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Formation of aligned CrN nanoclusters in Cr-delta-doped GaN

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Abstract

Cr-delta-doped GaN layers were grown by radio-frequency plasma-assisted molecular-beam epitaxy on GaN template substrates. Cr flux was supplied without nitrogen flow during Cr-delta-doping. Cr incorporation into a narrow thin layer region was confirmed with the depth profile measured by secondary ion mass spectrometry. Structural properties and Cr atom alignments were studied with transmission electron microscopy. It was found that Cr-delta-doped GaN layers were coherently grown with Cr or CrGa nanoclusters in the delta-doped region for low temperature growth (350, 500 °C). It was also found that aligned CrN nanoclusters (approximately 5 nm vertical thickness) with NaCl-type structure were formed in the delta-doped region for the growth at 700 °C.

1. Introduction

We have reported the ferromagnetic magnetic characteristics for the first time in thin films of rare-earth (RE)-doped GaN, such as GaGdN [1] and GaDyN [2], and transition metal (TM)-doped GaN; GaCrN [3]. Since they show very high Curie temperatures above room temperature, this material system has attracted much attention as spintronic materials. However, first-principles Monte Carlo simulation recently showed that the effective exchange interactions in GaCrN and GaMnN are short range, while GaMnAs and ZnCrTe have a longer interaction range [4]. This simulation method fails to predict the Curie temperature of diluted magnetic semiconductors (DMSs), in particular for wide-gap DMSs. The Katayama-Yoshida group [4] simulated spinodal nanodecomposition and found that, by controlling the decomposition dimensionality, various characteristic phases occur in DMSs such as a three-dimensional (3D) Dairiseki phase and a one-dimensional (1D) Konbu phase, in which the super-paramagnetic blocking temperature of GaCrN with a Konbu phase could be higher. In addition, the Newman group [5] reported that columnar morphology with very high Cr concentration formed in the AlCrN samples, which show Curie temperatures above 900 K. So nanosized magnetic clusters in the semiconductors are interesting, because they will show peculiar magnetic characteristics [6]. Such nanomagnetic materials can be used to fabricate nanomagnetic memories with a density of terabits per square inch and other novel nanospintronics devices [4, 7].

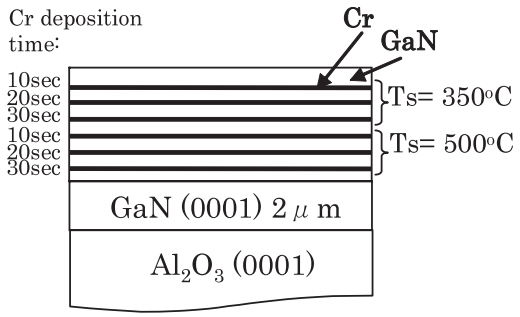


Figure 1. Schematic layer structures and growth temperatures for sample A.

In this study, in order to obtain nanosized magnetic clusters in GaN, Cr-delta-doped GaN layers were grown on GaN(0001) template substrates at various growth conditions by radio-frequency plasma-assisted molecular-beam epitaxy (RF-MBE). Cr depth profiles, structural properties and Cr atom alignments of the samples were studied.

2. Experimental procedure

Cr-delta-doped GaN layers were grown by RF-MBE on 2 μm thick GaN(0001) templates, which were deposited by metal–organic chemical vapor deposition on Al_2O_3(0001) substrates. After thermal cleaning of the template substrate surface, a

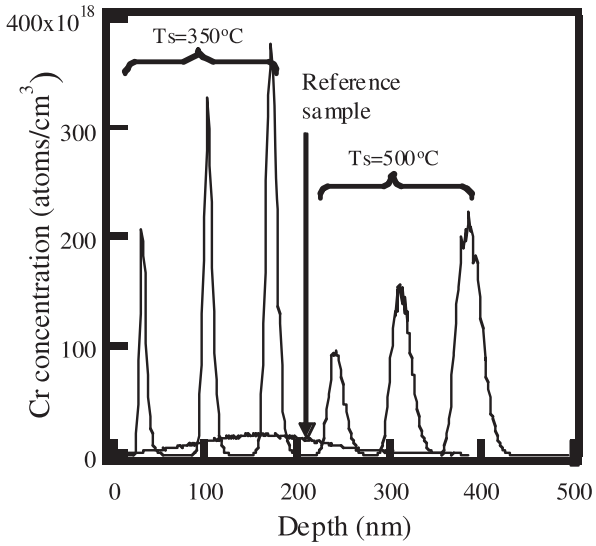


Figure 2. Cr depth profile for sample A measured with SIMS.

50 nm thick GaN buffer layer was grown at 700 °C. Four samples were grown. The layer structure of sample A is shown schematically in figure 1. Cr-delta-doping layers with 30, 20 and 10 s Cr deposition times were grown at 500 and 350 °C. These layers were separated by 70 nm thick GaN spacer layers. The other samples B, C and D have 10 cycles of Cr-delta-doping layers (20 s deposition time) and 8 nm thick GaN layers (120 s growth). Samples B and C were grown at 350 and 500 °C, respectively. In the growth of sample D, Cr-delta-doping layers were deposited at 500 °C, while 8 nm thick GaN layers were grown at 700 °C. Cr flux during deposition was 1.0×10^{-8} Torr for all these samples. For sample A, the depth profile of Cr was studied with secondary ion mass spectroscopy (SIMS), where the ^{52}Cr signal was detected using O^- as a primary ion. Samples B, C and D were characterized with x-ray diffraction, cross-sectional transmission electron microscopy (XTEM) and x-ray absorption fine structure (XAFS) analysis.

3. Results and discussion

In order to investigate the relationship between incorporation of Cr atoms and growth conditions, sample A with two growth temperatures (500 and 350 °C) was studied with SIMS. The SIMS depth profile of Cr for sample A is shown in figure 2. Peak Cr concentrations for the 350 °C-grown three Cr-doped layers are larger than those for the 500 °C-grown three layers. The Cr depth profiles for the former three layers are sharper than the latter three layers. These observations correspond to the smaller diffusion coefficient of Cr at 350 °C than at 500 °C. From this profile, the amount of Cr atoms deposited for 20 s was estimated as 2×10^{14} atoms cm^{-2} at both 350 and 500 °C.

The Cr depth profile for the GaCrN reference sample grown with the same Cr flux, where Cr was supplied during GaN layer growth, is also shown in figure 2. Cr concentration for the reference sample is much less than that for the Cr-delta-doped layers. It implies that the delta-doping technique can increase the Cr concentration at the same Cr cell temperature.

Figure 3 shows cross-sectional TEM photos for sample B grown at 350 °C and sample C grown at 500 °C. A lot of stacking faults are observed in sample B (figures 3(a) and (b)), where the formation of cubic GaN was confirmed. This corresponds to the previous observation that the Cr doping enhances the formation of cubic GaCrN for the growth of GaCrN at low temperatures [8]. Figures 3(c) and (d) for sample C indicate that Cr-delta-doped GaN layers are coherently grown on the GaN template, and keep their structure similar to the h-GaN template. No Cr-related clusters were observed in figures 3(a)–(d), though Cr or CrGa nanoclusters are considered to form, as discussed below.

Figure 4 shows the XTEM photo for sample D, where Cr-delta-doping was conducted at 500 °C, but GaN spacer layers were grown at 700 °C. Two typical areas are observed in

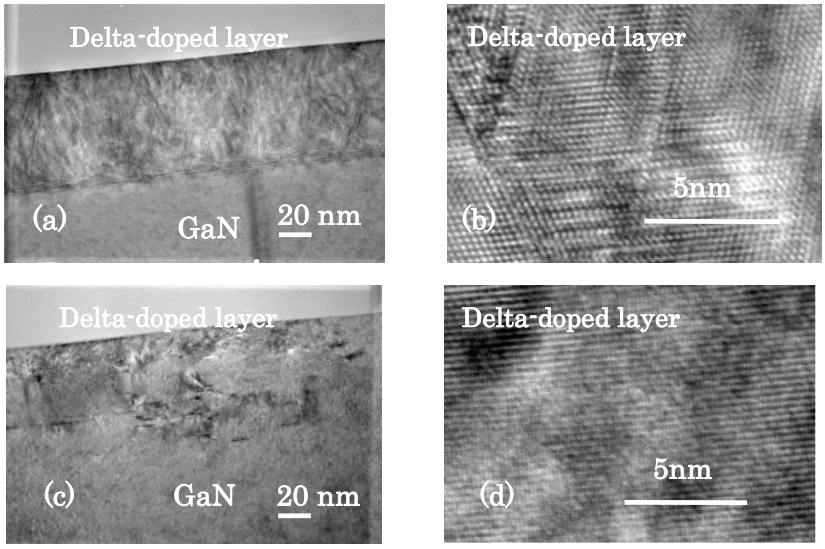


Figure 3. XTEM photos for sample B ((a), (b)) grown at 350 °C and C ((c), (d)) grown at 500 °C.

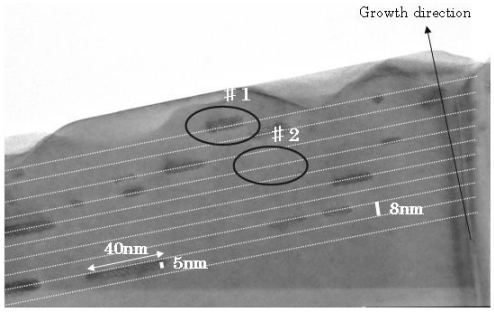


Figure 4. XTEM photo for sample D grown at 700 °C.

the Cr-delta-doped GaN layers: one are clustering areas (dark areas labeled #1); the other are epitaxially grown areas (light area labeled #2). The thickness of each clustering area along the growth axis is approximately 5 nm and these areas are exclusively arranged on the 10 parallel planes corresponding to the location of Cr deposited layers during MBE growth.

The clustering area observed in sample D is not developed in samples B and C. This indicates that there are two possible reasons: one is that Cr atoms form several monolayers of thin delta-doped layers preserving the h-GaN structure; the other is that Cr atoms diffuse into the GaN layers. It is also difficult to observe the difference between Cr atoms and Ga atoms selectively because the electron scattering factors of their atoms are close.

Energy-dispersive spectroscopy (EDS) measurements were conducted on both clustering area #1 and epitaxially grown area #2 in figure 4. Cr signal intensity is much larger at clustering area #1 than at epitaxially grown area #2, indicating that most of the Cr atoms are in the clustering areas. Furthermore, the electron diffraction (ED) pattern from the area including the clustering one (figure 5(a)) shows both diffraction spots from GaN with wurtzite-type structure and CrN with NaCl-type structure, while the ED pattern from the epitaxially grown area shows GaN spots only. These facts suggest that the clustering areas mainly consist of CrN with NaCl-type structure. The relationship of the crystal lattice direction between epitaxially grown GaN and clusters of CrN characterized by the ED pattern is as follows: GaN(0001) ∥ CrN(1$\bar{1}$1), GaN[10$\bar{1}$0] ∥ CrN[110].

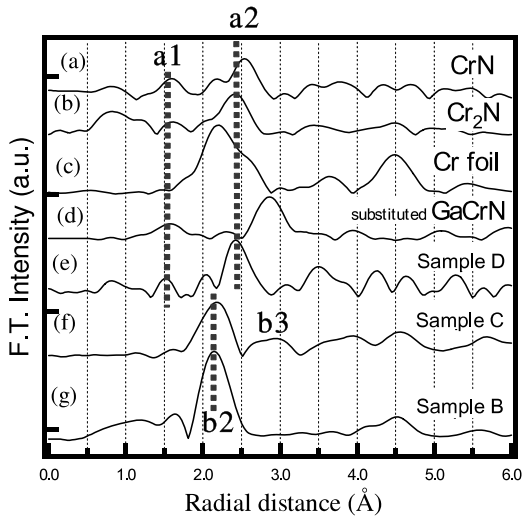
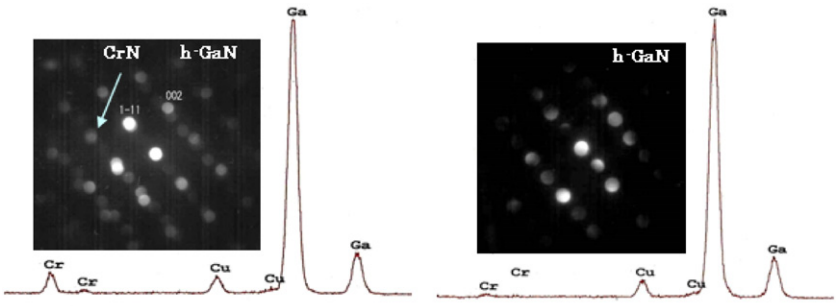


Figure 6. Radial distribution functions around Cr atoms obtained from XAFS measurements.

X-ray absorption fine structure (XAFS) analyses were used to investigate local crystal structure around Cr atoms. Figure 6 shows the radial distribution functions around Cr atoms for samples B, C and D (figures 6(g), (f) and (e), respectively). For comparison, data for (a) NaCl-type CrN, (b) Cr2N, (c) Cr foil and (d) Cr-substituted GaCrN are also shown in figure 6.

For sample D (function (e)), the radical distances for the peak **a1** from the first-nearest N atoms and the peak **a2** from the second-nearest Cr atoms approximately agree with those for the NaCl-type CrN (figure 6(a)). Therefore, the local structure around Cr atoms in sample D is NaCl-type CrN. On the other hand, the peak positions for samples C and B (figures 6(f) and (g)) are different from those for the NaCl-type CrN. Best fitting using the XAFS equation indicated that the peak **b2** corresponds to the first-nearest Ga or Cr atoms [9]. These observations indicate that in sample B grown at 350 °C and sample C grown at 500 and 500 °C, there are almost no Cr–N bonds and suggest that nanoscale Cr or CrGa clusters may be formed, which cannot be detected with TEM. No formation of Cr–N bonds is due to no supply of N flow during Cr deposition. To form the atomic layer formation of CrN, a



(a) Clustering area #1 (b) Epitaxially grown area #2

Figure 5. Electron diffraction patterns and EDS spectra for region (a) #1 and (b) #2 of figure 4.

supply of flowing N is needed during Cr deposition. This is a topic for a separate paper, where we will report the formation of tetrahedral arrangement of Cr–N bonds; zinc-blende or wurtzite structure CrN.

4. Summary

Cr-delta-doped GaN samples were grown at varied temperatures by RF-MBE. Delta-doping was confirmed by SIMS. Structural analysis with TEM showed that Cr-delta-doped GaN layers were coherently grown with Cr or CrGa nanoclusters in the delta-doped region for low temperature growth (350, 500 °C). CrN nanoclusters with NaCl-type structure were formed in the GaCrN for growth at 700 °C. Using the delta-doping technique, aligned CrN nanoclusters can be produced.

Acknowledgments

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