 1/10 of that of MOCVD.

\$2. Growth Apparatus and Methods

Figure 1 shows a schematic diagram of the reactor. It is essentially the same as the system used for growth of GaAs⁷⁾. There are two chambers in the source zone of the quartz reactor tube, but only one chamber were substantially used for the growth of AlAs. The second one is for Ga source for growth of AlGaAs in the future. The quartz reactor tube was coated with carbon by decomposing As(CH₃)₃ at 800 °C The DMAC A1(CH₂)₂C1--or TMA were supplied by bubbling high purity He through the liquid of these materials, The AsC1, was also supplied by bubbling He+1%H, through it, and reacted with the DMAC or TMA to produce A1C1, and A1C1.

Temperature of the deposition zone was maintained the same as that of the source zone (700°C-800°C). Deposition can be obtained by introducing H_2 gas from another independent path, since the aluminum chloride is reduced by the H_2 . This is principle of the flat temperature zone method^{5,6)}.

The growth conditions tried so far are as follows;

| | bubbler temperature AsCl ₃ temperature | |
|------------|---|--|
| DMAC: | 13°C, (20°C) 5°C13°C | |
| TMA : | 20°C, 25°C 13°C25°C | |
| flow rates | He for DMAC or TMA 200cc/min | |
| | He + $1\%H_2$ for AsCl ₃ 200cc/min | |
| | H ₂ for by path 200cc/min | |
| | He for Ga chamber 200cc/min. | |

\$4. Results and Discussions

4.1 Growth rate against AsCl₂/TMA ratio

Figure 2 shows the growth rate vs V/III ratio for the case that Al is supplied by TMA. The growth temperature was 755°C. The growth was observed in the V/III ratio range of 0.53<V/III<1.0. When the DMAC was used as the Al source, the V/III ratio was 0.35<V/III<0.48 which was slightly smaller than that for TMA. This is probably due to the fact that the DMAC has Cl atom compared with TMA. The maximum growth rate of 3.2 um/hr was obtained for TMA and AsCl. temperatures of 25°C and 20°C, respectively, (V/III = 0.65).

A cleaved surface of the grown layer observed by SEM is shown in Fig.3(a). The AlAs layer can be clearly observed without staining. The surface of the grown layer was mirror like as shown in Fig.3(b), when the V/III ratio was about 0.65 and the growth temperature was less than 750°C.





Fig.1, Schematic diagram of the single flat temperature zone Chloride VPE system used in this experiments.





Fig.3, (a) SEM photograph of the cleaved surface of the grown layer. (b) Photograph of the grown surface.

The reason why growth is obtained only for a certain range of V/III ratio is inferred as follows: When the partial pressure of $AsCl_3$ is too low, of course, the growth is not obtained. If all the Al is converted to $AlCl_3$, it is expected that the maximum growth rate is obtained when $AsCl_3/DMAC = 0.66$ or $AsCl_3/TMA = 1$, since the following reaction should occurs;

A1(CH₃)₂Cl+(2/3)AsCl₃+H₂=A1Cl₃+(1/6)As₄+2CH₄ (1) A1(CH₃)₃+AsCl₃+(3/2)H₂=A1Cl₃+(1/4)As₄+3CH₄ (2) In the experiments, the maximum growth rates were obtained for AsCl₃/DMAC = 0.43 and AsCl₃/TMA = 0.65. These values are about 2/3 of the estimated values by the above reactions. The reason is not made clear yet, but one possibility is that the aluminum chloride is not only AlCl₃ but also AlCl and about 1/3 of the aluminum chloride produced at the source zone is AlCl. Therefore, the optimum V/III ratio decreases from the values estimated by Eqs.1 & 2.

If the $AsCl_3$ partial pressure becomes too high for forming ($AlCl + AlCl_3$), excess Cl atoms are conveyed to the deposition zone as HCl, and etch the GaAs substrate. Therefore, the etching rate increases quickly with increase of the AsCl₃ partial pressure.

4.2 Dependence on the growth temperature

Growth rate against inverse of absolute temperature is shown in Fig.4. The Al source is and the bubbler temperatures of TMA and TMA AsC1, were 25°C and 20°C, respectively. For temperature range less than 760°C, the growth rate increases exponentially against the inverse of absolute temperature with increase of the temperature. This means that the growth is kinetically limited in this temperature range even for the AlAs growth as the case of GaAs growth by the flat temperature zone method 6,7). The activation energy estimated from the gradient is 38 Kcal-/mol, which is about 2/3 of that for GaAs growth with the same system '). The growth rate seems to saturate at the temperature range over 770°C, indicating that the growth is diffusion limited in this temperature range.



Fig.4, Growth rate against inverse of absolute temperature. Al source is TMA. Bubbler temperatures are 25°C for TMA and 20°C for AsCl₃.

4.3 Composition profile

An example of composition profile of the AlAs epitaxial layer measured by a sputtering Auger Electron Spectroscopy (AES) is shown in Fig.5. The values are not normalized in this figure. Since a GaAs capping layer is not grown, the surface of the epitaxial layer is oxidized, but the inside seems to be a perfect AlAs. At the interface, Al composition increases gradually over about 150 nm instead of an abrupt change. We have to investigate furthermore whether this is inherent to this growth system or can be solved by changing the growth condition and the reactor tube shape. However, since InGaAsP laser diode can be grown by the hydride VPE by adopting a sophisticated reactor chamber⁸⁾, the same abruptness and the same kind of thin layers should be obtained for AlGaAs layers grown by the Chloride VPE, once AlAs layer is proved to be grown by a chloride transport method.

When the composition of AlAs layer is measured by the AES, a few % of oxygen is always detected, but this does not necessarily mean that the oxygen actually exists in the grown layer, because a few % of oxygen was detected even in established MBE grown AlAs. During the sputtering by Ar, the surface of AlAs layer is thought to be oxidized by residual oxygen gas in the measurement chamber.

4.4 Electrical properties of the grown layer

The Hall measurement was performed on an AlAs layer grown on a semi-insulating GaAs substrate by putting electrodes directly on the AlAs layer. The growth conditions and thickness are as follows: DMAC=13 C, $AsCl_3=7^{\circ}C$, growth temperature = 785°C, thickness=2µm. Only one AlAs layer has been measured so far, but the results are as follows: Carrier density is 1.5×10^{15} cm⁻³, and mobility is 482 cm²/V.sec. The mobility is high enough compared with the one ($\mu = 294$ cm²/V.sec) reported so far on an epitaxial AlAs layer(2), so the quality of the grown layer is thought to be reasonbly good.

\$5. Summary

It was demonstrated that AlAs layer can be grown at relatively low temperatures (700°C-800°C) by Chloride VPE method without using poisonous AsH₂ gas for the first time.

Al was supplied as DMAC --Al(CH₃)₂Cl-- or TMA --Al(CH₃)₃--, and As was as AsCl₃. The growth was obtained for 0.35 < AsCl₃/DMAC < 0.48 and 0.53 < AsCl₃/TMA < 1.0. For a larger V/III ratio, gas etching occurred. The growth rate was 2 - 4 um-/min. Growth was kinetically limited when the growth temperature is less than 760°C, and the activation energy was 38 Kcal/mol. The surface was mirror like in this temperature range.



Fig.5, Composition profile of the AlAs layer measure by a sputtering AES.

Acknowledgments

The authors would like to express their sincere thanks to Profs. H.Seki and A.Koukitsu for their valuable suggestions on thermodynamic calculations and experiments, and to Prof. M.Kawabe and Mr. Shimizu for their help on the AES measurements.

This work was supported by the Scientific Research Grant-in-Aid for Special Project Research on "Alloy Semiconductor Electronics," from the Ministry of Education, Science and Culture of Japan.

Reference

- M.Ettenberg, A.G.Sigai, A.Dreeben, and S.L. Gilbert, J. Electrochem. Soc. <u>118</u>, 1355 (1971)
- 2) A.G.Sigai, M.S.Abraham, and J.Blanc, J. Electrochem. Soc. <u>119</u>, 952 (1972).
- K.H.Bachem and M.Heyen, GaAs and Related Compounds, Viena, 1980, p65.
 K.M.Bachem and M.Heyen, J. Crystal Growth,
- K.M.Bachem and M.Heyen, J. Crystal Growth, 55, 330 (1981).
- 5) A.Koukitsu, H.Seki, and M.Fujimoto, Japan. J. Appl. Phys. <u>15</u>, 1591 (1976).
 6) A.Koukitsu, S.Kouno, K.Takashima, and H.Seki,
- 6) A.Koukitsu, S.Kouno, K.Takashima, and H.Seki, Japan. J. Appl. Phys., <u>23</u>, 951 (1984).
 7) F.Hasegawa, T.Yamate, T.Yamamoto, Y.Nannichi,
- 7) F.Hasegawa, T.Yamate, T.Yamamoto, Y.Nannichi, A.Koukitsu and H.Seki, Japan. J. Appl. Phys., <u>24</u>, 1036 (1985).
- A.Usui, Y.Matsumoto, T.Inoshita, T.Mizutani, and H.Watanabe, GaAs and Related Compounds, Oiso, Japan, 1981, p137.