Applied Surface Science 258 (2011) 525–529

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

The important role of Mn^{3+} in the room-temperature ferromagnetism of Mn-doped GaN films

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ARTICLE INFO

Article history:
Received 27 May 2011
Received in revised form 18 August 2011
Accepted 18 August 2011
Available online 25 August 2011

PACS:
61.10.Nz
61.72.Vv
75.50.Pp
81.05.Ea
81.15.Fg

Keywords:
Laser assisted molecular beam epitaxy
Room-temperature ferromagnetism
Annealing temperature
Gallium manganese nitride
Mn valence
BMP

ABSTRACT

Mn-doped GaN films ($Ga_{1-x}Mn_xN$) were grown on sapphire (0 0 0 1) using Laser assisted Molecular Beam Epitaxy (LMBE). High-quality nanocrystalline $Ga_{1-x}Mn_xN$ films with different Mn concentration were then obtained by thermal annealing treatment for 30 min in the ammonia atmosphere. Mn ions were incorporated into the wurtzite structure of the host lattice by substituting the Ga sites with Mn^{3+} due to the thermal treatment. Mn^{3+}, which is confirmed by XPS analysis, is believed to be the decisive factor in the origin of room-temperature ferromagnetism. The better room-temperature ferromagnetism is given with the higher Mn^{3+} concentration. The bound magnetic polarons (BMP) theory can be used to prove our room-temperature ferromagnetic properties. The film with the maximum concentration of Mn^{3+} presents strongest ferromagnetic signal at annealing temperature 950 °C. Higher annealing temperature (such as 1150 °C) is not proper because of the second phase Mn_xGa_y formation.

1. Introduction

In recent years, dilute magnetic semiconductors (DMSs) have earned much attention due to the potential candidates to realize semiconducting and magnetic properties on the same chip. The ferromagnetic (FM) $Ga_{1-x}TM_xN$ with Curie temperature above room-temperature can be formed by doping the transition metal (TM) into GaN, which is an important potential utility of a magnetic wide band gap semiconductor [1]. The different experimental magnetic behaviours, such as the paramagnetism [2], ferromagnetism [3] and superparamagnetism [4], are observed and discussed. Curie temperature over a wide range of temperature is reported in literature [3,5].

The mean-field Zener model was studied by Dietl et al. [1] to predicate the ferromagnetism with T_c above room-temperature. He suggested that it can be realized in the p-type Mn-doped GaN with the hole concentration larger than $3.5 \times 10^{20}/cm^3$. The theoretical work states that ferromagnetism is facilitated by interaction between the Mn^{2+} ions and holes but the experimental results show significant discrepancies and most of the ferromagnetic films show n-type and even high resistive behaviour [6], which is in contradiction to the Zener model [1]. Furthermore, a typical argument for the unexplained ferromagnetism has been attributed to formation of ferromagnetic clusters (Mn_xN_y) or segregations [7], but they are not observed in our fabricated films. Therefore, the mechanism of magnetic interaction of the Mn^{2+} or Mn^{3+} ions in GaN is highly controversial.

In our study, we find that the Mn^{3+} (not Mn^{2+} for the Zener model [1]) ion plays an important role in the origin of room-temperature ferromagnetism. The Bound Magnetic Polarons (BMP) theory [8] is used to explain the origin of room-temperature ferromagnetism. The influence of annealing temperature on Mn concentration, internal defects, optical band gap, Mn related valence states and magnetic properties has been studied in our research.

2. Experimental details

The Mn-doped amorphous gallium nitride thin films were deposited on the sapphire substrates (0 0 0 1) using Laser assisted

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doi:10.1016/j.apsusc.2011.08.075

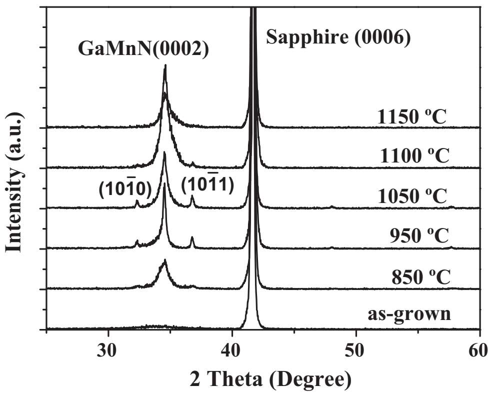

Fig. 1. XRD patterns of GaMnN films on the Sapphire (0 0 0 1) substrate before and after annealing at different temperatures.

Molecular Beam Epitaxy (LMBE). The 248 nm excimer laser (25 ns pulse width and 200 mJ pulse energy) was used at an incident angle of 45° to ablate the sintered $Ga_{0.95}Mn_{0.05}N$ targets. The fixed distance between the target and the substrate was 5 cm. The deposition took 45 min in a nitrogen atmosphere (1.4 Pa) on the sapphire substrates heated to 800 °C. Subsequently, the samples were placed on a quartz carrier and annealed in a tube furnace for 30 min. 99.999% pure Ammonia gas was used as an ambient with flow rate of 500 ml/min. The annealing temperature was varied in the range from 950 to 1150 °C.

The structural and the compositional analyses were carried out by XRD (Rigaku D/max-rB) spectroscopy and Zeiss supra55 field emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). The X-ray photoelectron spectra (XPS) were recorded with an ESCALAB 250 X-ray Photoelectron Spectrometer. The optical measurements were performed with U-4100 Spectrophotometer at normal incidence at room-temperature. The Raman measurements were carried out in backscattering configuration with a Jy-HR800 laser Raman spectrometer using the 473 nm line of a solid laser as an excitation source. The magnetic hysteresis loops were obtained at room-temperature by MicroMag 2900 alternating gradient magnetic field meter (AGM).

3. Results and discussion

3.1. Structural characterization

The XRD measurements of the annealed $Ga_{1-x}Mn_xN$ films with the various temperatures from 850 to 1150 °C are shown in Fig. 1. The diffraction peaks at around $2\theta = 34.50°$, 32.38° and 36.81° due to GaN (0 0 0 2), (1 0 $\bar{1}$ 0) and (1 0 $\bar{1}$ 1) respectively, are observed for all of the annealed films. These three peaks correspond to the hexagonal GaN wurtize structure. The dominant diffraction peak observed at $2\theta = 41.76°$ for all films owning to sapphire substrates. No peak other than the above four appeared in the spectra of all treated films, which indicates that the other phases like Mn_4N and Mn_xGa_y [9] have not formed. The c-axis lattice constants ($d_{c\text{-axis}}$) calculated with the help of the formula $d_{c\text{-axis}} = \lambda/\sin\theta$ varies with the annealing temperature. Such values of lattice constants are given in Table 1. The value of *c*-axis lattice constants ($d_{c\text{-axis}}$) will increase if the Ga sites are replaced by Mn ions having the larger radius. In our calculation, the maximum $d_{c\text{-axis}}$ is obtained when the doped GaN films are annealed at 950 °C. We believe that the most of Ga atoms have been replaced by Mn in such films. The decrease in $d_{c\text{-axis}}$ values with the increasing temperature within the range 1050–1150 °C is due to the tensile stress release at the higher annealing temperature.

Table 1
Mn concentration (x) and $d_{c\text{-axis}}$ of samples annealed at different temperatures.

Annealing temperature (°C)	Mn concentration x (at%)	$d_{c\text{-axis}}$ (Å)
850	6.20	5.1864
950	6.92	5.1952
1050	6.50	5.1922
1100	6.60	5.1864
1150	6.90	5.1802

The manganese concentrations (x) of the films obtained by EDX are listed in Table 1. The Mn concentrations of the annealed films are higher than that of the target. O'Mahony [10] proposed that heats of vaporisation of Ga (264 kJ/mol) and Mn (280 kJ/mol) are quite close, it is likely that a great ability of Mn to form a nitride is the determining factor in influencing the Mn:Ga ratio, and more manganese nitride might be expected to be formed under the conditions typically used for laser deposition. We believe that a minor variation in Mn:Ga ratio with annealing temperature is because of evaporation of few Mn atoms and loss of GaN in annealing process.

3.2. Raman analysis

Typical Lorentz fitted Raman spectra of GaMnN films annealed at 850 and 950 °C is given in Fig. 2(a and b) respectively. Three peaks (Fig. 2(a)) at 561, 531 and 574 cm^{-1} can be noticed suitably fit in the Raman spectra within the range 500–620 cm^{-1}. The peaks at 561, 531 cm^{-1} are attributed to the E_2^H and A_1 (TO) phonon modes of GaMnN [11]. Third peak at 574 cm^{-1} is described at the end of this section. Lorentz fitting reveals another peak at 576 cm^{-1} as shown in Fig. 2(b). This peak is caused by the substrate. The peak at 574 cm^{-1} (Fig. 2(a and b) is due to LVM of Mn–N bond [12]. If the impurity atom replaces the heavier host lattice atom, atomic

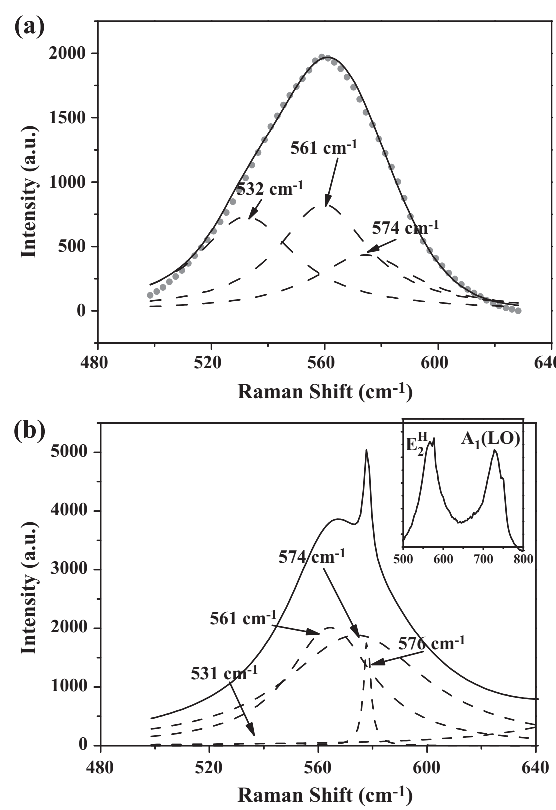

Fig. 2. Lorentzion fitted Raman spectra of GaMnN films annealed at (a) 850 °C and (b) 950 °C. The inset shows the Raman spectra of film annealed at 950 °C in rang 500–800 cm^{-1}.