Structural and Optical Properties of Ultra-high Pure Hot Water Processed Ga_2O_3 Thin Film

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Thin film based gas sensor is an advanced application of thin film especially Ga_2O_3 (GO) thin film gas sensor is useful for high temperature gas sensor. The effect of moisture or environment on thin film properties has more influence on gas sensing properties. Radio Frequency sputtered Ga_2O_3 thin film was synthesized and processed in ultra-high pure hot water at 95 °C for different time durations. The structural properties were verified by the Xray Diffraction technique and the observed spectra revealed the formation of hydroxyl compound of Gallium (Gallium Oxide Dueterate – GOD) on the surface of the thin film and evidenced for structural defects as an effect of moisture. Decreased crystallite size and increased dislocation density was showed the crystal defects of prepared film. From the Ultra Violet – Visible spectra, decreased optical transmittance was noticed for various processing time. The formation of needle like GOD was confirmed using Field Emission Secondary Electron Microscope (FESEM) images.

Keywords: Ga_2O_3 thin film, structural properties, surface defects, optical properties, hot water process.

1. INTRODUCTION

In recent years resistive gas sensors based on metal-oxide semiconductors have been investigated intensively, for sensing oxygen or harmful gases in a wide range of temperatures from room temperature up to 1000 °C [1]. Because of toxic and short resources life of ITO, ZnO and SnO_2 or the other materials are considered for the alternative materials to ITO [2]. Below 700°C gallium oxide exhibits sensitivity to reducing gases (CO, H_2, CH_x) on the basis of reactions at the surface of the material [3]. Ga_2O_3 thin film has been studied as a promising dielectric material for various device applications due to its somewhat high dielectric constant (10 – 14) and large band gap (~ 5eV). Ga_2O_3 thin films have been used in luminescent phosphors, high temperature sensors, deep-UV transparent oxides and dielectric coatings for solar cells [4 – 6].

Ga_2O_3 material has high potential to be a new generation of optoelectronic devices applied as transparent conductive oxide [7]. The conductivity of Ga_2O_3 material depends on the atmospheric condition so that it is suitable for gas sensor application [8]. It is also possible that there is predominant effect of surrounding environment on the device due to chemical reactions. After coating of Ga_2O_3 thin film, no report has been published about the further oxidation behavior in moisture based environment. Hot water oxidation has already used to oxidize solid uranium metal [9]. The hot water process will also affect the physical properties of the thin film material as a result of hydrothermal treatment. Qiu et al. [10] have discovered and reported on the synthesis of crystalline ZnO film by direct reaction of ultra-high pure water and metallic Zn film. Our group has also studied the influence of ultra-high pure hot water on the properties of various oxide thin films [11 – 13]. For gas sensing application, the surface of thin film is very important and should be analyzed.

Normally, Ga_2O_3 thin film prepared by sputtering using different targets showed more oxygen deficiency [14]. An amorphous Ga_2O_3 thin film may be utilized as a good gas sensor with oxygen deficiency [15]. Annealing or processing environment was influenced the surface structure of β-Ga_2O_3 nanostructure. Jangir et. al., reported the photoluminescence of β-Ga_2O_3 nano structure in moist environment especially at 800 °C using N_2 gas as carrier gas [16]. There are no reports on the influence of hot moister on Ga_2O_3 thin films.

In order to understand more, it is necessary to study the influence of hot moisture condition or hot water for various process times on the properties of Ga_2O_3 thin film surface at moderate temperature. In this study, the prepared Ga_2O_3 thin film is processed in ultra-high pure hot water for different time durations and reported their structural and optical properties.

2. EXPERIMENTAL DETAILS

2.1. Ga_2O_3 thin film synthesis

Ga_2O_3 thin film were deposited using pure Ga_2O_3 (99.99 % purity) target (3 inch in diameter and 4 mm in thickness) on commercial glass substrates by RF sputtering (Edwards make, Model-Auto 500) at room temperature. The chamber was initially evacuated to high vacuum of 7.2×10^{-6} mbar and fixed as base pressure. High pure Ar (99.999 %) was used as sputtering gas. The substrates were cleaned ultrasonically by rinsing in acetone bath and isopropyl alcohol. The cleaned substrates were loaded into the chamber and evacuated the chamber to reach the vacuum of 8.5×10^{-6} mbar. In order to remove the surface oxidation of the target, pre-sputtering was carried out for 5 min before starting deposition at Ar pressure of 3.2×10^{-3}. Substrate to target distance of 7 cm was kept constant for all depositions. All coatings were made in 200 W RF

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power at chamber pressure of 8.2 x 10^{-3} mbar. The coating was continued up to 2 h and the thickness of samples was measured by optical method as 125 nm. To get the uniform thickness, rotary drive system was used and 25 RPM was fixed.

2.2. Ultrahigh pure water treatment and characterization

Ultra-high pure hot water (resistivity more than 18.2 MΩ cm) treatment of Ga_2O_3 thin film was performed at 95 °C, in a magnetic stirrer. The hot water treatment was performed at four different times (1 h, 2 h, 3 h and 4 h). The crystalline nature of the Ga_2O_3 thin films was investigated by using a high resolution X-ray diffraction (HRXRD, X'pert-PRO, Philips, Netherlands) technique. A Cu Kα (k = 1.54056 Å) source was used, and the scanning range was between 2θ = 20° and 80°. The transmittance of processed samples was measured in the visible range using Shimadzu UV-1800 UV/Vis/NIR scanning spectrophotometer (Shimadzu). The transmittance was automatically calibrated against that of a bare glass substrate as a reference sample, and the refractive index and extinction coefficient were obtained from the transmittance curve. PL and Raman spectra of the samples were also measured at room temperature by Jobin Yvon HR 800 UV using 325 nm lines of a He-Cd laser and Ar laser as the excitation source respectively. The surface morphology of the processed Ga_2O_3 thin film was also tested using Field Emission Scanning Electron Microscope (FESEM) (Nova NanoSEM 450). New paragraph must be indented in the first line by 0.6 cm.

3. RESULTS AND DISCUSSION

3.1. Structural properties

The crystalline qualities of the Ga_2O_3 thin films for different processing time were evaluated using XRD spectra and the observed results are given in Fig. 1. It includes the XRD spectrum of as grown Ga_2O_3 thin film by RF sputtering. All the XRD peaks have been indexed thereby confirming the formation of β-Ga_2O_3 monoclinic structure (JCPDS Card No. 760573) along with gallium oxide deuterate (JCPDS Card No. 700537). In ultra-high pure hot water treatment, there may be a contact between the thin film surface and water molecule. In general, water vapor or water molecules react with the metal oxides in two ways. At low temperatures, water is adsorbed (ads) in its molecular form according to the following equation:

$$H_2O_{gas} \rightarrow H_2O_{ads} \rightarrow H_2O^{\bullet}_{ads} + e^{-}. \quad (1)$$

At high temperatures (780 °C and above), the adsorption of OH group dominates according to the following equation [17]:

$$H_2O_{ads} + O_0^{x} \rightarrow 2OH; \quad (2\,a)$$
$$OH + e^{-} \rightarrow OH^{-}. \quad (2\,b)$$

The dominating mechanism is adsorption of the OH groups according to Eq. 2 a, b. In our hot water process, the OH groups are adsorbing on the surface of Ga_2O_3 thin film and forming the gallium oxide deuterate as trace basis which is already confirmed by observing a strong peak nearly at ~ 2θ = 21° in XRD spectra (see Fig. 1).

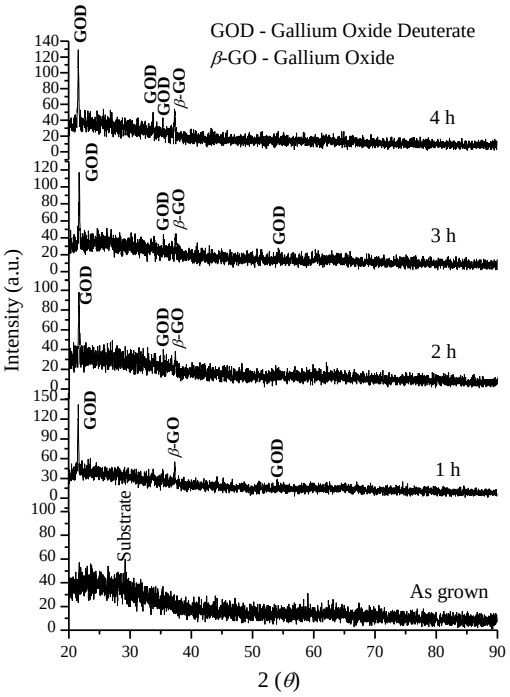


Fig. 1. XRD spectra of as grown and hot water processed Ga_2O_3 thin film for various process times

The XRD spectra show that the as-grown sample shows amorphous nature [5, 10] and improved crystallinity after processing in ultra-high pure hot water at 95 °C. Fig. 1 also shows that the (401) oriented β- Ga_2O_3 phase could be observed for all hot water processed samples along with a predominant peak at 2θ ~ 21.55 which is related to (110) oriented gallium oxide deuterate (GOD). Because of the reaction of OH group at the surface of the thin film, it is expected to form GaO_x group which creates surface states as defects [16]. This is the indication of surface defects as a result of hot water process. From Fig. 1, the amorphous nature of the sample could be revealed for all samples and this amorphous nature could bring desired insulating property for the thin films [18].

The observed structural parameters are summarized in Table 1. From the Table 1, the observed intensity is low for the samples processed at 2 h duration and increases gradually with processing time increases. From the XRD spectra, the crystallite size of (401) oriented peak of β-Ga_2O_3 thin film is calculated using Debey-Scherrer formula [19]:

$$D = 0.94\lambda / \beta \cos\theta, \quad (3)$$

where λ is wavelength (in Angstrom), β is the broadening of diffraction peak (in radians), θ is the Bragg diffraction angle and plotted against processing time in Fig. 2. It shows that the crystallite size decreases as processing time increases.

The dislocation density is mainly based on the crystallite size and hence it differs as a result of change in crystallite size. Dislocation density is one among the structural defects parameters and defined as the length of dislocation lines per unit volume of crystal, was evaluated from the following relation [20]:

$$\delta = 1 / D^2 \quad (4)$$

and the data are plotted as shown in Fig. 2 (inset).

Table 1. Structural properties of hot water processed Ga_2O_3 thin film

Obs., 2-Theta °	Std., 2-Theta °	*d* (Obs.), Å	*d* (Std.), Å	FWHM, 2-Theta °	hkl	JCPDS card No.	Compound
1 h							
21.561	21.66	4.11822	4.099	0.114	110	700537	GOD
37.329	37.38	2.40697	2.403	0.082	401	760573	GO
54.183	54.36	1.69144	1.686	0.100	221	700537	GOD
2 h							
21.604	21.66	4.11005	4.099	0.111	110	700537	GOD
35.375	35.37	2.53533	2.536	0.088	021	700537	GOD
37.346	37.38	2.40594	2.403	0.079	401	760573	GO
3 h							
21.674	21.66	4.09696	4.099	0.126	110	700537	GOD
35.428	35.37	2.5317	2.536	0.023	021	700537	GOD
37.488	37.38	2.39715	2.403	0.094	401	760573	GO
54.21	54.36	1.69065	1.686	0.113	221	700537	GOD
4 h							
21.578	21.66	4.115	4.099	0.153	110	700537	GOD
33.784	33.88	2.65098	2.643	0.066	130	700537	GOD
35.428	35.37	2.5317	2.536	0.023	021	700537	GOD
37.301	37.38	2.40871	2.403	0.162	401	760573	GO

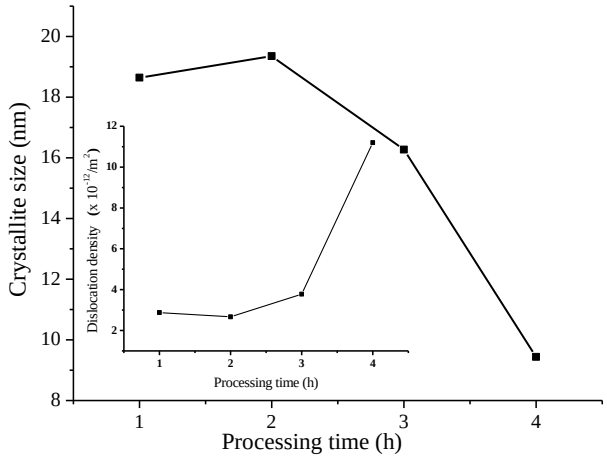


Fig. 2. Variation in crystallite size and dislocation density of hot water processed Ga_2O_3 thin film for various time durations

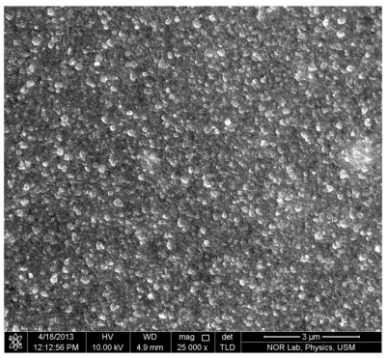
According to the equation, the crystallite size of the film decides the dislocation density and increases with processing time increases.

3.2. FESEM analysis

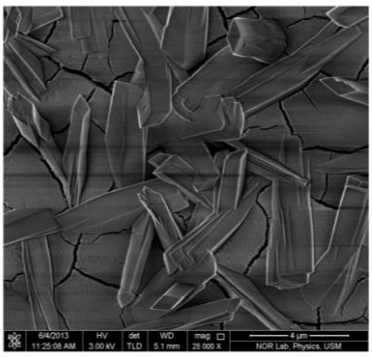
In order to confirm, the surface image of hot water processed Ga_2O_3 thin film treated at 4 hours duration was captured using FESEM as shown in Fig. 3 a – b. Since the images of all other samples processed at different time duration has similar structure as shown in Fig. 3 b, the image of samples processed at 4 h duration is presented and taken for consideration for discussion. Fig. 3 a shows the surface image of as grown Ga_2O_3 thin film and shows that the uniform surface with uniform size of the particles (Fig. 3 a). It clearly indicates that the needle like Gallium Oxide Dueterate is spread over on the surface of Ga_2O_3 thin film after processing (Fig. 3 b). Fig. 3 clearly distinguishes the processed and unprocessed Ga_2O_3 thin film and the cracks were also observed on the surface of thin film in the processed thin film.

3.3. Optical studies

The UV spectra of as-grown and ultra-high pure hot water processed thin film samples are given in Fig. 4.



a



b

Fig. 3. FESEM images of: a – as grown; b – hot water processed Ga_2O_3 thin film at 4 h duration in ultra-high pure media

It shows that the as grown samples show higher transmittance value than processed samples. Moreover, the oscillating behavior of transmittance spectra reveals the uniform thickness of the film.

Fig. 4 also depicts that the high transmittance value could be observed for all processed samples in the UV region than visible and IR region. Among the processed samples, the Ga_2O_3 sample processed at 2 h duration shows higher transmittance than other samples. Low value in transmittance could also be observed for the samples processed at 3 h duration and the oscillating behavior of

the curve for these samples is also reduced.

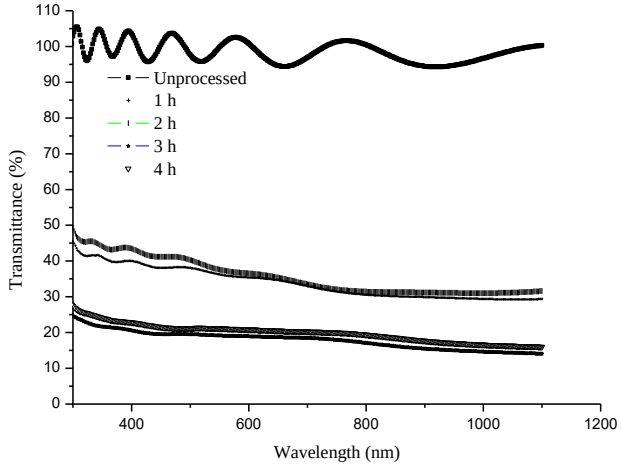


Fig. 4. Transmittance spectra of as grown and hot water processed Ga_2O_3 thin film at various processing times in ultra-high pure media

4. CONCLUSIONS

RF sputtered Ga_2O_3 thin film was synthesized on glass substrates and post processed with ultra-high pure hot water for various process times. XRD spectra revealed the formation of highly intensive peak of Ga_2O_3 phase and Gallium Oxide Deuterate phase and exhibited the effect of hot water process. Decreased crystallite size was noticed with 4 h hot water processed samples. The optical properties also evidenced the formation of defects as reduced transmittance for the effect of ultra-high pure hot water treatment. Overall, it is suggested that the formation of hydroxyl group on the surface of Ga_2O_3 thin film sensor is possible when it operates at high temperature in presence of moisture environment.

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