Ga$_2$O$_3$ films for electronic and optoelectronic applications


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(Received 9 August 1994; accepted for publication 4 October 1994)

Properties of Ga$_2$O$_3$ thin films deposited by electron-beam evaporation from a high-purity single-crystal Gd$_3$Ga$_5$O$_{12}$ source are reported. As-deposited Ga$_2$O$_3$ films are amorphous, stoichiometric, and homogeneous. Excellent uniformity in thickness and refractive index was obtained over a 2 in. wafer. The films maintain their integrity during annealing up to 800 and 1200 °C on GaAs and Si substrates, respectively. Optical properties including refractive index ($n = 1.84 \text{--} 1.88$ at 980 nm wavelength) and band gap (4.4 eV) are close or identical, respectively, to Ga$_2$O$_3$ bulk properties. Reflectivities as low as $10^{-5}$ for Ga$_2$O$_3$/GaAs structures and a small absorption coefficient ($\approx 100 \text{ cm}^{-1}$ at 980 nm) were measured. Dielectric properties include a static dielectric constant between 9.9 and 10.2, which is identical to bulk Ga$_2$O$_3$, and electric breakdown fields up to 3.6 MV/cm. The Ga$_2$O$_3$/GaAs interface demonstrated a significantly higher photoluminescence intensity and thus a lower surface recombination velocity as compared to Al$_2$O$_3$/GaAs structures.

I. INTRODUCTION

Dielectric films find a wide range of applications from passivation of surface states in various types of conventional and low-dimensional devices to metal-insulator-semiconductor field-effect devices. The lack of stable dielectric films providing a low interface state density is still a serious drawback of III-V semiconductors. Different dielectric materials including Si$_3$N$_4$, SiO$_x$, Al$_2$O$_3$, and Ga$_2$O$_x$ have been used in combination with dry, liquid, and photoelectric materials including Si$_3$N$_4$, SiO$_x$, Al$_2$O$_3$, and Ga$_2$O$_x$.

Recently, Aydil et al. achieved passivation of surface states during a NH$_3$ or H$_2$ plasma treatment at room temperature by removal of excess As and As$_2$O$_3$ and subsequent formation of a Ga$_2$O$_3$ film (a few monolayers thick) on the GaAs surface. The observed increase in photoluminescence intensity indicated a decrease of surface recombination velocity, which is related to the midgap interface state density, by several orders of magnitude. Furthermore, Ga$_2$O$_3$ films are chemically stable on GaAs as demonstrated by thermochemical phase diagrams. This paper reports on properties of dielectric Ga$_2$O$_3$ films deposited by electron-beam evaporation from a high-purity single-crystal Gd$_3$Ga$_5$O$_{12}$ source.

II. FILM FABRICATION

Electron-beam deposition imparts only a small amount of energy into the surface and is compatible with existing semiconductor processing schemes. Other Ga$_2$O$_3$ thin-film fabrication techniques using oxidation of evaporated Ga in an O$_2$ plasma may cause severe surface damage prior to deposition and did not produce dielectric Ga$_2$O$_3$ films. The compound Gd$_3$Ga$_5$O$_{12}$ source material represents a chemical combination of the relatively covalent oxide Ga$_2$O$_3$, which volatilizes near 2000 K, and the pretransition oxide Gd$_2$O$_3$, which has a boiling point of 4000 K. The compound Gd$_3$Ga$_5$O$_{12}$ decrepitates during heating by electron beam, slowly releasing Ga$_2$O$_3$. The deposition rate is kept low at about 0.5 Å/s in order to maintain a high purity of the deposited Ga$_2$O$_3$ film.

III. FILM CHARACTERIZATION

The Ga$_2$O$_3$ films were analyzed by ellipsometry and Auger depth profiling for uniformity and homogeneity, respectively. Furthermore, the Ga$_2$O$_3$ films were characterized by Rutherford backscattering spectroscopy (RBS) for areal densities and atomic composition including stoichiometry, as well as impurities. X-ray photoelectron spectroscopy (XPS) of Ga$_2$O$_3$ films was performed in order to determine the oxidation state of the Ga$_2$O$_3$ films. The microstructure and the phase of Ga$_2$O$_3$ films were analyzed by transmission electron microscopy (TEM). The etching behavior and the temperature integrity of Ga$_2$O$_3$ films was investigated up to annealing temperatures of 1200 °C. Spectroscopic ellipsometry measurements were done in order to determine the refractive index $n$ and the absorption coefficient $\alpha$. Optical transmission and reflection measurements provided further optical...
properties including band gap and reflectivity, respectively. Dielectric properties of Ga_{2}O_{3} films were evaluated on metal/Ga_{2}O_{3}/semiconductor structures. Finally, the Ga_{2}O_{3}/air exposed (100)GaAs interface was evaluated by photoluminescence measurements.

**A. Homogeneity and uniformity**

Figure 1 shows the Auger depth profile of a 955 Å thick Ga_{2}O_{3} film deposited at a substrate temperature of 125 °C with an O₂ partial pressure of 2×10⁻⁴ Torr in the deposition chamber. This result demonstrates the excellent depth homogeneity of the Ga_{2}O_{3} films. The areal uniformity of a Ga_{2}O_{3} film deposited at Tₛ=40 °C without introduction of additional oxygen is illustrated in Fig. 2. The standard deviations of the thickness and of the refractive index over a 2 in. wafer are 4 Å (0.5%) and 0.001 (0.05%), respectively. Similar results were obtained when oxygen was introduced into the chamber during deposition.

**B. Atomic composition and density**

The Ga_{2}O_{3} films were characterized by Rutherford backscattering spectroscopy for areal densities and atomic composition including stoichiometry. The measurements were performed using He⁺ ions at 1.8 MeV in random direction and at a 175° detection angle. Experimental results were compared to theoretical simulations in order to obtain the areal densities of the oxide layers and the respective O/Ga atomic ratio. Measured RBS spectra and the corresponding simulations are shown in Fig. 3. Experimental results indicate homogeneous and stoichiometric gallium oxide films with 40% Ga and 60% O for moderate substrate deposition temperatures and introduction of additional oxygen into the deposition chamber. Nonstoichiometric films were obtained for elevated substrate deposition temperatures (e.g., 44% Ga and 56% O for Tₛ=350 °C). The oxidation state of these films is further investigated by XPS in the next section. The film thicknesses separately measured by ellipsometry were used to compare the volume density of the deposited oxide films to the bulk Ga_{2}O_{3} density. For introduction of oxygen into the deposition chamber (p₂=2×10⁻⁴ Torr), the calculated film densities for lower Tₛ were between 60% and 68% of the bulk density using the bulk density of α-Ga_{2}O_{3} (6.44 g/cm³, Ref. 23). For higher substrate temperatures Tₛ between 200 and 350 °C, the film density increases to approximately 80% of the bulk density. If no excess oxygen is introduced, film densities between 70% and 74% of the bulk density were obtained for Tₛ=40 °C.

**FIG. 1.** Auger depth profile of a 955 Å thick Ga_{2}O_{3} film deposited at a substrate temperature of 125 °C with an O₂ partial pressure of 2×10⁻⁴ Torr in the deposition chamber. The analysis was done by using 4 keV Ar ions and the sensitivity factors for Ga and O were calibrated against pressed Ga₂O₃ powder. The nominal sputter rate is 65 Å/min.

**FIG. 2.** Refractive index and thickness uniformity of a Ga₂O₃ film over a 2 in. wafer. This film was deposited at Tₛ=40 °C without introduction of additional oxygen into the deposition chamber. Thickness and refractive index (measured at λ=830 nm) are (85.4±4) Å and 1.916±0.001, giving a relative standard deviation of 0.5% and 0.05%, respectively.

**FIG. 3.** Rutherford backscattering spectra measured on Ga₂O₃ films deposited with introduction of additional oxygen into the deposition chamber. An excellent agreement between simulated and experimental curves indicates homogeneous and stoichiometric gallium oxide films with 40% Ga and 60% O for substrate temperatures of 40 and 125 °C.
We consider Gd to be the dominant impurity in our Ga₂O₃ films and the existence of Gd was detectable. We estimate the relative concentration of this element to be, in general, lower than 0.1 at. % (Fig. 4). The two measured spectra shown in Fig. 5 (solid and dotted lines) were taken at different normal-to-beam angles (tilt angle θ) in order to stimulate different geometry configurations. Only small differences were detected in the relative energy positions between the two different tilt angles. The dashed line in Fig. 5 simulates the case of homogeneous distribution of Gd throughout the entire oxide film. The actual elemental distribution, however, is sharp and its peak position does not shift with the tilt angle θ, reflecting the existence of a narrow region, probably the surface region, where the Gd tends to segregate during film deposition.

C. Oxidation state

X-ray photoelectron spectroscopy of Ga₂O₃ films was performed in order to determine the oxidation state of the Ga₂O₃ films. A Perkin–Elmer 5600 series XPS spectrometer equipped with a monochromatic Al Ka x-ray source was used. High-resolution spectra were acquired using an x-ray power of 350 W. The aperture was set at 800 μm and the pass energy at 29 eV, giving a 0.72 eV full width at half maximum for the Ag 3d₅/₂ line. Depth profiling was done in situ by Ar sputtering using an ion gun at 4 keV. An area of 2×2 mm² was sputtered at a rate of ~100 Å/min. The surface composition at each step was calculated from the integrated areas of the core-level peaks using known sensitivity factors. The elemental gallium to Ga₂O₃ ratio was calculated by curve fitting the Ga 2p₃/₂ peak using predominantly Gaussian component peaks. Since the difference between the Ga 2p₃/₂ and the Ga L₃M₄½M₅½ peaks is used for chemical state identification, the reported peak positions were not compensated for surface charging. The Auger peak position refers to the Ga L₃M₄½M₅½ line.

Figure 6 shows the XPS depth profile of a Ga₂O₃ film on GaAs deposited at a substrate temperature of 125 °C and with no introduction of additional oxygen into the chamber. The Ga 2p₃/₂ core levels for Ga₂O₃ and elemental Ga are shown in the left figure. The Auger peak position (right plot) refers to the Ga L₃M₄½M₅½ line. The low binding-energy shoulder of the Ga 2p₃/₂ peak in the Ga₂O₃ film indicates the presence of elemental gallium in this film. The estimated mole fraction of elemental Ga is about 5%.

FIG. 4. Rutherford backscattering spectrum measured on a Ga₂O₃ film deposited at Tₛ = 40 °C with introduction of additional oxygen into the deposition chamber. The relative concentration of Gd, which is considered to be the main impurity in our Ga₂O₃ films, was estimated to be, in general, lower than 0.1 at. %.

FIG. 5. Rutherford backscattering spectra were taken at different normal-to-beam angles θ=10° (solid line) and 57° (dotted line) in order to stimulate different geometry configurations. The dashed line simulates the case of homogeneous distribution of Gd throughout the entire oxide film.

FIG. 6. XPS depth profile of a Ga₂O₃ film deposited on GaAs at a substrate temperature of 125 °C and with no introduction of additional oxygen into the chamber. The Ga 2p₃/₂ core levels for Ga₂O₃ and elemental Ga are shown in the left figure. The Auger peak position (right plot) refers to the Ga L₃M₄½M₅½ line. The low binding-energy shoulder of the Ga 2p₃/₂ peak in the Ga₂O₃ film indicates the presence of elemental gallium in this film. The estimated mole fraction of elemental Ga is about 5%.
energy is associated with Ga$_2$O$_3$. Suboxides such as GaO and Ga$_2$O, which were reported to be unstable and may exist only far away from equilibrium, were not detected in these films. The estimated mole fraction of elemental Ga is about 5%. As expected, elemental Ga was not detected in stoichiometric gallium oxide films. Figure 7 shows the XPS depth profile of a Ga$_2$O$_3$ film on Si deposited with introduction of oxygen ($p_{ox}=2 \times 10^{-4}$ Torr) into the chamber at a substrate temperature of 40 °C. The energy difference of the Ga $2p_{3/2}$ (1119.6 eV) and the Ga $L_3M_{45}M_{45}$ (425.7 eV) peaks in the Ga$_2$O$_3$ film is 693.9 eV and no low binding-energy shoulder in the Ga $2p_{3/2}$ peak could be observed within the oxide film. There is, however, evidence of elemental Ga at the Ga$_2$O$_3$/Si interface with the Ga $2p_{3/2}$ peak at 1117.8 eV and the Ga $L_3M_{45}M_{45}$ peak at 420.4 eV, giving an energy difference of 697.4 eV.

**D. Microstructure**

Ga$_2$O$_3$ films deposited and annealed under different conditions were investigated by transmission electron microscopy. The samples were prepared by chemical thinning using a grid-masking technique and inspected using a Philips 420 TEM operated at 120 kV. In general, the microstructure of the films was uniform and as-deposited films were amorphous. Figure 8 shows the plan-view TEM micrographs and the corresponding electron-diffraction patterns of Ga$_2$O$_3$ films deposited on GaAs at substrate temperatures of (a) 40, (b) 125, and (c) 350 °C. The diffraction patterns indicate the amorphous nature of all the films within the entire range of deposition conditions. As described in Sec. III B, the film deposited at 350 °C became Ga rich with a corresponding increase in the volume density. This is also reflected by a much finer morphology revealed in the corresponding TEM micrograph. TEM cross-sectional micrographs of a Ga$_2$O$_3$ film (a) after deposition at $T_r=40$ °C on a GaAs substrate and (b) after subsequent annealing at 800 °C for 30 s in N$_2$ are shown in Fig. 9. The GaAs/Ga$_2$O$_3$ interface and the

FIG. 7. XPS depth profile of a Ga$_2$O$_3$ film on Si deposited with introduction of oxygen ($p_{ox}=2 \times 10^{-4}$ Torr) into the chamber at a substrate temperature of 40 °C. Left and right plots show the Ga $2p_{3/2}$ core levels for Ga$_2$O$_3$ and elemental Ga as well as the Ga $L_3M_{45}M_{45}$ Auger line, respectively. Like in all investigated stoichiometric gallium oxide films, elemental Ga was not detected.

FIG. 9. Cross-sectional TEM micrographs of Ga$_2$O$_3$/GaAs interfaces for (a) as deposited at 40 °C and (b) after annealing at 800 °C for 30 s in N$_2$.

FIG. 8. Plan-view TEM micrographs and the corresponding electron-diffraction patterns of Ga$_2$O$_3$ films deposited on GaAs substrate at temperatures of (a), 40, (b) 125, and (c) 350 °C.
Ga$_2$O$_3$ surfaces were observed to be planar to the nanometer scale even after annealing at 800 °C. Since the integrity of Ga$_2$O$_3$ on GaAs is preserved, these films can be used for high-temperature annealing of implants in GaAs. Annealing of Ga$_2$O$_3$ films at temperatures above 700 °C leads to a distinct change in the microstructure from an amorphous to a polycrystalline phase. As expected, the grain size increases with annealing temperatures. Figure 10 shows the plan-view TEM micrographs and the corresponding electron-diffraction patterns for Ga$_2$O$_3$ films (a) on GaAs annealed at 800 °C and (b) on Si substrate annealed at 1200 °C in O$_2$ for 30 s. The continuous diffraction rings from the fine grain film break into spotty patterns for the large grain film. The measured lattice spacings are plotted in Fig. 11(a) along with the published x-ray powder patterns for (b) α-Ga$_2$O$_3$ and (c) monoclinic Ga$_2$O$_3$. The majority of the lines match with the α-Ga$_2$O$_3$, while a few lines match the monoclinic Ga$_2$O$_3$, which indicates that the dominant crystalline phase is α-Ga$_2$O$_3$.

E. Etching behavior and temperature integrity

The etching behavior of Ga$_2$O$_3$ films was investigated both as a function of deposition conditions and annealing temperature. The annealing was done in N$_2$ or O$_2$ atmosphere for 30 s. Figure 12 shows the etch rate of Ga$_2$O$_3$ films in a 10% HF solution at room temperature. The etch rate decreases with increasing substrate temperature during deposition as well as with annealing temperature. Note that the etch rate of as-deposited Ga$_2$O$_3$ films at $T_s$=350 °C is significantly lower than the etch rate of SiO$_2$ (200 nm/min) fabricated by plasma-enhanced chemical-vapor deposition at the same substrate temperature. In agreement with the refractive index, absorption, and RBS measurements, the decrease in etch rate with increasing substrate temperature during deposition and with rising annealing temperatures below 700 °C can be attributed to improved film densities. A new quality is observed for Ga$_2$O$_3$ films annealed at temperatures equal or higher than 700 °C, which may be related to the change from an amorphous to a polycrystalline phase as revealed by TEM measurements. These films do not etch even in a concentrated HF solution and the water sensitivity which is observed for amorphous Ga$_2$O$_3$ films disappeared. In general, the refractive index of amorphous Ga$_2$O$_3$ films was altered within a range of approximately −1.5% and +1% after soaking in de-ionized water for 60 h at room temperature, whereas polycrystalline Ga$_2$O$_3$ films were found to be stable.

Furthermore, the refractive index measured before and after annealing was used to evaluate the temperature integrity of Ga$_2$O$_3$ films. Figure 13 shows the relative change in refractive index versus annealing temperature for a Ga$_2$O$_3$ film deposited on a Si substrate at $T_r$=125 °C and an oxygen partial pressure of 2×10$^{-4}$ Torr in the deposition chamber. After a small, initial decrease in refractive index, the refractive index slightly increases with annealing temperature in an O$_2$ or N$_2$ atmosphere and the film maintains its integrity up to our maximum annealing temperature of 1200 °C. Annealing in a reducing ambient (15% H$_2$, 85% N$_2$), however, leads to a drastic decrease in refractive index for annealing temperatures over 700 °C and eventually to decomposition of the film.
film. Ga$_2$O$_3$ films deposited on GaAs maintain their integrity up to annealing temperatures of 800 °C (Fig. 14).

F. Optical properties

Spectroscopic variable angle ellipsometry measurements were done between 400 and 1700 nm in order to determine the refractive index $n$ and the absorption coefficient $\alpha$ as a function of wavelength. Figure 15 shows $n$ and $\alpha$ measured at 980 nm wavelength for Ga$_2$O$_3$ films deposited at substrate temperatures between 40 and 350 °C. The refractive index $n$ is within a range of 1.841–1.885 at 980 nm wavelength for all substrate temperatures $T_s$ used during deposition. This refractive index is close to $n = 1.91$ which is given in Ref. 23 for bulk Ga$_2$O$_3$. The slight increase in refractive index with substrate temperature for films deposited with introduction of additional oxygen into the chamber may be attributed to higher film densities. The measured absorption coefficient is very small ($\sim$100 cm$^{-1}$) and almost independent of $T_s$, indicating the nonabsorbing nature of these films.

FIG. 13. Relative change in refractive index vs annealing temperature for a Ga$_2$O$_3$ film deposited on a Si substrate at $T_s = 125$ °C and an oxygen partial pressure of $2 \times 10^{-4}$ Torr in the deposition chamber.

FIG. 14. Relative change in refractive index vs annealing temperature for a Ga$_2$O$_3$ film deposited on a GaAs substrate at different deposition conditions.

FIG. 15. Refractive index $n$ and absorption coefficient $\alpha$ measured at 980 nm wavelength for Ga$_2$O$_3$ films deposited at substrate temperatures between 40 and 350 °C. The absorption coefficient is very small ($\sim$100 cm$^{-1}$) and almost independent of $T_s$, indicating the nonabsorbing nature of these films.

FIG. 16. Measured reflectivity vs wavelength of a Ga$_2$O$_3$/GaAs structure. The measured reflectivity minimum is $<10^{-5}$ at 885 nm wavelength, which is in excellent agreement with the simulation data. The film thickness is 1170 Å.
The optical transmission was measured within a wavelength range of 185–600 nm for Ga$_2$O$_3$ films deposited on fused silica disks using a Perkin–Elmer spectrophotometer. According to a definition for materials with residual absorption, the band gap of Ga$_2$O$_3$ films was determined to be 4.4 eV (Fig. 17). The same band gap was reported earlier for bulk Ga$_2$O$_3$.28

**G. Dielectric properties**

Ti/Au dots of different diameters (50, 100, 200, and 500 μm) were evaporated on 40–4000 Å thick Ga$_2$O$_3$ films deposited on n$^+$-GaAs substrates. Figure 18 shows the dc breakdown field of 400–500 Å thick Ga$_2$O$_3$ films measured by applying a voltage ramp of approximately 1 V/s to the metal–insulator–semiconductor structure at room temperature. A breakdown field of 3.6 MV/cm was measured for Ga$_2$O$_3$ films deposited at 40 °C without excess O$_2$ in the evaporation chamber. If additional oxygen was introduced into the evaporation chamber, the breakdown field is about 3.1 MV/cm within the entire range of substrate temperatures during deposition. The specific resistivity of these films is found to be of the order of 10$^{12}$–10$^{13}$ Ω cm at room temperature. In an earlier work,30 we also reported a static dielectric constant of Ga$_2$O$_3$ films between 9.9 and 10.2, which is in close agreement with $\varepsilon_r$= 10.2 measured for single-crystal Ga$_2$O$_3$ platelets.31 Furthermore, like for other dielectrics, the current transport mechanisms in metal/Ga$_2$O$_3$/semiconductor structures were found to be controlled by the insulator bulk properties.

In order to evaluate the stability of dielectric properties of Ga$_2$O$_3$ films on GaAs with temperature exposure during processing, Ti/Au dots were evaporated on annealed films and, subsequently, the dc breakdown field was measured. As indicated in Fig. 19, the dc breakdown field degrades only by 6% for typical processing temperatures up to 400 °C. The breakdown field, however, degrades rapidly for annealing temperatures above 550 °C.

**H. Interface properties**

The Ga$_2$O$_3$/air exposed (100)GaAs interface was investigated by a photoluminescence study using an argon-ion laser (λ= 514.5 nm) operated at an optical power density of 50 W/cm$^2$. Dispersion and detection were done using a Spex 1877 triple monochromator and a Princeton Instruments liquid–nitrogen-cooled CCD camera, respectively. The integration time was 120 s. A particular structure was prepared (see inset of Fig. 20) in which the photoluminescence intensity is highly sensitive to the GaAs surface recombination velocity. Subsequently, 400 Å thick Ga$_2$O$_3$ and Al$_2$O$_3$ films were deposited on this structure by electron-beam evaporation. The photoluminescence intensity increased after deposition of a Ga$_2$O$_3$ film and, as indicated in Fig. 20, the pho-
toluminescence intensity is significantly higher for an air exposed (100)GaAs surface having a deposited Ga$_2$O$_3$ film compared to the same structure with a deposited Al$_2$O$_3$ film. Thus a lower surface recombination velocity is obtained for the Ga$_2$O$_3$ coated sample.

IV. CONCLUSIONS

Properties of dielectric Ga$_2$O$_3$ films deposited by electron-beam evaporation from a high-purity single-crystal Gd$_3$Ga$_2$O$_{12}$ source were reported. Thin-film properties including stoichiometry, microstructure, phase, homogeneity, uniformity, and temperature integrity as well as optical and electrical characteristics make these films well suited for electronic and optoelectronic applications. Furthermore, our deposition technique is compatible with integrated vacuum processing schemes using surface plasma passivation techniques or molecular-beam epitaxy in order to produce dielectric/III–V semiconductor interfaces with low density of interface states.

ACKNOWLEDGMENTS

We would like to thank G. P. Schwartz, R. A. Gottscho, R. L. Opila, T. D. Harris, L. C. Feldman, R. Becker, H. S. Luftman, and R. J. Fischer for many useful discussions. Special thanks to U. K. Chakarabarti and R. L. Masaitis for spectroscopic ellipsometry and Auger spectroscopy measurements, respectively. M. Passlack gratefully acknowledges support by the Deutsche Forschungsgemeinschaft. We are also grateful to N. K. Dutta, A. Y. Cho, and D. V. Lang for their support.


14 See, for example, A. Callegari, P. D. Hoh, D. A. Buchanan, and D. Lacey, Appl. Phys. Lett. 54, 332 (1989).


