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Low temperature deposition of Ga_2O_3 thin films using trimethylgallium and oxygen plasma

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Gallium oxide (Ga_2O_3) thin films were deposited by plasma-enhanced atomic layer deposition (ALD) using trimethylgallium as the gallium precursor and oxygen plasma as the oxidant. A wide ALD temperature window was observed from 100 to 400 °C, where deposition rate was constant at ∼0.53 Å/cycle. X-ray photoelectron spectroscopy survey scans indicated the presence of gallium, oxygen, and carbon elements with concentrations of ∼36, ∼51.8, and ∼12.2 at. %, respectively. As-deposited films were amorphous; upon annealing at 900 °C under N_2 atmosphere for 30 min, polycrystalline β-Ga_2O_3 phase with a monoclinic crystal structure was obtained. Refractive index and root mean square roughness of the annealed Ga_2O_3 film were higher than those of the as-deposited due to crystallization. © *2013 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4758782]

I. INTRODUCTION

Gallium oxide (Ga_2O_3) is a wide band gap material with good thermal and chemical stability, high dielectric constant, and large band gap (∼4.9 eV).[1,2] Combination of these properties enables Ga_2O_3 thin films to be used in various applications, including solar cells,[3] gas sensors,[4] deep-UV photodetectors,[5] field-effect transistors,[6] and spintronics.[7] The growth of Ga_2O_3 films has been accomplished by techniques, such as magnetron sputtering,[8] electron beam evaporation,[9] pulsed laser deposition,[10] molecular beam epitaxy,[11] metal-organic chemical vapor deposition (MOCVD),[12] vapor phase epitaxy,[13] and sol-gel process.[14]

Several studies have been reported for the atomic layer deposition (ALD) of Ga_2O_3 thin films using different precursors. First report on the plasma-enhanced ALD (PEALD) of Ga_2O_3 using oxygen (O_2) plasma was published by Shan *et al.*[3] Their study, in which $[(CH_3)_2GaNH_2]_3$ was used as the gallium (Ga) precursor, presented the structural, electrical, and optical properties of the deposited films.[15,16] Ga_2O_3 and mixed Ga_2O_3-TiO_2 films have also been grown by PEALD using $[(CH_3)_2GaNH_2]_3$ and $Ti(NMe_2)_4$ precursors in order to obtain films with large dielectric constant and low leakage current for electronic device applications.[1,17,18] Another study is about the fabrication of metal/insulator/semiconductor capacitors by using Ga_2O_3 as the insulating layer.[19] Ga precursor used in this study was not mentioned by the authors. Besides PEALD, few studies regarding the growth of Ga_2O_3 films using thermal ALD were reported as well. Dezelah *et al.*[20] employed $Ga_2(NMe_2)_6$ together with H_2O to obtain Ga_2O_3 thin films. This process exhibited an ALD window between 170 and 250 °C with a growth rate of 1 Å/cycle. Recently, Lee *et al.*[21] reported the deposition of Ga_2O_3 thin films via both ALD and MOCVD using a new Ga precursor, dimethylgallium isopropoxide (Me_2GaO^iPr). A narrow ALD window (280–300 °C) was reported for the process, and growth rate was found to be 0.28 Å/cycle in this region.

In this study, we report on the growth of Ga_2O_3 thin films using trimethylgallium (TMG) and O_2 plasma as the Ga source and oxidant, respectively. To the best of our knowledge, PEALD of Ga_2O_3 films at such low temperatures using TMG has not yet been reported. Chemical, structural, and morphological characterizations of the films are also presented.

II. EXPERIMENT

Ga_2O_3 thin films were deposited by PEALD using TMG as the Ga precursor and O_2 plasma as the oxidant. Experiments were carried out in a Fiji F200 ALD reactor (Cambridge Nanotech) with a base pressure of ∼0.20–0.25 Torr. Solvent-cleaned Si (111) substrates were loaded into the reactor through a load lock. Ga_2O_3 films were then deposited on these substrates at temperatures starting from room temperature to 400 °C. Ar was used as the carrier gas with the flow rates of 60 and 200 sccm for TMG and O_2, respectively. For the optimization of growth parameters, 150 cycles were deposited at 250 °C, where one cycle consisted of 0.015 s TMG (precursor bottle temperature ∼6 °C)/5 s Ar purge/2–60 s (25 sccm, 300 W) O_2 plasma/5 s Ar purge. Postgrowth annealing of Ga_2O_3 films was performed in a rapid thermal annealing system (ATV-Unitem, RTP-1000-150) under 100 sccm N_2 flow.

Chemical compositions and bonding states of the Ga_2O_3 thin films were determined by x-ray photoelectron spectroscopy (XPS), using a Thermo Scientific K-Alpha spectrometer equipped with a monochromatic Al Kα x-ray source. Surface morphologies and root mean square (rms) roughnesses of the films were investigated by using an atomic force microscope (AFM, Asylum Research, MFP-3D) in the contact mode. Grazing-incidence x-ray diffraction (GIXRD) measurements were performed in a PANanalytical X'Pert PRO MRD diffractometer operating at 45 kV and 40 mA, using Cu Kα radiation ($\lambda = 0.15418$ nm). Initial scans were performed within the range of 10°–90° by using 0.1° step size and 0.5 s counting time. For the crystalline samples, additional data were obtained within the same 2θ range by the summation of eight scans, which were performed by using 0.1° step size and 10 s counting time. Ellipsometric spectra of the Ga_2O_3 thin film samples were measured at three angles of incidence (65°, 70°, and 75°) within the wavelength range of 300–1000 nm by spectroscopic ellipsometry (VASE, J. A. Woollam). Cauchy dispersion function was used for modeling the optical

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constants and estimating film thicknesses. Prior to depositions, native oxide thicknesses of the Si (111) substrates were measured by spectroscopic ellipsometry, which were then used for estimating the thicknesses of deposited Ga_2O_3 layers using the $Si/SiO_2/Ga_2O_3$ model.

III. RESULTS AND DISCUSSION

In order to optimize growth parameters needed for the self-limiting deposition of Ga_2O_3 thin films, effect of TMG dose, O_2 plasma duration, and Ar purge time were studied. Doubling the TMG dose from 0.015 to 0.03 s (precursor bottle temperature ~6 °C) did not affect the deposition rate remarkably, indicating that 0.015 s is high enough for surface saturation. Figure 1(a) shows the deposition rate of Ga_2O_3 films as a function of O_2 flow duration. Experiments were carried out by using various durations ranging from 2 to 60 s. Deposition rate has saturated for O_2 flow durations starting from 10 s. Although 10 s was acceptable, 20 s was used for the following Ga_2O_3 depositions. The effect of purge time on growth rate was also investigated. Five seconds of Ar flow were found to be sufficient for completely purging excess precursors and gaseous byproducts. In order to study the effect of temperature on growth rate, 150 cycles with 0.015 s TMG and 20 s O_2 plasma were deposited at different temperatures (28–400 °C). A wide ALD temperature window was observed from 100 to 400 °C [Fig. 1(b)], where deposition rate was constant at ~0.53 Å/cycle. In Fig. 1(c), Ga_2O_3 film thicknesses were plotted as a function of the number of PEALD cycles. Films deposited at 250 °C exhibited a linear growth behavior. Slope of the linear fit corresponded to deposition rate observed within the ALD window.

Chemical compositions and bonding states of the deposited Ga_2O_3 thin films were studied by XPS. Survey scans detected peaks of Ga, oxygen (O), and carbon (C) with the concentrations of ~36, ~51.8, and ~12.2 at. %, respectively, for the film deposited at 250 °C. Almost same elemental compositions were measured for the films deposited at different temperatures within the ALD window. The reason of C found in the samples was asserted to be due to surface contamination. To prove this claim, bulk films were reached by applying ion beam etching by using Ar ions with energy of 2 kV. C was not detected in the bulk films obtained by

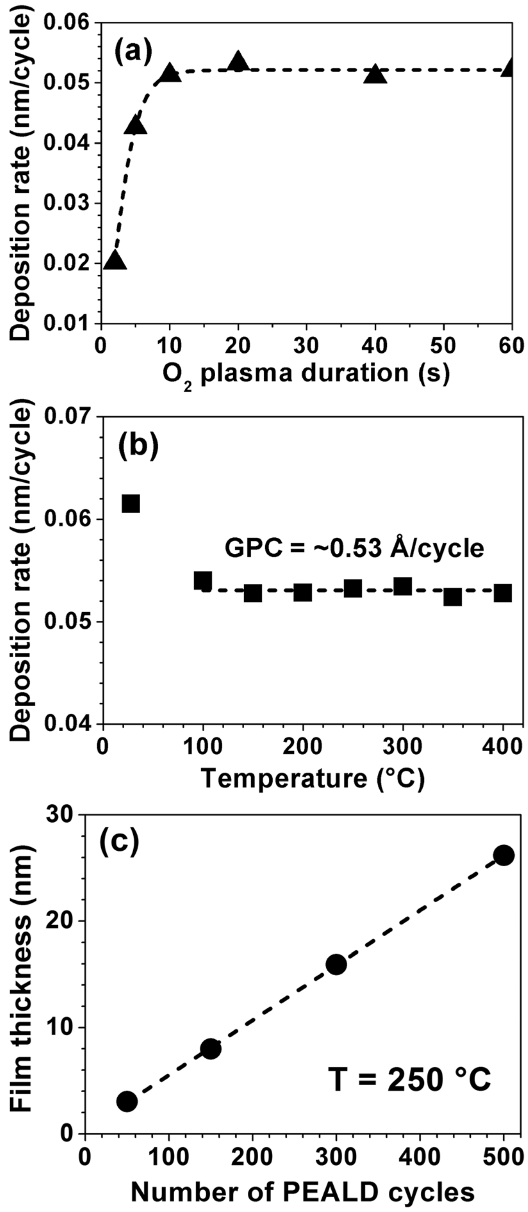

FIG. 1. Growth rate of Ga_2O_3 thin films as a function of (a) O_2 plasma flow duration at 250 °C, and (b) deposition temperature. TMG dose and O_2 plasma flow rate were constant at 0.015 s and 25 sccm, respectively. (c) Ga_2O_3 film thickness as a function of the number of PEALD cycles.

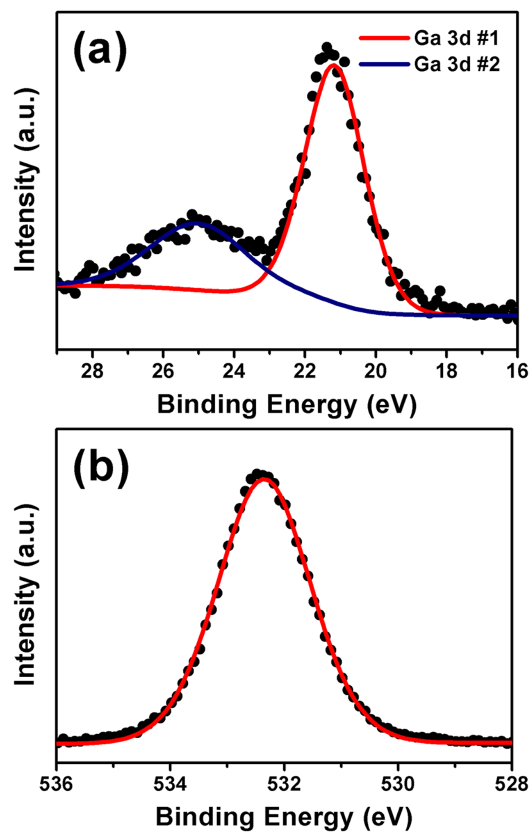

FIG. 2. (Color online) (a) Ga 3d and (b) O 1s high resolution XPS scans of ~26 nm thick Ga_2O_3 thin film deposited at 250 °C.

60 s etching. Ga 3d high resolution XPS spectrum taken from the surface of ~26 nm thick Ga_2O_3 sample was fitted by using two subpeaks as shown in Fig. 2(a). Subpeak #1, with a binding energy of 21.2 eV, confirmed the presence of Ga–O bond in the samples. Subpeak #2 (~25 eV), on the other hand, was related to the contribution from O 2s core level.[22] The effect of this contribution on XPS survey scan results is also noteworthy, which leads to an overestimation of the Ga atomic concentration in deposited films. Figure 2(b) is the O 1s high resolution XPS spectrum taken from the sample surface. Binding energy position of the O 1s (532.3 eV) core level was well consistent with the literature.[23]

Figure 3 shows the GIXRD patterns of as-deposited and annealed Ga_2O_3 films. Although these patterns belong to a film deposited at 250 °C, PEALD-grown Ga_2O_3 thin films were found to be amorphous in the as-deposited state irrespective of their deposition temperature. Upon annealing at 900 °C for 30 min under N_2 atmosphere, polycrystalline β-Ga_2O_3 films with a monoclinic crystal structure were obtained (ICDD reference code: 00-011-0370). Among all the five different allotropic modifications of Ga_2O_3, β-Ga_2O_3 is known to be the most stable and frequent one reported for thin films.[24] In order to determine the annealing temperature at which crystallization starts, as-deposited samples were also annealed at 500, 600, 700, and 800 °C for 30 min under N_2 atmosphere. GIXRD patterns of these samples indicated that crystallization starts at 600 °C. Crystallinity of the β-Ga_2O_3 films increased with annealing temperature.

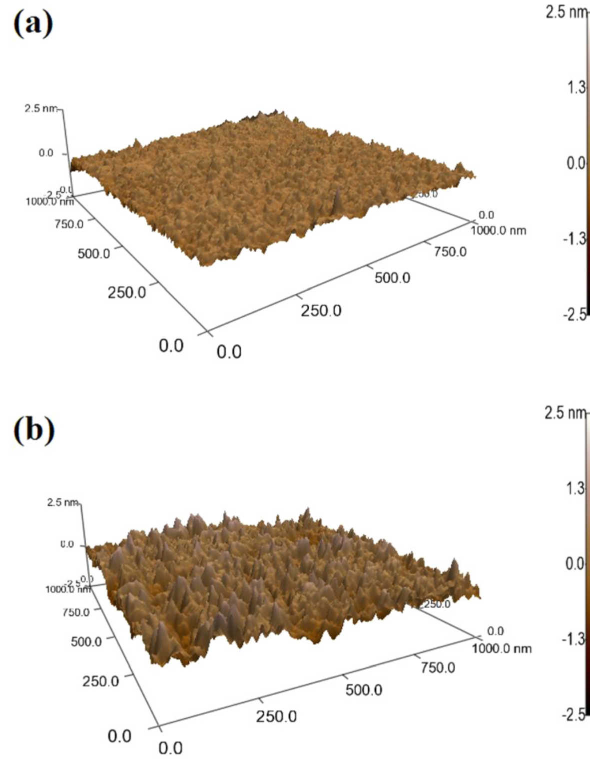

FIG. 4. (Color online) 3D surface morphologies of (a) as-deposited (250 °C) and (b) annealed ~26 nm thick Ga_2O_3 thin films.

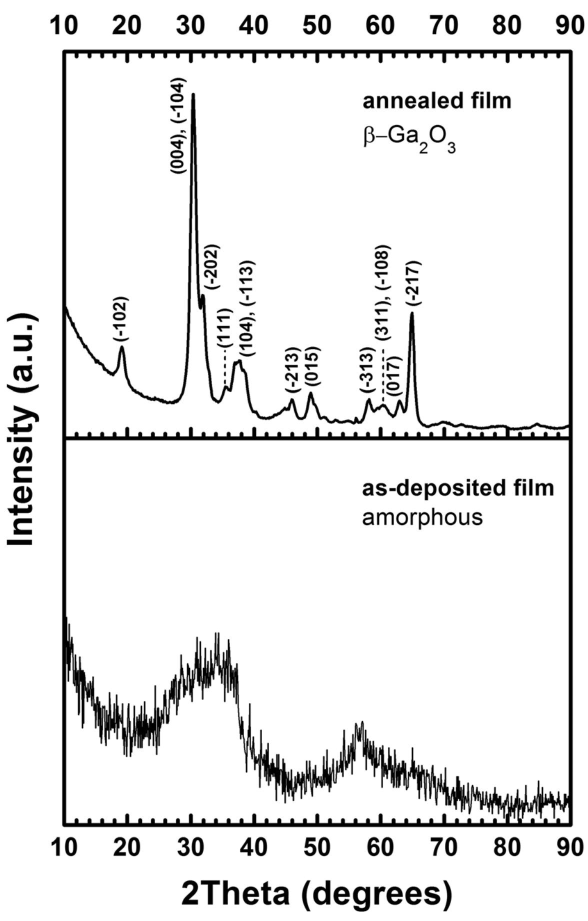

FIG. 3. GIXRD patterns of as-deposited and annealed ~26 nm thick Ga_2O_3 thin films. Film deposited at 250 °C was amorphous in the as-deposited state. GIXRD pattern of the annealed film reveals a polycrystalline structure and corresponds to the β-Ga_2O_3 phase.

AFM analyses were performed for revealing the surface morphologies and measuring the rms roughnesses of ~26 nm thick Ga_2O_3 thin films deposited on Si (111) substrates. Figures 4(a) and 4(b) show 3D AFM topographies of the as-deposited and annealed samples, respectively. rms roughness value, which was measured from a 1 μm × 1 μm scan area, increased from 0.16 to 0.37 nm after annealing at 900 °C for 30 min. Increase in the rms roughness value after annealing was attributed to the formation of grains upon crystallization.

Thicknesses and optical constants of Ga_2O_3 thin films were estimated by modeling the spectra measured by spectroscopic ellipsometry within the wavelength range of 300–1000 nm. Ellipsometric spectra of the as-deposited and annealed Ga_2O_3 thin films (500 PEALD cycles) were modeled by the Cauchy dispersion function using Si (0.5 mm)/SiO_2 (1.83 nm)/Ga_2O_3 layer structure. The thickness of the as-deposited film was measured as 26.2 nm, which did not change remarkably after postgrowth annealing. Refractive index values, on the other hand, increased from 2.05–1.86 to 2.09–1.92 for 300–1000 nm spectral range (Fig. 5). These results again indicate structural enhancement upon annealing at 900 °C.

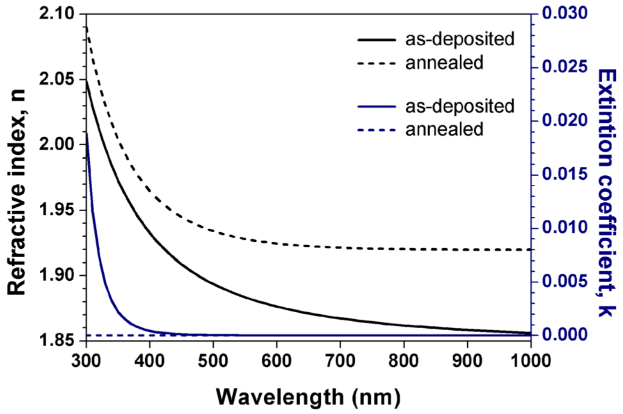

FIG. 5. (Color online) Optical constants of as-deposited (250 °C) and annealed ~26 nm thick Ga_2O_3 thin films.

IV. SUMMARY AND CONCLUSIONS

Ga_2O_3 thin films were deposited via PEALD at temperatures starting from room temperature using TMG and O_2 plasma. A wide ALD window ranging from 100 to 400 °C was observed with a constant deposition rate of ~0.53 Å/cycle. XPS studies confirmed the presence of Ga_2O_3, and C detected in the survey scans was attributed to surface contamination. Although as-deposited films were amorphous, annealing at 900 °C for 30 min under N_2 atmosphere resulted in crystallization. Upon postgrowth annealing, polycrystalline β-Ga_2O_3 thin films with monoclinic structure were obtained, which also exhibited higher refractive indices and rms roughnesses when compared to their as-deposited counterparts.

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