Fabrication of GaN/GaN:Mn core/shell nanowires and their photoluminescences

Ungkil Kim, Han-Kyu Seong, Myoung-Ha Kim, Heon-Jin Choi

Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, South Korea

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ABSTRACT

We report on the fabrication of GaN/GaN:Mn core/shell nanowires (NWs) using a two-step metalorganic chemical vapor deposition (MOCVD) and chloride-based chemical vapor transport (CVT) process. Structural analyses indicated that the heterostructure NWs were single crystalline and exhibited a core/shell and lozenge structure. The photoluminescence (PL) of the core/shell NWs showed a peak at a center wavelength of 454 nm, which was red-shifted compared to those of GaN and GaN:Mn NWs. This outcome indicates the accumulation of excited carriers at the interfaces that would be helpful in developing novel magnetism in diluted magnetic GaN:Mn semiconductors.

1. Introduction

Spintronics, which can utilize both the spin and the charge of an electron simultaneously, can be used in the creation of novel devices based on the spin and charge of electrons. This field has been the subject of much research as the downsizing of devices is now associated with critical issues such as short channel- and/or hot carrier effects that degrade the performance of devices significantly [1,2]. Semiconductors doped with a transition metal, known as diluted magnetic semiconductors (DMSs), are the most promising candidates for such applications [3]. DMSs based on GaN have been extensively studied due to their wide band-gap, which is essential for realizing ferromagnetism above room temperature [4]. In a previous study, the authors investigated the magnetism of a GaN:Mn DMS system by utilizing NWs, which have a number of advantages over thin films when studying ferromagnetism in DMSs [5]. Specifically, they offer thermodynamically stable features and are typically single crystalline and free of defects. Thus, the effect of defects and a non-uniform distribution of dopants as typically observed in DMSs prepared by non-equilibrium processing (e.g., molecular beam epitaxial process) are safely excluded. The free-standing nature of NWs makes it possible to exclude the effects of thermal- and lattice mismatches of the substrate and make it possible to determine the intrinsic magnetism under fully relaxed states [6]. Single crystalline GaN:Mn NWs show ferromagnetic magnetoresistance near room temperature, spin-dependent transport and, importantly, p-type characteristics, which have not been thus far shown in thin film studies [5].

According to mean field theory, room-temperature ferromagnetism and its charge-driven modulation, which are essential in device applications, require high carrier densities (for example, a concentration of holes of approximately $10^{20}/\text{cm}^3$ in GaN:Mn) [4]. However, such a high carrier concentration could be scarcely achievable via the simple doping of a transition metal in wide band-gap semiconductors. One approach to achieve a high carrier concentration involves the co-doping of a secondary dopant, which creates a shallow acceptor level in the band-gap [7,8]. Another approach that has not been studied in detail is the creation of heterostructures in which the carriers are confined at the interfaces [9,10]. In fact, limited studies of the thin film heterostructure of GaN:Mn on GaN or AlN have shown some evidence that the magnetic properties can be tuned [11–13]. It is worth noting that the heterostructure of NWs can confine the carriers two-dimensionally, whereas a thin film heterostructure confines one-dimensionally. Hence, distinct magnetic as well as optical and electrical properties can be expected in the NWs. In this study, we reported on the fabrication of single crystalline GaN/GaN:Mn core/shell NWs in a two-step MOCVD and CVT process, and their optical properties. The results indicate that the carriers are possibly confined at the interfaces between the core and the shell in these heterostructure DMS NWs.

2. Experimental procedure

To fabricate GaN/GaN:Mn core/shell NWs, GaN NWs were initially synthesized on Si substrates deposited Ni catalysts in a MOCVD system at 900 °C. Trimethylgallium (TMG) and ammonia gas (NH3) were used as Ga and N precursors, respectively. Hydrogen gas (H2) was used as a carrier gas to transfer the Ga precursor and as a diluent gas to regulate the concentration of the mixture containing TMG vapor and...
After growing the GaN NWs, the substrates were placed in a CVT system to grow the GaN:Mn shell layer, where solid metallic Ga and manganese dichloride (MnCl₂) powder were used as Ga and Mn precursors. The temperature of the furnace was increased to 750 °C under a flow of NH₃ and maintained for 10 min.

3. Results and discussion

Fig. 1a shows a scanning electron microscopy (SEM) image of GaN NWs grown on Si substrates using the MOCVD system. The synthesized GaN NWs are formed a triangular structure (inset in Fig. 1a) with diameters of ~100 nm. The triangular structure results from the two-fold symmetry along the [1 ¯ ¯ 0] crystallographic direction by the hydrogen reaction environment and as a result of the Ni catalyst in the TMG metal-organic system [14]. Fig. 1b shows a SEM image of the NWs after the CVT process. The diameter and length of the NWs is < 200 nm and several micrometers, respectively.

Fig. 2 shows transmission electron microscopy (TEM) images of the NWs after the CVT process. The difference in contrast between the core and the shell of the NWs indicates that the NWs indeed have a two-layer structure (Fig. 2a). The single crystalline nature without defects can be seen from the high-resolution TEM (HRTEM) image of the GaN:Mn shell layer (Fig. 2b). The selected-area electron diffraction (SAED) pattern further demonstrated that the core/shell NWs were a wurtzite structure and grew along the [210] direction (Fig. 2c). Fig. 2d shows the representative composition determined by an energy dispersive X-ray spectroscopy (EDS) analysis of the shell layer in the NWs. The average Mn concentration as measured from ten NWs was 4 at.% and it is believed that the Mn dopants are homogeneously distributed within the shell lattice [5].

Fig. 3 shows the PL spectra of GaN, GaN:Mn, and GaN/GaN:Mn core/shell NWs measured at room temperature. A He-Cd laser with a wavelength of 325 nm was used as an excitation light source for the PL measurements. The peak positions of GaN (black) and GaN:Mn NWs (red) are 374 nm (3.31 eV in photon energy) and 426 nm (2.91 eV in photon energy), respectively. The emission peak of the GaN NWs is the same as the reported values of GaN NWs [14, 15]. The emission peak in GaN:Mn NWs is ascribed to the Mn²⁺ acceptor level in the band-gap of the GaN NWs [16]. In a previous study by the authors, Mn ions were believed to have formed the acceptor level in the GaN band-gap because GaN:Mn NWs showed p-type electrical characteristics [5]. Furthermore, the difference in the emission energy between GaN and GaN:Mn NWs is 0.4 eV, which is identical to the reported value of the acceptor level in the thin film [11]. In the case of the GaN/GaN:Mn core/shell NWs (green), the main peak position is 454 nm (2.73 eV in photon energy). This emission energy may arise from a recombination in the depletion layer, as explained below in detail.

Fig. 4 shows a schematic energy band diagram for the possible mechanism of PL emission from the NWs. The peak at 3.31 eV is related to the band-gap emission in GaN NWs (Fig. 4a). Fig. 4b shows the possible mechanism of the emission in the GaN:Mn NWs. The excited electrons are grounded from a conduction band to the Mn acceptor level in the GaN band-gap [5, 11]. In the GaN/GaN:Mn core/shell NWs, a schematic band diagram can be constructed as shown in Fig. 4c. In this band-gap structure, the electrons excited in the GaN:Mn shell layer are subject to be transferred to the depletion region as they have a low energy state, and recombination occurs in the depletion layer rather than in the shell layer. It can thus show the emission energy peak at 2.73 eV. This red-shift in PL is worth noting because heterostructures in the NWs can confine and accumulate the carriers at the interfaces. It is well known that distinctive electrical- and optical properties can be achieved in many electronics by such a carrier confinement [17, 18]. Specifically, according to mean field theory, unique magnetism in DMS can be
achieved by the carrier confinement [4]. In this regard, heterostructure DMS NWs could be a nanoscale building block to realize novel magnetic- as well as optical- and electrical properties.

4. Conclusions

In summary, we fabricated single crystalline GaN/GaN:Mn core/shell NWs in a two-step MOCVD and CVT process. The PL from the GaN/GaN:Mn core/shell NWs showed a peak centered at the wavelength of 454 nm, that was red-shifted toward a longer wavelength as compared to GaN and GaN:Mn NWs. This may due to a recombination between the excited electrons transferred from GaN:Mn shell layer to the depletion layer and the Mn²⁺ hole level in the depletion region near the GaN:Mn shell. This indicates that excited carriers are accumulated into the interface of the core and the shell layer. This accumulation of carriers at the interfaces in heterostructure NWs would be helpful to realize unique magnetic properties, according to mean field theory, as well as distinctive optical and electrical properties.

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References