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Low temperature Ga_2O_3 atomic layer deposition using gallium tri-isopropoxide and water

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ABSTRACT

Ga_2O_3 atomic layer deposition (ALD) was carried out using gallium tri-isopropoxide (GTIP) as a gallium source and H_2O as an oxygen source at a low temperature (150 °C). The Ga_2O_3 ALD films show amorphous, smooth, and transparent behavior. The growth behavior and a variety of optical, structural, and electrical properties were investigated by various measurements. The growth behavior of Ga_2O_3 ALD using GTIP reveals a typical ALD process, and Ga_2O_3 films on glass substrates show outstanding transmittance (over 90%). The Ga:O ratio was measured as 1:1.7 by the Rutherford backscattering spectrometry, and auger electron spectroscopy confirmed that there was no carbon impurity (under the detection limit). The surface morphology was investigated through an atomic force microscope analysis, and all of the films deposited at 150, 200, and 250 °C showed smooth and featureless characteristics. Ga_2O_3 ALD thin film shows excellent leakage current (1×10^{-11} A at 1 MV/cm) and a very suitable breakdown field (6.5–7.6 MV/cm) as compared to previously reported Ga_2O_3 films. Also, the dielectric constant of the films is similar to that of conventional Ga_2O_3 films (about 9.23).

1. Introduction

Gallium oxide (Ga_2O_3) thin films have been studied as gas sensor devices, nanoscale optoelectronic devices, passivation layers for GaAs based microelectronics and dielectric layer [1,2]. Also, gallium oxide thin films have been prepared by various methods, such as magnetron sputter deposition [3], electron beam evaporation [4], pulsed laser deposition [5], laser ablation, chemical vapor deposition (CVD) [6,7] and atomic layer deposition (ALD) [1,8,9]. Among these methods, ALD is a growth method based on sequential, self-limiting surface reactions. As a result of the surface-reactions growth, the ALD process provides excellent thickness control and excellent conformal coverage on substrates. For these reasons, ALD is deemed a powerful technique to obtain high-quality thin films for a variety of materials including oxides, nitrides, and various types of metals [10]. In previous results of Ga_2O_3 films in vapor deposition, many researchers investigated various film properties of Ga_2O_3 thin films in terms of gallium precursors.

However, most gallium precursors require a temperature that exceeds 300 °C for deposition on a substrate, including gallium tris-hexafluoro acetyl acetonate (470 °C) [6], gallium alkoxide (300 °C) [11], gallium trichloride (450 °C) [12], trimethyl gallium (500 °C) [13], and triethyl gallium (470 °C) [14]. Although Ga_2O_3 films have feasible insulator and passivation properties in microelectronics, the high process temperature may limit their applicability to next-generation electronics such as flexible and transparent electronics. In addition, the chemical vapor deposition process with various Ga precursors usually incorporates unintentional impurities (C and Cl etc.) in the deposited films due to incomplete thermal reactions. Thus, it is important to select a precursor and process based on a low temperature for next-generation electronics.

In this work, Ga_2O_3 thin films were deposited by an ALD method using gallium tri-isopropoxide (Ga(OiPr)3, GTIP) as a Ga precursor at a low temperature (150 °C). The optical, chemical, and electrical properties of the ALD Ga_2O_3 films were investigated. The Ga_2O_3 films showed an amorphous phase, a smooth surface, a carbon-free composition, and high transparency, even at 250 °C. In addition, the electrical properties of the Ga_2O_3 thin films exhibit an excellent breakdown voltage (7.56 MV/cm at 250 °C) and a feasible amount of leakage current (1.92×10^{-11} A at 1 MV/cm) despite the mid-level bandgap energy (5.4 eV).

2. Experimental details

ALD Ga_2O_3 films were deposited on various substrates (Si, glass, and carbon) at 150 °C, 200 °C and 250 °C by using GTIP and H_2O. N_2 gas was used as a carrier gas at a flow rate fixed at 50 sccm. The GTIP precursor was held in a stainless steel canister and was heated to 120 °C, and the H_2O was maintained at 25 °C to control the source of the vapor pressure. The ALD Ga_2O_3 sequence was as follows: GTIP pulse time–N_2 purge–H_2O pulse–N_2 purge. To analyze the thickness, the refractive index, and optical bandgap of the Ga_2O_3 thin films,

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spectroscopy ellipsometry (SE, J. A. Woollam Co.) was conducted. Cauchy modeling was adopted to extract film thickness, considering in low energy regime without an adsorption. Tauc–Lorentz modeling was also adopted to extract optical parameter under adsorption energy regime. These spectra were extracted from a simple three-phase model, which is comprised of a Si substrate, Ga_2O_3 over-layer, and an ambient layer. Rutherford back-scattering spectroscopy (RBS, 2 MeV He^{2+}) was performed to obtain the film composition.

The Auger electron spectroscopy (AES, SAM-4300) depth profile was conducted to confirm the carbon impurity in the Ga_2O_3 thin films. The crystal structures of the Ga_2O_3 films were examined by X-ray diffraction (XRD, Rigaku diffractometer) using two theta method with CuK_α radiation ($\lambda = 1.5418$ Å). The surface morphology was observed using an atomic force microscope (AFM, Digital Instruments; Dimension 3100). The surface roughness of a typical 5 μm × 5 μm area was investigated using non-contact mode by 4 μm thickness, width 30 μm, and length 125 μm tips. The film transmittance was measured using ultraviolet visible spectroscopy (UV–VIS). The transmittance of the films was measured in the wavelength range of 300 to 800 nm. Current–voltage (I–V) and capacitance–voltage (C–V) measurements were taken to investigate the breakdown voltage, leakage current level, and dielectric constant. In an I–V and C–V test, 40 nm ALD Ga_2O_3 films were deposited on Si substrates. Patterned Al dots (100 nm thickness) of various sizes ranging from 60 μm to 1000 μm diameter were evaporated on Ga_2O_3 film/silicon substrates.

3. Results and discussion

The Ga_2O_3 ALD films were deposited at a low deposition temperature (150 °C to 250 °C) using GTIP as the gallium source and H_2O as the oxygen reactant. The self-limiting characteristic of these two surface reactions is demonstrated at a growth temperature of 250 °C, as shown in Fig. 1. When the GTIP precursor dose increases to 2.0×10^{-6} mol/cm^2, the growth rate (thickness per cycle) of the Ga_2O_3 films increases drastically and then saturates to 0.25 nm/cycle. This behavior reveals that both half-reactions become saturated for reactant exposures over 2.0×10^{-6} mol/cm^2 and that additional reactant exposure results in no additional growth. This tendency suggests that Ga_2O_3 films using GTIP as a precursor involve a conventional self-limiting surface reaction, which is a general ALD behavior. Also, the refractive index of Ga_2O_3 films exhibits a constant value (about 1.72) even when the GTIP dose increases drastically. In previous results [15,16], some groups reported that Ga_2O_3 films have a refractive index of about 1.84 when deposited by pulsed laser deposition and chemical vapor deposition (CVD). The deposited films usually show a monoclinic β-phase Ga_2O_3 structure due to the high deposition temperature. This difference in the refractive index may originate from the crystallinity of the Ga_2O_3 film between amorphous and poly-crystal structures.

Fig. 2 shows the growth rate and refractive index of Ga_2O_3 films depending on the deposition temperature. As the deposition temperature increases from 150 °C to 250 °C, the growth rate and refractive index exhibit no significant changes (0.25 nm/cycle and 1.72, respectively). This indicates that the deposition temperatures are precisely within the ALD process window due to the self-limiting surfaces of each precursor. As shown in Figs. 1 and 2, the Ga_2O_3 films are governed by typical ALD characteristics, as shown not only by the saturated growth rate but also by the process temperature window [10].

To investigate the stoichiometry of and impurity in the Ga_2O_3 films, the thin films were measured by RBS and AES. Fig. 3 shows the typical RBS spectra of Ga_2O_3 films when deposited on a carbon substrate at 250 °C. The RBS spectrum of the Ga_2O_3 films is Ga:O = 1:1.7, which shows an oxygen-rich phase. The AES depth profiles of Ga_2O_3 films were also determined (not shown here), showing no carbon impurity (under detect limit, 0.5 at.%) in the Ga_2O_3 films. Interestingly, earlier Ga_2O_3 films showed a Ga-rich phase (oxygen deficiency) with a few carbon impurities when deposited at temperatures that exceeded 300 °C with a dimethyl-gallium-isopropoxide precursor [2]. This likely occurred in that the generation of oxygen deficiencies in Ga_2O_3 films arose due to the high process temperature. Thus, the Ga_2O_3 ALD films display stoichiometry similar to that of Ga_2O_3 due to the low deposition temperature.

Fig. 4 shows the crystal structure and surface roughness of Ga_2O_3 films depending on the deposition temperature. Fig. 4(a) exhibits no specific peaks at all deposition temperatures according to the XRD patterns, meaning that there is no secondary phase of the Ga_2O_3 films. Earlier reported Ga_2O_3 films deposited by plasma enhanced ALD showed an amorphous phase at 200 °C, and the crystal structure of Ga_2O_3 was observed when the annealing temperature exceeded 700 °C. This amorphous phase may have affected the capacity of the film to form a smooth surface. To confirm the surface morphology of Ga_2O_3 films, an AFM analysis was performed as a function of the deposition temperature. Fig. 4(b), (c) and (d) display AFM images of 40 nm Ga_2O_3 films, demonstrating clearly smooth surfaces independent of the deposition temperature. The root mean square values of the films deposited at 150, 200, and 250 °C are 3.35, 4.11, and 3.98 Å respectively. This roughness is very similar to that of previous Ga_2O_3 films deposited with other precursors [1,9,13].

Fig. 5 shows the transmittances of the Ga_2O_3 thin films deposited at various temperatures. The optical transmission was measured by UV–visible light within a wavelength range of 400–800 nm for 40 nm Ga_2O_3 films on glass substrates. All of the thin films show outstanding optical transmission (over 90% in visible light range (550 nm)). Also, there are no significant differences in the transmission characteristics between 150 °C and 250 °C. These results demonstrate the strong potential of these films for application as antireflection and dielectric coatings for solar cells and flexible electronics. In addition, the Ga_2O_3

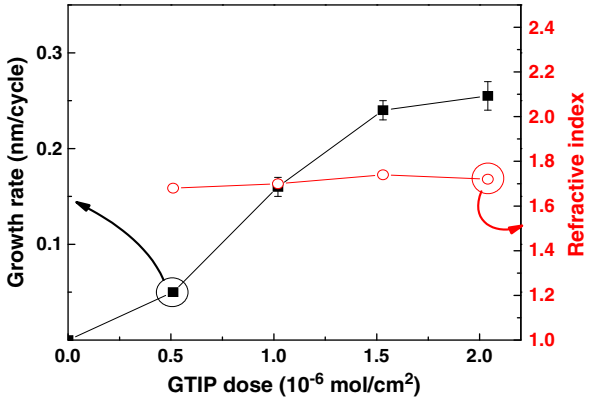

Fig. 1. The growth rate (thickness per cycle) of Ga_2O_3 thin film as a function of the GTIP dose. The growth temperature was 250 °C.

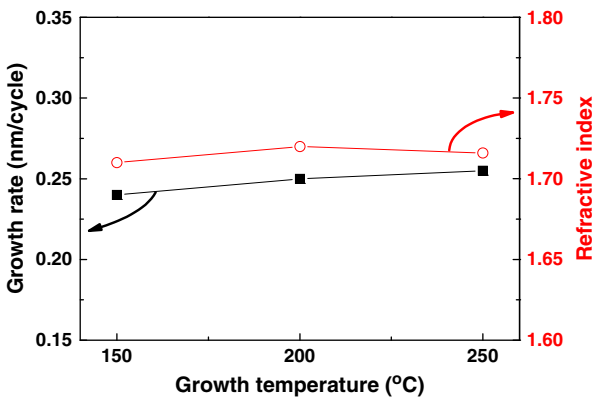

Fig. 2. The growth rate (thickness per cycle) and refractive index of Ga_2O_3 thin films as a function of the growth temperature.

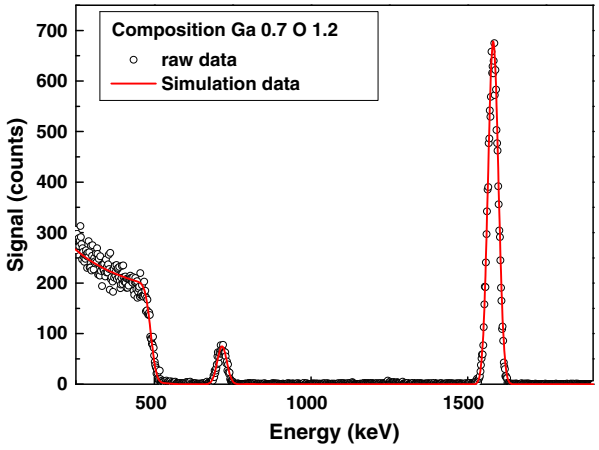

Fig. 3. Rutherford backscattering spectrum from a Ga_2O_3 sample grown at 250°°C.

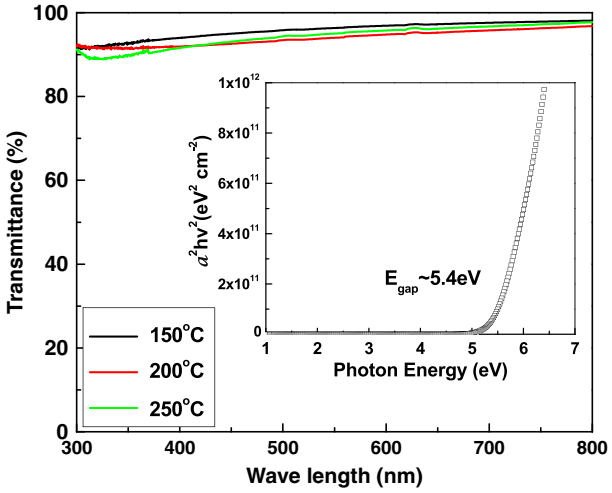

Fig. 5. The transmittance of Ga_2O_3 as a function of the growth temperatures on a glass substrate. The optical bandgap is estimated to be 5.4 eV as measured by SE and shown in the inset.

material has a direct bandgap. The absorption coefficient of the direct bandgap material is determined by the equation below [16]:

$$\alpha(h\nu) \propto \left(h\nu - E_g\right)^{1/2}. \quad (1)$$

The inset of Fig. 5 depicts a plot of the relative absorption coefficient $[\alpha(h\nu)]2$ against the photon energy $h\nu$. A sharp absorption edge is clearly observed. The sharp absorption edge can be determined by linear fitting. The optical bandgap energy as determined from the obtained SE spectra was about 5.4 eV at 250 °C in the Ga_2O_3 films, which is a feasible value compared to that in earlier results [16–18]. Also, there were no significant changes of the optical bandgap with an increase in the deposition temperatures.

To investigate the dielectric properties of Ga_2O_3 thin films, I–V and C–V tests were measured with 40 nm thick Ga_2O_3 thin films. Fig. 6 shows the leakage currents (A) of Ga_2O_3 films as a function of the electrical field (MV/cm). As the deposition temperature increases from 150 °C to 250 °C, the leakage current trend improves from 1.3×10^{-10} A to 1.9×10^{-11} A at 1 MV/cm. The breakdown field properties of the Ga_2O_3 films also improve from 6.5 to 7.6 MV/cm. Interestingly, these electrical properties (leakage current and breakdown field) of the Ga_2O_3 ALD films with a GTIP precursor are superior to those in earlier studies [15,16,19]. Moreover, the electrical properties without a post-annealing process are better than any other Ga_2O_3 films annealed with other precursors [9,15,16]. Although the origins of the outstanding properties are still unclear, they are likely related to the thermal ALD growth mechanism and the GTIP precursor. Many previous Ga_2O_3 films have been deposited by physical vapor

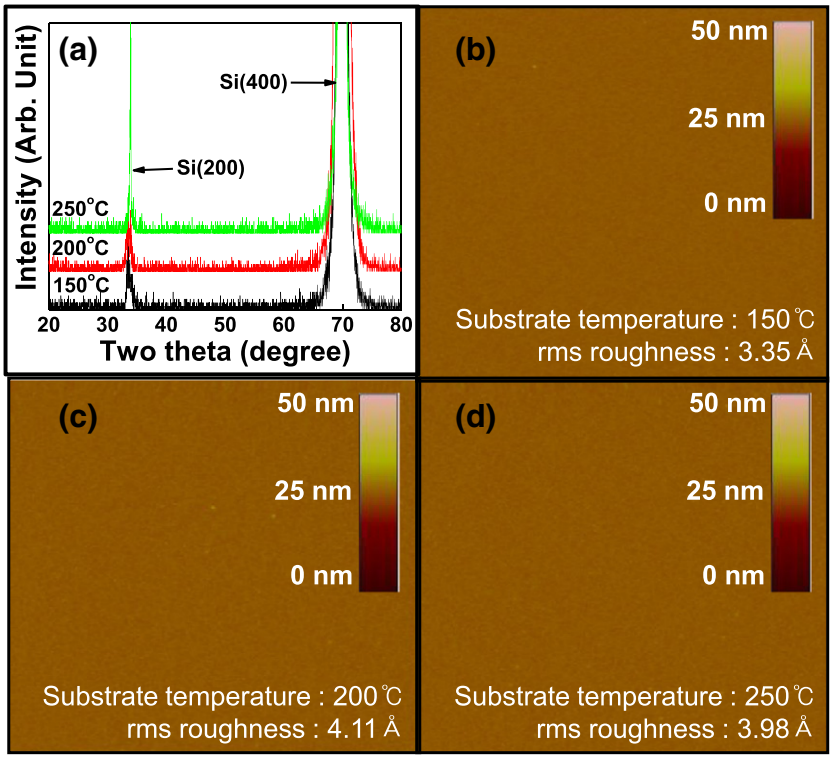

Fig. 4. (a) XRD patterns of Ga_2O_3 thin films deposited at different temperatures, (b–d) AFM images of 40 nm thick Ga_2O_3 thin film surfaces grown at 150, 200 and 250 °C.

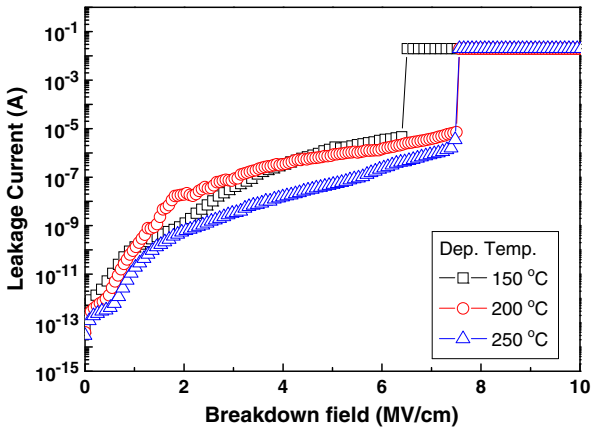

Fig. 6. Leakage current of Ga_2O_3 thin films grown at various substrate temperatures.

deposition and chemical vapor deposition, with the results usually showing a Ga-rich phase (oxygen deficiency), unintentional impurities, and the β-phase structure in the Ga_2O_3 films. However, the Ga_2O_3 ALD films are deposited while incorporating a self-limiting surface reaction, which suggests a complete reaction between GTIP and water without any incorporated by-products. Also, the oxygen-deficient Ga_2O_3 films show n-type semiconductor properties due to the generation of electron carriers as a result of oxygen vacancies. The Ga_2O_3 ALD films are very smooth and slightly oxygen-rich, showing amorphous properties. These findings are closely linked to the improved electrical properties. Capacitance–voltage (C–V) measurements were also taken at a frequency of 100 kHz. The dielectric constant of the Ga_2O_3 ALD films at 250 °C was found to be about 9.2, which is similar with that of other Ga_2O_3 films [9,15,19].

4. Conclusion

High-quality Ga_2O_3 thin films were deposited using a thermal ALD technique with an alternating supply of the reactant source, a gallium precursor of GTIP, and with H_2O at a low temperature. The growth rate of the Ga_2O_3 films became saturated at 0.25 nm/cycle at 250 °C and the ALD process window ranged from 150 °C to 250 °C. The stoichiometry of the Ga_2O_3 ALD films is Ga:O = 1:1.7 and there is no carbon impurity in the films. The Ga_2O_3 films show outstanding transmittance (over 90%) with an optical bandgap energy level of 5.4 eV. The smooth and amorphous Ga_2O_3 films have excellent electrical properties, including a low leakage current (1×10^{-11} A at 1 MV/cm at 250 °C) and a high breakdown field (7.6 MV/cm at 250 °C). Because the Ga_2O_3 films using the GTIP precursor have several advantages, such as a low-temperature process, high transmittance, and excellent electrical properties, these Ga_2O_3 ALD films are promising materials for use in various applications, including anti-reflection films, thin film encapsulation materials, as well as dielectric and passivation materials for next-generation electronics.

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