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MOCVD growth and electrical studies of p-type AlGaN with Al fraction 0.35

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Abstract

We present a study on the high performance p-type $Al_xGa_{1-x}N$ ($x = 0.35$) layers grown by low-pressure metalorganic chemical vapor deposition on AlN template/sapphire substrate. The influence of growth conditions on the p-type conductivity of the $Al_xGa_{1-x}N$ ($x = 0.35$) alloy is investigated. From the Hall effect and I–V transmission line model measurements, a p-type resistivity of 3.5 Ω cm for $Al_xGa_{1-x}N$ ($x = 0.35$) epilayers are achieved. To the best of our knowledge, this is the lowest resistivity ever measured for the uniform p-type AlGaN with Al fraction higher than 0.3. The Mg and impurities (O, C and H) of the atom concentration in the epi-layers are analyzed by means of SIMS depth profiles, which reveal the dependence of impurities incorporation on the III elements and growth temperature.

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Keywords: A1. Doping; A3. Metalorganic chemical vapor deposition; B1. Nitride; B2. Semiconducting aluminum compounds

1. Introduction

$Al_xGa_{1-x}N$ alloys have a direct wide band gap ranging from 3.4 eV (GaN) to 6.2 eV (AlN), which is well suited for the realization of deep ultraviolet (UV) optoelectronic devices. However, it is rather difficult to develop high conductivity n-type and p-type AlGaN alloys with high Al fraction, which are indispensable for achieving high performance in these devices. A number of groups have reported the impressive progress of high Al-content n-type AlGaN via Si–In co-doping at a reduced and high temperatures [1,2]. However, the achievement of high Al-content p-type AlGaN remains a significant challenge. Two main factors limit the p-type conductivity of AlGaN alloy: (i) the high activation energy for the substitutional Mg acceptor, the primary p-type dopant in GaN, is high (150–210 meV) [3–5], and becomes higher as the value of x in $Al_xGa_{1-x}N$ increases [6]. (ii) When increasing the Al fraction, the AlGaN epi-layer usually exhibits higher defect densities [7], which can compensate for the dopants. Several groups have reported successful MOCVD growth of uniform p-type AlGaN epitaxial layers using Mg as a dopant [8–12]. Most of the investigations focus on p-type AlGaN epilayers with an Al fraction that is less than 20%. Recently, Jeon et al. [13] reported that the viability of low resistivity p-AlGaN doping is constrained by two competing mechanisms, namely, a minimum dosage of Mg acceptors required to overcome the background defects and an incorporation ceiling above which structural defects occur.

In this paper, we report on the MOCVD growth and electrical studies of high Al fraction p-type AlGaN epilayers with improved conductivities. Under suitable growth conditions, p-type conduction of $Al_xGa_{1-x}N$ ($x = 0.35$) with resistivity of 3.5 Ω cm at room temperature were achieved. To the best of our knowledge, this is the lowest resistivity ever measured for the uniform p-type AlGaN with an Al fraction higher than 0.3.

2. Experimental procedure

Mg-doped AlGaN epitaxial layers were grown in a low pressure MOCVD reactor (Aixtron 200/4 HT-S), using

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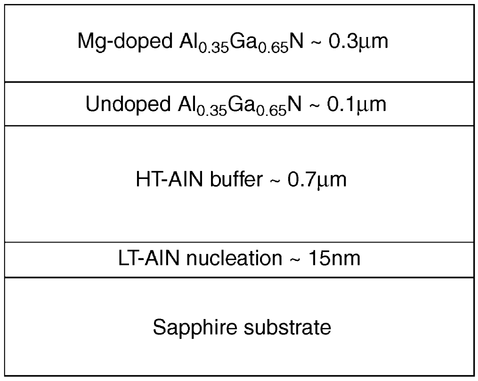

Fig. 1. Schematic drawing of epi-growth structure on sapphire substrate.

Trimethylgallium (TMGa), trimethylaluminum (TMAl), ammonia and biscyclopentadienylmagnesium (Cp_2Mg) as Ga, Al, N and Mg precursors, respectively. The buffer structures included: a 15 nm thick, low-temperature (600 °C) AlN nucleation layer, high temperature (1150 °C) 0.7 μm AlN template, and undoped AlGaN transitional layer (0.1 μm). After deposition of these layers, 0.3 μm thick Mg-doped AlGaN layers were grown using different growth parameters. Fig. 1 shows a schematic drawing of the sample structure. The H_2 was used as a carrier gas during AlN and AlGaN growth. Details on the growth process can be found elsewhere [14]. No additional conductive layers that could have influenced the conductivity measurements were found. The Mg-doped samples were thermally activated in N_2 ambient at 850 °C for 10 min, which resulted in a p-type conduction verified by the Hall measurement (standard Van Der Pauw). It was found that the optimum thermal activation temperature for Mg-doped AlGaN is higher than that of Mg-doped GaN, which is activated using 750 °C for 15 min.

X-ray diffraction was performed using a Bruker D8 system, delivering a CuKα1 line. To obtain the resistivity of the p-type AlGaN layers, the Current-voltage (*I–V*) transmission line model (TLM) and Hall effect measurements (commercial Lakeshore model 7512 Hall Measurement System) were performed. Ni/Au (10 nm/100 nm) metallization contact was fabricated on the p-type AlGaN surface for Hall measurement. After metallization, the samples were step annealed 60 s at 700 °C and 120 s at 850 °C in flowing N_2 ambient. *I–V* measurements were carried out by an HP 4142B Modular DC source.

3. Results and discussions

Before the deposition of the AlGaN layer, the growth processes of the 0.7 μm AlN template were optimized. The advantages of using an AlN epitaxial layer as a template for defect density reduction of the subsequent AlGaN layers have been demonstrated in several previous experiments [15,16]. After optimization, X-ray symmetric diffraction (0 0 0 2) revealed narrow full width at half maximum (FWHM) for both rocking and $\omega - 2\theta$ scan peaks: 323 arc s for rocking scan and 298 arc s for $\omega - 2\theta$ scan, respectively. The application of a high quality AlN template as a buffer layer is one key to improve the electrical properties of the subsequent p-type AlGaN layer. The UV optical transmission was performed on the as-grown samples. The optical transmission spectrum shows a sharp cut-off at 284 nm along with well-defined Fabry–Perot oscillations (not shown here) due to the high-quality of the material and the smooth surface [14].

Different from binary semiconductor alloys, the ternary AlGaN alloys possess two kinds of III elements (Ga and Al) which are in a competitive combination during the epitaxial growth. Two series of the Mg-doped AlGaN layers are grown keeping the TMGa flow rates of 22.5 μmol/min and 40.4 μmol/min, respectively. The Al fractions in AlGaN layers are changed by altering the TMAl flow rate. During all AlGaN layers growth, the reactor pressure and growth temperature are kept 50 mbar and 1050 °C, respectively. The used V/III ratios are in the range of 600–1200 during the deposition. The growth rate changes between 0.5 and 1.2 μm/h. Fig. 2 shows the dependence of an AlN mole fraction in the layers on the TMAl/(TMAl + TMGa) mole flow ratio. For the TMGa flow at 22.5 μmol/min, the Al composition in the solid phase is evident larger than the input ratio in the vapor phase. A quasi-thermodynamic analysis of the MOVPE growth of AlGaN alloy using TMGa, TMAl and ammonia had been proposed [17]. The Al atoms are preferentially incorporated into the AlGaN alloy because the reaction equilibrium partial pressure of Al is significantly lower than that of Ga. Therefore, the Al fraction in the solid AlGaN alloy is higher than that in the vapor phase. While for the TMGa flow of 40.4 μmol/min, the Al incorporation in the layer is at a relatively low level. With the TMAl flow increasing (TMAl/(TMAl + TMGa) to 0.42, the Al fraction

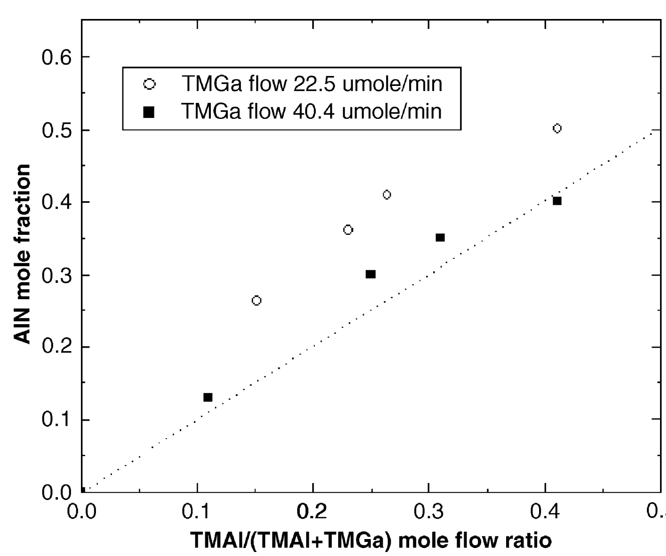

Fig. 2. The dependence of an AlN mole fraction in the layers on TMAl/(TMAl + TMGa) a mole flow ratio at $T = 1050$ °C, and $P = 50$ mbar.

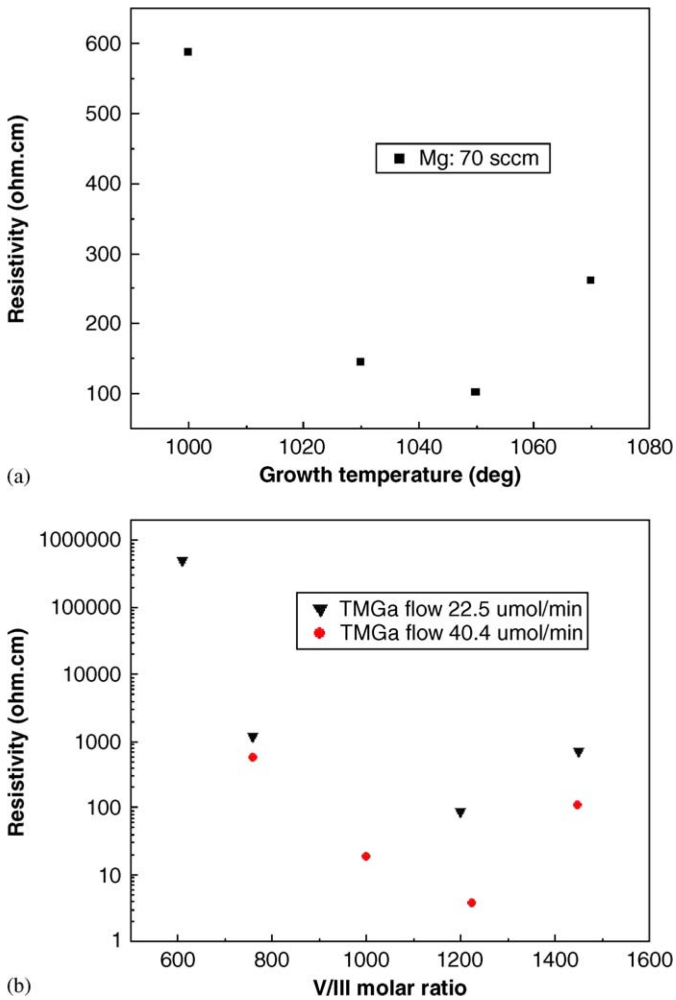

Fig. 3. Resistivity of the p-type $Al_xGa_{1-x}N$ ($x = 0.35$) epilayers as a function of (a) the growth temperature and (b) V/III molar ratio and group III element flow.

in AlGaN alloy is lower than that in the vapor phase. This phenomenon can be explained by the remarkable vapor phase reaction of TMAl and NH_3 with an increasing TMAl flow; even the growth is at a low reactor pressure and high temperature. Our experimental results are consistent with the quasi-thermodynamic analysis, and subsequently verify that the thermodynamic process controls the MOCVD growth of AlGaN alloy. It is implied that the electrical properties of the p-type AlGaN can be affected by changing the thermodynamic growth conditions.

Fig. 3(a) shows the resistivity of p-type AlGaN (Al = 0.35) layers as a function of growth temperature. The V/III mole ratio and Cp_2Mg flow are kept at 1200 and 0.536 μmol/min (Cp_2Mg/(TMAl + TMGa) is 9.25×10^{-3}) during all of the growths. As shown in Fig. 3(a), as the reactor temperature increases from 1000 to 1070 °C, the resistivity values first decrease from about 600 to 100 Ω cm, and then increase to about 250 Ω cm. The results show that the most suitable growth temperature for the p-type AlGaN (Al = 0.35) was in the range of 1030–1050 °C in this reactor.

To explore the influence of the growth conditions on the electrical properties of the p-type AlGaN epilayers, two series of the Mg-doped AlGaN layers were grown at 1050 °C. The TMGa flow rate was 22.5 μmol/min and 40.4 μmol/min for the first and second series, respectively. Al fraction in AlGaN alloy was maintained at 35% in all of the samples by adjusting the TMAl flow rates to 6.7 and 17.9 μmol/min. Fig. 3(b) summarizes the room-temperature resistivity of the samples from both series as a function of the V/III molar ratio. As shown in this figure, the variation of the resistivity as a function of the V/III molar ratio shows a similar trend for both series, indicating that the resistivity of the p-type AlGaN alloy has a remarkable dependence on the V/III ratio. For the samples of the first series, the Mg-doped AlGaN reveal a high resistance ($>1 \times 10^7$ Ω cm) at a V/III ratio of 610, and a minimum resistivity of 89.3 Ω cm at a V/III ratio of 1200. The decrease of the resistivity of the samples with increasing of the V/III ratio is consistent with the compensation by nitrogen vacancies in the p-type doping of GaN [18]. Compared to the samples of the first series, the resistivity of samples from the second series was much lower (more than one order of magnitude) which was due to the increase of the III-element precursors flow (namely the growth rate) at the same V/III ratio. The minimum resistivity (3.5 Ω cm) was achieved at a V/III ratio of 1225. After a V/III ratio of about 1200, the resistivity values starts to increase in both series. A relatively low V/III ratio should be used to obtain high crystalline quality AlGaN epilayers, by increasing the surface mobility of adsorbed Al species. We suspect the resistivity increase is due to degradation of the AlGaN crystalline quality at a high V/III ratio.

SIMS depth profiles of Mg and impurities (O, C and H) atoms were performed in the selective samples after annealing. As shown in Fig. 4, the Mg concentration in the AlGaN layer is approximately 2×10^{19} atoms/cc. It is

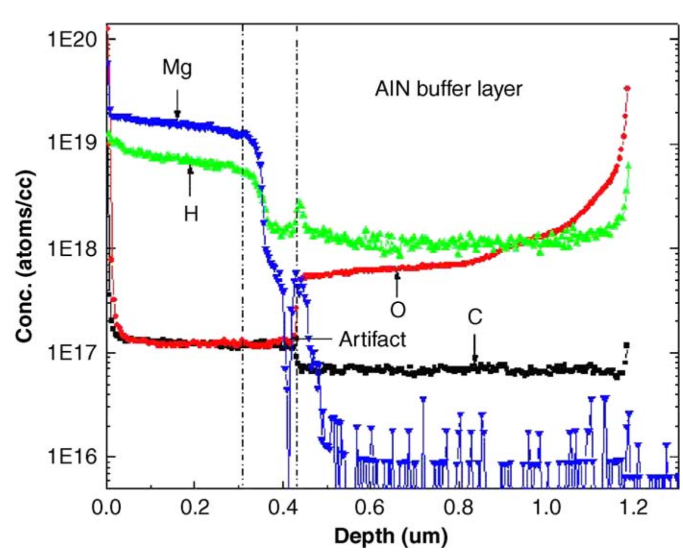

Fig. 4. SIMS profiles of Mg and impurities (O, C and H) atoms in the epilayer.

noticed that the H concentration has a variation similar to the variation of the concentration of the Mg atoms, where the H concentration is about half of the Mg concentration in the p-type AlGaN layer. This correlation between Mg and H has been previously observed in a p-type GaN [5]. The O and C atom concentrations show remarkable gradient at the interface of AlN buffer and the AlGaN layer. It is widely accepted that the O contamination in GaN is mainly due to ammonia. But compare that to the AlGaN growth, the ammonia flow rate is approximately one order of magnitude lower during AlN deposition, while the O concentrations in AlN (6×10^{17} atoms/cc) are about four times of magnitude higher than that in the AlGaN part (1.5×10^{17} atoms/cc). This provides evidence that the O incorporation is determined not by ammonia flow, but by the Al atoms during AlGaN growth, due to the high reactivity of Al and O. This is very different to GaN growth. The C atoms concentrations are 6×10^{16} and 1.5×10^{17} atoms/cc in AlN and AlGaN parts, respectively. The nature of C-related states in GaN and AlGaN is complex and not well understood at present. It is observed that the C concentration decreases as the growth temperature is raised in the GaN and AlGaN epilayers [19]. The lower C impurity concentration in the AlN parts can be ascribed to the higher growth temperature (1150 °C), compared to that of AlGaN (1050 °C). It should also be noted that both the O and C incorporation did not show dependence on the Mg dopant.

4. Conclusion

In summary, we have demonstrated p-type conductivity in Mg-doped $Al_xGa_{1-x}N$ ($x = 0.35$) epilayers. The influence of growth conditions (growth temperature, V/III molar ratio and group III element flow rate) on p-type conductivity was investigated. It was found that a proper V/III ratio and a relatively high growth rate were needed to improve the electrical characteristics of the p-type AlGaN epilayers. A p-type resistivity of $3.5\,\Omega\,\mathrm{cm}$ and a hole concentration of $>5 \times 10^{17}\,\mathrm{cm}^{-3}$ for $Al_xGa_{1-x}N$ ($x = 0.35$) were obtained under optimized growth conditions.

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