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Research Article

Optical Properties of One-Dimensional Structured GaN:Mn Fabricated by a Chemical Vapor Deposition Method

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Group III nitride semiconductors with direct band gaps have recently become increasingly important in optoelectronics and microelectronics applications due to their direct band gaps, which cover the whole visible spectrum and a large part of the UV range. Major developments in wide band gap III–V nitride semiconductors have recently led to the commercial production of high-temperature, high-power electronic devices, light-emitting diodes (LEDs), and laser diodes (LDs). In this study, GaN nanowires were grown on horizontal reactors by chemical vapor deposition (CVD) employing a vapor-solid mechanism. Many studies have described how to control the diameters of wires in the liquid phase catalytic process, but one-dimensional nanostructures, which are grown using a noncatalytic process, are relatively unexplored due to the challenge of producing high-quality synthetic materials of controlled size. However, vapor-solid mechanisms to make synthesized nanowires are simple to implement. We obtained results from GaN nanostructures that were a preferential *c*-axis orientation from the substrate. The morphology and crystallinity of the GaN nanowires were characterized by field-emission scanning electron microscopy and X-ray diffraction. The chemical compositions of GaN with Mn were analyzed by energy dispersive X-ray spectroscopy. Optical properties were investigated using photo luminescence and cathode-luminescence measurements.

1. Introduction

As a wide band gap semiconductor having a direct gap-type band gap, GaN is a material that has been studied since the 1970s for the purpose of applying various photoelectric elements and protection films, including blue luminous elements [1]. GaN has been actively researched all over the world. Since GaN has consecutive solid solubility with III–V series nitride semiconductors, such as InN (Eg = 1.92 eV) and AlN (Eg = 6.2 eV), it forms ternary series nitride homogenous solid solutions such as InxGa1-xN and GaxAl1-xN. Because the composition of a band gap can change to a linear function depending on the composition of these ternary-series nitrides, it is possible to manufacture luminous elements and light-receiving elements that include all of the red visible ray fields of ultraviolet rays by controlling the composition of III–V nitrides [2, 3].

Gallium nitride (GaN) is one of the most common semiconductor materials since it has a wide band gap of 3.39 eV and very good chemical stability. It is a very ecofriendly material that does not contain substances such as As and Hg [4, 5]. With its strong electron affinity, GaN has especially superior voltage characteristics such as electron mobility, saturated electron velocity, and electric field breakdown, as well as superior optical characteristics. Thus, it has numerous applications related to optical and electronic elements [6]. Sapphire, SiC, Si, and GaAs substrates are used to grow GaN semiconductors. The homoepitaxy growth method, which grows GaN on a GaN substrate, has recently attracted attention to reduce lattice defects [7].

In addition to green and red optical elements produced using GaAs and InP compound semiconductors, blue wavelength optical elements using GaN make it possible to fabricate displays that have natural colors. These displays have high potential for application in fields related to graphics and visual display terminals such as instrument panels of electronic devices [8–11]. Due to the development of high-speed broadband information and communication networks

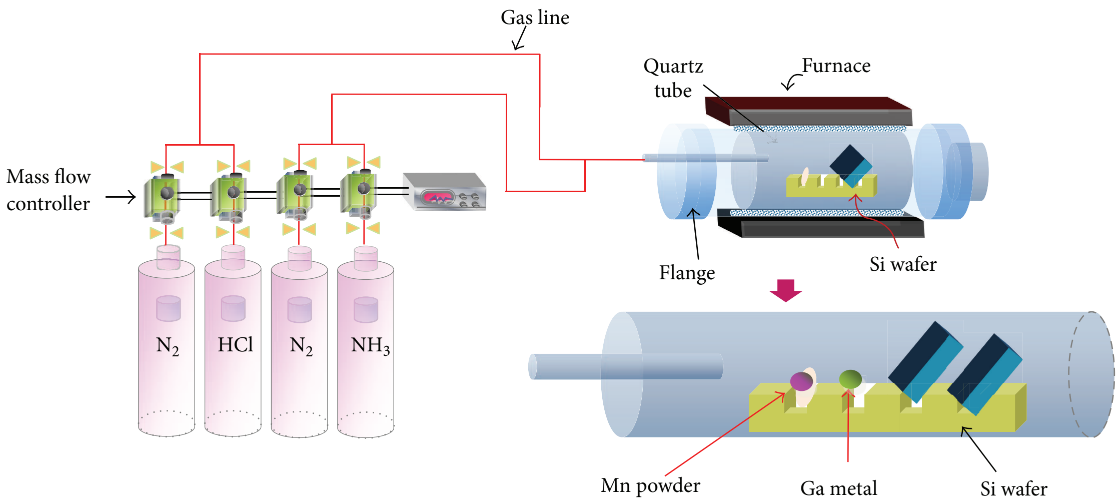


Figure 1: Schematic experimental setup for the growth of GaN and doped Mn.

and the expansion of fiber to the home (FTTH), there is also increased demand to transmit and process high-capacity broadband information. In this field, the capacity of an optical information processing system is in inverse proportion ($1/\lambda^2$) to the square of luminous source wavelength used for the system. Thus, if a short-wavelength semiconductor laser using GaN in the blue and ultraviolet ray domain is developed, it will be possible to effect a large increase in the rate of information processing [12–14].

In this paper, we have performed a systematic study of the properties of Mn-doped GaN nanowires.

GaN doped with Mn is a candidate for spintronics devices since a Curie temperature above room temperature has been reported. Additional interest in wide-gap nitride semiconductors arises when they are doped with transition metal Mn, due to their potential use in spintronics devices. The aim of this study was to improve the understanding of how the manganese is incorporated into the GaN layers, and how this process affects the defect structure of these wires.

2. Experimental

2.1. Materials and Reagents. For the growth of Mn-doped GaN wires, we used Ga metal (purity of 99.99%, density of 5.904 g/mL at 25°C, mp 29.8°C) and Mn powder (≥99%, −325 mesh, density of 7.3 g/mL at 25°C, mp 1244°C), with high-purity N_2 (99.999%) as a carrier gas and NH_3 (99.9995%) as a reaction gas. A mass flow controller (MFC) was used to regulate the partial pressures of N_2 and NH_3 gases. A silicon wafer substrate (100) was used for the growth of the GaN wires.

2.2. Experiments and Analysis. To grow GaN nanowires, we employed the chemical vapor deposition (CVD) method, and the configuration used for experiments is shown in Figure 1.

After a certain amount of gallium metal (≒100 mg) and manganese powder (≒5 mg) was put into the alumina boat, the substrate was inserted into the frame in the back of the boat, and then it was placed in the center of a tube furnace. While the temperature of the tube furnace was increased to achieve the reaction temperature according to each set of conditions (Table 1), N_2(99.999%), NH_3 (99.9995%), and HCl (N_2 mixture gas, 10 mol%) gases were injected. The heating rate was 5°C/min, and the holding time was 1 hour. During this time, the temperature and the total flow were regulated in the ranges of 950–1400°C and 490–625 sccm, respectively. The location of the gallium metal was occasionally changed with that of the manganese powder. Images of synthesized GaN nanowires were analyzed through field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7000F) to determine the growth conditions, and the wires were also qualitatively analyzed through energy dispersion X-ray spectroscopy (EDS). The crystal structure was analyzed through X-ray diffraction (XRD, Rigaku, *D*/max-2500/PC), and, for an analysis of the optical characteristics, photo luminescence (PL) and cathode luminescence (CL) measurements were taken.

Table 1: Experimental operating parameters.

No.	Temperature (°C)	N_2 (SCCM)	NH_3 (SCCM)
a	1000	175	150
b	1050	175	150
c	1100	175	150
d	1200	175	150
e	1300	175	150
f	1400	175	150

3. Results and Discussion

3.1. Growth of GaN Nanowires. Figure 2 shows GaN nanowires grown on the surface of a Si substrate observed through FE-SEM at various reaction temperatures. The experiment was conducted by increasing the flux of N_2 gas and NH_3 gas by 150 sccm, and the furnace temperature was increased

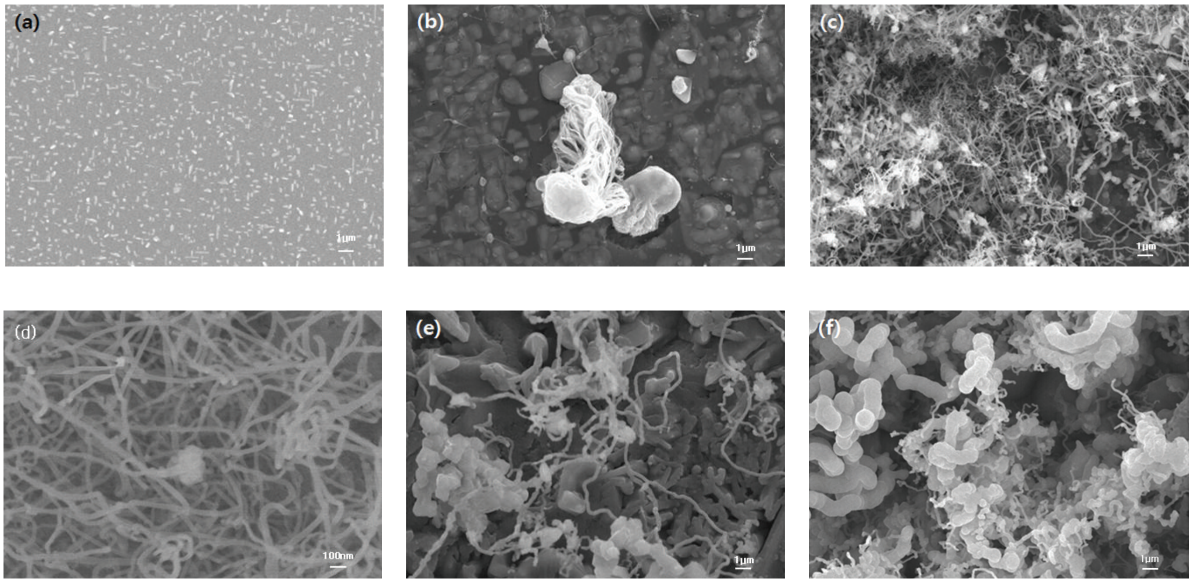


Figure 2: Structural characteristics of GaN:Mn nanowires grown on Si substrates at different temperatures: (a) 1000°C, (b) 1050°C, (c) 1100°C, (d) 1200°C, (e) 1300°C and (f) 1400°C.

5°C/min, and the reaction time was maintained for 1 hour. As shown in the FE-SEM picture of Figure 2, the experiment was carried out for 1 hour in the following conditions: (a) 1000°C, (b) 1050°C, (c) 1100°C, (d) 1200°C, (e) 1300°C, and (f) 1400°C.

As shown in Figure 2(a), GaN was not deposited on the surface of the Si substrate for a reaction temperature of 1000°C. However, in Figures 2(b), 2(c), 2(d), 2(e), and 2(f), GaN was deposited on the surface of the Si substrate for higher temperatures. As shown in the FE-SEM image, Figure 2(b) shows that GaN started growing at 1050°C, but only a fraction of the Si substrate showed GaN growth. On the other hand, Figures 2(c) and 2(d) show that GaN nanowires grew throughout the temperature range of 1100°C to 1200°C. In Figures 2(d), 2(e), and 2(f), GaN nanowires were produced, but they were thicker than those shown in Figure 2(c). It was also observed that lumps of wires were created in places. In particular, it was observed in Figure 2(f) that wires were created on the surface of a large-sized lump, but when the temperature was 1400°C, there was a high probability that the Si substrate could melt away. Thus, no additional experiments were conducted at temperatures above 1400°C. Overall, when other variables were fixed, and the reaction temperatures varied, the GaN started being deposited at over 1050°C, and its growth was best at temperatures between 1100°C and 1200°C.

3.2. XRD Analysis. Figure 3 shows XRD measurements of GaN nanowires. Based on the XRD diffraction pattern, we found peaks in the (0002) direction and (0004) direction in the GaN Wurtzite structure. Thus, the crystal structure of GaN grown is a Wurtzite structure having lattice constants where $a = 3.189$ Å and $c = 5.185$ Å.

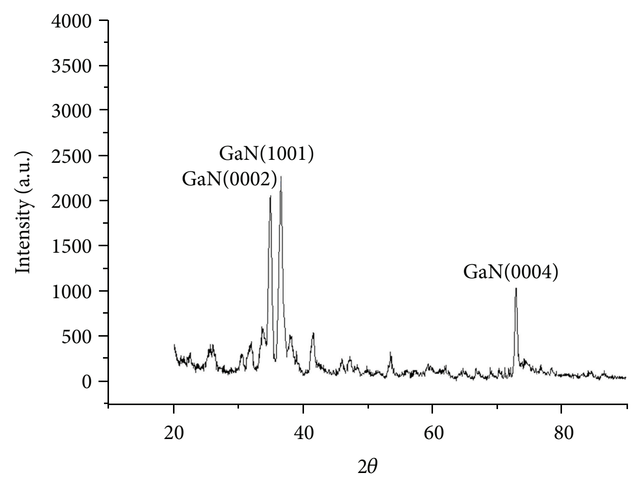
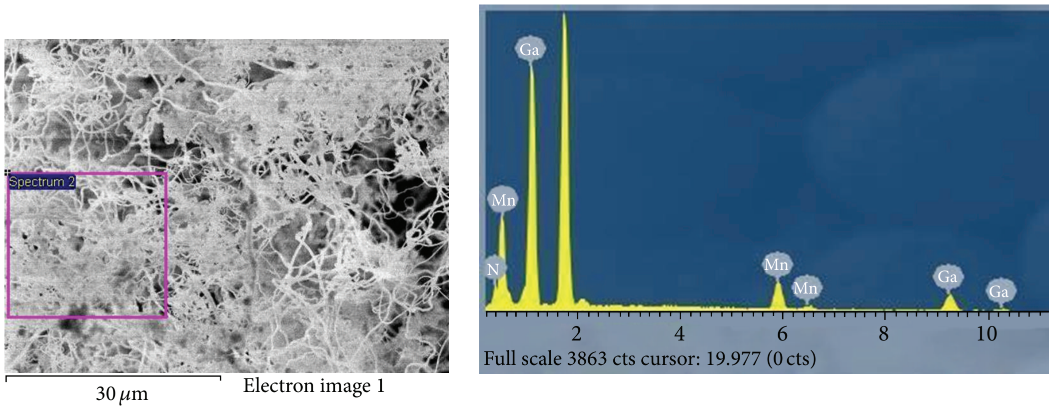


Figure 3: XRD pattern of GaN:Mn nanowires.

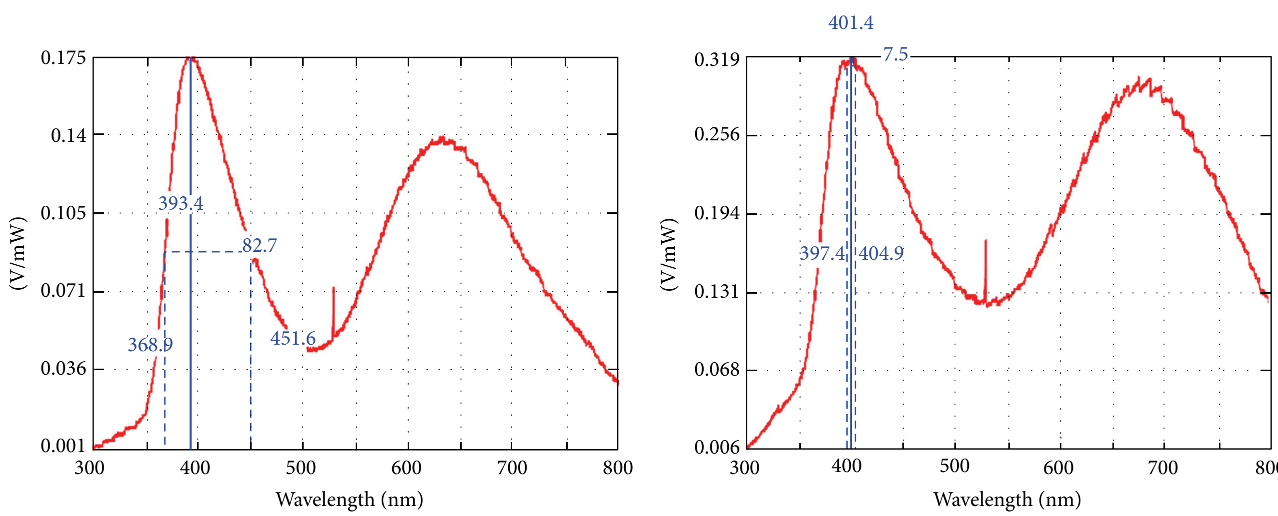
3.3. EDS Analysis. Figure 4 shows EDS measurements of GaN nanowires to determine the chemical composition of the GaN nanowires. Analyses of regions where GaN nanowires were deposited showed that they were chemically composed of Ga, N, and Mn. As a result, nanowires grown with those components deposited were found to be GaN. Interestingly, too much Mn was detected, although it was used for doping, and thus another experiment was carried out, regulating the amount of Mn to find the correct amount to use for proper doping based on the EDS results.

3.4. PL Analysis. Photoluminescence (PL) was measured to investigate the light-emitting characteristics of GaN doped



(a) (b)

Figure 4: Typical EDS spectrum data of the GaN:Mn nanowires.



(a) (b)

Figure 5: PL spectrum of GaN:Mn nanowires (a) PL data of GaN nanowires and (b) PL data of GaN:Mn nanowires.

with Mn. Figure 5 shows the PL analysis of the GaN nanowires (Figure 5(a)) and the PL analysis of the nanowires where GaN was doped with Mn (Figure 5(b)). The value of the GaN light-emitting wavelength was 393.4 nm. When the GaN was doped with Mn, the light-emitting wavelength was 401.4 nm. We found that as the amount of Mn doping increased, the light-emitting wavelength increased up to 700 nm (red), the maximum. In addition, even when the experiment was carried out with the same ratio of Ga metal to Mn powder, the value of the light-emitting wavelength was found to be 644.4 nm while keeping the temperature maintained at 1300°C.

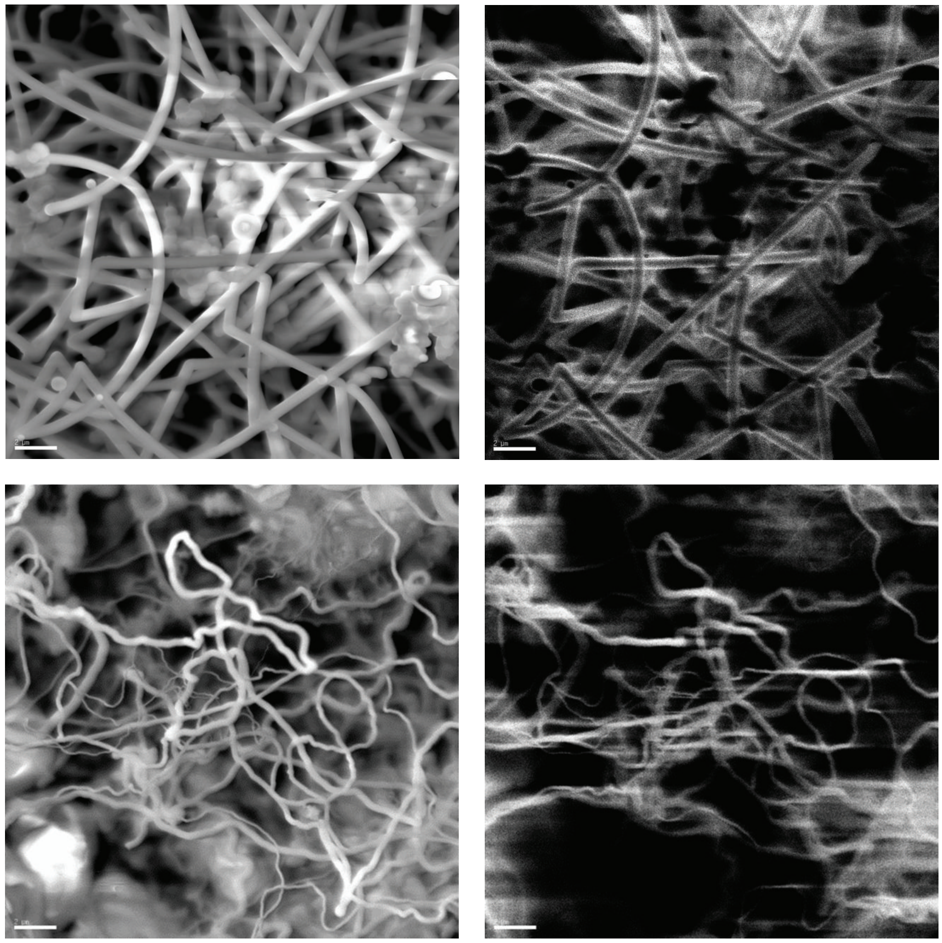
3.5. CL Analysis. Cathode-luminescence(CL) indicates luminescence caused by the recombination of positively charged holes made by incident electrons inside a crystal phosphor with electrons mainly floating on the conduction band. Figure 6 shows CL images of GaN nanowires grown on the surface of the Si substrate [14].

4. Conclusion

We succeeded in depositing nanostructured GaN on the surface of a Si substrate using the CVD method. The optimal conditions for the growth of GaN were determined by regulating the reaction temperature, the flux of reaction gases, the mixture ratio of gallium metal and manganese powder, and whether to use HCl gas and control of the reaction time [15]. The optimal conditions through the CVD method were 1200°C in temperature, 165 sccm in the flux of NH_3 gas, 1 hour of deposition time, and 20 : 1 in terms of the quantity (g) ratio of Ga metal to Mn powder [16].

GaN nanowires were deposited on the surface of a Si substrate using the CVD method, as observed through field-emission scanning electron microscopy (FE-SEM). As a result, we found that as-grown GaN nanowires were between 90 and 200 nm in diameter [17, 18].

XRD and EDS analysis of the crystal structure and chemical composition of GaN nanowires deposited on the surface



(a) (b)

Figure 6: CL data of GaN:Mn nanowires (a) SEM image and (b) CL image.

of a Si substrate using the CVD method and showed that the wires had wurtzite structure.

Measurements of the light-emitting characteristics of Mn-doped GaN nanowire PL showed blue light emission. This study demonstrates the potential for applying GaN nanowires in blue light-emitting diodes (LEDs) [19, 20].

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