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Effect of Substrate Temperature on Structural, Morphological, and Optical Properties of Gallium Oxide Thin Films Deposited by RF-Sputtering

Fevkani YILDIZ[1], Hulya AKCAY[1], Aykut ASTAM[2], Mutlu KUNDAKCI[1,*]

[1]*Atatürk University, Faculty of Science, 25000 Erzurum, Türkiye*
[2]*Erzincan Binali Yıldırım University, Faculty of Science and Literature, 24000, Erzincan, Türkiye*

Highlights

- This paper focuses on deposited Ga_2O_3 thin films at various temperatures by RFMS.
- Effect of Ts on the structural, morphological and optical properties of films was studied.
- The crystallinity properties of synthesized thin films strongly depend on the Ts.
- Bandgap energy of the gallium oxide films decreased with increasing Ts.

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Abstract

In this paper, gallium oxide (Ga_2O_3) thin films at various substrate temperatures (Ts) were grown on Indium Tin Oxide (ITO), glass, p-type silicon by radio-frequency magnetron sputtering (RFMS). We investigated how structural, morphological and optical properties change with various Ts. XRD results of thin films grown on p-type silicon substrate suggest that crystallinity properties of synthesized thin films strongly depend on the Ts. From SEM and AFM analyses of Ga_2O_3 thin films grown on p-type silicon substrate, it was observed that when the temperature increased, a porous structure appeared, and the grain size changed depending on the Ts. Moreover, obtained results from the absorption measurements, the bandgap energy of Ga_2O_3 thin films grown on the p-type silicon substrate decreased with increasing substrate temperature.

1. INTRODUCTION

Gallium oxide (Ga_2O_3) has garnered great attention from researchers due to its superior material properties. Ga_2O_3 is an ultra-wide-bandgap semiconductor material (4.7 – 5.3 eV), and its electrical conductivity varies from insulator to conductor, depending on the growth conditions [1, 2]. Furthermore, it exhibits high transparency from ultraviolet (UV) to the visible range [3, 4]. Such materials are suitable for applications in ultraviolet optoelectronics [5], high-power electronics [6], solar-cell energy conversion [7], and high-temperature gas sensors [8, 9].

Ga_2O_3 exhibits semiconductor characteristics. At temperatures higher than 773 K, its n-type conductivity may be attributed to surplus or lack in the crystalline structure [10]. It is a metal oxide material with five phases: (β-, α-, γ-, ε-, and δ-). Among these five phases, β- with a monoclinic structure is the most determined and extensively studied phase [11]. β- is a direct bandgap semiconductor material with a bandwidth of nearly 5.0 eV [2]. Due to these properties, studies on Ga_2O_3 have predominantly focused on the β phase. Because of its wide band gap, β- exhibits photoconductivity against deep UV light, making it useful as a luminescent material in various applications such as flat panel displays and UV detectors [12, 13].

Thin films of gallium oxide have been grown using various thin-film growth techniques, including MOCVD (Metal Organic Chemical Vapor Deposition) [14], plasma-assisted MBE (Molecular Beam Epitaxy) [15], the sol-gel process [16], and RF (Radio Frequency) magnetron sputtering [17].

*Corresponding author, e-mail: kundakci@atauni.edu.tr

In this article, we grew thin films using the radio-frequency magnetron sputtering (RFMS) technique at substrate temperatures of 150 °C, 300 °C, and 450 °C at an 8 mTorr deposition pressure. An elaborate analysis of optical, morphological, and structural properties was conducted to specify the effects of the substrate temperature at an 8 mTorr deposition pressure.

2. MATERIAL METHOD

Ga_2O_3 thin films were grew onto ITO (Indium Tin Oxide), p-type silicon and glass wafers by RFMS. During the growth, 99.99% pure gallium oxide ceramic used as target material. Wafers were cleaned thoroughly using the RCA procedure. The RCA cleaning procedure is a method used to remove alkali, organic ions, and heavy metal pollutants present on the surface of the wafers.

All films deposited at base pressure of 8×10^{-3} Torr and different substrate in the temperature range of 150-450 °C. Deposition of samples were carried by holding RF power constant at 50 W. Details of deposition parameters are shown in Table 1. From a distance of 7 cm from the substrate, the target was placed on a sputter gun. The deposition was carried out for 120 minutes, at 8 mTorr. The rate of argon flow is kept constant at 35 sccm during the deposition. The thickness of deposited thin films were measured by surface profile metrology P7 (KLA-tensor). Moreover, we measured thicknesses of thin films by using RF magnetron sputter sensor. We compared these values and calibrated the RF magnetron sputter sensor value achieved using profile meter. Thus, we achieved thin films with a thickness of 50 nm at different temperatures at 8 mTorr growth pressure. We kept the substrate rotation speed constant to ensure a homogeneous coating on the substrate surface. The schematic diagram of device is shown in Figure 1.

Ga_2O_3 thin films were analyzed by performing optical, morphological, and structural measurements. Structural measurements were carried out using a D-2 Phaser Bruker diffractometer with CuKα (λ= 1.5406 Å) as X-ray source. The detector scan changes from 20° to 80°. SEM (Scanning electron microscopy) analysis was performed by using Zeiss Sigma 300 model. We performed the optical characterization of the samples at room temperature using the LAMBDA 1050 Ultra viole/Visible/NIR spectrophotometer. In this study, absorption measurements were taken at wavelengths of 200 to 600 nanometers.

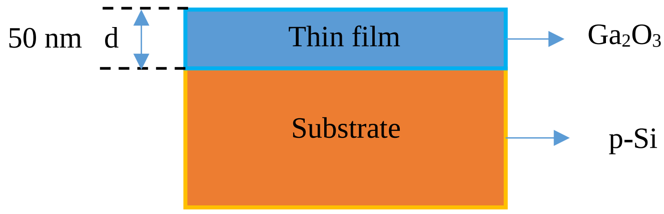


Figure 1. *The schematic diagram of device*

Table 1. *The growth paramters of thin film depositions within different substrate temperature (Ts)*

RF Power (Watt)	T_s (°C)	Ar (sccm)	Growth pressure (Torr)	Growth time (Min)	Film thickness (nm)
50	150 300 450	35	8×10^{-3}	120	50

3. THE RESEARCH FINDINGS AND DISCUSSION

3.1. Structural Analysis

Thin films were grown at different substrate temperatures (Ts) and were analyzed with XRD measurements. No peaks were observed in the XRD plots of thin films grown on ITO substrate under 8 mTorr pressure. XRD patterns of thin films deposited on the ITO substrate (not shown) exhibited their own characteristic peaks. Thus, the ITO substrate was not used in other depositions. XRD patterns of thin films deposited on the glass substrate (not shown) were found to be amorphous. No peaks were observed in the XRD plots of thin films grown on the glass substrate under 8 mTorr pressure, as expected. It seems that changing the substrate temperature has no effect on the crystallinity properties of films grown on the glass and ITO substrates under these conditions. The process of forming gallium oxide film can be challenging to control. The quality, structure, and properties of the film can vary significantly depending on the conditions in which it is formed, including temperature, pressure, and gas environment [18]. It is possible that the insufficient interfacial reaction at the substrate-film interface is the reason why gallium oxide thin film cannot be deposited on the surfaces of ITO and glass substrates under these conditions [19]. X-ray diffraction patterns of deposited films grown on p-type silicon at 8 mTorr pressure are shown in Figure 2. The results of X-ray diffraction prove the formation of the crystal phase on the p-type silicon surface in samples whose substrate temperature is changed. The locations of all diffraction peaks are in suitable agreement with the literature (JCPDS Card No. 96-200-4988).

X-ray diffraction patterns of films grown on p-type Si were observed at 30° and 64° at 8 mTorr pressure. These peaks shifted about 0.1 degree compared to the literature. This shift may be due to contamination and impurities during growth.

We observe that, while the peak intensities change with increasing Ts from XRD analysis, the locations of diffraction peaks do not change for all deposited films. Therefore, we can say that the degree of crystallinity of the grown films is highly dependent on the Ts.

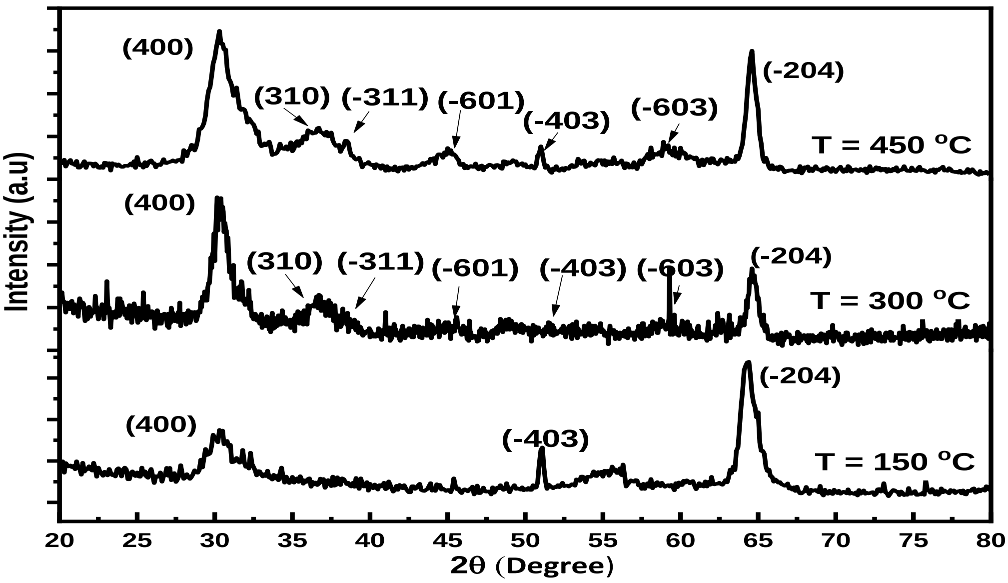


Figure 2. *The X-Ray diffraction patterns of the deposited films at various substrate temperatures*

The grain sizes deposited on p-type silicon was calculated from the XRD data by Scherrer's equation [20]. Calculated average values are shown in Table 2

$$D = \frac{k\lambda}{\beta \text{Cos}\theta} \qquad (1)$$

In this equation, D is the grain size, β is the FWHM (half-height full width) of the peak, λ is the X-ray wavelength, k = 0.9 is a constant and θ is the Bragg's diffraction angle.

Table 2. *Some structural parameters of Ga_2O_3 films deposited on p-type silicon substrate under different substrate temperatures*

Growth Pressure (mTorr)	Substrate Temperatures (˚C)	Miller indices (hkl)	Observed 2θ (Degree)	Grain Size (D) (nm)	Literature (D) (nm)

8	150	(400)	29.90	19.88	15 to 23 nm (from 500 to 900 ˚C)[21]
		(-204)	64.28		
	300	(400)	30.27	27.45	14 to 35 nm (from 300 to 600 ˚C)[22]
		(-204)	64.53		
	450	(400)	30.84	33.99	10 to 40 nm (from 500 to 800 ˚C)[19]
		(-204)	64.60		

3.2. Surface Morphology

In this study, Ga_2O_3 films were coated with 5 nm thick gold in a vacuum environment. Thus, excessive accumulation of electrons in the material is prevented and the excess electrons are discarded. In this way, better SEM image was obtained due to the conductivity of Au.

The SEM images of gallium oxide thin films grown on p-Si substrate at 8 mTorr pressure at 150 ˚C, 300 ˚C, 450 ˚C are shown in Figure 3.

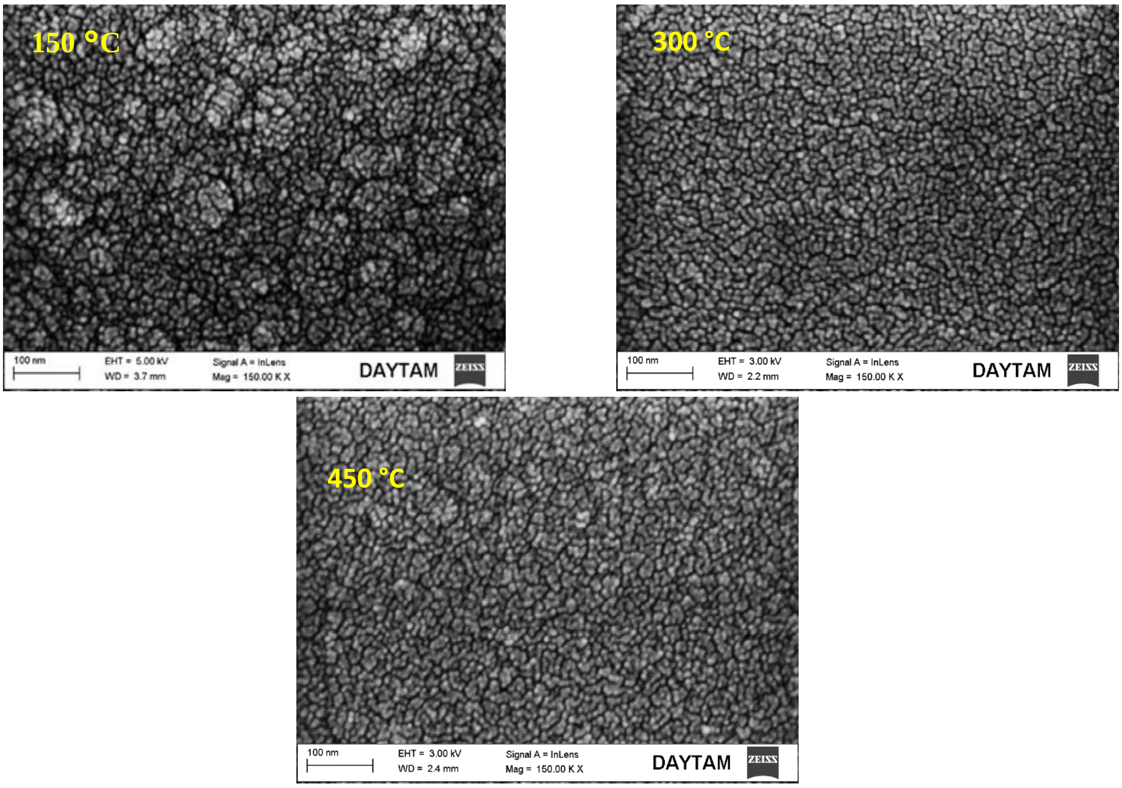


Figure 3. *Top views of Ga_2O_3 thin films prepared at 150 ˚C, 300 ˚C, 450 ˚C substrate temperatures*

In Figure 3, SEM results show the effects of Ts on the thin films grown on silicon at 8 mTorr pressure. The SEM images of the deposited thin films with different Ts display the crystalline deposition structures by increasing the Ts. According to the SEM images, the growth in the form of agglomeration in the thin film structure at 150 °C temperature seems more pronounced. A well-defined microstructure and homogeneous dispersion of intensive particles can be seen in films deposited at 300 °C and 450 °C. The dense morphology seen at 300 °C temperature is more or less similar when the Ts is increased to 450 °C. It is observed that the granular structures are distinct and homogeneous in all films. As temperature increases, atoms on the film surface become more mobile. When films are grown at 450 °C, small and dense particles with a spherical shape can be observed in SEM images. Both SEM images and XRD data reveal that films grown at 450 °C have better crystalline quality and a larger grain size. The SEM analyses indicate that the grain size of the material increases with increasing Ts.

We conducted an AFM measurement on films to study how substrate temperature affects its surface roughness. The films were deposited at temperatures ranging from 150 to 450 °C, and the results are shown in Figure 4. The RMS (Root mean square) surface roughness of the films deposited at 150, 300, and 450 °C was 0.83, 1.84, and 3.10 nm, respectively. This indicates that the surface roughness increases as the growth temperature increases. This observation is consistent with the SEM results that also showed an increase in the grain size of the films as the substrate temperature increased. It is believed that high substrate temperature can cause the overgrowth of grains, resulting in a rough surface.

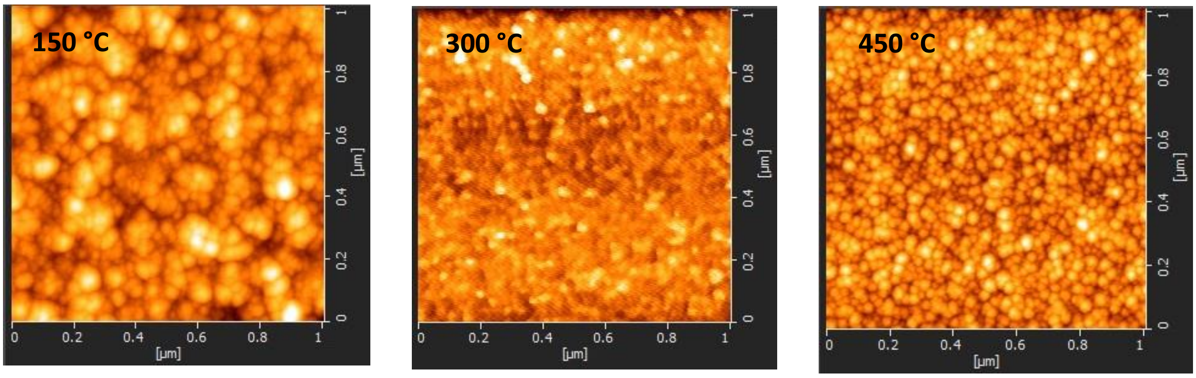


Figure 4. *AFM views of Ga_2O_3 thin films prepared at 150 ˚C, 300 ˚C, 450 ˚C substrate temperatures*

3.3. Optical Properties

The design of many important optoelectronic and photonic devices is based on controlling the value of the bandgap. The bandgap energy (E_g) is defined as the difference between the energy of the valence band's maximum point and the conduction band's minimum point. Direct optical band values were calculated by using the Tauc relationship as given below [23, 24]

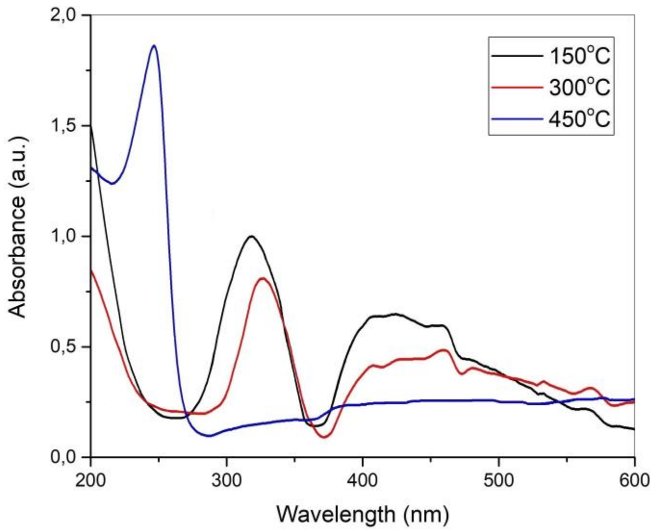
$$(\alpha h\nu)^2 = c(h\nu - E_g). \quad (2)$$

Where $h\nu$ is energy of the incident photon, c is a constant, α is the absorption coefficient and E_g is the direct optical bandgap energy of the material used. The absorption coefficient α, of the films is calculated the relation (3) [25, 26]

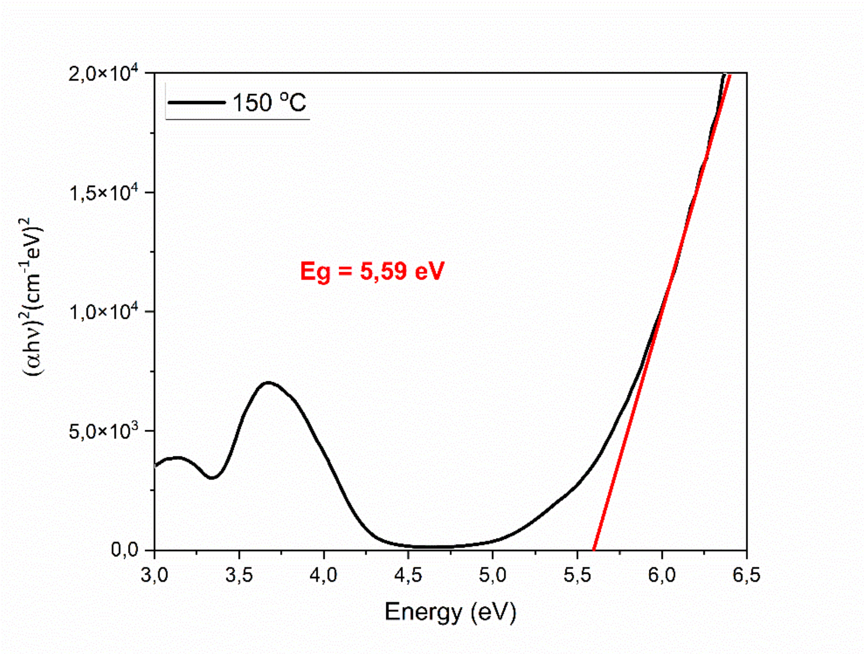
$$\alpha = \left(\frac{1}{t}\right) \ln\left[\frac{T}{(1-R)^2}\right] \quad (3)$$

where R is the reflectance, T is the transmittance, and t is the thickness of the film. The plots obtained and the absorption data for Ga_2O_3 thin films deposited on p-type silicon substrate at 8 mTorr pressure are demonstrated in Figure 5. Linear plots are obtained in the high absorption region when plotting $(\alpha h\nu)^2$ vs $h\nu$. These linear plots suggesting direct allowed transitions across E_g of Ga_2O_3 films.

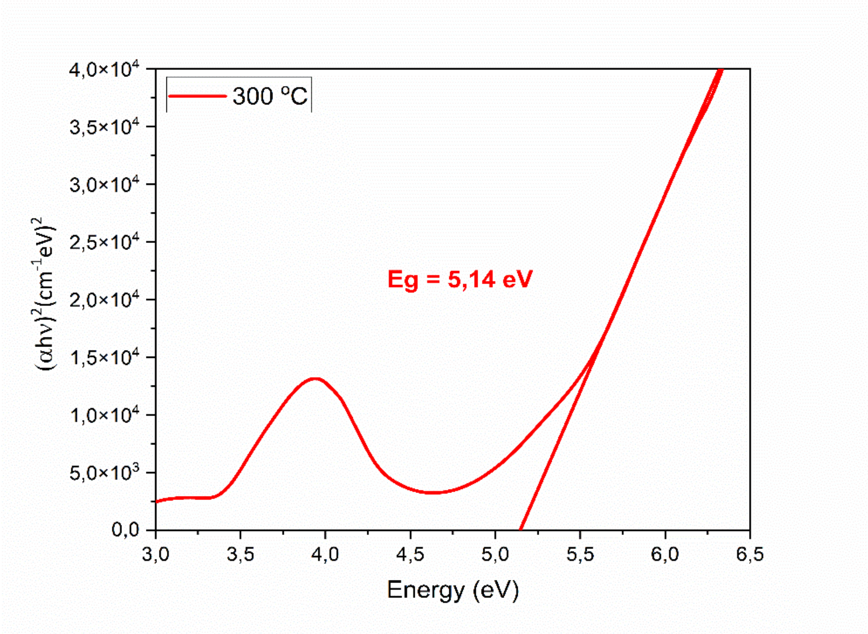
By using equation [3], optical E_g values of Ga_2O_3 thin films deposited on p-type silicon substrate at 8 millitorr pressure at $150\ °C$, $300\ °C$ and $450\ °C$ temperatures are calculated and given below.


2,0
1,5
1,0
0,5
0,0
Absorbance (a.u.)
200
300
400
500
600
Wavelength (nm)
150°C
300°C
450°C

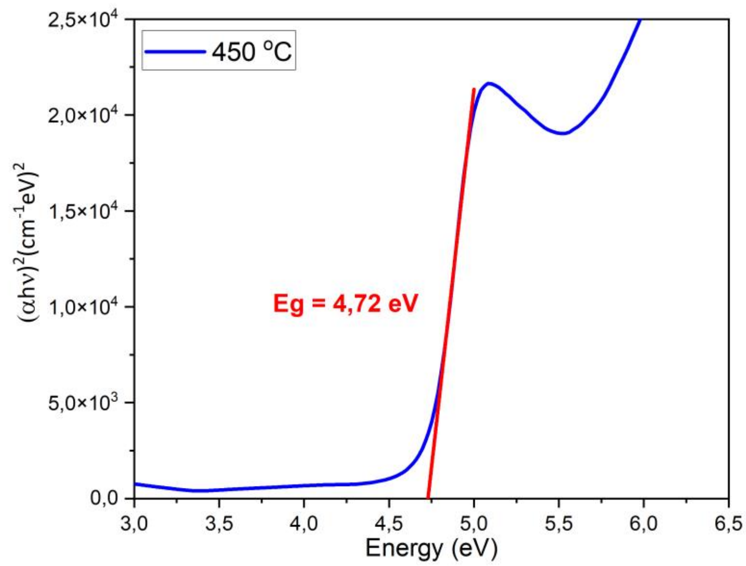
(a)


2,0×10^4
1,5×10^4
1,0×10^4
5,0×10^3
0,0
(αhν)^2(cm^-1eV)^2
3,0
3,5
4,0
4,5
5,0
5,5
6,0
6,5
Energy (eV)
150 °C
Eg = 5,59 eV

(b)



(c)



(d)

Figure 5. *Absorption spectrum and* $(\alpha h\nu)^2$ *vs hν plots for Graphene Oxide thin films deposited on p-Si substrate at 8 mTorr pressure and (b)* $150\ °C$*, (c)* $300\ °C$*, (d)* $450\ °C$ *temperatures*

The optical properties of Ga_2O_3 films deposited on p-type silicon were measured within a wavelength range of 200-600 nm. The bandgap of Ga_2O_3films was specified to be $5.59\ eV$, $5.14\ eV$ and $4.72\ eV$ at Ts of 150 °C, 300 °C and 450 °C, respectively. As seen from the Figure 5, the bandgap values decreased with increasing Ts at constant deposition pressure. Consequently, the bandgap value of the sputter grown Ga_2O_3materials can be adjusted by changing the substrate temperature at constant deposition pressure.

Fluctuations were observed in the low energy region of the absorption spectra of $\mathrm{Ga_2O_3}$films grown at $150\ °C$ and $300\ °C$ substrate temperature. The fluctuation is thought to be caused by micro-inclusions of different phases as specify by Zhou et al. [27].

Table 3. *Optical E_g (bandgap energy) values of Ga_2O_3 films grown on p-Si for different temperatures*

Substrate Temperature (˚C)	Optical Bandgap (eV)	Literature (Optical bandgap) (eV)
150˚	5.59	5.17 to 4.66 eV (from 25 to 800 ˚C)[19]
300˚	5.14	5.04 to 4.19 eV (from 500 to 900 ˚C)[21]
450˚	4.72	5.17 to 4.96 eV (from 25 to 600 ˚C)[22]

4. CONCLUSIONS

Ga_2O_3thin films were produced on ITO, p-type Si, and glass by RFMS deposition at substrate temperatures of 150 °C, 300 °C and 450 °C at an 8 mTorr deposition pressure. In this study, the primary reason for using various growth conditions is to examine the effect of growth conditions on the morphological, structural, and optical properties of the thin film. Additionally, the use of different substrate temperatures aims to investigate the effect of the substrate on the crystallinity and some physical properties of the film. The morphological, structural, and optical properties of the films were evaluated.

No peaks were observed in the XRD plots of thin films grown on ITO substrate under 8 mTorr pressure. XRD patterns of films produced on the ITO substrate exhibited their own characteristic peaks. XRD patterns of thin films prepared on the glass substrate were found to be amorphous, regardless of the chosen substrate temperature value at 8 mTorr pressure.

XRD patterns of thin films prepared on p-type silicon substrate were observed at 30˚ and 64˚ at 8 mTorr pressure. These peaks shifted about 0.1 degrees compared to the literature. This shift may be due to contamination and impurities during growth. This result supports the idea that the crystallization of the films can be changed by altering the substrate temperature.

SEM measurements provide important knowledge about the morphological structure of the grown films. When SEM analyses of films deposited on p-type silicon substrate are evaluated, agglomeration growth is more evident at 8 millitorr pressure. Crystal boundaries are clear, and no linear defects are observed. More significant aggregation was observed in gallium oxide thin film structures at lower temperatures. Additionally, according to the Scherrer formula, the grain size is larger at higher temperatures. As the temperature increases, the porous structure appears, and the grain size increases with the rising substrate temperature. This is typical for oxide materials in general [28].

Band gaps of the films have been determined from the absorption measurement. As shown in Table 3, gallium oxide films deposited on p-type silicon substrate have bandgap energies of 5.59 eV, 5.14 eV, and 4.72 eV at of 150 °C, 300 °C and 450 °C at 8 mTorr growth pressure, respectively. The bandgap energy of the gallium oxide films deposited on the p-type silicon substrate decreased with increasing T_s. As a result, we can state that the bandgap energy of the materials depends on the substrate temperature.

CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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