

Cr Atom Alignment in Cr-Delta-Doped GaN

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Abstract. Structural properties and Cr atom alignments in Cr-delta doped GaN grown by molecular beam epitaxy are studied with transmission electron microscopy and X-ray absorption fine structure (XAFS) measurements. It is found that the environment around Cr atoms in delta-doped samples is dramatically changed under various growth conditions. The XAFS analysis of these synthesized layers suggests that new Cr-related complexes are grown.

Keywords: MBE, delta doping, Cr, GaN, TEM, XAFS

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INTRODUCTION

Dilute magnetic semiconductors (DMSs) have caught much attention for their potential applications in spin-dependent photonic and electronic devices in recent years. Of those, properties of InMnAs and GaMnAs have been particularly studied for device applications. In spite of this large effort, the Curie temperatures (T_C) of Mn doped GaAs and InAs still lie below 159 K [1] at present. This is a weak point in Mn-As-DMS systems for device applications. A modern theoretical calculation indicated that high concentrations of magnetic dopants and carriers are needed to increase the T_C [2]. Therefore, highly Mn doped GaAs is grown under high As pressure at low growth temperatures. Point defects such as As-anti sites and interstitial Mn or As can be easily induced. Recently, spatially separated type doping, called delta doping, of Mn atoms in GaAs has been performed. Nazmul *et al.* [3] made DMS heterostructures consisting of Mn delta-doped GaAs and p-type AlGaAs layers. They also examined their postgrowth annealing, leading to significant improvement in its T_C to as high as 250 K. The delta doping of Mn atoms allows formation of locally high concentration of magnetic moments which exceed the solubility limit in the bulk matrix.

On the other hand, some GaN based DMSs such as GaMnN and GaCrN experimentally showed room temperature ferromagnetism [4,5]. In our previous study [6], we have reported that the solubility limit of

Cr atoms evaluated through X-ray absorption fine structure (XAFS) analysis of $\text{Ga}_{1-x}\text{Cr}_x\text{N}$ is below $x = \sim 0.03$. One of the methods to surpass the limited low solubility may be application of delta doping. Although elucidating the local environment around delta dopants gives fundamental information about DMS, few publications were found. To our knowledge, only one report on delta doping in GaN based DMSs is found in the literature [7]. In this paper, we describe the arrangement of Cr atoms delta-doped in GaN layers, grown under several conditions, by XAFS analysis.

EXPERIMENTAL

We have grown Cr-delta doped GaN layers using molecular beam epitaxy (MBE) techniques on 2 μm -thick GaN(0001) templates. The GaN template layers were deposited by metal organic chemical vapor deposition on Al_2O_3 (0001) substrates. After thermal cleaning at 700 °C, 50 nm-thick GaN buffer layers were grown on the templates at 700 °C. The continuous growth with the three-types of Cr-delta doped samples (Sample 1, 2 and 3) on the buffer layers was carried out as follows. Sample 1; Cr atoms were deposited at 500 °C for 20 sec at first. In succession, GaN layer was grown at 700 °C after elevating the temperature from 500 °C to 700 °C. This Cr / GaN bi-layer was grown in a 10 cycle. Sample 2; Cr / GaN bi-layers were grown at the same 500 °C for 20 sec in a 10 cycle. Sample 3 followed the same growth

conditions as sample 2 except the growth temperature of the bi-layers was 350 °C. Cr flux during deposition was 1.0×10^{-8} Torr for all these samples.

Structural properties of the grown film were examined by X-ray diffraction and transmission electron microscopy (TEM). XAFS were measured around Cr *K*-edge at room temperature in fluorescence mode using 19 SSD (Ge(Li)) detectors. The measurements were performed at BL-9A of the Photon Factory (PF) and BL01B1 of SPring-8. The incident X-rays were monochromatized by double Si(111) crystals. The energy was calibrated at the pre-edge of the Cu foil (12.7185 degrees).

RESULTS AND DISCUSSION

Figure 1 shows cross-sectional TEM images for samples 1, 2 and 3. In Figs. 1 (a) and (b), there are two typical areas in the Cr delta-doped GaN layers: one is clustering areas (dark areas); the other is epitaxially grown areas (light area). 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 the MBE growth. Energy dispersive spectroscopy (EDS) shows that most of the Cr atoms are in the clustering areas. Furthermore, electron diffraction (ED) pattern from the area including the clustering one (Fig. 2 (a)) shows both diffraction spots due to GaN with wurtzite type and CrN with NaCl type structures, 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 cluster of CrN characterized by ED pattern is as follows: GaN(0001) // CrN(1-11), GaN[10-10] // CrN[110].

Figs. 1 (c) and (d) for sample 2 indicate that Cr-delta doped GaN layers are coherently grown on the GaN template, and keep their structure similar to the h-GaN template. Therefore, it is difficult to distinguish the interface of the GaN template and the Cr delta-doped GaN layers. On the other hand, a lot of stacking faults are observed in sample 3 (Figs. 1 (e) and (f)). Clear Cr related clusters like sample 1 have not been observed in Figs. 1 (c) ~ (f). This indicates that the clustering area observed in sample 1 is not developed in samples 2 and 3. There are two possible reasons: one is that Cr atoms form several monolayers of thin delta-doped layer 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.

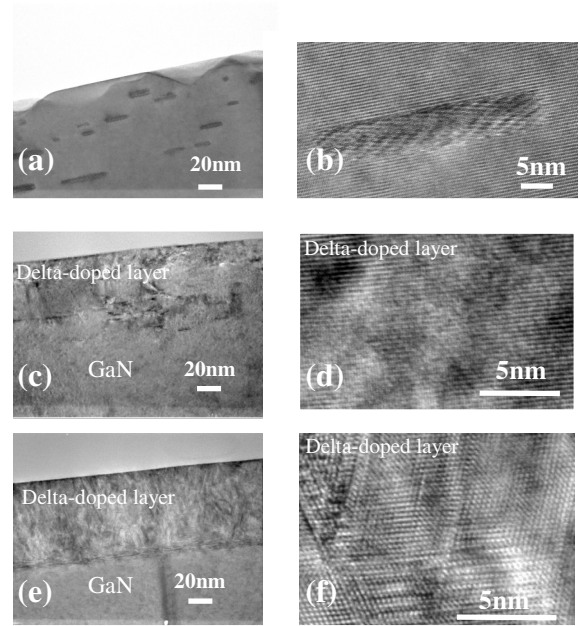


FIGURE 1. TEM images for sample 1 [(a), (b)], sample 2 [(c), (d)] and sample 3 [(e), (f)].

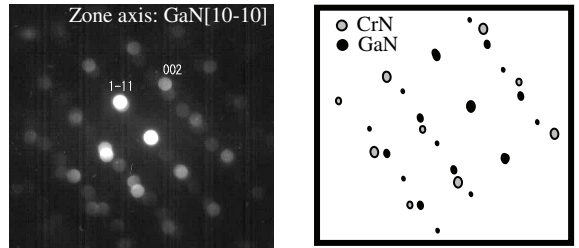


FIGURE 2. (a) Electron diffraction (ED) patterns for sample 1. (b) Simulated diffraction patterns of CrN and GaN.

XAFS data ($k^3\chi$) from the samples 1-3 are presented in Fig. 3, and the absolute magnitudes of their Fourier transforms (FT) are shown in Fig. 4. The results from Cr foil, CrN, Cr₂N and GaCrN [6] as reference samples are represented in each figure. Table 1 gives the best fitted values of the physical parameters for each FT peak using the McKale database. Here we are not able to fit well the first nearest neighboring peak (peak 1a in Fig. 4 (e)). However, the fitted values of the coordination number (N) and radial distance (R) for the second nearest neighboring peak (peak 1b) are determined to be 11.9 and 2.93 Å, respectively, closely corresponding to CrN. The first distinguishable peak in samples 2 and 3 appears around 2.2 - 2.3 Å, and are denoted 2a and 3a in Fig. 4, respectively, and the peak around 1.5 Å corresponding to that of the sample 1 is not explicitly observed, leading to the conclusion that there is no CrN formation. The peak 3a in Fig. 4 (g) consists of Cr-Ga and Cr-N, absorber-scatterer contribution, and their bond lengths are 2.46 and 2.17 Å, respectively.

The degree (R factor) of the curve fitting agrees better with Cr-Ga than Cr-Cr for the main component of the peak 3a. Therefore, the delta-doped Cr atoms in sample 3 are mainly surrounded by Ga atoms. However, it is difficult to fit the short distance side in the FT and the low k region in $k^3\chi-k$ for peak 3a with a one shell model with Cr-Ga (R factor is 1.14 %). Thus we tested a Cr-N bond at 2.17 Å, and as a result the R factor was dramatically improved to be 0.23 %. In Fig. 4 (f), the main component of the peak 2a is from Cr-Cr

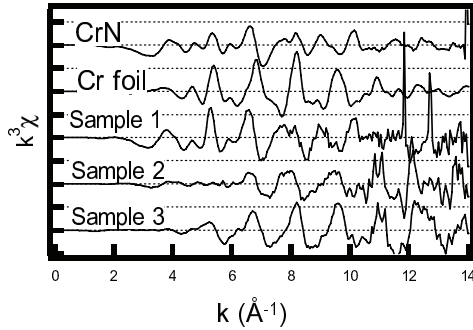


FIGURE 3. EXAFS (k) from CrN, Cr foil and samples 1-3.

scattering, being different from peak 3a. The Cr-N component as well as the case of peak 3a is also included in the peak 2a. An additional peak 2b is analyzed in sample 2. The radial distance of this peak 2b is close to that of substitutional Cr-Ga in GaCrN (Fig. 4 (d)). The results of curve fitting are given in Table. 1. It indicates that in sample 2 there are not only Cr-Cr bond systems but also Cr-N-Ga compound systems.

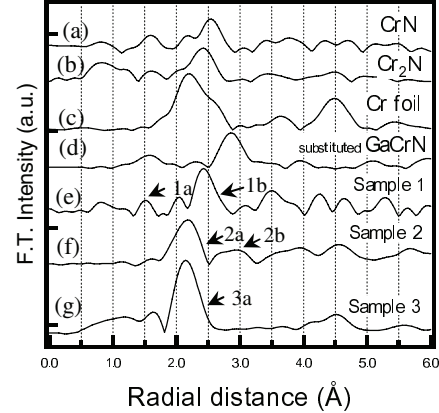


FIGURE 4. XAFS Fourier transforms magnitude from CrN, Cr₂N, Cr foil, Cr-substituted GaCrN [6] and samples 1-3.

TABLE 1. The best fitted physical parameter for each sample. The range of the FT is 1.8 ~ 16.0 Å and the range of the curvefitting 2.1 ~ 13.5 Å⁻¹ for all peaks.

Sample	Object Peak	Neighboring atom	N	R (Å)	ΔE	DW	MF	R factor (%)
CrN	1 st	N	3.45	2.11	4.62	0.01	6.21	4.29
	2 nd	Cr	6.25	2.96	0.30	0.05	6.93	1.57
Cr foil	1 st	Cr	5.97	2.87	10.71	0.07	6.73	0.73
	2 nd	Cr	7.10	2.49	12.9	0.07	7.49	
Sample 1	2 nd (Peak 1b)	Cr	11.9	2.93	-5.04	0.09	6.99	2.27
Sample 2	1 st (Peak 2a)	N	3.85	2.20	14.6	0.01	6.07	0.37
	2 nd (Peak 2a)	Cr	3.01	2.52	8.27	0.03	6.68	
	3 rd (Peak 2b)	N	1.67	3.04	11.4	0.20	12.58	0.16
	4 th (Peak 2b)	Ga	3.71	3.27	-4.71	0.07	6.68	
	5 th (Peak 2b)	Ga	0.66	2.99	-0.05	0.05	11.8	
Sample 3	1 st (Peak 3a)	N	1.84	2.17	-8.87	0.01	5.30	0.23
	2 nd (Peak 3a)	Ga	7.41	2.46	5.64	0.06	6.84	

In conclusion, we tried delta doping of Cr in GaN, and it is shown that the environment around Cr atoms is changed dramatically under the various growth conditions. We found new complexes of the Cr-N-Ga system. In alternation of growth temperature, we can produce a CrN nano-cluster (granular structure).

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