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Effects of high-temperature annealing on magnetic properties of V-doped GaN thin films grown by MOCVD

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ABSTRACT

Metal organic chemical vapor deposition (MOCVD) has been used to grow vanadium-doped GaN (GaN:V) on c-sapphire substrate using VCl_4 as the V source. The as-grown GaN:V exhibited a saturated magnetic moment (M_s) of 0.28 emu/cm^3 at room temperature. Upon high-temperature annealing treatment at 1100 °C for 7 min under N_2 ambient, the M_s of the GaN:V increased by 39.28% to 0.39 emu/cm^3. We found that rapid thermal annealing leads to a remarkable increase in surface roughness of the V-doped GaN as well as the electron concentration. The annealing also leads to a significant increase in the Curie temperature (T_C), we have identified Curie temperatures about 350 K concluded from the difference between the field-cooled and zero-field-cooled magnetizations. Structure characterization by x-ray diffraction indicated that the ferromagnetic properties are not a result of secondary magnetic phases.

1. Introduction

During the last few years, the manipulation of both the spin and the charge of the electron in semiconductors became a new challenge in modern microelectronics. To achieve this, diluted magnetic semiconductors (DMSs) with high magnetic ordering Curie temperatures and large spin polarizations of charge carriers have attracted considerable attention [1]. In the area of DMS related to III–V compound semiconductors, GaN have very recently received great interest, since its Curie temperature is higher than room temperature predicted by theoretical studies [2]. Although, recently GaN doped with Mn is the most intensively investigated in the group of III–V semiconductors, the systems with other transition metals as magnetic ions may also offer suitable properties. The theoretical study by first-principle calculation performed by Sato and Katayama-Yoshida [3] shows that V-, Mn-, and Cr-doped GaN are promising candidates for room temperature ferromagnetic (FM).

One of the important requirements for DMSs is the quality of the layers. Metal organic chemical vapor deposition is a mature technique for obtaining high-quality group-III nitride layers. We have reported the possibility of ferromagnetic behavior above room temperature for V-doped GaN (GaN:V) layers grown by MOCVD [4]. However, the annealing effect of GaN:V layer after growth by MOCVD on the structural and ferromagnetic behavior, has not yet been reported. Here, we report a study of the influence of annealing temperature on the structural and magnetic properties of GaN:V layers.

2. Experiment procedure

V-doped GaN layers were grown on Al_2O_3 (0001) substrates by MOCVD technique. Trimethylgallium (TMG), ammonia (NH_3), silane (SiH_4) and vanadium tetrachloride (VCl_4) were used as the precursors of gallium, nitrogen, silicon and vanadium, respectively. After thermal nitridation step for 7 min at 1080 °C under NH_3, N_2 and H_2, the SiN treatment was carried out at the same temperature. After treatment, the temperature was decreased at 600 °C to deposit GaN buffer layer. Finally, V-doped GaN take place at 1120 °C by introducing simultaneously TMGa and VCl_4 into the reactor. Specific details of the growth conditions have been reported elsewhere [5,6]. GaN:V layer were annealed at 1100 °C for 7 min in the nitrogen atmosphere. The x-ray diffraction (XRD) measurement was carried out using a Bruker D8 ADVANCE diffractometer equipped with a dynamic scintillation detector and a copper wavelength $K_{\alpha 1}$ radiation ($\lambda = 0.154056$ nm) in a symmetric Θ–2Θ geometry. The surface morphology of the GaN:V layers was observed with atomic force microscopy (AFM). Hall effect measurements were conducted by using the standard Vander Paw configuration.

The magnetic properties at room and low temperatures were analyzed using an alternating gradient field magnetometer

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(AGFM) and a superconductive quantum interference device (SQUID) magnetometer, respectively. For the measurements of FC and zero-field cooling (ZFC) magnetization versus temperature, the cooling process of the samples (in the case of FC) and the magnetization measurement were performed in the presence of 300 Oe.

3. Results and discussion

Shown in Fig. 1 are the XRD spectra of the undoped GaN, GaN:V(as-grown) and N_2 annealed GaN:V films at 1100 °C. It is observed that only diffraction peaks corresponding to GaN(0002), GaN(0004) and sapphire(0006) appear in the samples with and without annealing. No other peaks were observed in the XRD curves, suggesting that there is no phase separation or secondary phase precipitation by doping of V in GaN. But we cannot exclude the possibility of the formation of tiny amount precipitates or clusters, which are small enough to be detected in XRD measurement. Ternary phases (GaCrN) have been observed for Cr-doped GaN by Suemasu et al. [7]. Comparing the XRD curves in Fig. 1, we observe no change of peak position after doping and annealing, suggesting that there is no appreciable change in lattice parameter of GaN in our samples.

AFM was used to investigate the surface morphology of the as-grown and annealed samples. The typical AFM pictures of as-grown and annealed GaN:V films are shown in Fig. 2. The images were taken in an area of 10 μm × 10 μm. The surface morphology of GaN:V films changes after annealing. It is observed that the number of voids on the surface of the films increase with annealing temperature. The root mean square (rms) surface roughness of the as-grown films is about 98.64 nm Fig. 2(a). After annealing the surface of GaN:V becomes rougher as shown in Fig. 2(b). The roughness becomes about 108.30 nm. This change has not a significant effect on the peak positions observed by XRD. The high value of rms has the result of the doping source (VCl_4) in the presence of hydrogen as a carrier gas [8].

The magnetization versus magnetic field curves (M–H) at 5 K and 300 K before and after annealing are summarized in Fig. 3(a) and (b). The magnetic field was applied parallel to the sample surface. In the figures, clear saturation and hysteresis loops are observable, which provide evidence for the presence of ferromagnetic interactions at 5 K and 300 K in spite of their n-type conductivity [9]. Ferromagnetism at room temperature for n-type Mn-doped GaN has previously been reported [10]. The values of saturation magnetization (M_s) and coercivity (Hc) of the GaN:V at 5 K and 300 K are 0.45 emu/cm^3, 150 Oe and 0.28 emu/cm^3, 70 Oe respectively. The small coercivity and the small area under the hysteresis loop characterize these materials as ferromagnetic and these observations are consistent with those reported in other DMS [11]. Moreover, the values of Hc are higher than that of V-doped AlN (21 Oe) [12] and lower than that of V-doped ZnO (200 Oe) [13].

After annealing the GaN:V at 1100 °C in nitrogen ambient (N_2) during 7 min, the M_s (Hc) are increased (decreased) up to 0.52 emu/cm^3, 125 Oe and 0.39 emu/cm^3, 43 Oe at 5 K and 300 K respectively. These increases of saturation magnetization after annealing, which may imply that higher annealing temperature increases the amount of magnetic elements that contribute to ferromagnetism. The annealing temperature affects not only the diffusion of the dopant, but also the concentration of the intrinsic defects in the film, which in turn can influence its charge transport and magnetic properties. The annealing induced M_s enhancement of DMS materials has been explained by either the carrier-mediated mechanism [14]. In our system, the as-grown (V-doped GaN) has n-type with a carrier density of 6.98×10^{18} cm^{-3}, and the mobility about 100 cm^2/V s. Annealed sample investigated in this work revealing an increase in carrier density to 7.44×10^{18} cm^{-3}, and

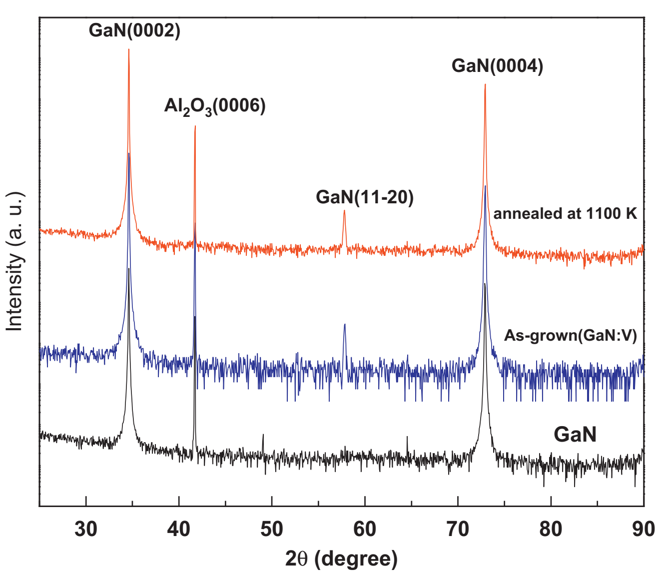

Fig. 1. XRD pattern (presented in a log scale) for GaN, the as-grown and N_2 annealed GaN:V.

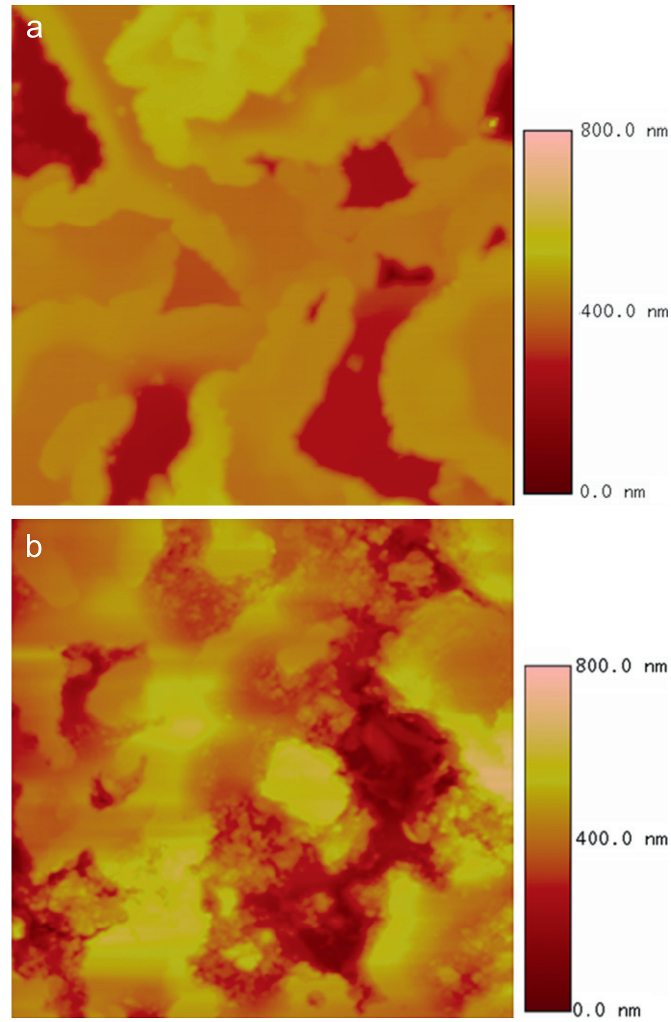

Fig. 2. AFM surface morphology of (a) as-grown and (b) GaN:V annealed at 1100 °C in N_2 ambient.