



Preparation of gallium oxynitride in the presence of iron through a citrate route

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ABSTRACT

Gallium oxynitrides were prepared in the copresence of various amounts of Fe³⁺ by ammonia nitridation of oxide precursors. Their crystallinity reduced in a compositional range up to 3 mol% and improved again above 4 mol% with an appearance of a nitride impurity. The product with 2 mol% of Fe³⁺ showed the maximum oxygen content of 21 mol% and minimum nitrogen content of 24 mol%. X-ray absorption spectroscopy, Mössbauer and magnetic measurements suggested a small amount of Fe₃O₄-like clusters in the oxynitride products. Density-functional calculations supported that the Fe-O-clustered system is more preferable than the statistical distribution of iron in the hexagonal gallium oxynitride structure.

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1. Introduction

Transition metal doped GaN has attracted a lot of interest in the field of carrier-induced ferromagnetism within diluted magnetic semiconductors [1]. Ferromagnetism was also reported in the low-temperature MBE-grown GaN with high Fe doping of 10¹⁹ cm⁻³ [2]. It appeared below 100 K and its origin was not clear. Precipitation of Fe_xN clusters was detected by TEM. Ferromagnetism with higher Curie temperature (~250 K) was also found out on high dose Fe implanted films of p-type GaN (~5 mol%) with subsequent annealing at 700–1000 °C [3–5]. Another research group reported room-temperature ferromagnetism on the similar p-type GaN film implanted with Fe⁺ ions [6]. An iron-doped GaN layer was grown epitaxially on GaN layer by MOCVD at 800–950 °C [7]. It showed a temperature-independent van Vleck paramagnetism of Fe²⁺. The reported magnetic behavior scatters among the iron-doped GaN samples as mentioned above.

Gallium oxynitride (Ga_{0.89}O_{0.11}(N_{0.66}O_{0.34}), isostructural to h-GaN, was obtained by the ammonolysis of a precursor prepared from an aqueous solution of gallium nitrate in addition of citric acid [8]. It was doped with 10 and 5 mol% Mn in the nitridations at

750 and 850 °C, respectively [9]. EXAFS measurements suggested a possible formation of manganese oxide clusters in the gallium oxynitride matrix of the nitrided product prepared at 750 °C. The product was paramagnetic down to 5 K although the nitrided product prepared at 850 °C showed an antiferromagnetic interaction in the gallium oxynitride matrix exhibiting a random distribution of oxygen and nitrogen atoms. Less than 1 mol% Cr³⁺ was also doped into the gallium oxynitride in a similar preparation route [10]. The product showed a Curie-like paramagnetism. The gallium oxynitride was doped with about 10 mol% Li⁺ randomly substituting Ga³⁺ [8]. The electrical conductivity was reduced because an excess amount of O₂⁻ was introduced with the doped Li⁺ substituting N³⁻. The solid solution limits of these cation dopings to the gallium oxynitride were strongly related to the site preference of doping cations, either for tetrahedral or octahedral sites. The preparation via the solution route offers the chance to obtain homogeneous solid solutions in a wide compositional range.

Ferric ion is found in tetrahedral environment either in wurtzite or zinc blende type FeN_x and in octahedral coordination in oxides [11–13]. Iron nitrides are thermally metastable due to their anti-bonding contribution in the highest occupied bands [14]. Iron particles were dispersed in AlN matrix to obtain granular magnetic film by a post annealing of Al_{1-x}Fe_xN sputter-deposited film. They precipitated because the bonding of iron to nitrogen in the nitride is not stable at high temperature. The granular film showed a magnetoresistance effect of 0.82% at room temperature [15].

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In the present study, the substitution of Ga^{3+} with Fe^{3+} in the gallium oxynitride was investigated by an ammonolysis of the oxide precursor prepared from a mixed metal citrate gel. The behavior of iron in the gallium oxynitride matrix was studied from its crystal structure, chemical analysis, magnetic measurement and quantum-chemical total-energy calculation.

2. Experimental

Ferric nitrate nonahydrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was mixed with gallium nitrate octahydrate $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$ in a Fe/Ga molar ratio of $x/(1-x)$ with $x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.10$ and 0.15 in about 20 ml of distilled water. These nitrates were purchased from Wako Pure Chemical Co. in 99.9% purity. Their metal contents were confirmed by ICP analysis (Shimadzu, ICPS-1000IV) before use. Equimolar anhydrous citric acid (Wako Pure Chemical Co., 98.0%) was added to the mixed aqueous solution against the total amount of nitrates. The mixed solution was heated on a hot plate under stirring to form a viscous gel. The brown gel was fired at 350°C for 1 h to result in a grey fluffy precursor. After grinding, it was then nitrated at 750°C for 10 h in ammonia (Sumitomo Seika Chemicals Co., 99.999%) using a flow rate of 50 ml/min. A yellow powderous product was obtained after cooling to room temperature. The residual ammonia was purged from the reaction tube with argon gas.

Powder X-ray diffraction was measured with a diffractometer (PANalytical, X'pert-MPD) with monochromatized Cu-K α radiation. The X-ray absorption measurement of the Fe and Ga-K edges was performed at BL-7C of the Photon Factory in KEK, Tsukuba. The incident X-rays were monochromatized by using a double-crystal monochromator with a Si(1 1 1) surface. The fluorescence mode was applied for the samples doped with a small amount of Fe. The EXAFS interference function, $\chi(k)$, was extracted from the measured absorption spectra using the standard procedure [16]. Magnetic properties were measured in a temperature range of 5–380 K and a magnetic field of $-5 \times 10^7/4\pi$ A/m to $+5 \times 10^7/4\pi$ A/m with a MPMS-5S (Quantum Design). Mössbauer spectrometer (Topologic Systems 220) using Co^{57} as a γ -ray source was operated to take the transmission spectrum at room temperature. Nitrogen and oxygen contents were analyzed by EMGA-620W (Horiba) using Si_3N_4 (R003 supplied by Ceramic Society of Japan) and $\alpha\text{-Fe}_2\text{O}_3$ as reference powder.

The electronic-structure calculations were performed within the framework of density-functional theory (DFT) with the Vienna *ab-initio* Simulation Package (VASP) [17,18], using ultrasoft pseudopotentials (USPP) of Vanderbilt type [19] with a kinetic energy cutoff of 500 eV; the crystal orbitals were expanded in plane waves. Correlation and exchange terms between the electrons were described by the generalized gradient approximation (GGA) of Perdew and Wang [20]. All results rely on well converged structures with respect to the k -point sampling. Forces were relaxed to values below 1 eV/nm and stresses below 2 kbar. The simulation box was the same as used in our previous work [10], which contains 194 atoms, except that Cr^{3+} is replaced by Fe^{3+} . In addition several different anion as well as cation distributions were investigated.

3. Results and discussion

Gallium oxynitride was prepared at 750°C in copresence of various amounts of Fe^{3+} through citrate route. It crystallized in wurtzite type structure up to 2 mol% of Fe^{3+} just as the nitrated product without Fe^{3+} . Its crystallinity became much worse up to 3 mol% of Fe^{3+} as shown in Fig. 1. The relative XRD peak intensity slightly changed above 3 mol% of Fe^{3+} ; the 0 0 2 diffraction line showed the largest intensity. A small amount of impurity appeared

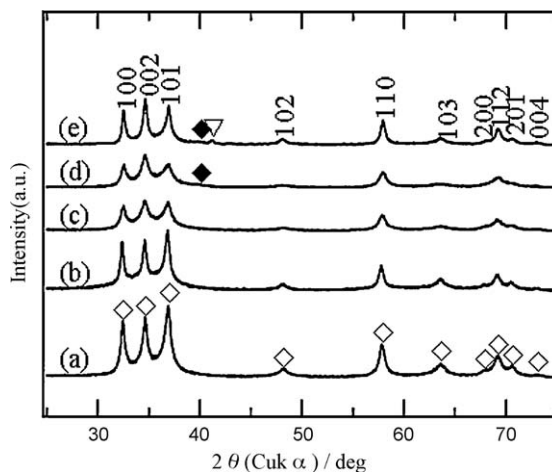


Fig. 1. X-ray diffraction patterns for the Fe-doped gallium oxynitrides. The doping amounts were (a) 0 mol%, (b) 2 mol%, (c) 3 mol%, (d) 4 mol% and (e) 10 mol%. Diffraction lines were assigned for the gallium oxynitride marked with open diamond, impurities of Fe_3GaN with filled diamond and Fe_4N with open triangle.

above 4 mol% of Fe^{3+} and the impurity might be assigned to Fe_3GaN isostructural to Mn_3GaN [21]. Fe_4N also appeared above 10 mol% Fe^{3+} as another impurity. The hexagonal lattice parameter was $a = 0.3188(4)$ nm, independent from the Fe^{3+} content, and only the c -parameter slightly expanded from $c = 0.5179(5)$ nm for the pure gallium oxynitride to $0.5188(6)$ nm in a compositional range above 3 mol%. The enhanced 0 0 2 diffraction intensity, XRD line broadening and the slight expansion in the lattice parameter c might be related to a partial stacking disorder from ABABAB in the wurtzite lattice to ABCABC in the products doped with Fe. A similar relative intensity change has been reported on gallium oxynitride prepared in the presence of NiGa_2O_4 [22].

Both oxygen and nitrogen contents were analyzed in the oxynitride products. The oxygen content was about 20 mol% in the compositional range of 2–3 mol% Fe^{3+} as depicted in Fig. 2. A small amount of the coexisting Fe^{3+} introduced about 10 mol% of additional oxygen to the nitrated products. Nitrogen content decreased in about 15 mol% in the same Fe^{3+} compositional range. Thus, the small amount of Fe^{3+} in the gallium oxynitride released nitrogen and took up the additional oxygen in the nitrated products. Cation vacancies found in the pure gallium oxynitride have been eliminated by the Fe^{3+} doping [8]. The thermally metastable nature of iron nitrides has been recognized, especially on those with smaller nitrogen contents such as Fe_{16}N_2 [23]. The

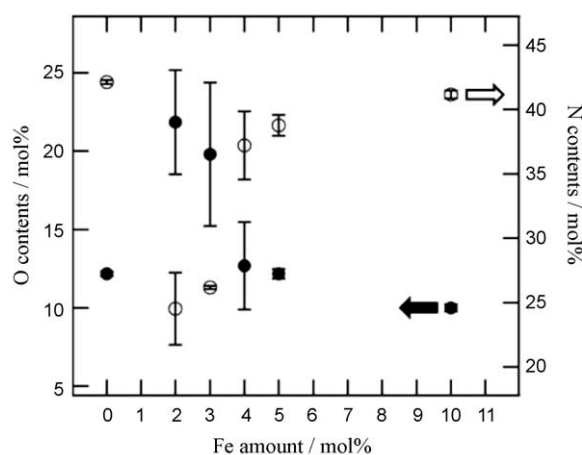


Fig. 2. Variation of oxygen and nitrogen contents against the amount of doped Fe. Filled and open circles stand for the contents of oxygen and nitrogen, respectively.

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