SELECTION OF PRECURSORS AND THEIR INFLUENCES ON III-NITRIDES GROWN BY MOCVD

Gu Xing and Ye Zhi Zhen
State key lab of silicon materials, Zhejiang University, China, P.R
guxing@mail.hz.zj.cn or guxing@hznc.com

Abstract

Selection of precursors exerts significant influences on the III-nitrides thin films grown by MOCVD. The common and novel precursors of group III, nitrogen, n-doping and p-doping which are used in the growth of III-nitrides are presented and their characteristic are discussed. Some major precursors that have distinctive effects to the sample’s properties, such as TMGa and TEGa, are compared in details.

Keywords: precursor, III-nitrides, GaN, MOCVD, TMGa, TEGa

I - INTRODUCTION

Aluminium nitride, gallium nitride and indium nitride and their alloys are commonly known as “III-nitrides”. These materials have superior intrinsic properties such as wide range of direct transition-type energy band gap, strong bond between nitrogen and each group atom, high thermal conductivity and high electron saturation velocity, which make them one of the most promising materials for applications to short wavelength light emitters such as light emitting diodes, laser diodes and photodiodes in visible and ultraviolet regions, as well as high-power electronic devices [1-5]. MOCVD is one of the most successful technologies for the growth of III-nitrides [6-9] (another one is MBE [9-10]). As a well developed technology, it can grow III-nitrides thin films with atomically sharp interfaces. Also MOCVD is the most promising method of choice for the growth of high quality III-nitrides films for mass production and particularly for devices. The selection of precursors is a procedure of great importance in the MOCVD technology, which exert significant influences on the microstructure, morphology, electronical properties and optical properties. In this paper, the common and novel precursors of group III, nitrogen, n-doping and p-doping are presented and their characteristic are discussed. Some major precursors that have distinctive effects to the sample’s properties are compared in details.
II - GENERAL CRITERIA FOR THE METALORGANIC PRECURSORS

Precursors are the source materials for each element (Al, Ga, In, N, Si, Mg and so on). They can come in the form of solid, liquid or gas depending on the growth condition. The investigation of metalorganic precursors for the growth of semiconductor has already received widespread attention [11]. The cumulative efforts on MOCVD over many years allow the fundamental properties of an ideal precursor to be defined. It should (1) have a good volatility (possibly higher than 0.1 torr at around 300K) (2) have a good thermal stability during its evaporation and transport in the gas phase and (3) decompose cleanly on pyrolysis without contamination of the growing film. What’s more, it should have high purity and be non-toxic and non-pyrophoric when possible. Since it is often used in a limited amount, it also should be stable in the container over a long period. To provide a stable vapor pressure, liquid precursors are better than solid and gaseous ones. The common chemical precursors for the growth and doping of III-nitrides are listed in Tab.1 and Tab.2.

Tab.1 The most common chemical precursors for the growth and doping of III-nitrides.

<table>
<thead>
<tr>
<th>Element</th>
<th>Chemical formula</th>
<th>Chemical name</th>
<th>Pressure (298K)</th>
<th>A</th>
<th>B</th>
<th>Melt point (°C)</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>(CH₃)₃Ga</td>
<td>TMGa</td>
<td>238</td>
<td>1825</td>
<td>8.50</td>
<td>-15.8</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td></td>
<td>(C₂H₅)₃Ga</td>
<td>TEGa</td>
<td>4.79</td>
<td>2530</td>
<td>9.19</td>
<td>-82.5</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>Al</td>
<td>(CH₃)₃Al</td>
<td>TMAi</td>
<td>14.2</td>
<td>2780</td>
<td>10.48</td>
<td>15</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td></td>
<td>(C₂H₅)₃Al</td>
<td>TEAl</td>
<td>0.041</td>
<td>3625</td>
<td>10.78</td>
<td>-52.5</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>In</td>
<td>(CH₃)₃In</td>
<td>TMIn</td>
<td>1.75</td>
<td>2830</td>
<td>9.74</td>
<td>88</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td></td>
<td>(C₂H₅)₃In</td>
<td>TEIn</td>
<td>0.31</td>
<td>2815</td>
<td>8.94</td>
<td>-32</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>Zn</td>
<td>Zn(C₂H₅)₂</td>
<td>DEZn</td>
<td>8.53</td>
<td>2190</td>
<td>8.28</td>
<td>-28</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>Mg</td>
<td>Mg(C₅H₅)₂</td>
<td>CP₂Mg</td>
<td>0.05</td>
<td>3556</td>
<td>10.56</td>
<td>175</td>
<td>Pyrophoric</td>
</tr>
</tbody>
</table>

Vapor pressure of metalorganic compounds are calculated in the terms of expression: \( \log_{10} P(\text{Torr}) = \frac{A-B}{T(\text{K})} \)

Compared with GaAs by MOCVD [12,13], the growth of III-nitrides are much safer, because of the avoidance of using lethal hydride such as AsH₃ and/or PH₃ as the group δ sources. Although not well characterized, the group-III metalorganics appear to be nontoxic [14]. However, most of the metalorganic compounds are pyrophoric and can be dangerous even in the limited quantities generally used, since even a small leak can lead to the ignition of hydrogen carrier gas. Usually an inert gas, such as helium [15] and/or nitrogen [16], is used together with hydrogen as the carrier.
Tab.2 Other common chemical precursors for the growth and doping of III-nitrides.

<table>
<thead>
<tr>
<th>Element</th>
<th>Chemical formula</th>
<th>Chemical name</th>
<th>Physical state at 298K</th>
<th>Toxicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>(C₂H₅)₂GaCl</td>
<td>DEGaCl</td>
<td>Liquid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GaH₃N(CH₃)₃</td>
<td>TMAG</td>
<td>Solid</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>(CH₃)₃AlN(CH₃)₃</td>
<td>TMAI-TMN</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂AlH</td>
<td>DMAIH</td>
<td>Liquid</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td></td>
<td>AlH₃ N(CH₃)₃</td>
<td>TMAA</td>
<td>Solid</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>In</td>
<td>C₂H₅(CH₃)₂In</td>
<td>EDMIn</td>
<td>Liquid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₃)₃InP(CH₃)₃</td>
<td>TMIn-TMP</td>
<td>Solid</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>N₂</td>
<td>Nitrogen</td>
<td>Gas</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>NH₃</td>
<td>Ammonia</td>
<td>Gas</td>
<td>Corrosive</td>
</tr>
<tr>
<td></td>
<td>N₂H₄</td>
<td>Hydrazine</td>
<td>Gas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH₃)₃CNH₂</td>
<td>Tertiarybulyamine</td>
<td>Liquid</td>
<td>Toxic</td>
</tr>
<tr>
<td></td>
<td>C₆H₅NHNH₂</td>
<td>Phenylhydrazine</td>
<td>~Liquid</td>
<td>Toxic</td>
</tr>
<tr>
<td>Zn</td>
<td>DMZn</td>
<td>Dimethyl-zine</td>
<td>Liquid</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>Si</td>
<td>SiH₄</td>
<td>Silane</td>
<td>Gas</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td></td>
<td>Si₂H₃</td>
<td>Disilane</td>
<td>Gas</td>
<td>Pyrophoric</td>
</tr>
<tr>
<td>Ge</td>
<td>GeH₄</td>
<td>Germane</td>
<td>Gas</td>
<td>Toxic</td>
</tr>
<tr>
<td>S</td>
<td>H₂S</td>
<td>Hydrogen sulfide</td>
<td>Gas</td>
<td>Toxic</td>
</tr>
<tr>
<td>Se</td>
<td>H₂Se</td>
<td>Hydrogen selenide</td>
<td>Gas</td>
<td>Lethal</td>
</tr>
</tbody>
</table>

III - PRECURSORS OF THE GROUP III

A series of MO compounds have been used as the precursors of group III element, as shown in Tab.1 and Tab.2. Among them the trimethyl compounds and triethyl compounds are used most frequently. Generally speaking, the trimethyl compounds have a higher vapor pressure than trimethyl compounds at the reaction temperature, thus make them react more easily at the
atmospheric reactors. Besides its relatively low vapor pressure, the more severe parasitic reaction further make the triethyl compounds not suitable for the AP growth, because the parasitic reaction is more inclined to happen at atmospheric pressure [17]. It has been reported that the pre-reactions between the precursors can leads to the formation of stable Lewis acid-base adducts and oligomers with simultaneous elimination of hydrocarbons [18-20]. At the AP circumstance, even the trimethyl compounds can react with the NH₃. The stable cyclic trimers [(CH₃)₂GaNH₂]₃ is produced in the case of TMGa [18] and the parasitic pre-reaction in the case of TMAI [21] can severely affect the quality of the film deposited in the AP-MOCVD reactors. In the low-pressure reactors, however, the triethyl compounds have been used successfully to grow high purity GaN with less carbon contamination [22]. It has also been observed that triethylaluminum, -indium, and -gallium sources decompose at lower growth temperatures compared to the trimethyl-equivalents [23], and thus a higher Ga/Al/In content in the gas phase can be achieved at a low temperature. Although the function is not clear, but it has been revealed that the concomitant use of methyl or ethyl analogues of group III elements offers a well-matched reactivity in the growth of alloy [24-25].

III.1 TMGa and TEGa

The choice of gallium precursors has greater impact to the films deposited, compared with the aluminum precursor [26]. TMGa and TEGa are the precursors used most frequently. Although their different effect in the growth of GaAs has been reported [27], these comparisons are not equivalent to the GaN growth due to the different growth conditions (e.g. the common growth temperature of GaAs is 600°C while GaN is over 1000°C). Generally speaking, TMGa is suitable to both AP-MOCVD and LP-MOCVD while TEGa only suitable to the LP-MOCVD. But TEGa has shown a series of advantages in the condition of the LP-MOCVD [22]. What’s more, the TEGa has a lower decomposition temperature (see Fig.1) and can be applied easily to the low temperature condition.

The kinetic model for the grown of GaN by TMGa and TEGa is different. In the case of TMGa, the reaction [29] G1 and G2 are taken place:

\[ \text{Ga}(\text{CH}_3)_3 \rightarrow \text{Ga}(\text{CH}_3)_2 + \text{CH}_3 \quad \text{(G1)} \]

\[ \text{Ga}(\text{CH}_3)_2 \rightarrow \text{GaCH}_3 + \text{CH}_3 \quad \text{(G2)} \]

Reaction G1 describes the homogeneous decomposition of TMGa with simultaneous loss of a methyl radical yielding dimethyl-gallium (DMGa). Dimethyl-gallium further decomposes to monomethyl-gallium (MMGa) via another loss of methyl radical. The highly mobile molecule MMGa acts as the determining species at the substrate, which has a long diffusion length [26]. TEGa, on the other hand, decomposed by β-elimination [30]:

\[ (\text{CH}_3 - \text{CH}_2) - \text{Ga} - \text{R} \rightarrow \text{CH}_2 = \text{CH}_2 + \text{H} - \text{Ga} - \text{R} \quad \text{G(3)} \]
Figure 1: Decomposition of TEGa and TMGa as a function of temperature by different carrier gas. (after ref.28)

Since the activation energy for this decomposition is low [31], highly reactive gallane (GaH3) molecule can be achieved and act as the growth determining species of TEGa. Because of its very small diffusion length gallium incorporates into the crystal close to the place where it arrives on the surface.

Thus the surface morphology of the GaN film is different. Fig.2 shows the AFM surface image for two GaN epilayer grown on the identical conditions except gallium precursors. The root mean square surface roughness of the samples grown by TMGa is 9.59Å while by TEGa is 16.4Å.

It is probably the different diffusion length that cause these differences. The small diffusion length of GaH₃ make the Ga atoms accumulate at the place where it arrives the surface and hence restrict the lateral growth, thus resulting in a relatively rough surface.

Figure 2. AFM surface images for GaN epilayers grown with (a) TMGa and (b) TEGa (after ref.32)
It has been reported that using TEGa as a substitute for TMGa can significantly reduce the carbon contamination in many occasions, such as in the growth of GaAs [27] or InGaAs [33]. In the case of GaN, the similar conclusion has also been drawn [22,32], as shown in Fig 3. This reduction of carbon can be contributed to the different reaction mechanism: the highly reactive methyl can bring more C and H contamination to the GaN deposited, compared with the steady C2H4. The carbon contamination often compensates with the background n-dopants (native defects or residual impurities such as Si and/or O) and thus makes the GaN film highly resistive. The SiH4 is used as an n-dopant to achieve conduction, and it has been reported that TMGa samples showed high resistivity than TEGa samples [35]. A higher flow rate of SiH4 is required to achieve conduction in the TMGa grown films, and the resulting mobility is also lower than the TEGa example [32].

Figure 3. SIMS depth profiles of O and C normalized to the GaN signal in samples grown with TMGa and TEGa (after ref.22)

Moreover, the deep levels caused by carbon are also different from the TMGa samples and the TEGa samples. Three distinct levels, which located at 0.14(E1), 0.49(E2) and 1.63±0.3eV(E3) have been found in the TMGa sample, while only the deep level of 1.63±0.3eV(E3) has been found in the TEGa sample [34], as shown in Fig.4. The origin of deep level E3 is further discussed [35], and Oxygen is thought to be responsible for it. This finding can further approve that the reaction mechanism between TMGa and TEGa is different, where the deep levels of E1 and E2 probably are caused by the C and/or H by the methyl decomposed from TMGa, for both substitutional carbon [36] and acceptor-H complexes [37] can be responsible for these levels. Another proof is the carbon from TMGa mainly enhance the D-A pair emission at about 378nm, which shows the carbon makes an acceptor level at nitrogen sites in GaN; the carbon from TEGa mainly enhance a deep emission at about 550nm, which shows the carbon may make deep levels at interstitial sites in GaN by C-C bonding in ethyl radicals [38]. Another hypothesis of this level is that it is caused by nitrogen vacancy-related complexes or extended defects [32]. Although the author hasn’t presented proof, this hypothesis is something of reasonable, because the GaH3’s mobility is lower than MMGa, thus the Ga atoms can be accumulated at the place they arrive the substrate and thus prohibit the N atoms from coming into their sites. As an evidence, the deep
emission at ~550nm is found to be suppressed in the GaN film with high crystallinity and few impurities [38].

The reduction in impurities helps to improve the crystallinity of the GaN. It is found that the FWHM of sample grown with TEGa is smaller than TMGa, indicating a better microstructure is achieved, as shown in Tab.3.

**Tab. 3 The result of X-ray rocking for GaN films (The data are from ref 32)**

<table>
<thead>
<tr>
<th>Value (arcmin)</th>
<th>Category</th>
<th>Sample with TMGa</th>
<th>Sample with TEGa</th>
<th>Priority of sample with TEGa</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWHM of (002)</td>
<td>Symmetric curves</td>
<td>9.982</td>
<td>8.043</td>
<td>Less screw dislocation and mixed dislocation</td>
</tr>
<tr>
<td>@-rocking</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FWHM of (102)</td>
<td>Asymmetric curves</td>
<td>11.472</td>
<td>10.970</td>
<td>Less threading dislocation</td>
</tr>
<tr>
<td>@-rocking</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FWHM of (102)</td>
<td>Angular rotation of columns</td>
<td>16.806</td>
<td>15.306</td>
<td>Neighboring columns are aligned better</td>
</tr>
<tr>
<td>hk-circle scan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An in situ normal reflectance measurement has been employed to investigate the growth mode of TMGa and TEGa, and the result is shown in Fig.5. It is clear that the island coalescence stage(σ), which exerts a profound influence on the quality of GaN, is different between the growth process with TMGa and with TEGa. In the case of TMGa, coalescence stage is much shorter, indicates the growth mode is changed from three dimensional to a quasi-two dimensional
rapidly; In the case of TEGa, such a period will continue for a longer time, the coalescence procedure is taken place gradually, and the growth mode is changed gradually, too.

III.2 DEGaCl

DEGaCl ((C₂H₅)₂GaCl) has been employed as an alternative gallium precursor [39-42]. The propose to use this precursor is to achieve a hydride vapor phase epitaxy (HVPE)-like growth mode, which can exploit advantages from both MOCVD and HVPE technologies, resulting in high growth uniformity and low carbon incorporation in the case of GaAs growth [41]. DEGaCl is also believed to decompose following the β-elimination reaction (G3), resulting in the formation of GaCl [39]. Thus the Cl-containing species within the MOCVD growth environment is provided, and associated with the reversible reaction G4 and G5:

\[
\text{GaCl}_3 + \text{NH}_3 \rightarrow \text{GaN} + \text{H}_2 + \text{HCl} \quad \text{G4}
\]

\[
\text{GaN} + \text{HCl} \leftrightarrow \text{GaCl} + \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{H}_2 \quad \text{G5}
\]

the HCl is presented near the GaN surface, which is believed to provide reaction pathways for the removal of surface structure and chemical defects and impurities. The surface morphology is also different between samples grown with TMGa and DEGaCl: the surface of DEGaCl-based samples exhibit a sharp faceted step edges, which is similar to the surface morphology grown by the HVPE (as shown in Fig.6).
III.3 aluminum and indium precursors

The facile β-elimination makes TEAl, a precursor with relatively low pressure, suitable for the growth of AlN in some cases [43-44], but TMAI is the Al precursor used most frequently. This is probably caused by the parasitic reaction, a pre-reaction which is most likely to appear when triethyl alkyls are used as the group III precursors at atmospheric pressure [45]. Generally, the adduct formed during the parasitic reaction will break up again when it is heated and thus has no adverse effect on crystal growth. But in some occasions the adduct undergoes severe elimination reaction and less volatile polymers are produced, so the precursors are exhausted even before the crystal growth [45]. To use the trimethyl compounds instead of the triethyl compounds, or use the low-pressure growth can both repress such a parasitic reaction.

TMAI, however, still has been reported to have a more severe parasitic reaction with the NH₃ at a higher pressure when compared with TMGa. (as shown in fig.7) Growth efficient, which is defined as the growth rate divided by the group III molar flow rate, serves as an indicator of the degree of the parasitic reactions. It has been found that the parasitic reaction is a problem at 200 torr when TMAI is employed, and that’s maybe the reason that why TEAl, the triethyl-equivalent of TMAI is so seldom employed [44] in the growth of III-nitrides.

Physical methods are also employed to repress the parasitic reaction. That is because the degree of the parasitic reaction is reactor-specific and the reactor’s geometry could be optimized to achieve a higher flow velocity, thus reduce the reactant’s residue time could be shortened [46]. Another way is to separate the reactants before they reach the substrate. For example, a quartz plate parallel to the substrate is employed in the two-flow MOCVD to separate the different precursors from parasitic reaction (as shown in Fig.8). Recently Matsumoto et al. succeeds to reduce parasitic reaction by suppressing convection suing a three-layered laminar flow reactor [48].

Fig. 6 Typical AFM images of the GaN surface morphology (after ref. 42)
Trimethylamine Alane (TMAA) is an aluminum precursor without any Al-C bonds. So by employing this precursor carbon incorporation in the epitaxial layers could be well controlled due to the avoidance of introducing alkyl groups. What’s more, due to it is more harder to conform volatile oxygen-contained impurities, a low concentration of Oxygen can be expected. However, as it has a relatively low vapor pressure (about 2 torr) and is easy to decompose (as shown in Fig. 9), it seems to be suitable to the low temperature growth with a reduced pressure [49].
TEIn is rarely used to grow III-nitrides. It is probably due to the parasitic reaction, too, because historically the parasitic reaction between TEIn and phosphine(PH₃) is extremely severe. Another factor must be taken into consideration is that a higher reactor pressure is needed to provide more active N atoms on the epilayer surface, which are necessary for the growth of GaInN, and obviously TEIn is not a good choice in this circumstance. In the MOCVD growth of III-nitrides, TMIn seems to be the solitary choice by now. Since it is a solid material at room temperature and has difficulty to provide a stable vapor pressure. Ludowise et al. have employed a series-connection of bubbles to conquer this problem [50]. Epichem Inc. has developed a novel precursor system to deliver TMIn. In this system, solid is suspended in an extremely low VP adduct solution, and the evaporated TMIn is continuously replenished by dissolution during the usage. It is claimed that by using this system a constant output of TMIn could be achieved while the vapor pressure remains the same as TMIn. [51]

IV. NITROGEN PRECURSORS

Ammonia is the most common nitrogen precursor for the MOCVD growth of III-nitrides. However, the high stability of ammonia requires the high temperatures for the epitaxial growth, thus leads to a high NH₃ partial pressure to avoid nitrogen loss during the growth and very high
V/III ratio (~$10^4$-$10^5$) are to be used. What’s more, the high temperature growth also adds difficulty to the growth of III-nitrides in some certain occasion. For example, the growth of InN is most difficult at a high temperature because its low decomposition onset makes a low temperature essential. So several new nitrogen compounds are now being evaluated as potential sources. These include N(CH$_3$)$_3$, Dimethylhydrazine((CH$_3$)$_2$NNH$_2$), phenylhydrazine ((C$_6$H$_5$)NHNH$_2$), triethylamine((C$_2$H$_5$)$_3$NH$_2$), Tertiarybutylamine(N(C$_4$H$_9$)H$_2$) and t-butylamine ((C$_4$H$_9$)$_3$CNH$_2$). It seems that most of these efforts are not successful. Using N(CH$_3$)$_3$ results produce no GaN epitaxial layer but Ga droplets[52]. For both triethylamine and t-butylamine, the growth was limited by too low V/III ratio, and in the case of t-butylamine, solid carbon deposit seems to be an intrinsic limitation to its use [53], and tertiarybutylamine also has high levels of carbon incorporated when used in the growth of AlN/GaN [53]. Phenylhydrazine has been demonstrated to have a reduced deposition temperature due to its relatively low thermal stability, and a significant reduction in the III-V ratio required to produce stoichiometric films was observed [54], but its poor volatility (only 0.043 torr at 300K) limits its use in a relatively high pressure circumstance. However, Dimethylhydrazine ((CH$_3$)$_2$NNH$_2$) seems to be a promising alternative precursor to NH$_3$: A reduced deposition temperatures can be achieved due to its lower thermal stability, and a sufficient nitrogen flux is available due to its good volatility(around 130 torr at 300K). It has been reported that stoichiometric, high quality GaN has been achieved using this precursor [55-56]. Anyway, the ammonia still remains the most widely and effectively employed nitrogen precursor in the MOCVD growth of III-nitrides.

Z.J.Liu et al. have reported to use the n-propylamine together with ammonia in the MOCVD process [57]. It is said that when a comparatively small amounts of n-propylamine(the ratio of ammonia flow to n-propylamine flow is about 10:1) is used, a significantly improved crystal morphology of GaN is obtained. It is believed that the n-propylamine could be a more effective source of NH$_2$, since the C-N bonding enthalpy is lower than the H-N bonding in the NH$_3$.

V. N-DOPANT PRECURSORS

A series of dopants have been investigated in the n-doping of III-nitrides, such as Ge(GeH$_4$) [57], sulfur(H$_2$S), Se(H$_2$Se) and Oxygen. But the Si is the most effective n-dopant in the n-doping of III-nitrides, because only Si has been used to achieve n-type conduction in all of GaN, Al$_x$Ga$_{1-x}$N [58] and Ga$_{1-x}$In$_x$N [59]. Currently, silane (SiH$_4$) is mainly used as the Si precursor. Akasaki et al. succeeded in controlling the n-type conductivity by SiH$_4$ doping in combination with the LT-buffer layer [60]. But SiH$_4$ is a toxic, pyrophoric gas that can form explosive mixtures in air. So it should be handled with equipment appropriately designed to take account of its pyrophoric and explosive nature, such as a well prepared storage and exhaust system.

Tetraethylsilane (TeESi) has been reported to be a novel alternative Si precursor, which can provide excellent n-type controllability and reproducibility as well as the low carbon incorporation in the growth of MOCVD growth of GaAs [61]. When it was employed in the growth of GaN [62-63], the electron concentration was observed to increase with the increase in the TeESi flow rate [62], and the activation energy for ionization of shallow donors was calculated to be 27meV [62-63].
VI. P-DOPANT PRECURSORS

Although theoretically the C could achieve the p-type conduction in III-nitrides, there are very few reports of doping the β-nitrides by incorporating unusually high amounts of C into the lattice[64]. The p-dopants III-nitrides are mainly from the group III elements. Among the group α elements, Mg is the only efficient species used as p-type dopant in MOCVD grown GaN [65-66]. Bis-cyclopentadienyl magnesium (Cp\textsubscript{2}Mg) is the most Mg precursor used most frequently. This precursor is a solid material and has a low volatility (0.04 torr at 300K). So heating above room temperature is required to achieve higher gas phase concentrations. However, the Mg mole fraction thus becomes unstable when its content decreases [63]. The alternative of Cp\textsubscript{2}Mg, the bis-methylcyclopentadienyl magnesium ((MeCp)\textsubscript{2}Mg, melting point=27°C) and bis-ethylcyclopentadienyl magnesium (ECp\textsubscript{2}Mg, melting point=–17°) are believed to be more useful, because they have lower melting point and higher vapour pressure. Though has a lower melting point than Cp\textsubscript{2}Mg, (MeCp)\textsubscript{2}Mg also need to be heated to achieve higher vapor pressure. This precursor has been reported to be used to fabricate high quality devices [67]. P-type conduction with hole concentration in the 10\textsuperscript{18} cm\textsuperscript{-3} range is achieved with post growth thermal annealing at 750°C in N\textsubscript{2} ambient [53]. However, it shows a poor dopant incorporation efficiency compared with Cp\textsubscript{2}Mg.(as shown in Fig.10) It is believed that the presence of methyl groups, which can strongly affect interactions with NH\textsubscript{3}, leading to increased precipitate formation in the growth chamber, or by forming more volatile Mg adducts at the surface [68].

![Fig.10 Atomic fraction of Mg in GaN as a function of the Mg flux ratio in the gas phase when using Cp\textsubscript{2}Mg and (MeCp)\textsubscript{2}Mg. Precursor fluxes \(\Phi_{\text{Mg}}\) and \(\Phi_{\text{TMG}}\) are given in mol/min. (after ref.68)](image)

ECp\textsubscript{2}Mg is liquid at room temperature, so it can provide a more stable vapor pressure compared with Cp\textsubscript{2}Mg. The GaN films using ECp\textsubscript{2}Mg shows p-type conduction after annealing [63]. It is commonly known that the procedure of post-growth treatments such as annealing (>600°C under nitrogen or vacuum) or low energy electron beam irradiation are required to break the Mg-H bond to activate the p-dopant [69-70]. The acceptor activation energy is estimated to be 163 meV for ECp\textsubscript{2}Mg[63] and 170meV for Cp\textsubscript{2}Mg, which is in accordance with the activation energy of Cp\textsubscript{2}Mg reported before[71].
Although Zn has been reported as a successful p-dopant in the growth of III-nitrides, the diethylzinc (DEZn) has been employed in the Mg-Zn co-doping. p-GaN film showing a low electrical resistivity (0.7 Ω·cm) and a high hole concentration (8.5×10^{17} cm^{-3}) was successfully grown without the degradation of structural quality of the film [73]. What’s more, the measured specific contact resistance has been lowered by one order of magnitude by using Mg-Zn co-doping (as shown in Fig.11).

Figure 11, (a) Comparison of the I-V characteristics for the only Mg-doped (dashed line) and Mg-Zn co-doped p-type GaN films(solid line), (b) Variation of resistance as a function of gap spacing for the only Mg-doped (Solid square) and Mg-Zn co-doped (solid circle) p-type GaN films.(after ref.72)

REFERENCES

[28] M. Pristovsek in Fundamental growth processes on different gallium arsenide surfaces in metal-organic vapor phase epitaxy, Doctoral Dissertation accepted by: Technical University of Berlin, Department of Physics, 2000-11-01
[34] W.I. Lee, T.C. Huang, J.D. Guo and M.S. Feng, Appl. Phys. Lett. 67(12), 1995
[38] Akihiko Ishibashi, Hidemi Takeishi, Masaya Mannoh, Yasufumi Yabuuchi and Yuzaburoh Ban, J. Electronic Materials, Vol. 25. No. 5 1996