β-Ga_2O_3 and related alloys grown by MOCVD on a Multi-wafer production system

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Abstract

We report on growth of β-Ga_2O_3 using multi-wafer small scale production MOCVD system with a loading capacity of up to seven two-inch wafers. The growth was conducted using TEGa and TMGa and pure oxygen. Films with thickness uniformity of ~7 % and growth rate of up to 1 µm/hr have been demonstrated. The growth of device quality β-Ga_2O_3 layers doped with Si and Fe impurities for n-type conductivity and compensation doping were also presented. Silane for Si and ferrocene for Fe were used as a precursor to dope the layers. Growth conditions influencing the incorporation of the two dopants were discussed. Additionally, a novel doping process with nitrogen which acts as compensating impurities in β-Ga_2O_3 is discussed. The benefits of using nitrogen to compensate residual conductance in β-Ga_2O_3 in comparison to the traditional Fe dopants is discussed.

INTRODUCTION

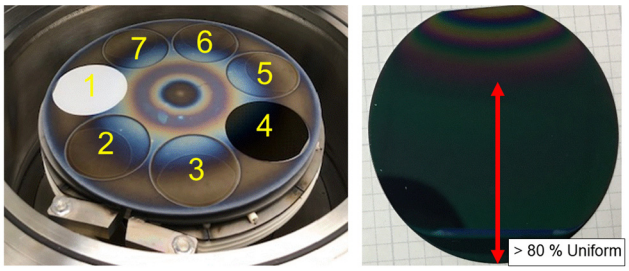
β-Ga_2O_3 has remarkable material properties that suits it for applications in high voltage power devices [1] and solar blind photodetectors [2]. The material has numerous attractive characteristics, including a large bandgap of ~ 4.9 eV and predicted electron mobilities (300 K) on the order of 100–300 cm^2/Vs [3]. Recently, our group demonstrated a record RT electron mobility of 176 cm^2/Vs by growing the epilayer using MOCVD [4]. Moreover, β-Ga_2O_3 has an estimated breakdown field of ~ 8 MV/cm, which is more than twice the breakdown field of GaN and SiC [1, 3], making it uniquely important for high power devices.

Epitaxial β–Ga_2O_3 thin films have been grown by MBE [5], MOCVD [6], and HVPE [7] methods. Except HVPE, the other growth methods are limited by extremely slow growth rate (< 0.7 µm/hr) [3, 8], making them unsuitable for mass production where thick layers are desirable for practical power devices. In MOCVD, the limitation is mainly due to unwanted gas phase reaction that depletes the precursors, thus reducing the growth rate. Agnitron's recent work in designing CIS-MOCVD system that separately injects the MO and oxygen sources has overcome this challenge, enabling the growth of device quality β–Ga_2O_3 at a fast growth rate [9].

Here, we will discuss the growth of Ga_2O_3 using multi-wafer CIS-MOCVD that can accommodate up to seven two-inch wafers. Films with thickness uniformity of ~7 % and growth rate of up to 1µm/hr have been demonstrated on 2" substrates using TEGa and TMGa precursors. The donor and deep accepter impurities doping in Ga_2O_3 thin films using the MOCVD growth methods is also presented. Controlled Si doping for n-type conductivity and Fe and N for compensation of residual conduction in the epilayers are discussed.

GROWTH OF β-Ga_2O_3 IN A MULTI-WAFER MOCVD REACTOR

Using the single wafer CIS-MOCVD system, our group recently demonstrated the growth of device quality β-Ga_2O_3 thin films with a growth rate of up to 10 µm/hr [9]. The fast growth rate had been achieved due to the CIS design which separately delivers the oxygen and MO precursors in the proximity of the substrate (showerhead to substrate separation ~1 cm). Unlike the commercial MOCVD, this prevents premature oxidation or parasitic reaction of the MOs, enabling them to reach the substrate surface undepleted, leading to fast growth rate.



(a) (b)

Fig.1. Images of (a) a wafer carrier with seven two-inch wafer pockets (pockets numbered 1 through 7) used in the multi-wafer MOCVD reactor for the growth of Ga_2O_3, (b) Ga_2O_3 thin film grown on Si wafer as shown in pocket 4 in (a). More than 80 % of the wafer is uniform. Sapphire wafer is shown in in pocket 1.

Here, the CIS method was implemented for a multi-wafer MOCVD reactor, which can load up to seven two-inch wafers (Figure 1(a)) to scale the MOCVD growth method for mass production. The multi-wafer system is based on the CIS design with three MO injection zones, which enables to independently control the MO distribution through each zone to achieve a uniform film on large area substrates. The growth was conducted using TEGa and TMGa and pure oxygen. Shown in Figure 1(b) is the Ga_2O_3 thin film grown on silicon

substrate with over 80 % of the wafer area covered with a uniform film. Films with growth rate of up to 1µm/hr have been demonstrated on a 2" sapphire substrates using both TEGa and TMGa precursors with an over all thickness uniformity of ~7 %.

The multi-wafer reactor was also used for the growth of Si doped and UID epitaxial β-Ga_2O_3 thin films on (010) β-Ga_2O_3 substrates. While the UID layer remains resistive, the doped sample has shown Hall mobility of ~ 90 cm^2/Vs at n=1.6x10^{18} 1/cm^3. The UID layer is expected to have high electron mobility but obtaining a good ohmic contact for accurate Hall measurement requires a complicated regrowth process [4]. These results clearly prove the capability of the CIS-MOCVD reactor for the growth of device quality β-Ga_2O_3 in high volume.

SILI CON DOPING IN A VMOCVD GROWN β-Ga_2O_3

In an MOCVD grown β-Ga_2O_3 layers, Si [8, 10] and Sn [8] are known as the most common doping impurities for achieving extrinsic n-type conductivity. Both impurities act as shallow donors. However, the use of Sn as a dopant for β-Ga_2O_3 grown by MOCVD is complicated for two reasons. The first is a pronounced memory effect. The second is the incoherency of Sn incorporation in β-Ga_2O_3 at high Sn doping levels (>10^{19} cm^{-3}) where it leads to a deterioration of the quality of the crystal and its surface. Moreover, the ionization efficiency of the Sn in the film is poor [8]. As a result, the use of Si appears to be the rational choice for n-type doping of MOCVD grown β-Ga_2O_3. In this study, we use a 40 ppm SiH_4/He as a source for Si to study its incorporation in an MOCVD grown Ga_2O_3 epitaxial films.

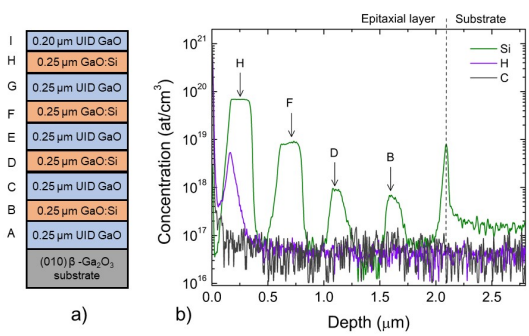


Fig.2. (a) Schematics of MOCVD grown β-Ga_2O_3multilayers doped with various concentrations of Si and O_2/TEGa ratios separated by UID layers. (b) SIMS depth profile of Si, H, and C for the multilayers in (a). The intentionally Si doped layers are marked with an arrow.

Here, multiple Si doped Ga_2O_3 layers with different concentration of Si are grown on a semi-insulating (010) β-Ga_2O_3 substrate in a single growth experiment. The growth rate for the layers is ~1µm/hr. The schematic representation of the Si doped layers is shown in Fig. 2 (a). The Si doped layers are separated by UID layers. Both for the doped and the UID layers, the O_2/TEGa ratio was varied to study its effect on the background concertation of Si, C, and H in the UID layers as well as the incorporation Si in the intentionally doped layers. The layers (A and B), (C and D), (E and F), and (G, H and I) are grown at O_2/TEGa ratios of 430, 1070, 2150, and 3220, respectively. The layers A, C, E, G and I are UID layers while the layers B, D, F, and H are intentionally Si doped layers with SiH_4/He flow rates of 2.3x10^{-10} mol/min, 2.3x10^{-10} mol/min, 2.3x10^{-9} mol/min, and 2.3x10^{-8} mol/min, respectively. The SIMS depth profiles for Si, C, and H in the layers are shown in Fig. 2 (b). At the film/substrate interface, the accumulation of Si is observed [10]. This accumulation of Si at the interface is similar to the phenomenon commonly encountered in MBE grown β-Ga_2O_3 which is frequently attributed to the adsorption of ambient contaminants onto the exposed substrate surface [11]. A similar contamination of the substrate surface might lead to the accumulation of Si at the film/substrate interface for the MOCVD grown β-Ga_2O_3 layers.

Figure 3 shows the Si concentration in the UID (blue trace) and intentionally Si doped (red trace) layers as a function of O_2/TEGa ratio and SiH_4/He flow rates. The increase of the O_2/TEGa ratio for the UID layers separating the intentionally doped layers yielded a similar background impurity concentration which is the detection limit of the SIMS instrument. However, for the intentionally doped layers the O_2/TEGa ratio appears to influence the incorporation of Si. The SiH_4/He flow rate in layers B and D is the same, but the concentration of Si atoms incorporated into the two layers is different. An increase in the O_2/TEGa ratio from 430 to 1073, led to the increase of Si atomic concentration from ~ 6x10^{17} to ~9x$10^{17}$$cm^{-3}$. This clearly indicates greater Si incorporation resulting from the increased oxygen flow. With the increase of the SiH_4/He and O_2/TEGa ratio, a Si concentration up to 7x10^{19} cm^{-3} was achieved. As indicated in the SIMS profile, a well-controlled Si doping of the Ga_2O_3 epilayer can be achieved by using SiH_4/He.

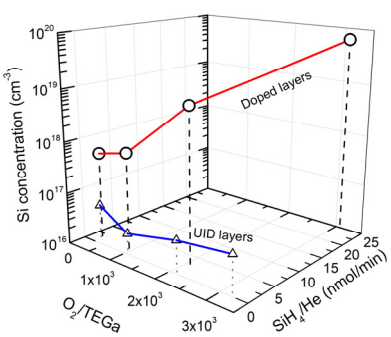


Fig.3. 3D graph showing the peak Si concentration as a function of O_2/TEGa ratio and SiH_4/He flow rate for the UID (blue) and Si doped (red) layers as measured by SIMS depth profile shown in Fig. 2(b).

The incorporation of carbon and hydrogen into the MOCVD grown Ga_2O_3 layers is anticipated due to the metalorganic precursors used for the growth of the films.

According to the DFT calculation studies carbon [12] and hydrogen [13] act as shallow donors in Ga_2O_3. However, the C and H concentrations throughout the layers grown by MOCVD (Fig. 2) remains unaffected with the measured SIMS values close to the detection limit (DL), effectively showing that no incorporation of the two impurities takes place even though it is hardly possible to avoid them. On the other hand, near the top surface of the layers an accumulation of H is observed. This could be attributed to the diffusion of H to the upper surface of the film during the growth process and the higher flow of SiH_4/He used for the heavy doping of the top layer.

The accumulation of Si at the interface (Fig. 2 (b)) has a deleterious effect on device performance, such as the lack of a sharp current pinch-off in FETs. One possible method to mitigate this is to dope the first few layers at the film/substrate interface with compensating dopants such as Fe or Mg. Additionally, the use of a N_2O grown insulating buffer layer could be an effective way to compensate parasitic conductance at the interface. In the next two sections, we will address the doping Ga_2O_3 with Fe and N using MOCVD method.

IRON DOPING IN AN MOCVD GROWN β-Ga_2O_3

In bulk Ga_2O_3 substrates, Si is the major background impurity with a typical carrier concentration of ~10^{17} cm^{-3} [14] making it an n-type material. This n-type conductivity is compensated by introducing Mg or Fe dopants which act as deep acceptors. Similarly, these dopants can be used to compensate unintentional n-type conductivity in the homoepitaxial Ga_2O_3 films. Here, we discuss the doping of Fe in an MOCVD grown Ga_2O_3 epitaxial film using ferrocene (Cp_2Fe) precursor as a source for Fe [15].

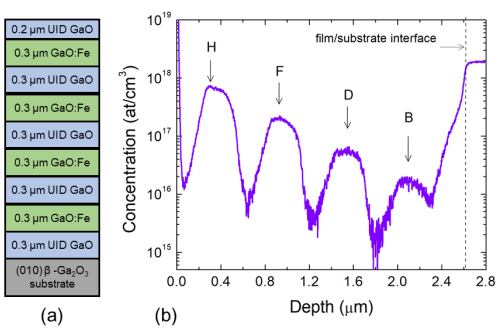


Fig. 4. (a) Schematic of MOCVD grown Ga_2O_3:Fe multilayers with various Fe concentrations separated by UID layers. The layers B, D, F, and H were Fe doped layers. (b) SIMS depth profile of Fe for the layers grown in (a).

Shown in Figure 4 (a) is the schematics of multiple, ~ 0.3 µm thick, layers grown with various concentrations of Fe doped layers separated by UID layers. The layers B, D, F, and H were grown by flowing 2.4 nmol/min, 4.4 nmol/min, 8.4 nmol/min, and 12.8 nmol/min, respectively, of Cp_2Fe. The O_2/TEGa ratio for the growth each layer is 430. Figure 4(b) shows the SIMS depth profile of the film showing the incorporation of Fe in the MOCVD grown layers. With the increase in the Cp_2Fe flow, an increase in the incorporation of Fe from ~ $2x10^{16}$ cm^{-3} (layer B) to ~ $8x10^{17}$ cm^{-3} (layer H) is observed. However, the interfaces between the Fe doped layers presented a V-shaped characteristic, showing the diffusion of Fe into the UID layers deposited to separate them. This diffusion of Fe into the UID layers is a common problem in GaN and Fe appears to behave in a similar fashion in Ga_2O_3 as well. In Ga_2O_3 thin films, the Fe diffusion tail can extend to a depth of ~1.5 µm [15], requiring the deposition of thick UID layers to block its effect on the active channels.

NITROGEN DOPING IN AN MOCVD GROWN β-Ga_2O_3

The other deep accepter doping impurity used for Ga_2O_3 is nitrogen [16]. H. Peelaers *et al*. [17] reported that N incorporates in the sites of both Ga and O, but the substitution of N on an O site acts as a compensating center with the deep energy level at >1.3 eV above the valance band maximum. Experimentally, Wong *et al*. demonstrated the doping of N into Ga_2O_3 substrates by ion implantation [16]. However, the ion beam carries substantial energy, which causes damage to the crystal structure of Ga_2O_3. As a result, post-implantation thermal annealing is required not only to remove the implantation damage but also to drive the N impurity in the intended site. This method, nevertheless, is unsuitable for doping of the homoepitaxial layers. Efficient doping of the

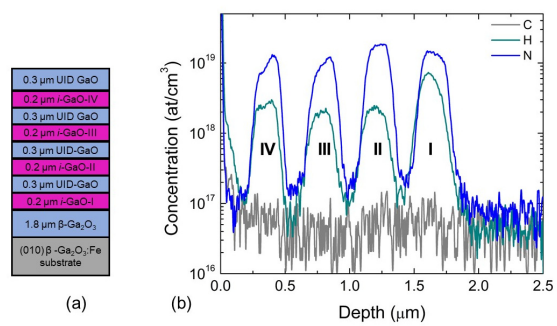


Fig. 5: (a) Schematics of MOCVD grown multilayers of β-Ga_2O_3 doped with N using N_2O, separated by UID layers. (b) SIMS depth profile of N, H, and C for the multilayered film in (a).

film can be achieved by introducing the N impurity precursor during the growth process.

Here, we show the doping of N into the MOCVD grown Ga_2O_3 by using nitrous oxide (N_2O) gas [15]. The N_2O is used both a source of oxygen and nitrogen in the growth of Ga_2O_3. The incorporation of N into the growing layer is significantly influenced by the process conditions, including the chamber pressure and flow rate of N_2O. To efficiently crack the N_2O for the growth of the film, growth pressure >100 Torr is required. Fig. 5 (a) shows the schematics of a multilayered Ga_2O_3 thin film grown with N_2O and pure oxygen. The N_2O grown layers (labeled as *i*-GaO) are grown by changing the

growth pressure and N_2O/TEGa ratio and separated by UID layers grown using pure oxygen. The *i*-GaO-I and *i*-GaO-II layers were grown at a chamber pressure of P_1 and N_2O/TEGa ratio of 4288 and 2144, respectively. Similarly, the *i*-GaO-III and *i*-GaO-IV layers were grown at a chamber pressure of P_2 (P_1>P_2>100 Torr) and N_2O/TEGa ratio of 4288 and 2144, respectively.

The SIMS depth profiles of N, H and C impurities in the layers grown with N_2O and oxygen are shown in Fig. 5 (b). The N_2O grown layers show an incorporation of N into the Ga_2O_3 films which drops to the detection limit (DL) in the UID Ga_2O_3 layers. The highest N incorporation (~$1.9x10^{19}$ cm^{-3}) is achieved for the *i*-GaO-II layer which is grown at a higher growth pressure (P_1) and lower N_2O/TEGa ratio of 2144. With the decrease in growth pressure, the incorporation of N into the N_2O grown layer is reduced. The UID layers between the N_2O grown layers don't contain any N, indicating that there is either very little or no diffusion of N out of the N_2O grown layers, which is consistent with the lower diffusion of N [16] observed in an implantation doped Ga_2O_3 substrate. However, the N doping is accompanied by the incorporation of H which virtually follows the same profile as N [see Fig. 5(b)]. This contrasts with the film grown using a pure oxygen precursor where there is no H incorporation observed. The use of N_2O may create a chemical byproduct that keeps the H in the growth chamber, but the exact cause of the H incorporation has yet to be understood. The incorporation of H along with N is undesirable as it effectively cancels the effect of N in the film given the shallow donor behavior of H. This requires the elimination, or at least the reduction, of H in the film while maintaining the N incorporation. This can be done either by annealing the film in vacuum or adjusting the growth conditions [18].

CONCLUSIONS

In summary, we demonstrated the viability of MOCVD to meet the demand for mass production of power devices based on Ga_2O_3. Multi-wafer CIS-MOCVD reactor that is capable of growing films on up to seven two-inch wafers in a single experimental run was used. Using TEGa and TMGa precursors, films with thickness uniformity < 10 % at a growth rate of ~1μm/hr have been demonstrated. UID and Si doped films have also been grown using the multi-wafer CIS-MOCVD. For the doped layer, RT Hall mobility of ~ 90 cm^2/Vs at n=$1.6x10^{18}$ $1/cm^3$ was measured. N-type conductivity and compensation doping of Ga_2O_3 using Si and Fe was studied. The incorporation of Si into the Ga_2O_3 thin film was dependent on the flow rates of SiH_4 and oxygen. For a constant SiH_4 flow, higher incorporation of Si was observed when the film is grown in an oxygen rich environment. Fe doping was conducted using ferrocene as a source for Fe. The increase in ferrocene flow rate leads to the incorporation of higher Fe into the film. However, Fe was observed to out diffuse into the UID layers, suggesting the need for the growth thick (~1.5 μm) UID layers to fully cap its effect from the active layers. N doping using N_2O for compensation was also studied. N, unlike Fe, was not observed to diffuse into the UID layers, making it an efficient compensating dopant. This is especially vital for film/substrate interface compensation where Si accumulation is common problem.

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ACRONYMS

CIS: Close Injection Showerhead
MOCVD: Metal Organic Chemical Vapor Deposition
MBE: Molecular Beam Epitaxy
HVPE: Halide Vapor Phase Epitaxy
MO: Metalorganic
TEGa/ TMGa: triethylgallium/trimethylgallium
UID: Unintentionally doped
SIMS: Secondary Ion Mass Spectrometry