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High indium incorporation in the growth of InGaAs on (100) GaAs by precursor alternating metalorganic chemical vapor deposition

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Precursor alternating metalorganic chemical vapor deposition에 의한 (100) GaAs 기판위로의 InGaAs 성장시의 높은 indium 유입

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Abstract – High indium incorporation was observed in InGaAs growth by precursor alternating metalorganic chemical vapor deposition (PAMOCVD). A possible mechanism of high indium incorporation into the crystal in PAMOCVD was proposed by considering the decomposition products of gallium and indium precursors, and thus the different adsorption behavior of the decomposed precursor molecules.

요 약 – precursor alternating metalorganic chemical vapor deposition (PAMOCVD)에 의한 InGaAs의 성장시에 높은 indium의 유입이 관찰되었다. gallium 과 indium의 전구물질의 분해의 차이 그리고 이에따른 분해된 전구물질 분자의 흡착행동의 차이를 고려함으로써 PAMOCVD 성장시의 결정내로의 높은 indium유입의 mechanism을 제안하였다.

I. Introduction

$In_xGa_{1-x}As$ is an important material for electronic and optical devices. InGaAs/InP based material system can be used for high electron mobility transistors (HEMTs) [1] and for semiconductor lasers in the infrared range of the optical spectrum [2]. InGaAs/GaAs is also an important material system. If the thickness of the InGaAs on GaAs does not exceed the *critical layer thickness*, the lattice mismatch between InGaAs and GaAs substrate can be elastically accomodated. With this strained layer technology, InGaAs/GaAs can be used in fabricating InGaAs/GaAs pseudomorphic HEMTs [1] and InGaAs/GaAs strained layer lasers [2]. Molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) are two most important techniques to grow InGaAs itself and InGaAs-related materials [3]. Due to high throughput and large area uniformity, MOCVD can be considered as the production tool for the fabrication of electronic and optical devices made of InGaAs based III-V compound semiconductors. Trimethylgallium (TMGa), trimethylindium (TMIn), and arsine (AsH_3) are one of the most widely used combinations of precursors for MOCVD growth of InGaAs, and there are many reports on MOCVD growth of InGaAs using TMGa, TMIn, and AsH_3 as the precursors [4].

Precursor alternating metalorganic chemical va-

por deposition (PAMOCVD) is a modification of MOCVD, in which, in case of InGaAs growth, group III precursors, TMGa and TMIn, and the group V precursor, arsine, are alternatively exposed to the substrate. If PAMOCVD growth is performed in a self-limiting regime, in which the growth rate is saturated at 1 monolayer per cycle, it is called as atomic layer epitaxy (ALE). Several advantages such as low temperature growth and high dopant-incorporation [5] made PAMOCVD and/or ALE important techniques in the fabrication of III-V compound semiconductors. With separate supply of group III precursors and group V precursors, and thus less gas phase parasitic reactions between group III and V precursors, PAMOCVD can be usefully used in InGaAs growth, in which thickness and composition uniformity is very difficult to achieve by MOCVD due to the parasitic gas phase reaction of TMIn and AsH_3. Compared with MOCVD, PAMOCVD (or ALE) shows less gas phase parasitic reaction of TMIn and arsine, and thus offers higher composition uniformities [6]. Composition control of ternary alloys such as InGaAs is very important for the fabrication of devices, and it is necessary to investigate the incorporation behavior of constituent atoms into the growing crystals. In this paper, high indium incorporation in PAMOCVD growth of InGaAs is reported, and the possible mechanism of high indium incorporation in InGaAs growth by PAMOCVD is suggested.

II. Experiments

The growth of $In_xGa_{1-x}As$ epitaxial layers was performed in an atmospheric pressure PAMOCVD system, which is described in detail in Ref. [7]. Trimethylgallium (TMGa) and trimethylindium (TMIn) were used for gallium and indium metalorganic precursors, respectively. The precursors were mixed, and then introduced into the reactor through the column III inlet of the reactor. Arsine (AsH_3, 100%) was used as an arsenic source and was introduced into the reactor through the column V inlet. The central flow was maintained to prevent intermixing of column III and column V precursors. Rotation made the substrate exposed alternatively to TMGa+TMIn flux and to AsH_3 flux. The graphite susceptor was heated by RF-induction. Thicknesses of grown layers were measured by optical microscope and confirmed by transmissiom electron microscope (TEM). The composition of the grown InGaAs layers were measured by x-ray diffraction. Hall technique was used to measure types and concentrations of carriers in the grown layers.

III. Results and discussion

Figures 1(a) and 1(d) show variations of compositions x (x^s) and growth rates g_r, respectively, of $In_xGa_{1-x}As$ layers grown by PAMOCVD with the molar ratio of TMIn/(TMGa+TMIn) in gas phase, which can be denoted as x^v. Thicknesses of grown layers were around 1 μm. The left and right vertical axes refer x^s and g_r, respectively. The growth temperature was 480°C, and the total molar flow rate of TMGa and TMIn precursors was kept at 1.2×10^{-5} moles/min. Arsine (100%) flow rate was fixed at 4.1×10^{-4} moles/min. The substrate exposure time to TMGa+TMIn, which was 0.2 sec, was the same as the exposure time to AsH_3. As x^v was varied from 0.26 to 0.5, x^s increased from 0.60 to 0.97. As x^v increased, the growth rate g_r also increased. The dark circle denoted as (b) in figure 1 shows the x^s versus x^v data for $In_{0.53}Ga_{0.47}As$ grown by MOCVD at 540°C, which is from Ref. [8]. Experimental data for lower growth temperatures were not available since it is almost impossible to grow InGaAs of good quality at the growth temperature lower than 540°C by MOCVD. From the comparison of (a) and (b) of figure 1, it can be found that, for $In_xGa_{1-x}As$ with x in the range of our experiments, the indium incorporation in

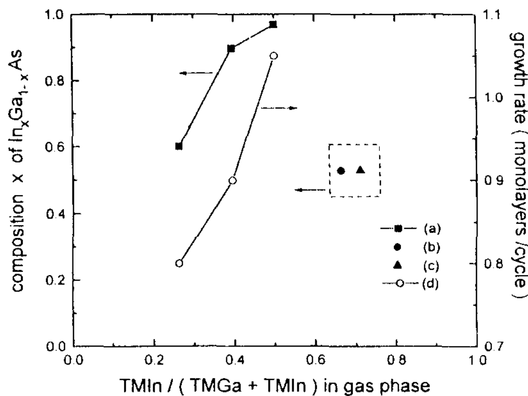

Fig. 1. variations of compositions x (x^s) (a) and growth rates g_r (d) of $In_xGa_{1-x}As$ layers grown by precursor alternating metal-organic chemical vapor deposition (PAMOCVD) with x^v. TMIn+TMGa and arsine exposure time was 0.2 sec, and arsine (100%) flow rate was fixed at 4.1×10^{-4} moles/min. The dark circle (b) shows the x^v versus x^s data for $In_{0.53}Ga_{0.47}As$ grown by MOCVD at 540°C, which is from Ref. [8]. The dark triangle (c) shows x^s versus x^v data obtained with an extrapolated k_{in} value of $In_{0.53}Ga_{0.47}As$ grown by MOCVD at 480°C, which can be estimated from Ref. [8].

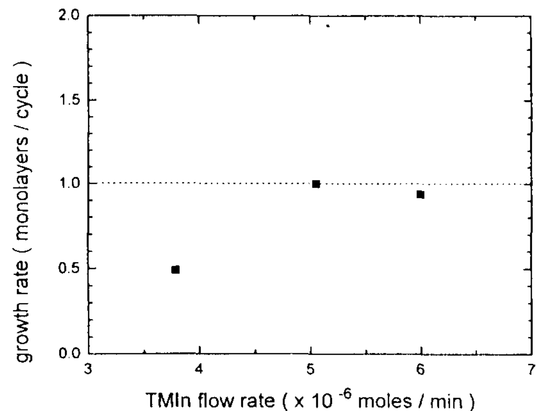

Fig. 2. variation of growth rates of InAs with TMIn flow rates. TMIn and arsine exposure time was 0.2 sec, and arsine (100%) flow rate was fixed at 4.1×10^{-4} moles/min.

PAMOCVD is much higher than in MOCVD *i.e.* PAMOCVD of InGaAs has a much larger indium distribution coefficient, which is defined as $k_{in}=x^s/x^v$, than MOCVD of InGaAs. The reason for this high indium incorporation can be attributed first to the lower growth temperature used in the PAMOCVD growth since k_{in} increases as the growth temperature decreases [8].

The lower growth temperature, however, is not considered to be the main cause of the difference between indium distribution coefficients of PAMOCVD and of MOCVD. The dark triangle denoted as (c) in figure 1 shows x^s versus x^v data obtained with an extrapolated k_{in} value of $In_{0.53}Ga_{0.47}As$ grown by MOCVD at 480°C, which can be estimated from the data in Ref. [8]. Compared even with an extrapolated data for the MOCVD growth at 480°C, the indium incorporation of PAMOCVD is much higher than that of MOCVD. This means that the low growth temperature in PAMOCVD is not the main cause of the high indium incorporation. Since MOCVD is done mostly in the mass-transport limited reaction regime, the composition of the growing crystal is mostly determined by the ratio of decomposed precursor molecules on the growth surface. PAMOCVD, however, is mainly a surface-reaction limited process, and the determination of the composition of the growing crystal involves complicated surface reactions. The main reason why the incorporation of indium into the growing crystal is higher in PAMOCVD than in conventional MOCVD can be possibly investigated by considering the difference in reaction of TMGa and TMIn with the growth surface. Since the PAMOCVD is mostly surface-reaction limited process, identification of decomposed products from TMGa and TMIn precursors can be important in understanding the incorporation process of indium and gallium atoms into the growing crystal. To find the difference between TMIn and TMGa decomposition processes, atomic layer epitaxy of InAs and GaAs was performed using TMIn and TMGa, respectively. The group V precursor was AsH_3 for both cases. Figures 2 and 3 show the variation of growth rates of InAs and GaAs, respectively, with corresponding precursor flow rates. Thicknesses of grown layers were around 1 μm. In case of InAs

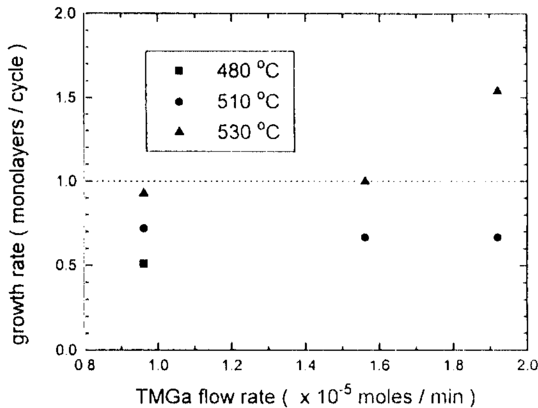

Fig. 3. variation of growth rates of GaAs with TMGa flow rates. TMGa and arsine exposure time was 0.2 sec, and arsine (100%) flow rate was fixed at 4.1×10^{-4} moles/min.

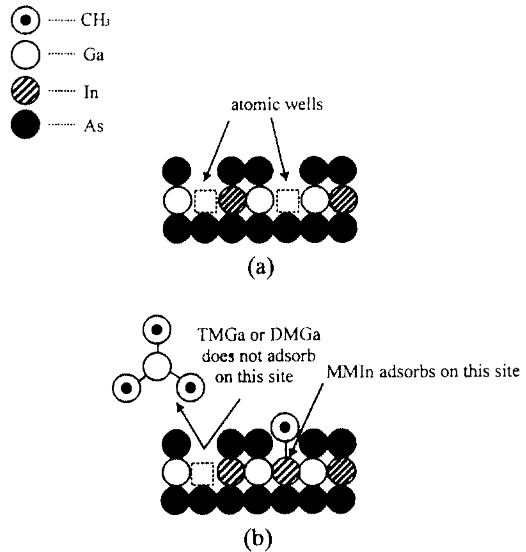

Fig. 4. Schematics of "atomic wells" on the growth surface (a) and the interaction of gallium- and indium-containing molecules with the surface (b). In (b), smaller MMIn can adsorb on the "atomic well" site while larger TMGa and/or DMGa cannot adsorb on "atomic well" sites because they are too large to adsorb on the "atomic wells".

growth at 480°C, the growth rates were saturated at one monolayer per cycle in the TMIn flow rate of 5.0-6.0×10^{-6} moles/min, while the growth rate of GaAs growth at 480°C was less than 1 monolayer per cycle. In case of GaAs growth, the growth rates started to reach 1 monolayer per cycle only at 530°C, at which a region of the growth rate saturation was found. According to the model of GaAs ALE proposed by Nishizawa *et al.* [9], the occurrence of growth rate saturation depends on species of gallium containing molecules on the growth surface.

They proposed that the species on the surface depends on the growth temperature, and the growth rate saturation occurs when monomethylgallium (MMGa) covers the growth surface, while growth rate is less than one monolayer per cycle when dimethylgallium (DMGa) and/or trimethylgallium (TMGa) cover the growth surface due to the large molecular sizes of DMGa and/or TMGa. With the assumption that the same model can be applied to the growth of InAs using TMIn and AsH_3, it can be suggested that the suface-covering species in InAs ALE at 480°C is monomethylindium (MMIn), while that in GaAs ALE at 480°C is dimethylindium (DMGa) and/or trimethylgallium (TMGa). Since DMGa and TMGa molecules are much larger than MMIn, it is much more difficult for DMGa and TMGa molecules to be adsorbed on the growing surface, especially at "atomic wells" as shown in figure 4, than for the MMIn molecules. The density of "atomic wells" on the growth surface can be quite large. DMGa and TMGa are bigger molecules and gallium in DMGa or TMGa adsorbs on every several lattice-sites [9]. Lattice-sites all of whose closest neighbor lattice-sites are occupied by DMGa or TMGa may not have any gallium- or indium-containing species adsorb on them. Accordingly, after gallium from the adsorbed DMGa or TMGa molecules incorporated into the crystal through the reaction with subsequently supplied AsH_3, many atomic wells can be formed on the lattice-sites which were surrounded by lattice-sites having DMGa or TMGa on. The "steric hindrance" effect [10] on DMGa and/or TMGa adsorptions on the growth surface,

especially on the "atomic well" sites, can result in much less incorporation of gallium into the growing crystal, and thus in much higher indium incorporation into the crystal. In case of MOCVD, in which TMGa, TMIn and AsH_3 are introduced into the reactor simultaneously, TMGa and/or DMGa may react with arsenic-containing molecules, and gallium atoms may have more chance of incorporating into the crystal. Easier adsorption of indium-containing molecules on the growth surface than that of gallium-containing molecules in PAMOCVD can also explain the experimental result of growth rate (g_r) increase with the increase of x^s. Higher adsorption of indium-containing molecules, which occupy smaller area of the growth surface than gallium-containing molecules, will lead to the increase of total number of indium- and gallium-containing molecules, resulting in higher growth rates. More works such as *in situ* identification of molecular species on the growth surface are needed to clarify the mechanism of the high indium incorporation in PAMOCVD of InGaAs at 480°C. As-grown samples showed n-type conductivity with concentrations around 1×10^{17} cm^{-3}.

IV. Summary

PAMOCVD was used to grow $In_xGa_{1-x}As$. In PAMOCVD growth performed at 480°C, indium incorporation into the growing crystal was much higher than gallium incorporation. Such a high incorporation of indium was suggested to be due to the adsorption difference between monomethylindium (MMIn) and dimethylgallium (DMGa) (or trimethylgallium (TMGa)), which are possible decomposition products of indium and gallium precursors on the growth surface at 480°C.

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