ABSTRACT

GROWTH AND CHARACTERIZATION OF FERROMAGNETIC SEMICONDUKTOR GaN:Mn THIN FILMS USING PLASMA ASSISTED METALORGANIC CHEMICAL VAPOR DEPOSITION(PA-MOCVD) METHOD

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The subject of this dissertation is the growth and characterization of GaN:Mn thin films using plasma assisted metal-organic chemical vapor deposition (PA-MOCVD) method. Gallium-Nitride Manganese (GaN:Mn) is a ferromagnetic semiconductor material or known as diluted magnetic semiconductor (DMS) which is very potential for spintronic device applications. Compared to conventional devices, spintronic device has many advantages, including higher data processing, more integrated device (*compact*), and lower energy consumed. To produce such device application, DMS is required to have a Curie temperature (T_C) higher than room temperature, high efficiency of spin injection (of around 100%) and should be compatible to the existing semiconductor technology.

Compared to the conventional III-V based DMS, theoretically GaN:Mn has many advantages, including its high Curie temperature i.e. above room temperature and is ideal for spin injection. From the experimental results, many groups have reported the growth of GaN:Mn thin films using MOCVD method besides other methods. These MOCVD-grown GaN:Mn thin films were reported to have Curie temperature above room temperature.

The objectives of this research are to investigate the physics of the growth of GaN:Mn thin films using PA-MOCVD method, and to understand mechanism of Mn incorporation into GaN:Mn, as well as to obtain the correct procedure to produce high quality of GaN:Mn thin films which is potential for spintronic device applications.

Prior to the growth, the numerical simulations were performed using FEMLAB Ver.2.1 (2000) software to provide specification of processes occurred in the growth of GaN:Mn using MOCVD method, which can be used as references of the growth of GaN:Mn using PA-MOCVD method. In this simulation, *trimethyl gallium* (TMGa), *cyclopentadienyl manganese tricarbonyl* (CpMnT) and ammonia were used as a precursor of Ga, Mn and N, respectively. From the simulation results, the temperature required for the growth of GaN:Mn should be maintained at 900 ^{o}C or above. The uniformity of the grown film can be achieved when the substrate is placed between 3.5 cm and 4.5 cm of susceptor radial distance. The flow rate of TMGa, NH_3 and CpMnT precursors as reference of growth parameters were found to be 0.08 sccm, 70 sccm, and 0.01 sccm, respectively.

The high growth temperature required for the growth of GaN:Mn using MOCVD may cause nitrogen dissociation which leads to the difficulty of producing single phase of GaN:Mn thin

films. In fact, high Mn concentration is necessary to improve the magnetic characteristics of GaN:Mn film. To overcome this problem, PA-MOCVD method was used in this work instead of MOCVD. The PA-MOCVD reactor is an extension from the previous thermal MOCVD reactor by incorporating microwave cavity as a cracking cell to produce nitrogen radical instead of NH_3, therefore the growth temperature can be reduced. This low growth temperature was expected to be able to improve magnetic characteristics of GaN:Mn thin films, which are demonstrated by the high T_C (above room temperature) and the high value of magnetic moment.

A series of growth and characterization of GaN:Mn thin films were carried out. The growth was conducted on Al_20_3 (0001) substrate. TMGa, UHP of nitrogen gas and CpMnT were used as a source of Ga, N and Mn, respectively. The Mn incorporation was then controlled by varying molar fraction of Mn/Ga source. The effect of V/III flux ratio and growth temperature on the Mn incorporation as well as the dependency of Mn incorporation on the magnetic, electrical and optical properties of grown films were also investigated. The crystal structure of the films was analyzed by XRD and HR-XRD, while SEM and AFM methods were used to analyze the films' surface morphology. Magnetic, electrical and optical properties were then investigated using VSM, Hall-van der Pauw and UV-Vis measurements, respectively.

The growth rate and Mn incorporation into GaN:Mn thin films are highly dependent on the growth temperature. The highest growth rate was achieved at growth temperature of 680^{o}C, while the highest Mn incorporation occurred at 700^{o}C. At V/III flux ratio of 600, the highest growth rate but the lowest Mn incorporation were achieved. Therefore the high growth rate does not lead to the high Mn incorporation. The Mn incorporation into GaN:Mn has a positive correlation with molar fraction of Mn/Ga, however the molar fraction of Mn/Ga does not affect the grwth rate of GaN:Mn.

From the analysis of XRD spectra, it was obtained that the highest Mn incorporation into GaN:Mn which would produce single phase GaN:Mn (0002) was 6.4 % at 650^{o}C of growth temperature. While at 700^{o}C of growth temperature, the maximum of Mn incorporation into GaN:Mn films that would still produce single phase film were 3.2 %. These XRD results were also confirmed by the HR-XRD results. Up to a concentration of 2.0 % at 650 ^{o}C of growth temperature and of 2.5% at 700 ^{o}C of growth temperature, it was found that increase of Mn concentration in GaN:Mn film would decrease the lattice constant and increase the FWHM value. This decrease in lattice constant and increase in FWHM value is believed due to solid solution, i.e. substitution on Mn atom into Ga atom site inside GaN matrix.

The AFM and SEM results also show that the surface roughness of the films is influenced by the Mn concentration. The high concentration of Mn and the high growth rate tend to increase the surface roughness.

The VSM measurement results show that all the grown samples were ferromagnetic at room temperature, therefore they have a Curie temperature above room temperature. The obtained values of magnetic coercivity, remanent magnetization and saturation magnetization were in the ranges of 300 - 800 Oe, 10.2 –34.4 emu/cm^3, and 20 – 39 emu/cm^3 respectively, depending on Mn concentration and the growth temperature. For the films grown at 650 ^{o}C, the highest value of Bohr magneton was obtained by a sample with Mn concentration of 2.0 %, namely 3.1

μ_B/Mn-atom. While for the films grown at 700 ^{o}C, the highest value of Bohr magneton was obtained by a sample with Mn concentration of 2.5 %, namely 3.7 μ_B/Mn-atom. And These VSM measurement results also confirm the solid solution argument for Mn concentration up to 2.0 % for films grown at 650 ^{o}C and up to 2.5% for films grown at 700 ^{o}C, as obtained by XRD measurements. For Mn concentration higher than those values, increase in Mn concentration will eventually decrease the magnetic moment value. This was believed from a relatively dominant contribution of antiferromagnetic from *nanocluster*, precipitate or Mn interstitial inside the film.

Based on measurement of electrical properties using Hall-van der Pauw method, it was found that all GaN:Mn samples were *n*-type with the highest value of carrier concentration of about 1.8 x 10 ^{19} /cm^3. It was also obtained that Mn incorporation in GaN:Mn leads to the decrease in carrier concentration, because Mn acts as acceptor and tends to compensate the carrier (electron). This low carrier concentration leads to the high carrier mobility and high resistivity of GaN:Mn film.

Based on results from UV-Vis measurement, it was obtained that band gap of GaN:Mn tends to increase with the increase in Mn concentration. This optical property was in agreement with the result from electrical property measurement, i.e. the film is more resistive for higher Mn concentration.

Keywords: GaN:Mn, PA-MOCVD, spintronics device, Curie temperature (T_C), DMS, SEM, AFM, EDX, XRD, HR-XRD, lattice constant, FWHM, Hall-van der Pauw, solid solution, VSM, single phase crystal, hysteresis curve, Bohr magneton, magnetic moment.