

Manganese doped gallium oxynitride prepared by nitridation of citrate precursor

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Abstract

Manganese doping of gallium oxynitride was investigated to obtain a magnetic semiconductor by nitriding a precursor in ammonia flow. The precursor was obtained by pre-firing a mixed gel made of Mn^{2+} and Ga^{3+} nitrates and citric acid in aqueous solution. The products were isostructural with hexagonal GaN. The doping limit was 10 and 5 at% in the samples nitrided at 750 and 850 °C, respectively. Chemical analysis of the products suggested that they were manganese doped gallium oxynitrides. Oxide and nitride ions were randomly distributed in the anion sites in the latter product. Manganese oxide cluster might be formed in the former. The product nitrided at 850 °C showed an antiferromagnetic interaction with a Weiss temperature $\theta = -38$ K, while the product nitrided at 750 °C was paramagnetic.

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1. Introduction

Manganese doped gallium nitride is theoretically expected to be a diluted magnetic semiconductor at room temperature [1]. The film prepared with 9 at% Mn by MBE was reported to have a Curie temperature of 940 K [2]. Another MBE film with 2 at% Mn was assumed to be ferromagnetic because it had a positive Curie temperature although it was basically paramagnetic with its low manganese concentration [3]. Hashimoto et al. reported two kinds of MBE films, namely paramagnetic and ferromagnetic GaMnN films with less than 2 and more than 10 at% Mn, respectively [4]. The latter phase was contaminated with ferromagnetic Mn-based compounds at above 50 K. These results on the thin films are controversial.

Manganese doping has also been studied using crystals obtained by an ammono-thermal technique at temperatures between 1200 and 1250 °C [5,6]. $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ($x < 0.1$) crystals were paramagnetic in the range $2 \text{ K} < T < 300 \text{ K}$. Antiferromag-

netic interaction, which may suggest the presence of super exchange, was observed at 2 K [5]. Crystals with 2 at% Mn were found to be paramagnetic in another investigation [6]. GaN crystals doped with 3d-transition metals were grown in high purity by the Na flux method [7]. Doping of <0.35 at% Mn was achieved, and the product was paramagnetic with $\mu_{\text{eff}} = 5.99 \mu_{\text{B}}$ corresponding to Mn^{2+} in high spin. The amount of Mn doping seems to be less than 2 at% in GaN single crystals grown at high temperature. The doping range was narrow and different between these reports.

Homogeneous mixing of cations can be easily achieved through preparations in solution. Mixed metal oxides and oxide solid solutions have typically been prepared at relatively low firing temperatures through homogeneous mixing by a variant of the Pechini method [9–12]. This method may enhance the Mn doping level in the case of nitridation at low calcination temperatures. Pyrochlore/fluorite type oxynitrides in $\text{RETa}(\text{O},\text{N})$ were prepared by ammonolysis of the amorphous oxide precursor through a citric acid route at the relatively low firing temperature of 900 °C [13]. Gallium oxynitride has been reported in spinel type structure under high temperature–high pressure condition [14]. “GaON” in which two kinds of close packed arrangements

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hc and fcc coexist has been prepared by ammonolysis of gallium double oxides [15]. Gas sensing behavior was recently reported on the “GaON” obtained through NiGa_2O_4 prepared by citrate method [16]. Formation of gallium oxynitride in ambient condition has not yet been reported for ammonolysis of the precursor containing gallium only as its cation through a citrate coordination polymer gel.

In the present investigation, the preparation of gallium oxynitride was studied by nitridation of the gallium oxide precursor prepared by a citric acid route in ammonia flow. The Mn doping behavior of gallium oxynitride was studied through a similar gel nitridation process. The overall changes in crystal structure and magnetic property were discussed in relation to the manganese doped GaN.

2. Experimental

Starting materials were gallium nitrate hydrate $\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($n=7-9$) and manganese nitrate hexa-hydrate $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ purchased from Wako Pure Chemicals in 3N purity. Both 1.28 g of the former and various amounts of the latter were mixed together with their equimolar amount of citric acid (Wako Pure Chemicals in 3N purity) and dissolved in 50 cm³ of distilled water. The solution was condensed to a gel on a hot plate under stirring. Brown precursors were obtained by firing the gel in the range between 300 and 400 °C for 1 h in crucibles. The precursors were amorphous. The precursor fired at 300 °C was found to contain 0.89 wt% residual carbon. There was only a trace amount of carbon in the precursor fired above 350 °C. The precursors were porous because water vapor and carbon dioxide evolved from the gel.

The precursor that was practically free of residual carbon was pulverized in an agate mortar and pestle. It was then nitrided in 5N ammonia (Nippon Oxygen Co.) flow in a mullite boat in the range between 750 and 850 °C for 10 h. The nitrided product was cooled down to below 100 °C in the ammonia flow and then taken out from the reaction tube after complete substitution of the ammonia in the tube with 4N argon for 1 h. There was no specific reason to use argon instead of nitrogen in the cooling. Color of the nitrided products changed from grayish yellow to light yellow with the nitridation temperature range. It was slightly more brownish with the manganese doping. The products obtained through nitridation of the precursor at 400 °C were contaminated with trace amounts of Ga_2O_3 , probably because the precursors were overoxidized. Thus, the precursors were used after firing the citrate polymer gel at 350 °C for 1 h. Some of the nitrided products were annealed in evacuated sealed silica tubes at 1000 °C for 10 h.

Powder X-ray diffraction was performed using X'pert MPD (PANalytical) with monochromatized Cu K α . Lattice parameters were refined by a least squares method using the well-defined diffraction lines 102, 110, 103, 200, 202, 104, 203, 210 and 211. Si was used as an internal standard. Nitrogen and oxygen contents were analyzed by EMGA EF-600 (Horiba) using Si_3N_4 (R003 supplied by Ceramic Society of Japan) and 3N Y_2O_3 as reference powders, respectively. Magnetic properties were measured over the temperature range 5–300 K under a magnetic field of 5 T with a MPMS-5S SQUID (Quantum Design). X-ray absorption of Mn and Ga-K edge was measured in the transmission mode at beam line BL-9A and BL-10B of the Photon Factory in KEK, Tsukuba. Details of the experimental procedure were given in Reference [17]. The EXAFS interference function, $\chi(k)$, was extracted from the measured absorption spectra using the standard procedure [18].

3. Results and discussion

The precursors derived from citrates of varying manganese content were nitrided at 750 °C. The products showed broad X-ray diffraction peaks. The positions of these peaks were similar, but their relative intensities were different from those of h-GaN, as shown in Fig. 1. The relative intensity of the 101

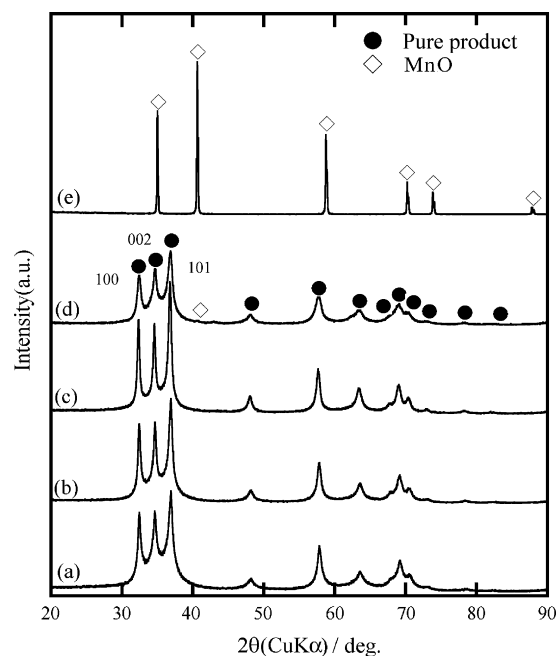


Fig. 1. XRD patterns of specimens nitrided at 750 °C of varying manganese content: (a) $x=0$, (b) $x=0.05$, (c) $x=0.10$, (d) $x=0.15$ and (e) $x=1.0$.

peak was much stronger in h-GaN than in the present product. A different intensity ratio for the three first diffraction peaks has been reported [15,16]. The second one was the most intense for “GaON” with the sphalerite type structure. There were three more additional peaks at $2\theta=40.02^\circ$, 86.51° and 96.41° . However the present product did not show these extra peaks. Hexagonal close packing in wurtzite is preserved instead of cubic closest packing in the sphalerite. Some amount of oxygen might be present in the wurtzite type crystal lattice partly substituting nitrogen of h-GaN.

In the compositional range above the solid solution limit of about 10 at% Mn, MnO impurities appeared and the diffraction peaks became broader, as shown in Fig. 1(d). The lattice parameters were $a=0.3184$ nm and $c=0.5179$ nm for the Mn-free nitrided product, as shown in Fig. 2. Both of these parameters were much smaller than the reported values for h-GaN, namely $a=0.31890$ nm and $c=0.51855$ nm [19] probably because a small amount of gallium vacancy was introduced with the partial substitution of nitrogen with oxygen. The lattice parameters gradually changed with the manganese amount up to $x=0.10$ and then reached almost constant values of $a=0.3175$ nm and $c=0.5187$ nm. The unit cell volume shrank from $V=45.47 \times 10^{-3}$ to 45.31×10^{-3} nm³ with Mn doping.

Crystallinity of the products was improved upon nitridation at 850 °C, as shown in Fig. 3. The relative peak intensity of the XRD peaks was more similar to that for h-GaN than the product at 750 °C. MnO impurity was observed even at 10 at% Mn, as indicated in Fig. 3(c). The hexagonal lattice parameters for the Mn-free specimen, namely $a=0.3189$ nm and $c=0.5183$ nm, were much closer to the h-GaN values than those for the sample nitrided at 750 °C, as shown in Fig. 4. The amount of gallium vacancy was reduced in the higher nitridation temperature.

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