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Large-Area MOCVD Growth of Ga_2O_3 in a Rotating Disc Reactor

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Gallium oxide is a wide-bandgap semiconductor material which is being developed for a range of electronic and electrooptic device applications. Commercial implementation of these devices will require production-scale technology for Ga_2O_3 film deposition. This work demonstrated deposition of uniform Ga_2O_3 films on both 50-mm-diameter (0001) sapphire and 200-mm-diameter (100) silicon substrates, using a rotating disc metalorganic chemical vapor deposition reactor. The source reactants were trimethylgallium and oxygen. The resulting Ga_2O_3 films were smooth, optically transparent, and highly insulating and had excellent thickness uniformity. Ga_2O_3 films deposited on (0001) sapphire at temperatures of at least 600°C and pressures of at least 45 Torr consisted of $(\bar{2}01)$-oriented β-Ga_2O_3 in the as-deposited state. The β-crystal structure was shown to be stable on annealing to 800°C, in either air or nitrogen atmosphere. A Ga_2O_3 film deposited at a lower temperature was shown to crystallize to a similar $(\bar{2}01)$-oriented β-Ga_2O_3 structure on postdeposition annealing at 800°C.

Key words: Ga_2O_3, thin films, MOCVD, epitaxy

INTRODUCTION

Recently, there has been significant interest in the semiconductor material Ga_2O_3 for a wide range of electronic and electrooptic device applications. Ga_2O_3 has a very attractive combination of properties, including a wide bandgap with measured values ranging from 4.4 eV to 4.9 eV,[1–3] a high breakdown field of 2.80 MV/cm to 5.70 MV/cm,[4,5] and a dielectric constant of 10.[4] In addition, high-quality β-Ga_2O_3 substrates can be produced by standard techniques,[6] and are now commercially available. Ga_2O_3 is being developed for a range of applications, including power semiconductor devices,[7] gas sensors,[8,9] transparent conductive oxides,[2] ultraviolet (UV) photodetectors,[3,10,11] and as gate dielectric layers for GaAs[4,12] and GaN[5] devices. Ga_2O_3 films could also be used as buffer layers for subsequent GaN film deposition.[13,14] These applications will require high-quality Ga_2O_3 films to be deposited on Ga_2O_3 or other substrates. Many techniques have been investigated for deposition of Ga_2O_3 films, including evaporation,[4,15] the sol–gel method,[3] chemical solution deposition,[9] spray pyrolysis,[16,17] radio frequency (RF) sputtering,[8,18] pulsed laser deposition,[2] atomic layer deposition,[19] molecular beam epitaxy (MBE),[7,12,20,21] and metalorganic chemical vapor deposition (MOCVD).[10,11,22–29]

Unlike competing wide-bandgap materials such as SiC, GaN, and diamond, Ga_2O_3 single crystals can be grown from the melt.[6] Large-area Ga_2O_3 substrates thus have the potential to become more economical and more readily available than any of these competing materials. Therefore, it is important to develop large-area film deposition technology for Ga_2O_3 films for use in wide-bandgap device applications. Deposition of Ga_2O_3 films by MOCVD offers many advantages for ultimate device fabrication, including conformal deposition over device topography and the capability for scale-up to high-volume production. Among the published studies of

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Ga_2O_3 film deposition by MOCVD, only one other research group[11,26] specifically identified the deposition system as one capable of scaling to large-area wafers. The rotating disc MOCVD reactor is a proven technology for achieving uniform film deposition on large-area substrates.[30,31] This work aimed to demonstrate large-area growth of device-quality β-Ga_2O_3 films using rotating disc MOCVD reactor technology.

EXPERIMENTAL PROCEDURES

All Ga_2O_3 film depositions were done in a rotating disc MOCVD reactor. The reactor has a 16-inch-diameter stainless-steel chamber. The gas flow geometry is vertical, from an upper showerhead. The substrate platter is a horizontal, high-speed rotating disc with diameter of 31.75 cm. The platter can be configured for single-wafer (200 mm or 300 mm) or multiple-wafer (150 mm or smaller) loads. The MOCVD reactants were trimethylgallium (TMGa) and oxygen. Argon was used as the carrier gas. The deposition temperature range investigated was 500°C to 650°C. The deposition pressure range was 4 Torr to 65 Torr. The O_2 flow rates were 750 standard cm^3/min (sccm) to 1800 sccm. The substrates used for the majority of the deposition trials were 50-mm-diameter (0001) sapphire wafers. Additional deposition trials were also done on 200-mm (100) silicon wafers.

For Ga_2O_3 films deposited on either (100) silicon or (0001) sapphire, thickness was determined by optical reflectance spectroscopy using white light. For Ga_2O_3 films on (100) silicon, no other characterization was done since the intention in this case was to demonstrate uniform deposition on large-area substrates. Ga_2O_3 films on (0001) sapphire were also characterized by x-ray diffraction for crystal structure and orientation, optical microscopy for general film morphology, and four-point probe for sheet resistivity. X-ray diffraction was done using Cu K_α radiation. Postdeposition annealing was done in a conventional tube furnace under flowing nitrogen or in a conventional box furnace in static air. All annealing trials were done at 800°C for 15 min, followed by furnace cool down to near room temperature.

RESULTS

The measured thickness of the MOCVD-deposited Ga_2O_3 films was generally in the range of 100 nm to 320 nm. All films were smooth and featureless as observed by optical microscopy up to 1500× magnification. All Ga_2O_3 films were insulating, with sheet resistivity beyond the measurement range of our equipment (10^{10} Ohms/square). The Ga_2O_3 films on sapphire substrates were visibly transparent. Results of initial MOCVD process optimization are summarized in Figs. 1, 2, and 3, which show the measured Ga_2O_3 film growth rate as a function of

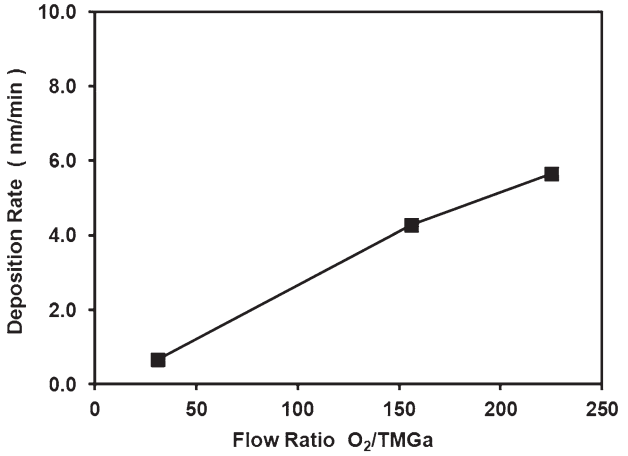

Fig. 1. Measured growth rate versus O_2/TMGa flow ratio for Ga_2O_3 films deposited on (0001) sapphire at 600°C and 15 Torr.

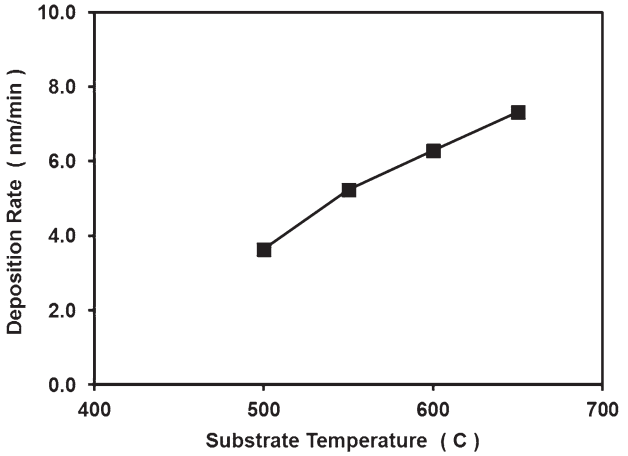

Fig. 2. Measured growth rate versus deposition temperature for Ga_2O_3 films deposited on (0001) sapphire at 45 Torr with O_2/TMGa flow ratio of 225.

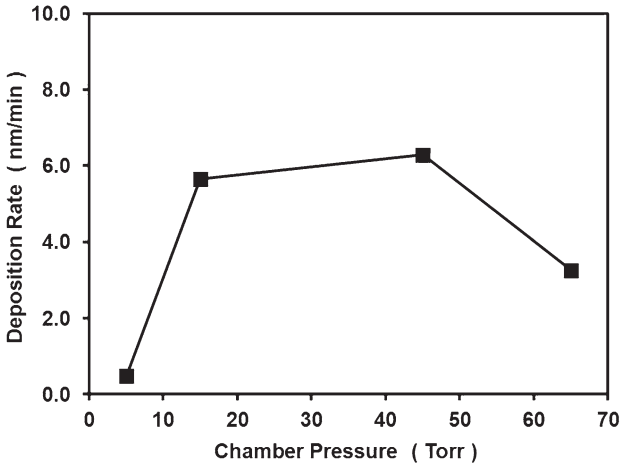

Fig. 3. Measured growth rate versus deposition pressure for Ga_2O_3 films deposited on (0001) sapphire at 600°C with O_2/TMGa flow ratio of 225.

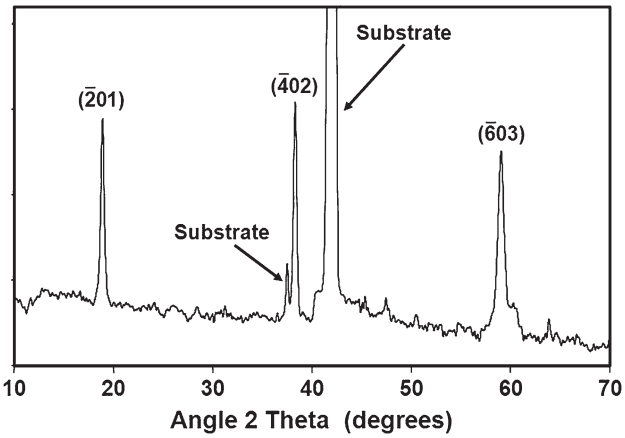

Fig. 4. X-ray diffraction results for Ga_2O_3 film deposited on (0001) sapphire at 600°C, 45 Torr, and O_2/TMGa flow ratio of 225.

the O_2/TMGa flow ratio, deposition temperature, and deposition pressure, respectively.

X-ray diffraction results for Ga_2O_3 films deposited at temperature of at least 600°C and pressure of at least 45 Torr indicated a $(\bar{2}01)$-oriented β-Ga_2O_3 structure, as shown in Fig. 4. All films deposited at lower temperature or pressure showed no x-ray diffraction peaks in the as-deposited condition. Postdeposition annealing was done on a Ga_2O_3 film deposited at temperature of 550°C, pressure of 45 Torr, and O_2/TMGa flow ratio of 225. This sample originally showed no x-ray diffraction peaks in the as-deposited condition. Annealing for 15 min at 800°C in air resulted in crystallization to a $(\bar{2}01)$-oriented β-Ga_2O_3 structure, with an x-ray diffraction pattern similar to that shown in Fig. 4. Two additional film samples deposited at 600°C, 45 Torr, and O_2/TMGa flow ratio of 225 were also postdeposition annealed in flowing nitrogen and in static air. X-ray diffraction analysis of these samples showed the $(\bar{2}01)$-oriented β-Ga_2O_3 structure in the as-deposited state. Each sample was annealed for 15 min at 800°C in the specified atmosphere. For both samples, the x-ray diffraction pattern was essentially unchanged, confirming the stability of the β-crystal structure on annealing to 800°C in both air and nitrogen.

Figure 5 shows a photograph of a 200-mm (100) silicon wafer with MOCVD-deposited Ga_2O_3 film of 90 nm nominal thickness. The insert in Fig. 5 shows a 50-mm single-side-polished (0001) sapphire substrate with an MOCVD-deposited Ga_2O_3 film of nominal 320 nm thickness. Figure 6 shows the measured thickness of the Ga_2O_3 film on (100) silicon, as a function of position across the wafer. From the data of Fig. 6, the thickness uniformity for the Ga_2O_3 film is 3.3% across the 200-mm wafer.

DISCUSSION

From the process optimization results, the best MOCVD process conditions for achieving high

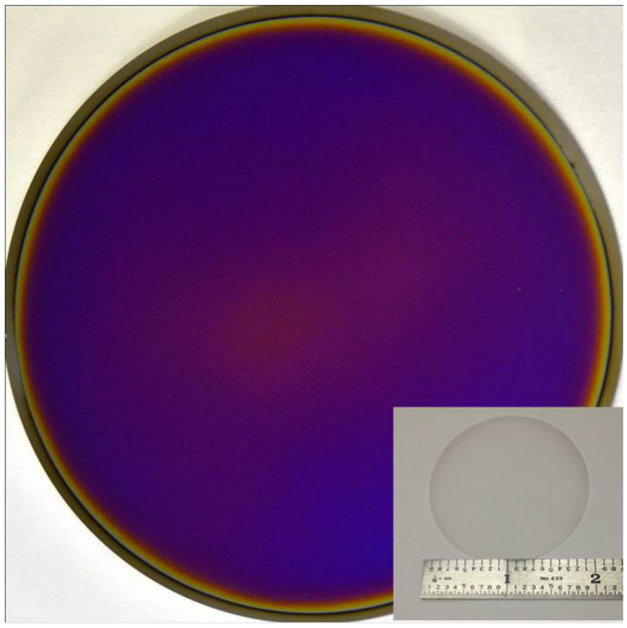

Fig. 5. Photograph of a 200-mm (100) silicon wafer with MOCVD-deposited Ga_2O_3 film of nominal 90 nm thickness. The insert shows an MOCVD-deposited Ga_2O_3 film of nominal 320 nm thickness, on a 50-mm single-side-polished (0001) sapphire wafer. The size scale in the insert is applicable for both images.

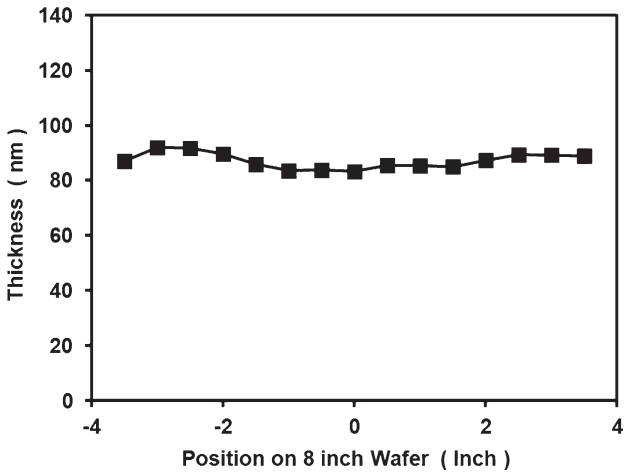

Fig. 6. Measured thickness of Ga_2O_3 film deposited on a 200-mm (100) silicon wafer, as a function of position across the wafer.

deposition rates and highly $(\bar{2}01)$-oriented β-Ga_2O_3 are pressure of 45 Torr to 65 Torr, temperature of at least 600°C, and O_2/TMGa flow ratio of 225. These optimum conditions are slightly different from those reported in other studies of Ga_2O_3 MOCVD,[11,26] which used lower O_2 flow rates. The higher O_2 flow rates used in this study are better suited to large chamber sizes for large-area Ga_2O_3 film deposition.

The $(\bar{2}01)$-oriented β-Ga_2O_3 structure has also been observed in several other studies of Ga_2O_3 films deposited on (0001) sapphire substrates by MOCVD[10,22–26,28] and by MBE.[20] The x-ray diffraction

technique used in this work cannot confirm epitaxy of the Ga_2O_3 film, since it does not measure rotational orientation within the film plane. However, other works have confirmed epitaxial ($\bar{2}01$)-oriented β-Ga_2O_3 films on (0001) sapphire through pole figure measurements[15] and by transmission electron microscopy.[28] Analysis using a crystal model showed the [201] direction of the β-Ga_2O_3 to be perpendicular to the sapphire {100} planes.[12] In light of these works, it is likely that the β-Ga_2O_3 films deposited on (0001) sapphire by MOCVD in this work are in fact epitaxial.

Postdeposition annealing has been shown to have a significant effect on the electrical and optical properties of β-Ga_2O_3 films on (0001) sapphire, as characterized by Hall measurements,[11] photoconductivity,[11] cathodoluminescence,[11] current–voltage (I–V) characteristics,[25,26] and photoluminescence.[26] Therefore, it is important to characterize the annealing behavior of the Ga_2O_3 films, in order to achieve optimum properties for the ultimate device application. The Ga_2O_3 films produced in this study were shown to maintain the β-crystal structure on annealing up to 800°C, in agreement with other annealing studies.[23,25] We did not observe any transformation to the α-structure, as has been reported by others.[26] The annealing atmosphere (air versus nitrogen) was shown to have no effect on the film quality as measured by x-ray diffraction in this study.

In summary, MOCVD in a rotating disc reactor was shown to be a production-worthy technique to produce Ga_2O_3 films for device applications. Deposition rates up to 7.3 nm/min were demonstrated for β-Ga_2O_3 films on (0001) sapphire substrates. We anticipate higher deposition rates can be achieved with higher precursor delivery rates. A thickness uniformity of 3.3% was demonstrated for an MOCVD-deposited Ga_2O_3 film on a 200-mm silicon wafer. Epitaxial ($\bar{2}01$) β-Ga_2O_3 films on (0001) sapphire were achieved by deposition at temperatures of at least 600°C and pressures of at least 45 Torr. Epitaxial ($\bar{2}01$) β-Ga_2O_3 films can also be achieved by postdeposition annealing of films deposited at lower temperatures and pressures. The epitaxial ($\bar{2}01$) β-Ga_2O_3 film structure was shown to be stable on annealing up to 800°C, as observed by x-ray diffraction.

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