High Mobility and High N concentration of GaN_xAs_{1-x} Thin Films Grown by Metal Organic Chemical Vapor Deposition

I. Hamidah[1)], A. Suhandi[1)], A. Setiawan[1)], and P. Arifin[2)]

[1)] Physics Laboratory, Dept. of Mechanical Engineering, Indonesia University of Education
Jl. Dr. Setiabudhi No. 229 Bandung 40154 Indonesia. Phone/Fax: 62-22-2020162
[2)] Lab. For Electronic Material Physics, Dept. of Physics, Bandung Institute of Technology
Jl. Taman Sari No 10 Bandung 40132 Indonesia, Phone/Fax: 62-22-2511848

Abstract*- GaN_xAs_{1-x} thin films had been successfully grown on semi-insulating GaAs (001) substrates by metal organic chemical vapour deposition (MOCVD) method. The precursors used were trimethylgallium (TMGa), dimethylhydrazine (DMHy), and tris-dimethylaminoarsenic (TDMAAs). GaN_xAs_{1-x} thin films of 1.2 – 2.4 μm thick were grown at the total reactor pressure of 50 torr, H_2 and N_2 flow rate of 300 sccm, temperatures range of 560 – 590°C, and the ratio of TDMAAs/TMGa and DMHy/TDMAAs flow rate of 4.5 and 0.8, respectively. The growth rate of GaN_xAs_{1-x} thin films are in the range of 0.8 - 1.6 μm/h. The N concentration of GaN_xAs_{1-x} thin films was studied by HR-XRD measurements and was calculated using Vegard's law from symmetric and asymmetric reflection. From this study, it found that the N concentration of GaN_xAs_{1-x} thin films were in the range of 4.9 and 5.5%. The measured electron mobility using Hall-van der Pauw method is in order of 3270 and 3380 $cm^2 V^{-1} s^{-1}$ at x = 4.9% and 5.5%, respectively.

I. INTRODUCTION

The ternary alloy GaN_xAs_{1-x} has attracted increasing interest in past few years both because of practical and fundamental points of view. It is because of their very unique physical properties and wide range of possible device applications such as optical interconnections, fast switching systems, and low band gap detector. More recently, promising results have been obtained in light emitting devices with wavelengths in the 1.3 or 1.55 μm with high temperature performance [1], due to large conduction band offsets between barrier and quantum well.

All long wavelength lasers grown today are fabricated using InGaAsP on InP. The high temperature performance of this laser is still unsatisfactory compared with that of short wavelength GaAs-based laser diodes (LDs). In past few years, (In)GaN_xAs_{1-x}, which could be grown lattice matched to GaAs substrate, was found to have a band gap in the telecommunication range of wavelength [2,3], with excellent high temperature performance for use in optical-fibre transmission systems.

Unlike all conventional ternary III-V semiconductor alloys, where the band gap energy of the alloy can be reasonably approximated as a weighted linear average of the band gaps of the parental binary compounds, the band gap of GaN_xAs_{1-x} has anomalous composition dependence. The concentration of nitrogen into GaAs drastically reduces the band gap. For example, the addition of only 2% of nitrogen to GaAs causes a dramatic decrease in band gap energy by about 0.4 eV [4], due to large electro negativity of N. By optimizing N concentration will vary the lattice constant of GaN_xAs_{1-x}, provide an opportunity to synthesize GaN_xAs_{1-x} that are lattice matched to Si. This will fulfill a long-sought desire for fabrication of optoelectronic and photonic devices based on the most-developed and most-mature Si technology, which not only offers advantages of the large-scale and low-cost fabrication, but also opens the door for integration of optoelectronic and microelectronic devices on a chip.

To obtain the high N concentration in GaN_xAs_{1-x}, the precursors used were TMGa, DMHy, and TDMAAs. The choice of precursors based on their advantages that are: TMGa is one alternative precursor because it has low pyrolysis temperature [5]. The advantage of DMHy compared to the often employed ammonia (NH_3) as precursor of atomic nitrogen, is its low decomposition temperature [6]. Consequently, no modification of MOCVD growth apparatus is required. TDMAAs is a precursor that does not need pre-cracking and has no direct As-H bonds which is believe has high toxicity and has no As-C bonds which cause low mobility [7]. However, N concentration in GaAs is difficult due to the large miscibility gap of the alloy. In addition, epitaxial growth of GaN_xAs_{1-x} still remains a problem, because the crystal quality deteriorates for higher N concentration leading to a remarkable degradation of the optical and electrical characteristics [8]. To date, in order to improve optical quality of GaN_xAs_{1-x}, two methods are mainly used those are ex situ rapid thermal annealing (RTA) and in situ rapid thermal annealing in a growth reactor [9].

The properties most studied of GaN_xAs_{1-x} are focused on its physical and optical properties, but few study about of GaN_xAs_{1-x} electrical properties. In this study, by using HR-XRD, we tried to clarify the influence of DMHy/TDMAAs ratio on the N concentration. In addition, using Hall-van der Pauw method, we investigated the influence of N concentration to the growth rate and the mobility of

GaN_xAs_{1-x} thin films grown by MOCVD.

II. EXPERIMENTAL PROCEDURE

GaN_xAs_{1-x} thin films were grown by MOCVD in a vertical reactor. The precursors (TMGa, DMHy, and TDMAAs) were introduced to the reactor by carrier gas H_2 purified by hydrogen purifier (Palladium diffuser, RSI-10). The schematic diagram of the reactor is depicted in fig.1. Semi-insulating GaAs (001) substrates were solvent cleaned and then etched in a 4:1:1 solution of H_2SO_4, de-ionized water, and H_2O_2 at temperature of 70°C for 30 seconds [10]. After loading into the growth reactor, samples were thermally cleaned for 10 minutes at 650°C under N_2 flux to dessorb remaining surface contaminants. GaN_xAs_{1-x} thin 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, while ratio of TDMAAs and TMGa were kept constant (V/III = 4.5), to achieve the optimum growth condition as reported in our previous paper [11]. During the growth, the reactor pressure was kept at 50 torr, and flux of dilute gas N_2 and H_2 were set at 300 sccm.

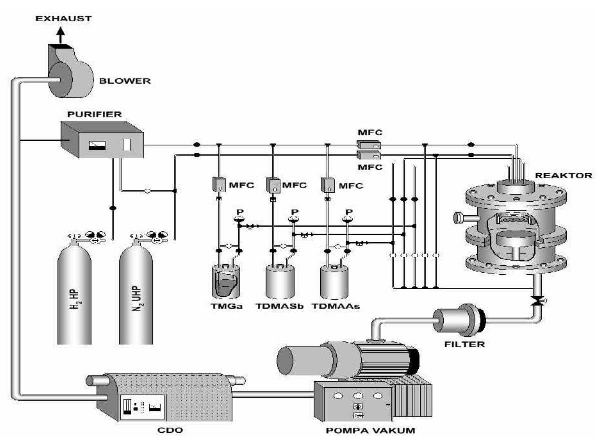

Fig. 1. Schematic diagram of Vertical reactor MOCVD.

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 concentration 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} thin films [12]. 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 GaN has been commonly assumed to be justified [13].

Electrical properties of GaN_xAs_{1-x} thin films, i.e. electron mobility were evaluated by Hall-van der Pauw method at room temperature. To measure these properties, indium paste was used as ohmic contact on films and the magnetic intensity was set in the range of 15 – 60 mT.

III. RESULTS AND DISCUSSION

The GaN_xAs_{1-x} growth rate is strongly dependent on substrate temperature in the range of 560 to 590°C, as shown in fig. 2. For these conditions, the TMGa, DMHy and TDMAAs flow rates were kept at 0.11, 0.4, and 0.5 sccm, respectively. The growth rate starts to increase at 560°C until temperature of 580°C. When the growth temperature is above 580°C, the growth rate decreases due to desorption of atoms of films from the substrate surface. The typical growth rate of GaN_xAs_{1-x} thin films is 1.1 μm/h

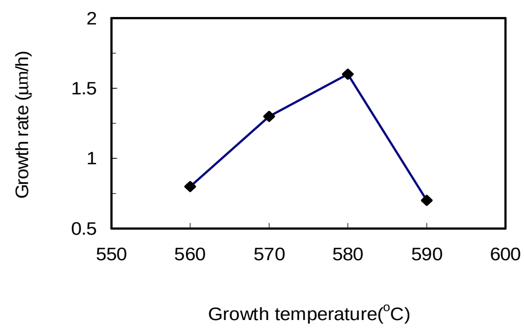

Fig. 2. Growth rate of GaN_xAs_{1-x} thin films.

Fig. 3 shows a typical HR-XRD (004) rocking curve of GaN_xAs_{1-x} thin film. GaN_xAs_{1-x} diffraction intensity peaks are clearly observed. From the separation between the GaAs and GaN_xAs_{1-x} diffraction intensity peaks, $a_\perp$ is estimated to be 5.598 Å and 5.591 Å, using formula:

$$d_{004} = \frac{a_\perp}{4} \qquad (1)$$

To calculate N concentration, asymmetric reflection had been 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 [14]. From the Bragg angle of the GaN_xAs_{1-x} (115) plane in fig. 4, the *d* spacing of the GaN_xAs_{1-x} (115) plane, d_{115}, is estimated to be 1.0865 Å and 1.0864 Å. The lattice parameter parallel to the (001) surface, a_{ll}, is related to the above-determined quantities ($a_\perp$ and d_{115}) by equation:

$$d_{115} = \left(\frac{2}{a_{11}^2} + \frac{25}{a_\perp^2} \right)^{-2} \qquad (2)$$

From this equation, a_{ll} is calculated to be 5.6109 Å and 5.6060 Å, which is close to the lattice constant of GaAs. This shows that GaN_xAs_{1-x} thin films were coherently grown on the GaAs surface. These results show that the asymmetric XRD mapping measurements can precisely determine the three-dimensional crystalline structures of the coherently grown epitaxial films.

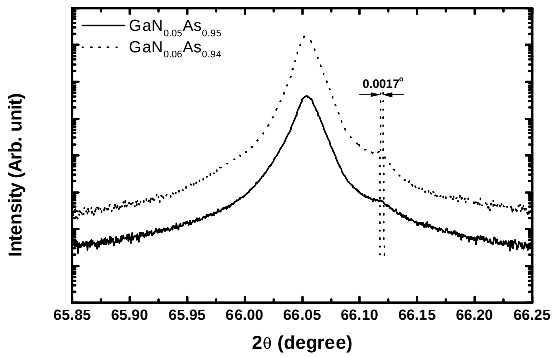

Fig. 3. XRD curve of GaN_xAs_{1-x} (004).

Lattice constant of cubic GaN_xAs_{1-x} thin films is expressed by:

$$a_0 = a_{//}\left(1 - \frac{c_{11}}{c_{11} - 2c_{12}}\frac{a_{//} - a_{\perp}}{a_{//}}\right) \tag{3}$$

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

$$x = \frac{a_o - a_{GaAs}}{a_{GaN} - a_{GaAs}} \tag{4}$$

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 [14]. 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 by this formula showed good agreements with N concentration measured by SIMS (secondary ion mass spectroscopy) [14]. It revealed that the N concentrations of GaN_xAs_{1-x} were in the range of 4.9 – 5.5%, and the lattice constants were 5.5975 and 5.5911 Å, respectively. From these results, we found that the higher concentration of N, the lower lattice constant. By increasing N concentration will decrease the lattice constant of GaN_xAs_{1-x}, provide an opportunity to synthesize GaN_xAs_{1-x} that are lattice matched to Si ($a_0 = 5.45$ Å). The misfit between film and substrate are 0.99 and 1.10 % for N concentration of 4.9 and 5.5%, respectively.

The dependence of the room temperature electron mobility with x in GaN_xAs_{1-x}, measured by standard Hall-van der Pauw method are depicted in fig.5. The measured electron mobility is in order of $3270\ cm^2\ V^{-1}\ s^{-1}$ at x = 4.9% and $3380\ cm^2\ V^{-1}\ s^{-1}$ at x = 5.5%. It can be seen that the mobility increases as the N concentration is increased. These results are agreed with the theory analyzed by Buyanova [4] that is m_e^* decrease if N concentration is increased and finally will enhance the mobility. Compared to the computation calculation using S-matrix theory (Born approximation), given by [15]:

$$\mu^{-1} = \frac{\sqrt{3m^* kT}}{e}\pi\left(\frac{m^*}{2\pi\hbar^2}\right)\left[\frac{dE_c}{dx}\right]^2 a_o^3 x \tag{5}$$

it can be estimated that the electron mobility is constant in the order of $1000\ cm^2\ V^{-1}\ s^{-1}$ for $x \geq 1\%$. The low mobility calculated by this method may be caused by using constant and high m_e^*, that is 0.12 m_e. Factors omitted in the calculation here is the influence of N-N nearest-neighbour pairs and clusters. The low mobility in dilute nitride alloys has significant consequences for potential device applications. For example, the low electron mobility combined with the short non-radiative life-time, limits the electron diffusion lengths and efficiency achievable in GaInNAs-based solar cells.

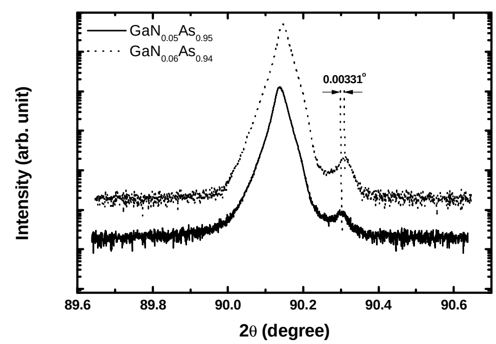

Fig. 4. XRD curve of GaN_xAs_{1-x} (115)

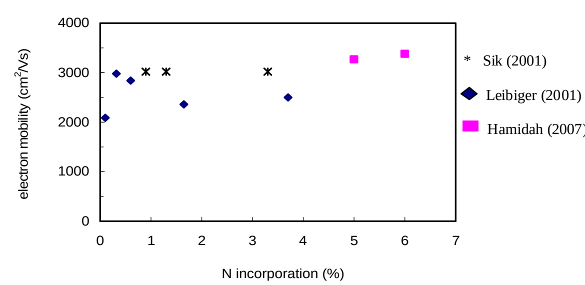

Fig. 5. Room temperature electron mobility, μ, in GaN_xAs_{1-x}.

The values obtained from the Hall-van der Pauw measurement are higher than that found in many samples, i.e. $\mu \sim 100\text{-}400\ cm^2 V^{-1} s^{-1}$ [16,17], but almost the same with the values observed by Leibiger [18] and Sik [19] in the range of 2090 – 3020 $cm^2\ V^{-1}\ s^{-1}$ (fig.5). Finally, the high mobility of the grown GaN_xAs_{1-x} thin films also opens opportunity for application of electronics devices.

IV. CONCLUSION

The growth rate of GaN_xAs_{1-x} thin films is strongly influenced by growth temperature. It revealed that the higher growth temperature the higher growth rate. The N concentration of GaN_xAs_{1-x} thin films was calculated using Vegard's law from symmetric and asymmetric reflection. From this study, it is revealed that the N concentration strongly depend on DMHy/TDMAAs flow ratio. The increase of DMHy/TDMAAs flow ratio, lead to the high N concentration in GaN_xAs_{1-x} thin films. It also revealed that the increase of N concentration will decrease the lattice constant of GaN_xAs_{1-x}, provide an opportunity to synthesize GaN_xAs_{1-x} that are lattice matched to Si. The dependence of the room temperature electron mobility with x in GaN_xAs_{1-x}, show that the mobility increases as N concentration is increased.

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