

Characteristics of p-type GaN Films Doped with Isoelectronic Indium Atoms

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The method of isoelectronic doping, is employed to prepare p-type GaN films using metalorganic chemical vapor deposition. With the addition of In atoms, the film surface becomes much smoother, and the corresponding hole concentration and resistivity are also improved, to $8.7 \times 10^{17} \text{ cm}^{-3}$ and $\gg 1 \Omega\text{-cm}$, respectively. More interestingly, it is found that an ohmic I-V characteristic can be obtained in such types of films without any dehydrogenation treatment.

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PACS. 68.55.Ln – Defects and impurities: doping, implantation, distribution, concentration, etc.

I. Introduction

The group III-nitride semiconductors have recently attracted much attention owing to a variety of applications in blue, green light-emitting diodes, violet laser diodes, as well as in semiconductor light bulbs [1-4]. Despite the number of advances being achieved, the realization of high conductivity p-type GaN material still remains a challenge, which hampers the rapid development of nitride-based laser diodes and bipolar devices [5]. For wide-bandgap material, due to the inherited deep acceptor energy level feature, a poor doping efficiency is usually a result in such types of semiconductor. However, the situation is even worse for GaN. This is because the doping of Mg atoms can itself generate lots of native donors, causing severe self-compensation effects which degrade the film properties. To enhance the hole concentration, several methods, in addition to a dehydrogenation process, have been employed to prepare p-GaN, including modulation doping, codoping of p-type dopants (e.g., Mg and Zn), ion-implantation of high density shallow Be acceptors, and conducting the growth in a hydrogen-free ambient atmosphere. In this study, we present an alternative way to prepare p-type GaN, by using isoelectronic indium codoped with Mg during the deposition. Clear improvements are found in terms of surface morphology and electrical properties when the film is also doped with In atoms.

II. Experiments

The isoelectronically indium-doped and Mg-doped p-type GaN films were grown on 2" C-plane (0001) sapphire substrates at $1110 \pm \text{C}$ using a low pressure metalorganic chemical vapor deposition (LP-MOCVD) method with a horizontal reactor. The samples were prepared by a nominal two-step growth method. A 300 Å low-temperature GaN nucleation layer was first

deposited at $520 \pm 5^\circ\text{C}$, followed by the direct growth of a $\approx 2 \mu\text{m}$ thick GaN:Mg layer without the introduction of a buffer layer between them. For sample preparation, electronic grade trimethylgallium (TMGa), ammonia (NH_3), and bis-cyclopentadienylmagnesium (Cp_2Mg) were used as the Ga, N, and Mg source precursors, respectively. When isoelectronic In doping was needed, trimethylindium (TMIn) diluted with hydrogen was used, which gave a solid In/Ga concentration ratio of $\approx 0.2\%$ in the film. The resultant surface morphologies were examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM) (DI-Nanoscope IIIa) using the tapping mode, while the Hall effect measurements were conducted at 300 K under a magnetic field of 1 T and a current of 10^{-4} A. Finally, a parameter analyzer (HP 4145B) was used to determine the current-voltage (I-V) characteristics of selected p-type GaN films.

III. Results and discussion

In an attempt to investigate the isoelectronic In effects on p-type GaN, two series of samples were prepared. One consists of conventional Mg-doped GaN films grown with a Cp_2Mg flow rate that varied from 100 to 495 sccm ($0.118 \mu\text{mol}/\text{min}$ to $0.585 \mu\text{mol}/\text{min}$). The other was of GaN:Mg films co-doped with isoelectronic In atoms prepared under essentially the same growth conditions, except for introducing a constant TMIn flow rate of $25.5 \mu\text{mol}/\text{min}$ (250 sccm) concurrently during the sample preparation. We note that there was a dramatic change in the film surface morphology, as revealed by the SEM micrographs in Fig. 1. For the Mg-doped GaN, many pockmarks, as expected, were spread all over the entire surface, stemming presumably from the large differences

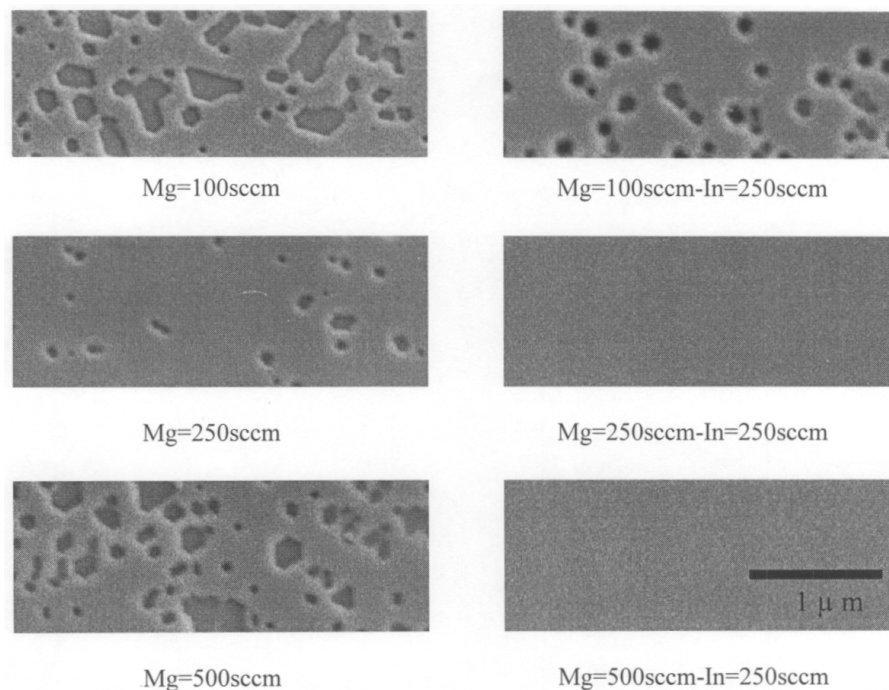


FIG. 1. SEM micrographs of (a) \gg (c) for GaN:Mg films grown with various Cp_2Mg flow rates from 100 to 495 sccm, and (d) \gg (f) for GaN:Mg films co-doped with In atoms.

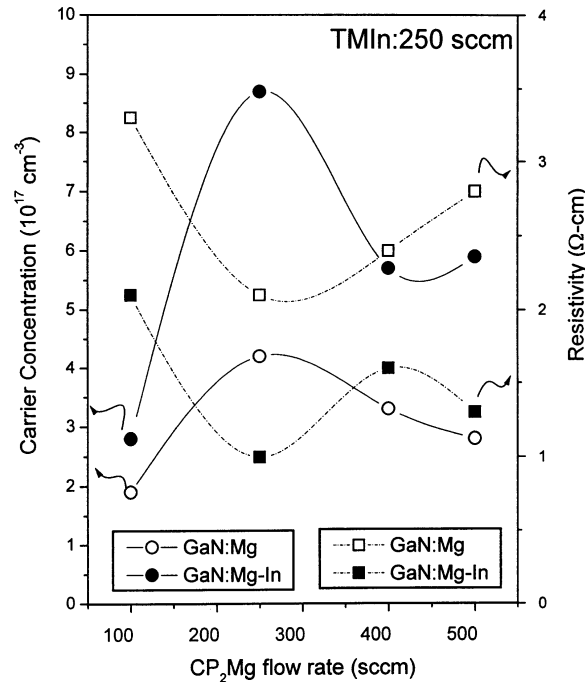


FIG. 2. Hall properties of p-type GaN and In-Mg codoped GaN films as a function of Mg source flow rate.

of the atomic size between the Ga and Mg constituents [6, 7]. Although the size of the defects varied with the Mg source flow rate, the corresponding density remained rather high, lying in the range of 10^8 - 10^9 cm^{-2} . On the other hand, as TMIn was added, the size and density of the defects decreased notably for the 100 sccm Mg-flow-rate sample. More striking results were observed on the films grown with higher Mg flow rates. They possessed a virtually featureless surface structure when codoped with In atoms. Consequently, the corresponding root mean squared surface roughness value improved from the typical 12.2-26.6 Å for conventional p-GaN films down to a value of 4.2 Å, when the film was doped with In. The progress in surface smoothness for In-doped p-GaN can be attributable at least partially to the better surface migration capability of In, as compared to that of Ga, on the growing interface [8, 9], and partially to the strain release of In doping in the Mg-doped GaN sample, because of the fact that the atom size of $\text{In} > \text{Ga}$ and that of $\text{Mg} < \text{Ga}$, which not only carries the growth to be in a layer-by-layer manner, but also effectively suppresses the induced dislocations, defects and stacking faults that commonly occur in the p-type GaN epitaxial layer.

In figure 2, we show the In doping effects on the Hall properties of p-type GaN films thermally annealed at 750 °C for 40 min as a function of the Mg source flow rate. The results for nominal Mg-doped p-GaN films are also included in this figure for comparison. In accordance with other reports, some of the typical electrical characteristics are observed for Mg-doped GaN films. The associated hole concentration increased initially with the Mg source flow rate, and tended to drop subsequently with a further increase of the Mg supply. The optimum carrier concentration and resistivity are $4.2 \times 10^{17} \text{cm}^{-3}$ and 2.1 Ω-cm, respectively. In regard to those

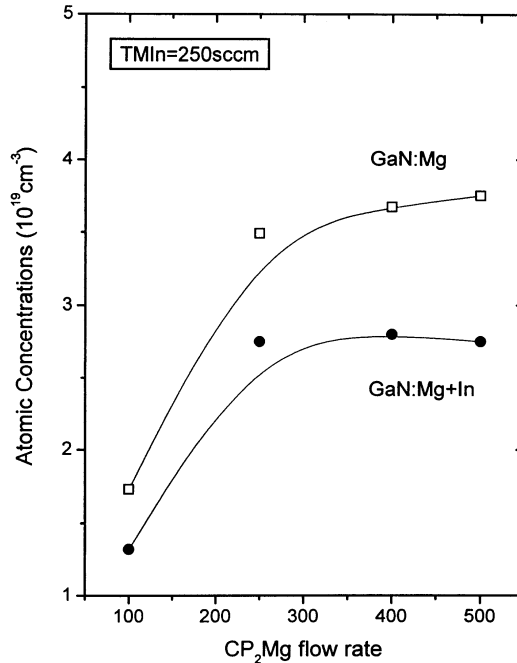


FIG. 3. Results of SIMS data for the solid Mg concentration for p-GaN and In-Mg codoped GaN films.

In-Mg codoped p-GaN films, their Hall properties basically showed a very similar tendency to that of shown by the Mg-doped films. Nevertheless, the entire film quality is improved. The resulting hole concentration reached $8.7 \times 10^{17} \text{ cm}^{-3}$ while the resistivity is reduced to $1 \Omega\text{-cm}$, indicating the good quality of our Mg-In codoped GaN film.

From the published literature, we learn that there are a number of factors that affect the hole concentration in p-GaN, which include the solid Mg concentration, the degree of self-compensation, the hydrogen passivation effect, and crystalline quality degradation. Among them, the solid Mg concentration is no doubt the most fundamental factor in determining the Hall properties of p-type GaN. It has been reported that the measured hole concentration in p-GaN tends to increase with the Mg concentration, up to the optimum doping level of $2\text{-}4 \times 10^{19} \text{ cm}^{-3}$, depending on the reactor is schematic design and various growth parameters. Beyond this point the doping efficiency drops significantly, due to a rapid increase in its donor concentration, which gives significant compensation effects in the film. Actually, the compensation seems inevitable for p-type GaN film, because the Mg doping itself can unintentionally induce native donor defects, with shallow-types dominating in the lightly doped samples and deep-types in the heavily doped ones.

For this reason, we carried out a second set of ion mass spectrometry (SIMS) measurements. The SIMS data in Fig. 3 reveal that the solid Mg concentration increased monotonically with the Mg flow rate for conventional GaN:Mg films; on the other hand, a saturation characteristic was observed in our In-doped samples. The increasing of the solid Mg concentration with the Mg flux, together with a decrease in the hole concentration in the Mg-doped samples, suggests that

our p-GaN films grown by the conventional method are all overdoped. The corresponding critical solid Mg concentration is conceivably not greater than $\approx 3.7 \times 10^{19} \text{ cm}^{-3}$. As for the In-doped samples, the low measured Mg saturation value indicates that the Mg solubility is being suppressed to a certain extent by the addition of In atoms, which can be partly credited to the increased competition of Mg atoms with In atoms in occupying the Ga sublattices. Based on the above arguments, we can infer that the increased hole concentration in In-doped p-GaN is not a direct result of an increasing Mg concentration in a solid, since an adverse effect is observed in our In-doped films.

It is certain that the mechanisms involved in p-GaN are rather complex in nature; we believe this is also true for the In-Mg co-doped GaN case. Definitely the study of isoelectric doping effects on p-GaN is still in its infant stage. Full comprehension is currently impossible and is beyond the scope of our discussion here, due to the limited information available from the aforementioned measurements. Nonetheless, the phenomena induced by In-doping in p-type GaN can be ascribed at least qualitatively to the following reasons: First, the In doping in such types of film keep the solid Mg concentration apart, slightly away from the overdoped situation. This keeps the film from generating a large density of Mg-related deep-donors, thus avoiding the occurrence of severe compensation effects, so that better Hall properties can be obtained. Second, it is generally believed that the higher the dislocation density, the less the resultant carrier density in the epitaxial film. It has been shown that adding In to conventional GaAs bulk crystals can greatly reduce the density of dislocations by pinning the dislocations at In atoms due to a larger radius of In than Ga [10]. This seemingly is also the case for p-GaN, as revealed by SEM micrographs (Fig. 1), where a much smoother surface morphology can be obtained when the film has In added. If the surface density has a certain proportionality with the dislocation density, and hence with its extended point defect concentration, we may reasonably anticipate that we can develop a lower compensation ratio in our In-doped p-GaN film.

Another likely effect caused by the In doping in p-GaN is the reduction of the nitrogen vacancy density. For In-containing alloys, we have found in our study that, regardless of the growth of GaN, InGaN or Mg-doped GaN the introduction here of In atoms during the epitaxy can always bring a sudden decrease in the Ga incorporation efficiency. This yields means a higher effective V/III ratio on the growing interface, which believably could help in reducing the formation of nitrogen vacancies in the solid. Although not all of these samples are suitable for deep-level transient spectroscopy measurement, we do find in undoped GaN film a notable decrease in the nitrogen vacancies [11]. We believe similar results can also occur in In-doped p-GaN film. Since the nitrogen vacancy functions as a shallow donor in GaN film and represents the major intrinsic compensation center for Mg doping in the 10^{18} to 10^{19} cm^{-3} range. The decrease of nitrogen concentration could indubitably enhance the hole concentration in the valence band.

Finally, it is known that hydrogen plays a key role in the p-type doping of GaN. When hydrogen is present in the solid, it passivates substitutional Mg by forming MgGa-N-H complex, resulting in a poor doping efficiency in as-grown GaN. Experimental data indicate that, under a similar solid Mg concentration, a p-GaN film with a lower hydrogen concentration usually could possess a higher carrier concentration. This is also observed in our In-doped GaN film. In Fig. 4, we show a typical impurity incorporation depth profile for both pure Mg-doped and In-Mg codoped GaN films. One can note that the Mg concentrations are about the same for both types of the samples, while the hydrogen concentration in the In-doped sample appears to be $\approx 50\%$ lower than that of Mg-doped film. Although thermal annealing in ambient nitrogen can remove

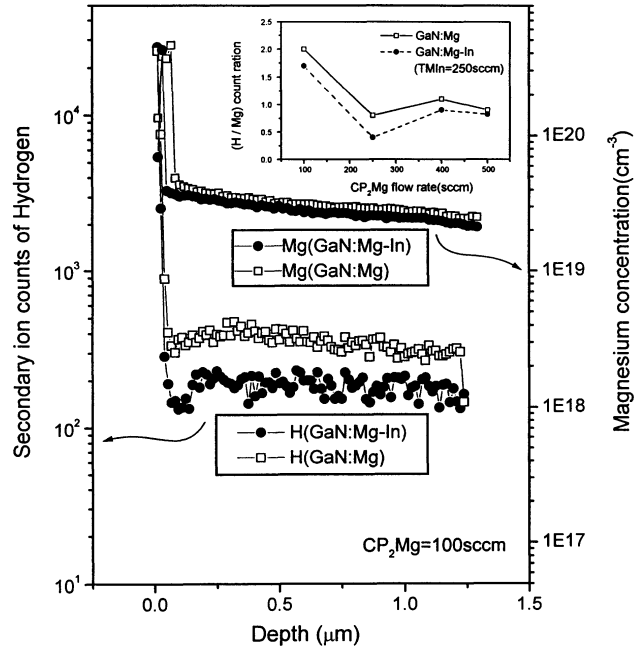


FIG. 4. SIMS depth profile of Mg concentrations for both pure Mg-doped and In-Mg codoped GaN films.

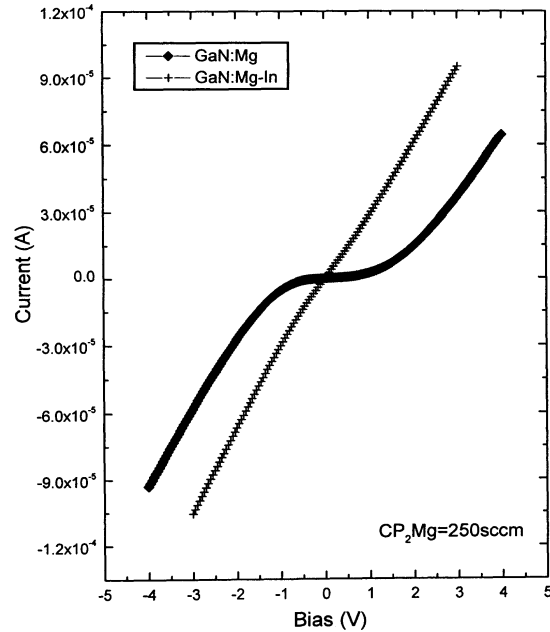


FIG. 5. I - V characteristics of as-deposited Mg-doped and In-Mg codoped GaN films without any dehydrogenation treatment.

hydrogen from the complex to some extent, complete dehydrogenation is difficult to accomplish for GaN, because of the thermal budget limitation. That is under thermal treatment a certain portion of the hydrogen ions remains in the solid where they will again form an Mg-H complex during the cooling to room temperature which degrades the properties of the film [12]. Thus, for p-type GaN growth, perhaps a better way to obtain a high hole concentration would be to grow a film with a lesser degree of hydrogen passivation. The less the hydrogen content, the higher the concentration of Mg atoms that can actively provide free holes to the valence band, and the better the device performance that can be obtained. Additionally, probably due to the lesser degree of hydrogen passivation, we did find some interesting electrical behaviors in our In-doped p-GaN. As shown in Fig. 5, a nearly ohmic I-V characteristic is readily attained in our as-deposited In-doped p-GaN film, which has seldom been reported by the MOCVD nitride community. For comparison, the typical characteristics of high resistivity and rectifying carrier transport behavior are observed, as expected, for our as-deposited Mg-doped GaN films.

IV. Conclusions

In summary, we have studied the isoelectronic In-doping effects on Mg-doped GaN films grown by MOCVD. The preliminary results indicate that when In atoms are added, the surface morphology is greatly improved, and a virtually featureless structure can be obtained, particularly for films grown at high Mg flow rates. Furthermore, comparatively good Hall properties are also displayed in these films. The resulting optimum hole concentration and resistivity are $8.7 \times 10^{17} \text{ cm}^{-3}$ and $1 \Omega\text{-cm}$, respectively. Perhaps the most striking result is the observance of a linear I-V characteristic on the as-deposited sample, which indicates the good Hall properties associated with such types of film. All of the above findings suggest that isoelectrical In doping is a viable technique, and has potential for the preparation of high quality p-type GaN material.

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