Ultra-Wide Band Gap Material Gallium Oxide, Technology, Properties, Characterization

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Abstract

Gallium oxide (Ga_2O_3) is a ultra wide-bandgap semiconductor (4.7 ~ 5.3 eV) that has garnered significant attention for its exceptional structural, optical, and electrical properties, which make it suitable for high-power electronics, UV photodetectors, and catalysis. Structurally, Ga_2O_3 exhibits polymorphism, with α-, β-, γ-, δ-, ε-, and κ-phases, among which β-Ga_2O_3 is the most thermodynamically stable under ambient conditions. Synthesis methods, including hydrothermal growth, sol-gel processes, RF/DC sputtering, atomic layer deposition (ALD) and molecular beam epitaxy (MBE) enable precise control over phase formation, crystallinity, and defect density.In the present work is demonstrated the reactive magnetron sputtering (DC) technology for formation β-Ga_2O_3. As substrate is used 2-inch, (0006) orientation and 400μ thickness sapphire wafer. Experiments are made in different condition (power, oxygen partial pressure, time, temperature etc.) for analyzing the best technological rout of growing Ga_2O_3 with good structural, optical and electrical properties. X-ray structural analysis (XRD) was measured and a small peak was identified at the diffraction angle $2\theta=20.5^0$. In terms of optical properties, transmission spectra were measured. The calculated optical band gap was ~ 5 eV. Electrically, Ga_2O_3 behaves predominantly as an n-type semiconductor due to oxygen vacancies. Undoped β-Ga_2O_3 exhibits high resistivity (~10^6 Ω·cm). Electrical measurements also were performed on an HP 4279A C-V Meter to obtain a C-V profile, and the thicknesses of the deposited films were calculated from the graphs and compared with the values measured on the profilometer.

Keywords: *Ultra wide band gap, technology, oxide, transmission spectra*

1. Introduction

In recent decades, semiconductors with a large band gap (SiC, GaN, AlN, ZnO) have gained great interest and wide application in technology and everyday life [1]. For many decades, devices based on silicon (Si) dominated the field of electronic devices. Substantial progress was achieved with the commercialization of the transistor in the 1980s, the creation of the bipolar junction transistor (IGBT) in the 1990s, and the production of the p-n junction transistor in the 2000s. Every significant improvement in devices based on silicon as the base semiconductor material has been due to the clever formation of the p-n junction. However, since 2010, devices based on other systems have entered the market, and the focus has shifted from p-n junction engineering to materials engineering. SiC-based diodes were introduced around 2010, and were soon followed by p-n junction (JFET) and metal-oxide-semiconductor (MOSFET) field-effect transistors [2-3]. Steady and continuous improvements in SiC material quality and better process control have led to a lower market value for this material. In 2019, SiC devices accounted for ~3% of the total power device market, and this is expected to increase to 12% by 2025 [4]. Another emerging class of optoelectronic devices is based on AlGaN/GaN high-electron mobility transistors (HEMTs) [5], which can be grown on inexpensive 200-mm-diameter silicon wafers, onto which a thin layer of GaN is grown by metal-organic chemical vapor deposition (MOCVD) [6]. Many other wide-bandgap materials are currently being investigated. Among them is diamond, which is considered the "ultimate material". However, technological obstacles (lack of effective n-type doping and surface conduction channels, as well as the lack of wafer fabrication and the difficulty of creating ohmic contacts) have long hindered the demonstration of devices based on this material. Aluminum nitride (AlN) is perhaps the most interesting wide-bandgap material, as it has high thermal conductivity and a very large band gap (6.2 eV), larger than that of diamond (5.5 eV). However, its production rates are very low and the wafer diameter is at most 2 inches.

In contrast to the wide bandgap materials listed above, the ultra-wide bandgap (4.7–4.9 eV) semiconductor gallium oxide (Ga_2O_3) is the only material that can be grown from the liquid phase and is therefore a potentially low-cost material. It forms five crystalline polymorphs. The β phase is the only stable polymorph above 1800 °C and 1 atm pressure. The use of melt-based growth techniques provides significant manufacturing advantages, cost, and scalability compared to vapor-deposition processes used for other wide bandgap semiconductors such as SiC, GaN, and AlN.

2. Experimental

In this article is presented formation gallium oxide by reaqtive magnetron sputtering technology. Magnetron sputtering technology is a well-known vacuum sputtering technology. The reagent gases, argon and oxygen, are 99.9999% pureity. As a substrate is used 2-inch, 400 μ thickness and (0006) orientation sapphire wafers and 2-inch, 400 μ thickness and (100) orientation silicon wafers for various measurements. The main thing in this technology is that liquid gallium with a purity of 99.99% is used as the target, and not a gallium oxide target. The vacuum chamber is equipped with a rotating system on which the sapphire sample is placed. During the deposition process, the sample is moved and placed on top of the gallium target on the magnetron, and the growth of the gallium oxide film on the sapphire begins. The chamber is also equipped with a residual gas analyser (RGA200), which is used to diagnose the gases contained in the initial vacuum and determine the ratio of the partial pressures of argon and oxygen during the gallium oxide deposition process. Experiments were conducted with the aim of determining the properties of gallium oxide thin films grown in pure oxygen on the one hand and in a mixture of argon and oxygen on the other hand. These properties are: deposition rate, thickness of the deposited layer, structural properties (XRD), electrical properties (C-V characterization) and optical properties (transmission spectra).

3. Results and Discussion

3.1 XRD Analysis

In the Fig. 1 and Fig. 2 is shown XRD patterns of Ga_2O_3 deposited in pure oxygen and mixed gases ($Ar+O_2$). Gallium oxide (Ga_2O_3 structure) was obtained on sapphire substrates by magnetron sputtering technology.

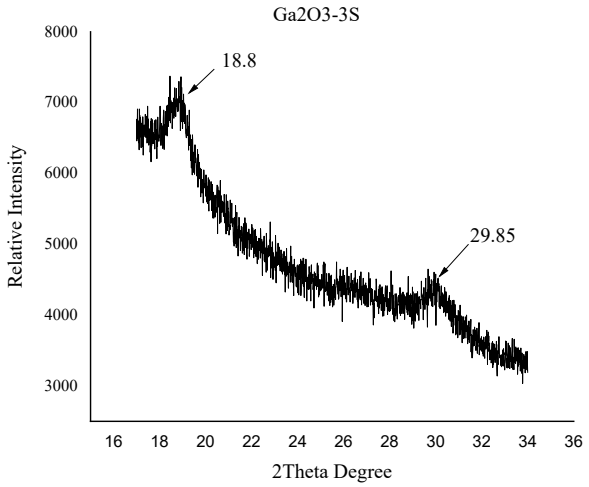

Fig. 1. XRD of Ga_2O_3 with pure oxygen

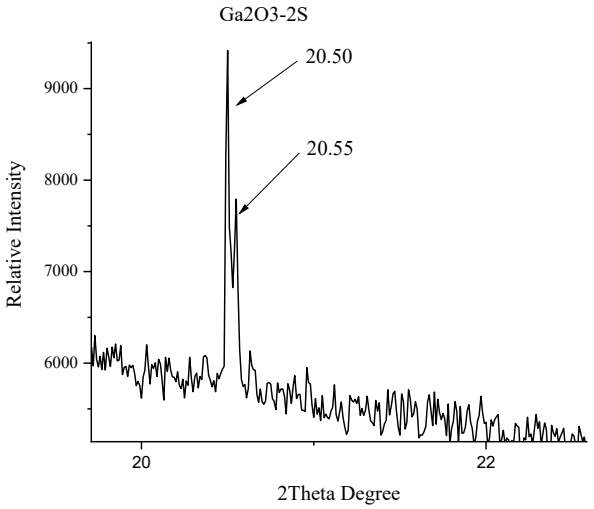

Fig. 2. XRD of Ga_2O_3 with $Ar+O_2$

X-ray structural analysis of Ga_2O_3 deposited in pure oxygen ambient showed that the obtained material is a material with a polycrystalline structure (Fig. 1). Distinct peaks are noted at diffraction angles: 18.8 and 29.85. XRD of sapphire does not match any of the above peaks, therefore they are Ga_2O_3 peaks [7].

In the case of Ga_2O_3 deposited in mixed gases (Fig. 2), the XRD peaks of sapphire and Ga_2O_3 overlap (they coincide when the diffraction angle is 41.70). Therefore, XRD was taken at different diffraction angle intervals. This method clearly revealed the peaks of Ga_2O_3 at diffraction angles: 20.55 and 20.50. It should be noted here that these peaks do not coincide with the XRD peaks characteristic of sapphire and emphasize the polycrystalline nature of the obtained Ga_2O_3 structure.

3.2 C-V Characterization

For measuring C-V characterition Ga_2O_3 was deposited on n-type silicon wafer creating metal-oxide-semiconductor (MOS) structure Fig. 3. As from the theory of C-V measurement known the C-V curve has three regions: accumulation, depletion and inversion regions. For high frequency measurement on the MOS structure is applied small sinusoidal oscillating (AC) signal on the voltage sweep. This is because equilibrium conditions imply that there is sufficient time for the inversion layer carrier concentration to respond to any changes in applied field. Any inversion layer must be formed from minority carriers generated in the depletion region and swept to the surface by the electric field. If the material quality of the silicon is good, carrier generation - recombination processes occur very slowly, with a time constant on the order of milliseconds. Therefore, for an applied AC voltage in the megahertz range, the response of the inversion layer is simply too slow to follow the signal and similar to ionized dopant impurity atoms, the inversion layer appears fixed with respect to the AC component of the bias. (Of course, the inversion layer does respond to the primary voltage sweep) [8].

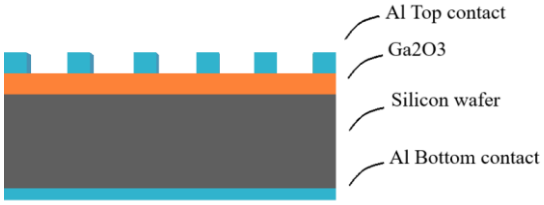

Fig.3 MOS structure of Ga_2O_3

As a previous case deposition is considered in pure oxygen and mixed gases ambient. The experiments were carried out in the several modes, in term of deposition time: 5 min, 15 min and 20 min. In the Fig. 4 and Fig. 5 is shown C-V patterns of Ga_2O_3.

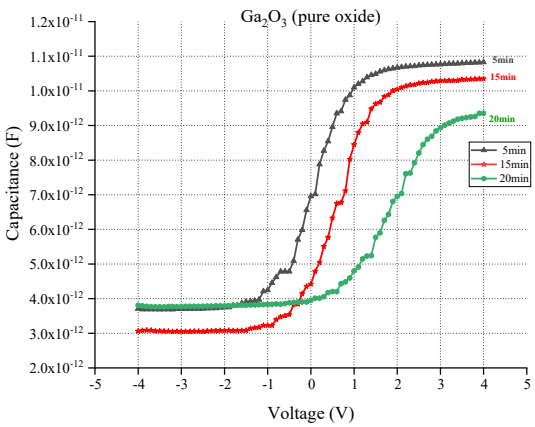

Fig. 4. C-V of Ga_2O_3 in pure oxygen

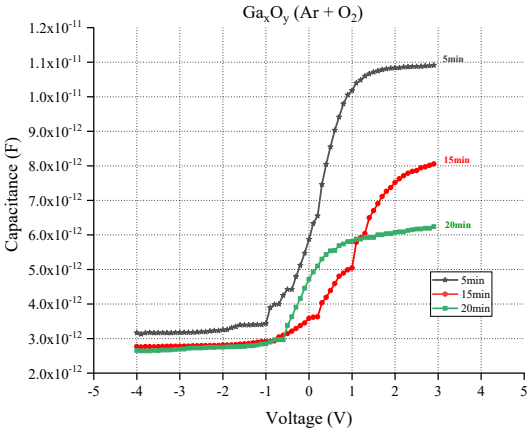

Fig. 5. C-V of Ga_2O_3 in mixed gases.

As can be seen from the graphs, for gallium oxides deposited at different deposition times (in both cases), the capacitance values in the saturation region change proportionally. Using the oxide thicknesses measured by profilometer and data from C-V measurement, using the known formula (1), was calculated the dielectric constant of gallium oxide.

$$C = \frac{\varepsilon \varepsilon_0 S}{d} \quad (1)$$

where ε is the dielectric permittivity of gallium oxide, $\boldsymbol{\varepsilon_0}$ - dielectric constant, S - the area of the top aluminum contact ($2.8 \cdot 10^{-5}$ sm^2), d - the thickness of gallium oxide (Å). Table 1. gives some technological and calculated parameters of gallium oxide.

Tab. 1. The text of the table caption will be here.

Deposition time, min	**Pure O_2, %**	**Thickness by profilometer, Å**	**Dielectric constant**	**Deposition rate, $Å/min$**
5	100	180	4.88	36
15	100	242	6.74	16.1
20	100	261	5.48	13.05
5	30	188	5.45	37.6
15	30	281	5.50	18.7
20	30	440	5.47	22

Calculated average dielectric constant for Ga_2O_3 is around 5.6. Different situation appears in the calculating deposition rate. In the case of pure oxygen initially it is greatest 36 $Å/\boldsymbol{min}$. For a big deposition times (15min and 20 min) surface of gallium covers by gallium oxide and prevents further sputtering. As a result, the surface resistance of the target increases and the sputtering current decreases. The latter leads to a decrease in the deposition rate till 13 $Å/\boldsymbol{min}$, approximately 3 times less. The same situation is observed in the mixed gases ambient. But small difference occurs in the deposition rate. Because of existing Ar the sputtering rate commonly rises and if we compare it to the previous case, the thickness of the deposited layer increases slightly, although for the same reason, the oxide deposited on the gallium target reduces the deposition rate.

3.3 Transmission Spectra.

For optical measurement Ga_2O_3 was deposited on sapphire wafers. Fig. 6 and Fig. 7 illustrates transmission spectra of C-V of Ga_2O_3 in pure oxygen and mixed gases ambient. Optical measurement was carried out on UV/VIS/NIR Spectrophotometer. Both curves have sharp minimum, corresponds to optic band gap respectively 4.2 eV and 4.7 eV for pure oxygen and mixed gases ambient.

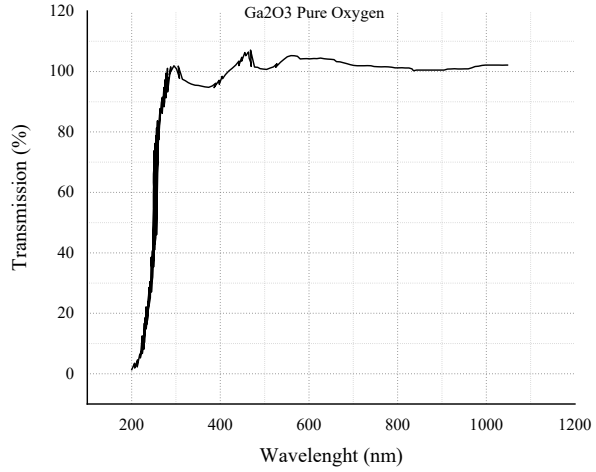

Fig. 6. Transmission spectra of Ga_2O_3 with pure oxygen

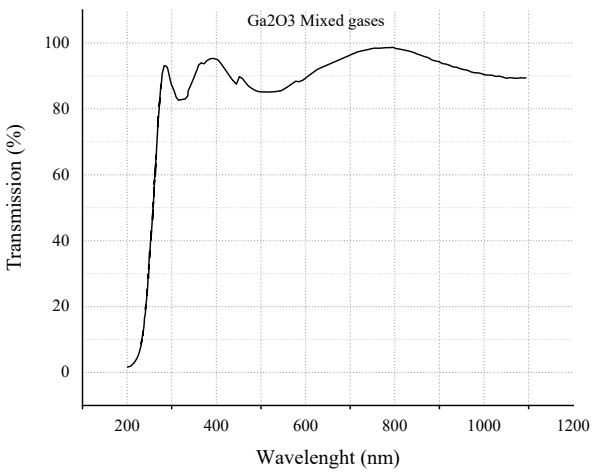

Fig. 7. Transmission spectra of Ga_2O_3 with mixed gases.

4. Conclusions

The conducted studies have shown that it is possible to obtain good quality gallium oxide thin films using reactive magnetron sputtering technology. X-ray structural analysis revealed the presence of polycrystalline gallium oxide inclusions. The dielectric constant of gallium oxide was calculated using the C-V method, which is on average equal to 5.6. The width of the optical band gap was calculated using the transmission spectra, which amounted to 4.2 ÷4.7 eV. From the results obtained, we can conclude that the gallium oxide obtained using the aforementioned technology will be fully compatible with the technology for creating opto-electrical devices. First of all, the creation of a memristor is intended, in which complete (pure oxygen ambient) and incomplete (mixed gases ambient) gallium oxides can be used as the active layer.

Acknowledgments

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