Effect of Growth Temperature and Mn Incorporation on GaN:Mn Thin Films Grown by Plasma-Assisted MOCVD

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Abstract. In this paper, the growth of GaN:Mn thin films by plasma-assisted metalorganic chemical vapor deposition (PAMOCVD) method is reported. The method used in this study, utilizes a microwave cavity as a cracking cell to produce nitrogen radicals, which in turn reduce the growth temperature. Trimethylgallium (TMGa), nitrogen (N_2) and cyclopentadienyl manganese tricarbonyl (CpMnT) were used as a source of Ga, N and Mn, respectively, while hydrogen gas was used as a carrier gas for both TMGa and CpMnT. The effect of growth temperature and Mn incorporation on structural properties and surface morphology of GaN:Mn films are presented. The growth of GaN:Mn thin films were conducted at varied growth temperature in range of 625 ^oC to 700 ^oC and the Mn/Ga molar fraction in the range of 0.2 to 0.5. Energy dispersive of X-ray (EDX) and X-ray diffraction (XRD) methods were used to analyze atomic composition and crystal structure of the grown films, respectively. The surface morphology was then characterized using both atomic force microscopy (AFM) and scanning electron microscopy (SEM) images.

A systematic XRD analysis reveal that maximum Mn incorporation that still produces single phase GaN:Mn (0002) is 6.4 % and 3.2 % for the film grown at 650 ^oC and 700 ^oC, respectively. The lattice constant and full width at half maximum (FWHM) of the single phase films depend on the Mn concentration. The decrease in lattice constant accompanied by the increase in FWHM is due to incorporation of substitutional Mn on the Ga sub-lattice. The maximum values of doped Mn atoms incorporated in the wurtzite structure of GaN:Mn as substitutional atoms on Ga sub-lattice are 2.0 % and 2.5 % at 650 ^oC and 700 ^oC, respectively. AFM and SEM images show that the film grown at lower growth temperature and Mn concentration has a better surface than that of film grown at higher growth temperature and Mn concentration.

Keywords: *GaN:Mn; PA-MOCVD; EDX; XRD; AFM; SEM.*

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1 Introduction

In recent years, ferromagnetism in diluted magnetic semiconductors (DMS's) have attracted great interests due to potential applications in spintronics, in which make it possible to combine the information processing and data storage in one material [1]. In spite of the potential attraction, low solubility of magnetic element (Mn) in the compounds such as GaAs and GaN makes it difficult to fabricate ferromagnetic III–V semiconductors and is known to be a major obstacle to overcome for the practical applications [2]. The magnetic effects on DMS's are roughly proportional to the concentration of the magnetic ions (Mn), therefore it is very important to suppress the formation of the secondary phase containing Mn [3].

Most of the initial works in DMS have focused on II-VI semiconductors in which a fraction of the group II sub-lattice was randomly replaced by Mn atoms [1]. In these materials, the presence of magnetic ions influences the free carrier behavior though the sp-d exchange interaction between the localized magnetic moments and the spins of the itinerant carriers. For practical application, DMSs are required to have two essential features: a Curie temperature (T_C) higher than room temperature and to be based on a typical semiconductor for which the carrier control technique is well established [4]. From this viewpoint, III-V-based DMSs can be considered promising materials for spintronics.

Recently, effort in the development of GaN:Mn based DMS has mainly focused on the improving of materials preparation. This paper reports the successfully growth of GaN:Mn material by plasma-assisted MOCVD method, in which requires growth temperature lower than that of conventional MOCVD, which is in range of 625-700 °C. The characteristics of the resulting films depend on the growth parameters used. Since MOCVD is generally regarded as the optimal technique for the growth of high quality III-nitrides, it is desirable to be able to produce ferromagnetic GaN:Mn by this method. The PA-MOCVD reactor is equipment extended in this work from the previous conventional MOCVD reactor by incorporating microwave cavity as a cracking cell to produce nitrogen radical instead of N_2, so that the growth temperature can be reduced.

In this work, the growth of GaN:Mn thin films PAMOCVD method is reported, with emphasize to the effect of growth temperature and Mn incorporation into GaN:Mn thin films on their structural properties and surface morphology. The concentration of Mn doped into a GaN semiconductor was determined by EDX analysis. A systematic XRD analysis was used to determine whether the grown films are to be attributed to the pure diluted GaN:Mn phase or not. In addition, the surface morphology of the films was then characterized using both AFM and SEM images.

2 Experiment

The MOCVD reactor consists of a water-cooled stainless-steel vertical reactor equipped with plasma-cracking cell. The combination of a root blower pump and a rotary vacuum pump were used as a pumping system. By using low power downstream plasma cavity (ASTeX), N-reactive was supplied from N_2 gas downward to the substrate. The plasma itself was generated by 2.45 GHz microwave at power of 200 W and was applied through a coaxial cable. The growth temperature is then monitored by a thermocouple inserted inside the heater. Gases were injected into the chamber from inlet located at the top of the reactor. Pneumatic valves were used to control the gas flow through the vent where the pressures of each gas lines were monitored. Mass flow controllers (MFC's) were used to determine the number of moles of TMGa, CpMnT and N_2 introduced into the chamber. The atomic composition of the film was determined from electron dispersive X-ray (EDX) measurement, while the surface morphology was analyzed using atomic force microscopy (AFM) and scanning electron microscopy (SEM) images. The structural properties and crystal orientation were investigated by means of X-ray Diffraction using CuK_{α} radiation.

The growth of GaN:Mn was performed on *c* plane sapphire substrate in a microwave inductively heated vertical MOCVD reactor. Trimethylgallium (TMGa) and high purity (99.99%) nitrogen were used as a source of gallium and nitrogen, while cyclopentadienyl manganese tricarbonyl (CpMnT) was used to dope the epilayers with manganese. The low temperature GaN buffer layer was grown at 500 ^{o}C for 10 minutes. The purpose of the GaN buffer layer is to overcome lattice mismatch between *c* plane sapphire substrate and the grown films. The growth parameters of GaN:Mn, including growth temperature, V/VIII flux ratio and Mn/Ga molar fraction were varied in the range of 625 to 700 °C, 440 to 1080 and 0.2 to 0.5, respectively. The operating pressure was set to 0.7 Torr. The growth was conducted for 2 h and the thickness of the films was 0.3 - 0.5 μm.

3 Results and Discussion

Ferromagnetic semiconductor GaN:Mn thin films have been successfully grown by PA-MOCVD method. EDX measurements clearly demonstrated the existence of the Mn atoms in the GaN:Mn thin films grown at 650 - 700 ^{o}C, depends on the Mn/Ga molar fraction. The higher molar fraction of Mn/Ga flux leads to the higher Mn incorporation into GaN:Mn thin film. At 625 ^{o}C of growth temperature, there is no Mn incorporation into GaN epilayer, because at this low temperature the growth is controlled by kinetics of chemical reactions which are highly depend on the thermal energy occurring at the substrate

surface. Meanwhile the thermal energy at this temperature is not high enough to produce chemical reaction needed for Mn incorporation into GaN epilayer.

The films grown at 650 ^{o}C with Mn concentration between 1.4 – 6.4 % were then analyzed using XRD system to determine their structural properties and crystal orientations. Here only peak associated with single phase of GaN:Mn (0002) was observed in addition to that of the sapphire substrate (Figure 1). Therefore, the maximum Mn concentration that can produce a single phase GaN:Mn is 6.4 % for 650 ^{o}C of growth temperature. Compared to the GaN peak, GaN:Mn films with 1.4 %, 2.0 % and 6.4 % of Mn concentration show the peak shifts at 2θ = 34.64, 2θ = 34.73 and 2θ = 34.61, respectively, which indicate a single phase wurtzite structure of GaN:Mn (0002). The highest value of the peak shift, i.e. ~ 0.16^{o}, was achieved by GaN:Mn film with 2,0 % of Mn concentration. The resulted peak shifts are lower than that of GaN:Mn film grown using ion implantation method, i.e. 0.357^{o} for 1.5 % of Mn concentration [5].

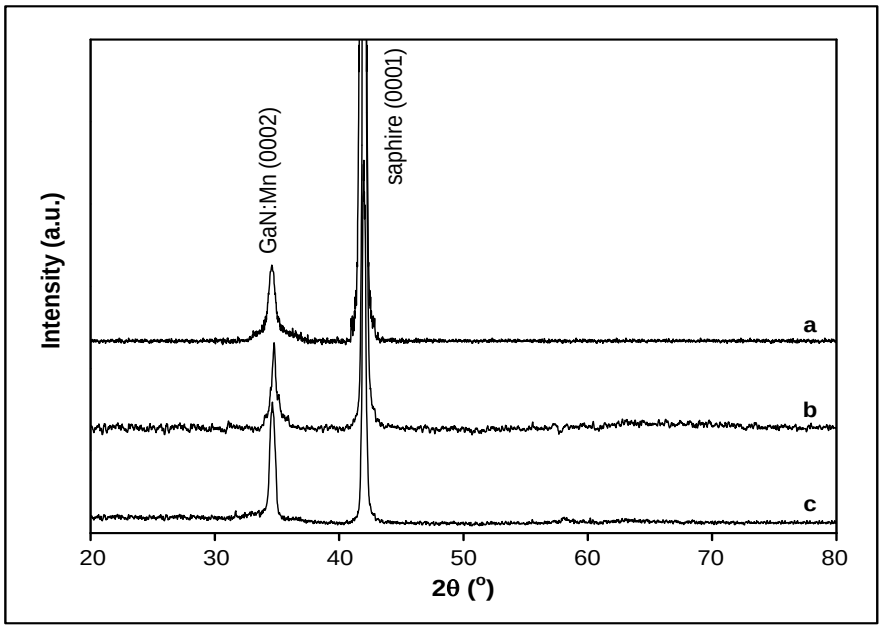

Figure 1 The XRD pattern of GaN:Mn for films grown at 700 ^{o}C with (a) 1.4 %, (b) 2.0 %, and (c) 6.4 % of MN concentration.

As the growth temperature is changed to 700^{o}C, the single phase of GaN:Mn can be observed for GaN:Mn films with Mn concentration up to 3.2 %. For a higher Mn concentration (i.e. 6.4 %) another peak begins to appear that is associated with Ga_xMn_y (Figure 2). The appearance of this second peak in the

XRD pattern is convinced due to structural degradation of the film due to nitrogen vacancy formation at high temperature.

The maximum Mn concentrations that can produce a single phase of GaN:Mn (0002) resulted in this work (6.4 % and 3.2 % at 650°C and 700°C, respectively) are higher compared to MOCVD-grown GaN:Mn films reported by other groups, i.e. 1.9 % [6] and 2.3 % [7].

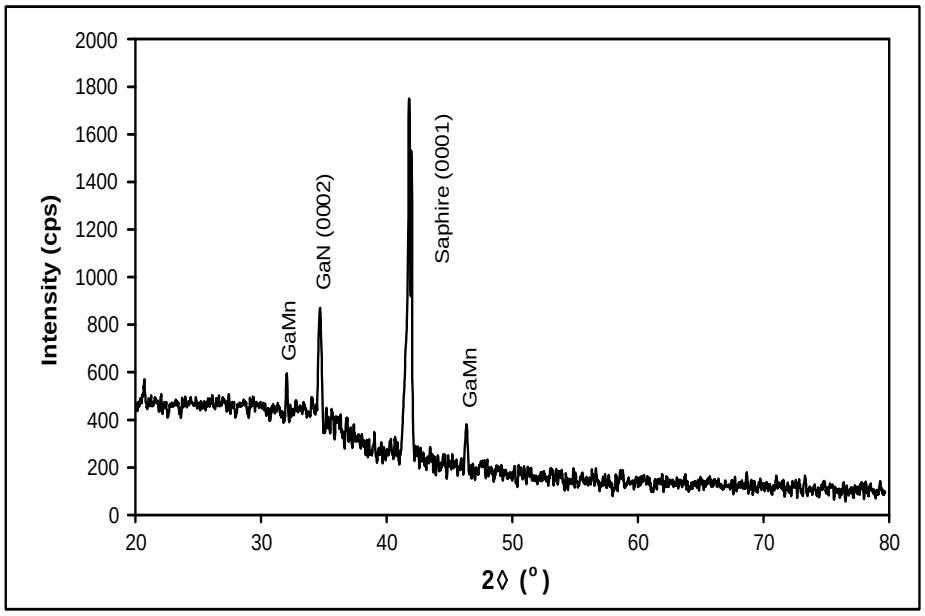

Figure 2 The XRD pattern of GaN:Mn for film grown at 700 °C with 6.4 % of Mn concentration.

Additional information about the structure of the GaN:Mn films are shown in Figure 3 and Figure 4, where the *c* plane lattice constant and full width half maximum (FWHM) are plotted versus the Mn concentration. The lattice constants of the single phase films grown at different growth temperature were found to vary with Mn concentration. The lattice constant of GaN:Mn films decrease when compared to an undoped GaN film grown under similar conditions. The decrease in lattice constant is due to incorporation of Mn substitutionally on the Ga sub-lattice. However, as the Mn concentration is increased beyond 2.0 % and 2.5 % for the films grown at 650 °C and 700 °C, respectively, the lattice constant began to increase. It indicates that all doped Mn atoms are incorporated in the wurtzite structure as substitutional atoms on Ga sub-lattice only for the GaN:Mn films with Mn concentration of $\leq$ 2.0 %

and $\leq$ 2.5% at 650 ^{o}C and 700 ^{o}C, respectively, leading to the solid solution GaN:Mn structure.

The FWHM values as shown in Figure 4 and Figure 5 tend to increase with increasing Mn concentration until 2% and 2.5 % at 650 ^{o}C and 700 ^{o}C of growth temperature, respectively. The maximum value of FWHM for different growth temperature occurs at the minimum in lattice constant. This supports the previous argument that at this Mn concentration, for a certain growth temperature, the GaN:Mn films are at maximum solubility for substitutional Mn in the Ga site [8]. Therefore the maximum solubility for substitutionaly Mn on Ga sublattice in GaN:Mn are 2.0 % and 2.5 % at 650 ^{o}C and 700 ^{o}C, respectively. These resulted values are higher than that of MOCVD-grown GaN:Mn films reported i.e. 1.5 % [6] and 1.8 % [7].

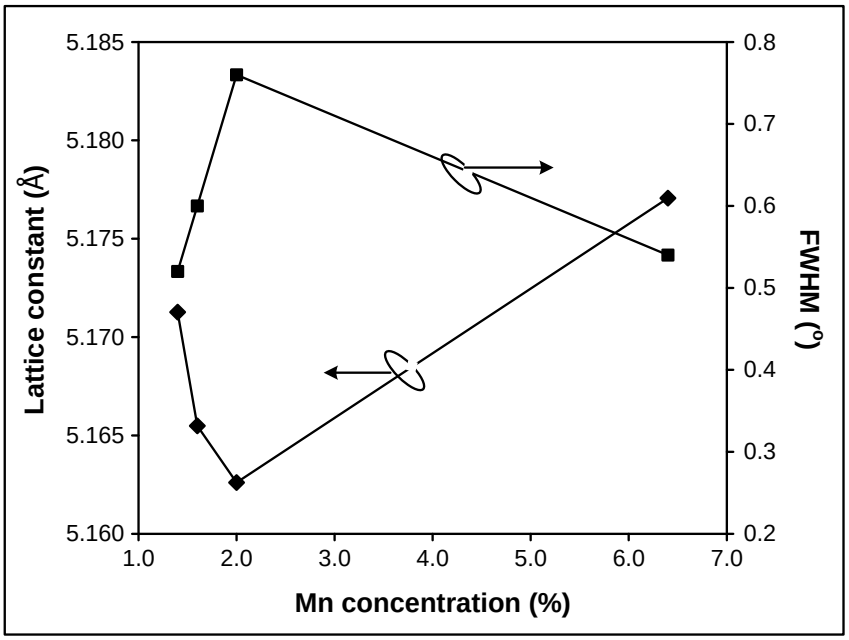

Figure 3 Lattice constants and FWHM values for single phase of GaN:Mn films grown at 650 ^{o}C.

The lattice constant of each sample shrinks up to 4.5 % compared to the undoped GaN sample grown at the same conditions, i.e. 0.56988 leading to the lattice contraction. These results are slightly lower than that of GaN:Mn film grown by MBE method, i.e. 0. 5% for 0.5 % of maximum Mn concentration [9] and indicates that the grown films are elastic. The elasticity of the films is considered due to the low growth temperatures

used in these works and the GaN:Mn and sapphire substrate lattice mismatch.

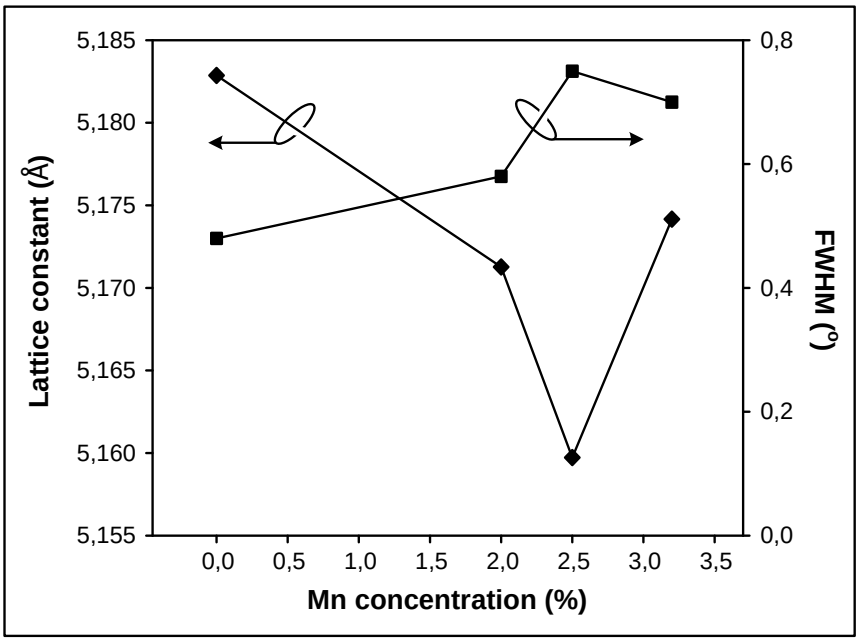

Figure 4 Lattice constant and FWHM values for single phase of GaN:Mn films grown at 700 ^{o}C.

This is consistent with lattice constant calculations for GaN:Mn based on a bond length model proposed by Reed [7]. By considering the bond length **b**, between the Ga and N atoms along the *c*-axis, allows for predicting the lattice constant corresponding to a specific Mn concentration (Figure 5). The bond length **b** can be calculated for the wurtzite crystal structure along *c* axis by the following equation:

$$\mathbf{b} = \frac{c_{GaN}}{2(1+\sin(19^o)} - \left[\frac{r_{Ga}+r_N}{2}\right] \tag{1}$$

where r_{Ga} and r_N are the atomic radii for Ga and N respectively, which give **b** = 0,9698 A^o.

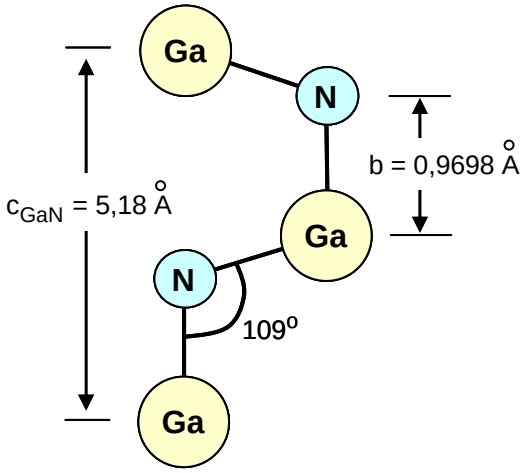

Figure 5 The atomic arrangement of the Ga and N atoms along *c* axis in the GaN wurtzite crystal structure [7].

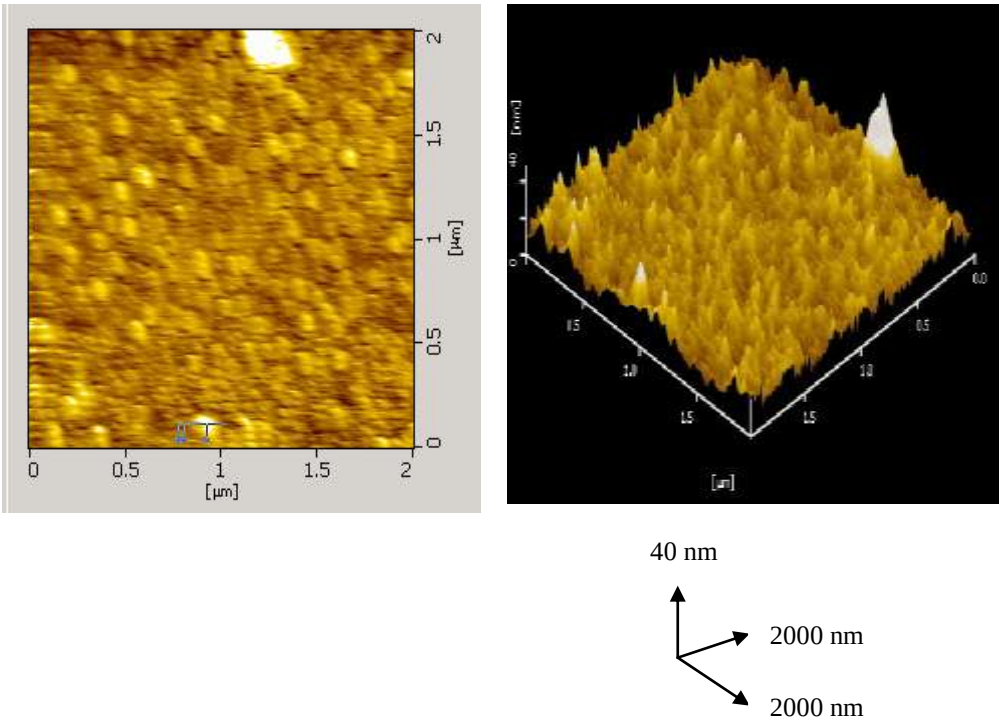

Figure 6 The 2D and 3D of AFM images for GaN:Mn film grown at 700 ^{o}C with 6.4 % of Mn concentration.

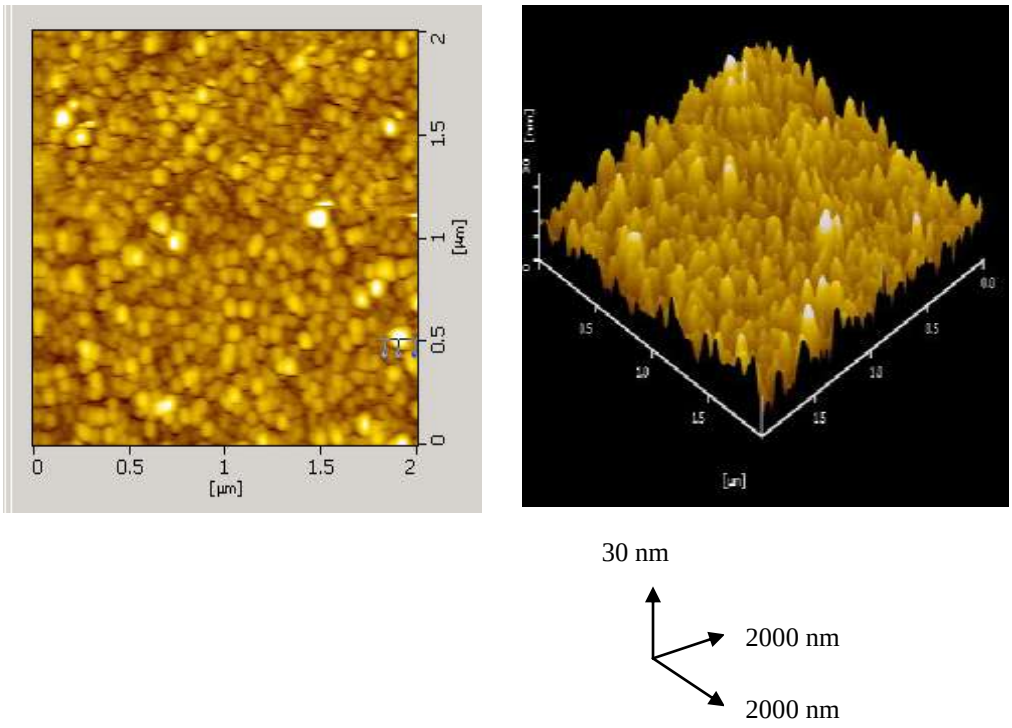

Figure 7 The 2D and 3D of AFM images for GaN:Mn film grown at 650 ^{o}C with 6.4 % of Mn concentration.

Next assume that 100 % MnN has the same crystal structure as GaN so that an upper boundary can be set for the model. Then substitute the atomic radii for Mn into equation (1) and assume that the **b** is the same as in GaN to predict the lattice constant for 100 % MnN with wurtzite crystal structure, this theoretical value is $c_{MnN} = 5{,}05\ A^o$. The Vegard's Law then applied to estimate the Mn concentration at low doses. The atomic radii for Ga, N and Mn are r_{Ga} = 1.218 A^o, r_N = 0.75 A^o and r_{Mn} = 1.12 A^o, respectively. Therefore since $r_{Ga} > r_{Mn}$, it is expected that the lattice would contract when Mn substitutes for Ga in the GaN lattice [7].

The effect of growth temperature and Mn concentration on the surface morphology were carried out by using AFM and SEM images, respectively. The surface morphology of GaN:Mn film grown at 700 ^{o}C with 6.4 % of Mn concentration determined by AFM images show clear areas (spots) of what

likely second phase precipitate on the surface (Figure 6). This suggests the primary mechanism for the decay of thermodynamically unstable GaN:Mn compound in nitrogen desorption and phase rearrangement of the surface in the absence of reactive nitrogen environment during MOCVD growth. This thermodynamic tendency for nitrogen vacancy formation would lead to structural degradation of the films. By changing the temperature to the optimum growth temperature (650 ^{o}C), the spots began to shrink indicating that the formation of second phase precipitate can be suppressed at this growth temperature (Figure 7).

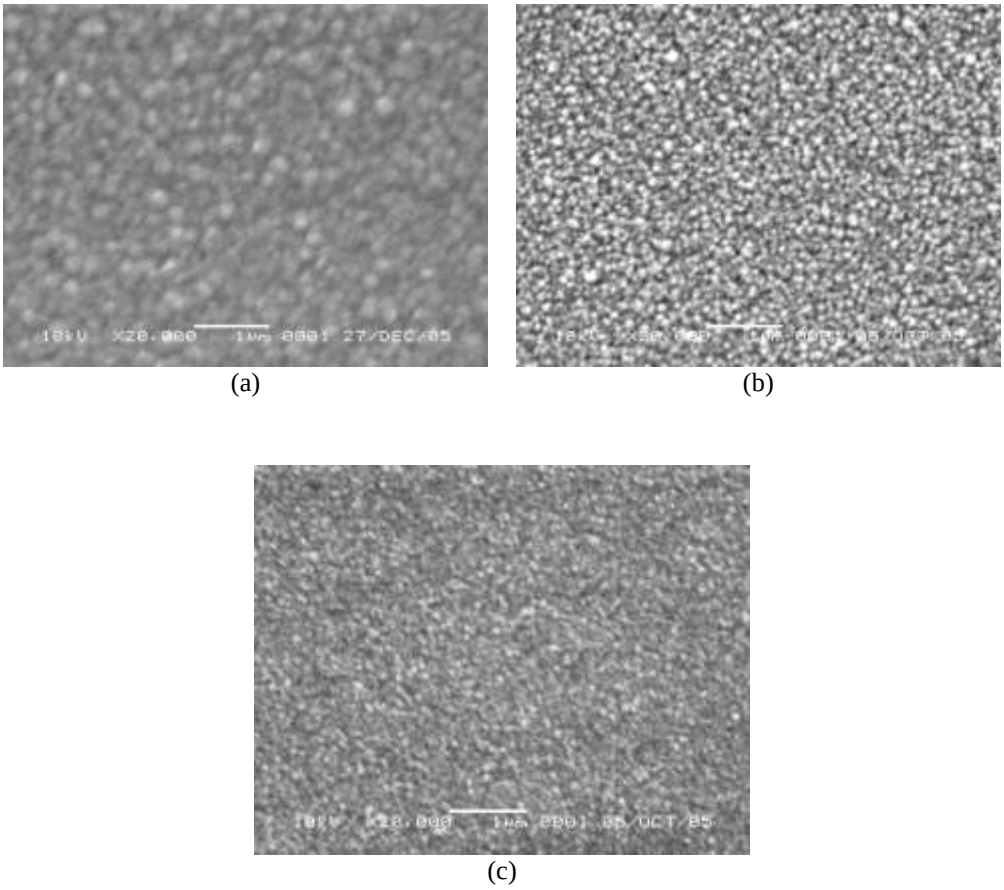

Figure 8 SEM images of 20,000 times enlargement for GaN:Mn films grown at 700^{o}C with (a) 6.4 %, (b) 2.5 %), and (c) 2.0 % of Mn concentration.

The SEM images of GaN:Mn films grown at 700^{o}C with different Mn concentration are shown in Figure 3. Homogeneous surface are shown for the films with 2.0 % and 2.5 % of Mn concentration. A higher Mn concentration (6.4%) could lead a macroscopic precipitation on film surface. The degree of roughening increases with increasing Mn concentration due to the incorporation of Mn atoms in GaN lattice leading to structural degradation of the films.

4 Conclusion

Our results demonstrate that PA-MOCVD method is an optimal method to produce single phase of GaN:Mn (0002) thin films without secondary phase. It seems that with PA-MOCVD method the epitaxy of single GaN:Mn DMS films can be resulted at the temperature lower than that of thermal MOCVD. A systematic XRD analysis do not reveal any clustering effect in the films for Mn concentration below 6.4 % and 3.2 % at 650 ^{o}C and 700 ^{o}C, respectively. For a higher Mn concentration, GaMn cluster is observed.

The lattice constant and full width half maximum (FWHM) of the single phase film are found to vary with Mn concentration. The decrease in lattice constant accompanied by the increase in FWHM was due to incorporation of substitutional Mn on the Ga sub-lattice in GaN:Mn. The maximum solubility of substitutionally Mn in GaN:Mn are 2.0 % and 2.5% at 650 ^{o}C and 700 ^{o}C, respectively. The surface roughness of the films determined from the AFM and SEM images show that the film grown at lower growth temperature and Mn concentration has a better surface than that of film grown at higher growth temperature and Mn concentration.

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