METALORGANIC CHEMICAL VAPOR DEPOSITION OF GaN_xAs_{1-x} ALLOYS USING TMGa, DMHy, AND TDMAAs

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ABSTRACT
GaN_xAs_{1-x} films have been successfully grown on GaAs substrates by metalorganic chemical vapor deposition (MOCVD) using trimethylgallium (TMGa), dimethylhydrazine (DMHy), and tris-dimethylaminoarsenic (TDMAAs). Decomposition process of TMGa, DMHy, and TDMAAs had been studied to understand the mechanics aspect for Ga, N, and As resulted. Nitrogen concentration in the films was determined by high-resolution x-ray diffraction measurements (HR-XRD). The measured nitrogen concentration was different in each sample if the ratio of DMHy and TDMAAs was different too.

Keywords: MOCVD, TMGa, DMHy, TDMAAs, HR-XRD

INTRODUCTION

Due to the large band gap bowing of GaN_xAs_{1-x}, makes it promising candidate for a wide range of semiconductor applications. Dilute nitride-based (In,Ga) (N,As) heterostuctures are promising for optoelectronic devices, such as lasers in the spectral range 1.3 – 1.55 μm with high-temperature performance [1]. Several researchers have demonstrated that metalorganic vapor phase epitaxy (MOVPE) is a promising technique for GaInNAs growth using DMHy as N sources [1-4]. DMHy is expected to have a lower pyrolysis temperature than that of NH_3, which enable the growth of high N concentration. In contrast, the optical characteristics are found to deteriorate with increasing N concentration [4].

In the search for alternative for group-V sources to replace the hazardous AsH_3 in MOMBE (metalorganic molecular beam epitaxy), TDMAAs has emerged as an excellent candidate, which release As at low temperature (250-450°C) [5-6]. Decomposition products of TDMAAs are As, reactive amino groups like $N(CH_3)_2$, aziridine ($HN(CH_2)_2$) and atomic hydrogen. Highly reactive amino groups react with other reactive hydrocarbons (from i.e. TMGa) forming volatile molecules and significantly reduce the amount of incorporated carbon impurities in GaAs [7].

TMGa is widely used as precursor in the epitaxial growth of GaAs from organometallic source. TMGa is commonly employed in the MOVPE growth process with low carbon incorporation levels resulting from the grown material [8]. In contrast, the use of TMGa in ultra high vacuum growth techniques such as chemical beam epitaxy (CBE) and MOMBE, leads to high very levels of carbon incorporation, which acceptor concentration ranging typically from 10^{19} – 10^{21} cm^{-3} [9]. Although such high acceptor levels are useful for certain specific application, it is generally more desirable to grow GaAs-based material with low impurity levels. Consequently, TMGa is the more commonly used precursors for MOVPE growth.

Concerning to the advantageous of precursors used in the growth of GaAs, in this paper we studied the properties of GaN_xAs_{1-x} films grown by MOCVD using TMGa, DMHy, and TDMAAs. HR-XRD and the standard Van der Paw-Hall effect measurement are applied for the analysis.

EXPERIMENT

GaN_xAs_{1-x} films were grown on (001) GaAs substrate by MOCVD in a vertical reactor. The precursors used were TMGa, DMHy and TDMAAs. The precursors were introduced to the reactor by carrier gas H_2 purified by hydrogen purifier (Palladium diffuser, RSI-10). Semi-insulating GaAs (001) substrates were solvent cleaned and then etched in a 4:1:1 solution of H_2SO_4, deionized water, and H_2O_2 in temperature of 70°C for 30 second [10]. After loading in the growth reactor, samples were cleaned for 10 minutes at 650°C under N_2 flux to desorb remaining surface contaminants. GaN_xAs_{1-x} films of 1.2 – 2.4 μm thick were grown at temperatures of 560 – 590°C for 90 minutes. To obtain variation of N concentration, ratio of DMHy and TDMAAs were varied between 0.8–1.0, while ratio of TDMAAs and TMGa varied between of 4-5. During growth the reactor pressure was kept at 50 torr, and flux of dilute gas N_2 and H_2 were set at 300 sccm, respectively. Detailed growth conditions are shown in table 1.

Table 1 Growth conditions and structures of the GaN_xAs_{1-x} films

Sample name	Growth temperature (^oC)	As/Ga ratio	N/As ratio	Film thickness (μm)	N conc.
A	560	4.5	0.8	$1.2x10^{-4}$	5.5
B	570	4.5	0.8	$1.95x10^{-4}$	5.5
C	580	5	0.8	$2.4x10^{-4}$	5.5
D	580	5	1	$1.05x10^{-4}$	4.9

High Resolution x-ray rocking curve measurement was performed using double crystal Phillips x-ray diffractometer (Phillips x'pert triple axis) with λ = 1.54056 Å ($K_{\alpha-1}$). The N composition of GaN_xAs_{1-x} was determined from (115) asymmetric reflections to take into account of strain-induced lattice constant change of the GaN_xAs_{1-x} films [11]. In order to determine the lattice parameter of the films perpendicular ($a_\perp$) and parallel (a_{ll}) to the (001) substrates surface, both symmetric and asymmetric reflection are usually measured by the conventional 2θ - θ scan method. However, by HR-XRD the lattice parameter are determined, but not directly determine the N concentration of GaN_xAs_{1-x}. Thus, the calculation of these values requires assumptions on the variation of the lattice parameters and of the elastic constants with x. A linear interpolation (Vegard's law) between the values of the GaAs and cubic type GaN has been commonly assumed to be justified [12].

RESULT AND DISCUSSION

1. Decomposition Process of TMGa

The possible decomposition routes of TMGa (fig. 1) had been studied by Aquino [13] using high resolution electron energy loss spectroscopy (HREELS). Previous desorption experiments [14] have shown that the dominant decomposition route for TMGa at GaAs surface involves the sequential loss of CH_3 groups from the surface, although some CH_3 groups also desorb as MMGa species (route 3). The formation of CH_2 species at elevated temperature indicates an additional decomposition pathway involving hydrogen abstraction from CH_3 groups bonded to the surface (route 2)[15].

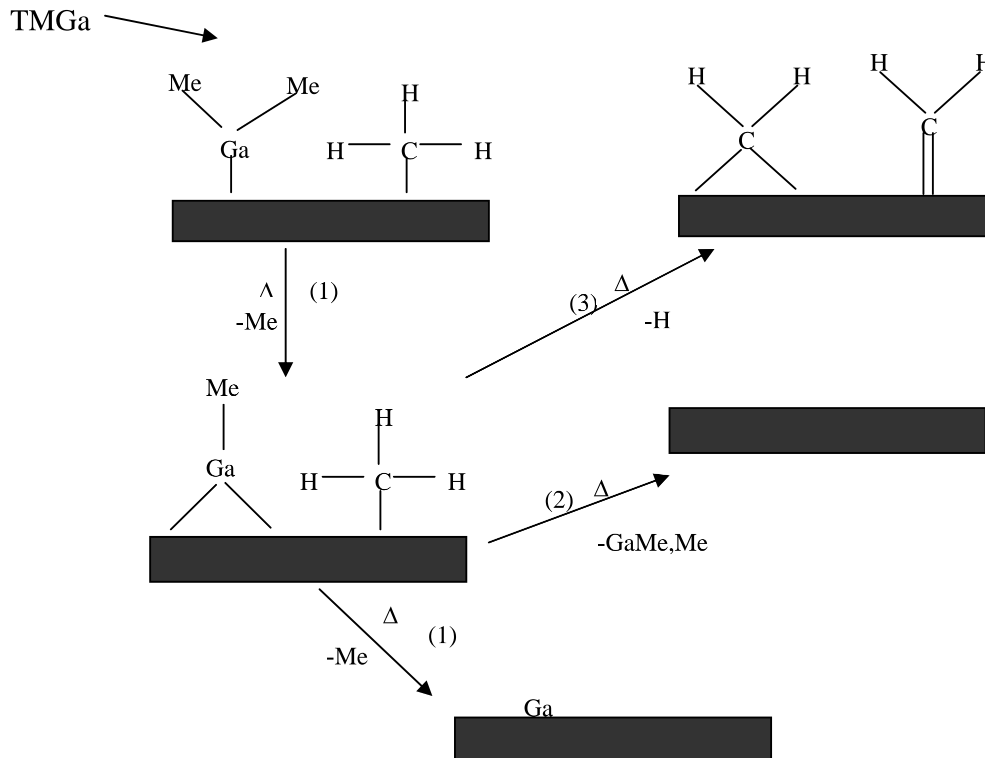

Fig.1. Decomposition pathway for TMGa.

2. Decomposition Process of DMHy

One possible alternate nitrogen source is DMHy. DMHy is a liquid at room temperature with a vapor pressure of approximately 157 torr [16]. Atomic layer growth (ALG) mechanism of AlN (Alumunium nitrida) by Robinson [17] using DMHy source. Fig. 2 summarizes the ALG growth mechanism by showing simplified growth model where only the predominant species that were observed by X-ray photoelectron spectroscopy (XPS) are shown. The initial decomposition of the source on the surface results in the delivery of the nitrogen as NH_x species.

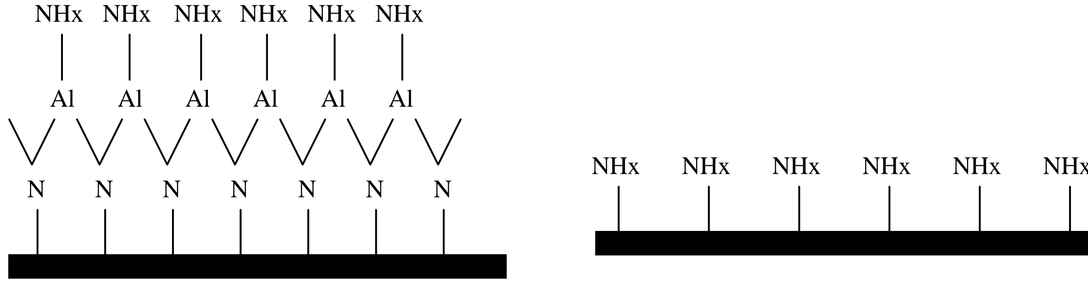

Fig.2. Atomic layer growth model for AlN using DMHy

3. Decomposition Process of TDMAAs

Mechanics aspects of decomposition of TDMAAs had been studied by Whitaker and co. worker [18] using technique of modulated beam mass spectrometry (MMBS). As the substrate temperature is increased above 470°C, a radical change of $AsNMe_2^+$ and $AsNMe^+$is observed increase in MMBS signals and As^+ decrease. With reference to the decomposition scheme of TDMAAs (fig. 3), there appear to be an increase in the desorption of high mass As-containing species (steps 1, 3, 5) at the expense of decomposition to form As atoms (step 6). Steps 2 and 4 probably continue to occur. It is also conceivable that the recombination of As and amine species (step 7) occurs at the expense of desorption of As (step 8).

Ga, N, and As resulted from decomposition of TMGa, DMHy, and TDMAAs is expected form GaN_xAs_{1-x} film on GaAs substrate with good quality.

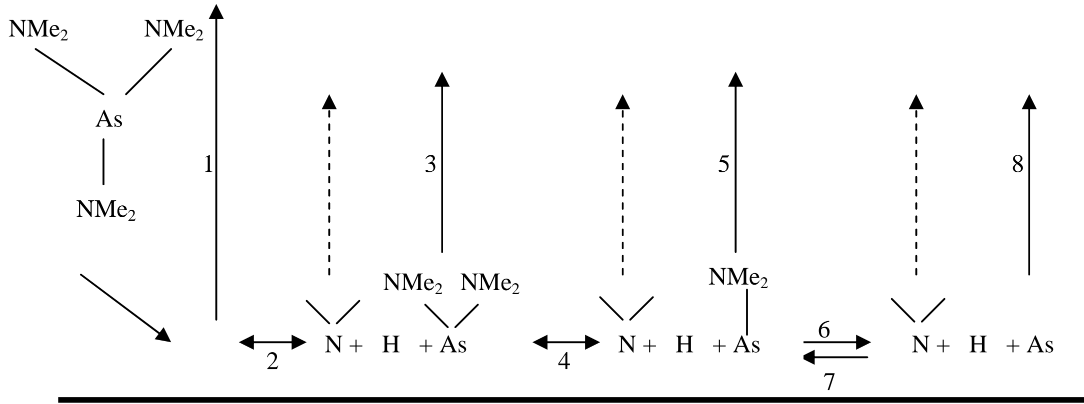

Fig.3. Decomposition scheme for TDMAAs.

4. Structural and Electrical Properties of GaN_xAs_{1-x} Films

Fig. 4 shows the GaN_xAs_{1-x} growth rate plotted as a function of the resiprocal substrate temperature. The GaN_xAs_{1-x} growth rate is strongly dependent on substrate temperature in the range of 560 to 590°C. For these conditions, the TMGa, DMHy and TDMAAs flow rate kept at 0.11, 0.4, and 0.5 sccm, respectively. Growth starts at about 560 ^{o}C, and the growth rate increases as the substrate temperature increases until it reaches 580°C. An Arhenius [19] curve fit to the growth rate data yields activation energy of 150.91 kJ/mol.

Fig. 5 shows a typical HR-XRD (004) rocking curve of GaN_xAs_{1-x} film. To calculate N concentration, asymmetric reflection was measured. It is well known that the inclination between the asymmetric plane of the substrate and that of the film is usually observed if the film is subject to a tetragonal distortion [20]. Lattice constant of cubic GaN_xAs_{1-x} films is expressed by:

$$a_0 = a_{ll}\left(1 - \frac{c_{11}}{c_{11} - 2c_{12}} \frac{a_{ll} - a_{\perp}}{a_{ll}}\right) \tag{1}$$

Where, C_{ll} and C_{12} are the elastic constant for GaN_xAs_{1-x} films. The N concentration, x, is estimated from a_0 assuming Vegard's law:

$$x = \frac{a_o - a_{GaAs}}{a_{GaN} - a_{GaAs}} \qquad (2)$$

Where, a_{GaN} is the lattice constant of cubic GaN (4.50 Å). Since the elastic constant of GaN_xAs_{1-x} is not available, linear interpolation was used for GaAs and cubic phase GaN. As for the possible bowing of the GaN_xAs_{1-x} elastic constant, the maximum error for the 5% N concentration was estimated by assuming the extreme cases of GaAs and GaN elastic constants, which were 5.06% and 4.52%, respectively. The N concentration calculated in this way showed good agreements with N concentration measured by SIMS (secondary ion mass spectroscopy) [21]. It was carried out that the GaN_xAs_{1-x} N concentration were in the range of 4.9 – 5.5%, and the lattice constant were 5.5975 and 5.5911 Å, respectively.

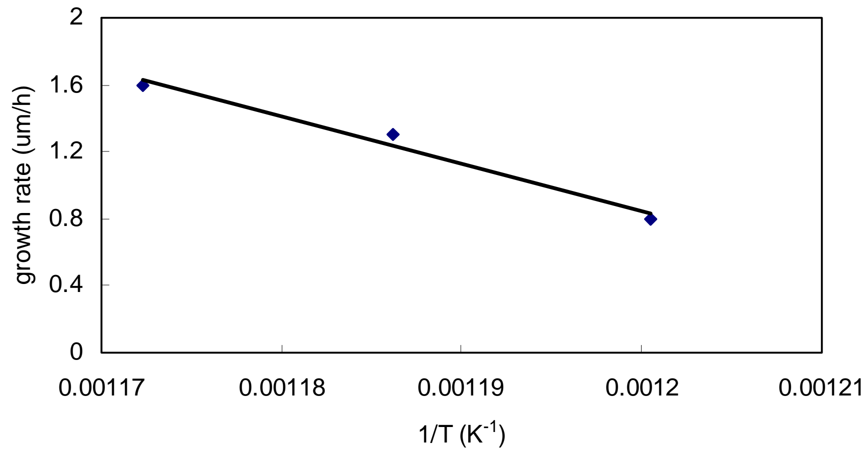

Fig.4. Growth rate of GaN_xAs_{1-x} films

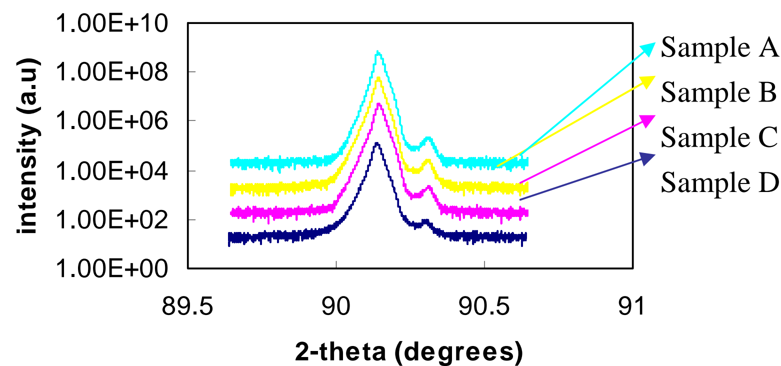

Fig. 5. Asymmetric reflection of HR-XRD of GaN_xAs_{1-x} films

For these measurements, we can see that there is no influence from the difference growth temperature and As/Ga ratio to N concentration in GaN_xAs_{1-x} film (sample A and B). N concentration in GaN_xAs_{1-x} film only influenced by variation of N/As (sample C and D).

CONCLUSIONS

Temperature of growth is strongly influence growth rate of these films. It revealed that the higher growth temperature the higher growth rate. The crystalline structures of GaN_xAs_{1-x} films grown on GaAs (001) substrates by MOCVD were studied by HR-XRD measurements. The N concentration of GaN_xAs_{1-x} films had been calculated using Vegard's law from symmetric and asymmetric reflection and it found that in our sample x is in the range of 4.9 – 5.5 %.

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