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XPS Depth Profile Study of Sprayed Ga_2O_3 Thin Films

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Abstract

Ga_2O_3 thin films were fabricated by spray pyrolysis method using gallium acetylacetonate as source material and water as oxidizer. The films were annealed at 450˚C for 60 minutes in argon atmosphere. X-ray photoelectron spectroscopy (XPS) depth profile studies were carried out to analyze the stoichiometry and composition of sprayed as-deposited and annealed Ga_2O_3 thin films. Surface layers and the inner layers of as-deposited and annealed films were found nearly stoichiometric.

Keywords

Ga_2O_3, Thin Films, x-Ray Photoelectron Spectroscopy, Depth Profiling

1. Introduction

Gallium oxide (Ga_2O_3) is considered a novel thin film material that can be used as transparent conducting electrode for optoelectronic devices [1] [2], light emitting sources [3] [4], gas sensors [5] [6] [7] [8], thin film transistors [9] and so on.

Gallium oxide thin films have been fabricated by electron-beam evaporation, chemical vapor deposition, high-frequency sputtering and atomic layer epitaxy (ALE) [5] [10] [11] [12]. In general, films prepared by these techniques result with incorporation of carbon impurities and are amorphous. Gallium oxide thin films have been fabricated using $GaCl_3$ and $Ga(NO_3)_3$ as source materials by means of the spray pyrolysis method [13] [14]. Spray pyrolysis is a low-cost non-vacuum technique to fabricate thin films over large areas.

In this work, gallium oxide thin films were fabricated by spray pyrolysis method using gallium acetylacetonate as source material of gallium. The gallium acetylacetonate is neither toxic nor expensive. It is also stable at room temperature. It is essential to have an idea of stoichiometry of surface and bulk of Ga_2O_3

film as it has a profound impact on device performance. In the present work, we investigated stoichiometry of Ga_2O_3 thin films using X-ray photoelectron spectroscopy (XPS) depth profiling.

2. Experimental Details

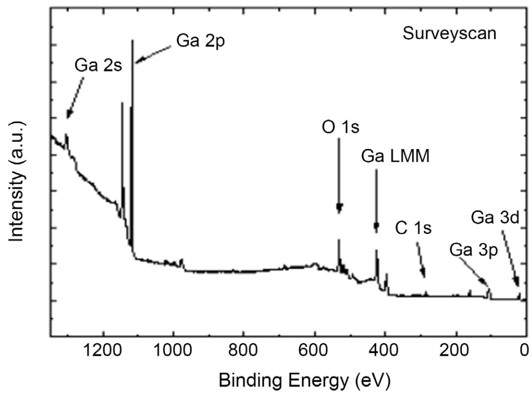
Alconox was used first for washing and scrubbing all the glassware. Afterwards, N_2 gas was used for drying them. An aqueous solution of (Conc) 0.05 M Gallium (III) Acetylacetonate ($C_{15}H_{21}GaO_6$, Sigma-Aldrich, 99.99%) has been used for precursor solution spray deposition. The precursor solution was added in a mixture of 50 ml deionized water and 50 ml methyl alcohol. Glacial acetic acid (5 mL/L) was added to improve the solubility of source material [15]. Substrate temperature was kept within ±5˚C of 350˚C by a hot plate with the help of a thermocouple. After film deposition, the substrates were cooled down slowly to room temperature. Substrates were then annealed at 450˚C for 60 min. in argon atmosphere. The annealing process shows a change in morphology of the Ga_2O_3 thin films. XPS was used to study the composition of the Ga_2O_3 thin films. A Kratos AXIS Ultra DLD XPS system using monochromatic Al Kα radiation (1486.6 eV) was used to obtain the XPS spectra. The pressure was maintained at 5×10^{-10} Torr. The binding energy value of contaminant carbon (C 1s 284.6 eV) was used as a reference. Ion sputtering of the sample was done with Ar^+ at 15 mA and 4000 eV for 10 min.

All the spectra was fitted using XPSPeak software version 4.1. Lorentzian-Gaussian type peaks was used to deconvolute the spectra.

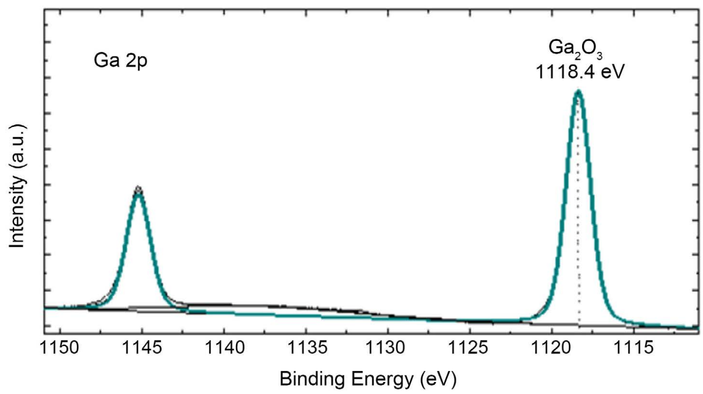
3. Results and Discussion

XPS analysis was used to investigate the composition.and chemical purity of as-deposited Ga_2O_3 thin films. As-deposited XPS survey spectrum of Ga_2O_3 is showed in **Figure 1(a)**. Ga 2s, 2p, 3p, 3d, Ga Auger, O 1s and C 1s peaks are clearly seen in the spectrum. Carbon contamination is present in almost all the preparations. The Auger peak position at 425.7 eV of Ga refers to the Ga $L_3M_{45}M_{45}$ line [10]. The Ga 2p intensity is very large compared to the other Ga peak intensity, and that is why we have reported just Ga 2p spectra of Ga compounds. High resolution spectra of Ga 2p and O 1s core level are shown in the **Figure 1(b)** and **Figure 1(c)** respectively. The position of the Ga $2p_{3/2}$ peak is 1118.4 eV. This binding energy is characteristic of Ga_2O_3 [16]. Suboxides such as GaO and Ga_2O and elemental Ga was not detected in gallium oxide films. The binding energy value 531.3 eV of O 1s is characteristic of Ga_2O_3.

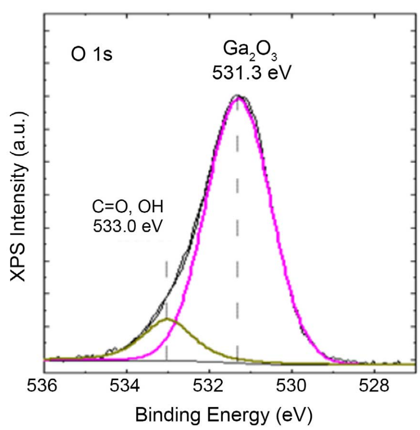
The XPS survey spectrum of as-deposited Ga_2O_3 thin film after 10 min. Ar^+ ion sputtering is showed in **Figure 2(a)**. Ga 2s, 2p, 3p, 3d, Ga Auger, O 1s peaks are clearly seen in the spectrum. Carbon contaminations were reduced to a low level after 10 min. Ar^+ ion sputtering. High resolution spectra of Ga 2p and O 1s core level are shown in the **Figure 2(b)** and **Figure 2(c)** respectively. No chemical shift in Ga 2p and a shift of 0.1 eV in O 1s core level were observed after 10 min. of Ar^+ ion sputtering.



(a)



(b)



(c)

Figure 1. (a). XPS survey spectrum of as-deposited Ga_2O_3 film; (b). High resolution XPS spectra of the Ga 2p core level of as-deposited Ga_2O_3 film; (c). High resolution XPS spectra of the O 1s core level of as-deposited Ga_2O_3 film.

The XPS survey spectrum of annealed Ga_2O_3 thin film is showed in **Figure 3(a)**. Ga 2s, 2p, 3p, 3d, Ga Auger, O 1s and C 1s peaks are clearly seen in the spectrum. The Auger peak position at 425.7 eV of Ga refers to the Ga $L_3M_{45}M_{45}$ line [10]. The Ga 2p intensity is very large compared to the other Ga peak intensity, and that is why we have reported just Ga 2p spectra of Ga compounds. High resolution spectra of Ga 2p and O 1s core level are shown in the **Figure 3(b)** and

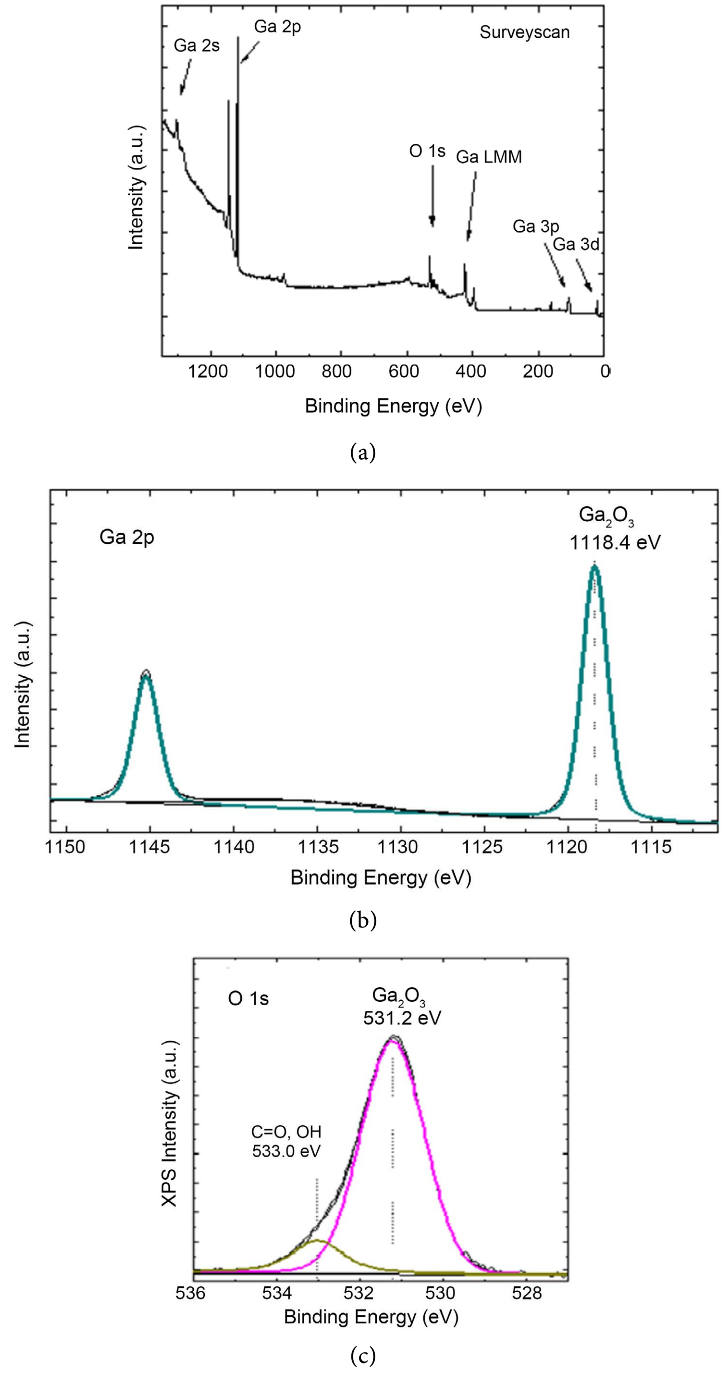
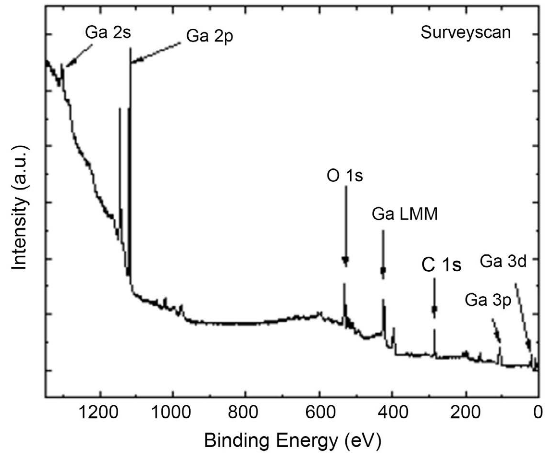
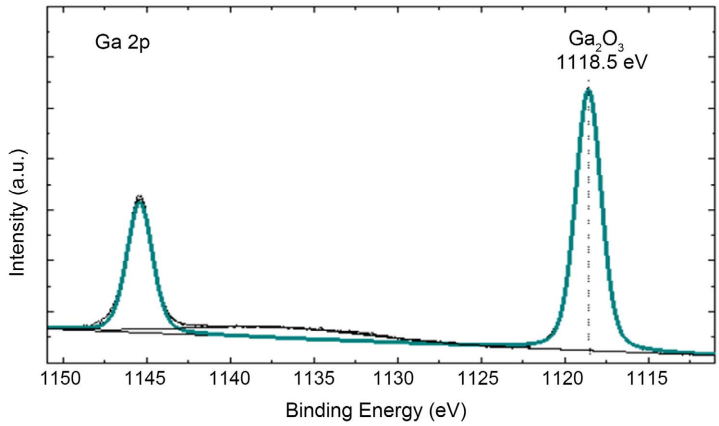


Figure 2. (a). XPS survey spectrum of as-deposited Ga_2O_3 film after 10 min. Ar^+ ion sputtering; (b). High resolution XPS spectra of the Ga 2p core level of as-deposited Ga_2O_3 film after 10 min. Ar^+ ion sputtering; (c). High resolution XPS spectra of the O1s core level of as-deposited Ga_2O_3 film after 10 min. Ar^+ ion sputtering.

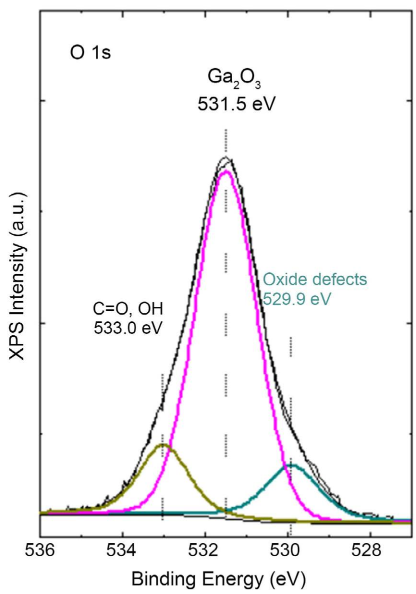
Figure 3(c) respectively. The position of the Ga $2p_{3/2}$ peak is 1118.4 eV. This binding energy is characteristic of Ga_2O_3 [16]. A chemical shift of 0.1 eV in Ga 2p and a shift of 0.2 eV in O 1s core level were observed in annealed Ga_2O_3 thin film compared to as deposited Ga_2O_3 thin film.



(a)



(b)



(c)

Figure 3. (a). XPS survey spectrum of annealed Ga_2O_3 film; (b). High resolution XPS spectra of the Ga 2p core level of annealed Ga_2O_3 film; (c). High resolution XPS spectra of the O1s core level of annealed Ga_2O_3 film.

The XPS survey spectrum of annealed Ga_2O_3 thin film after 10 min. Ar^+ ion sputtering is showed in Figure 4(a). Ga 2s, 2p, 3p, 3d, Ga Auger and O 1s peaks are clearly seen in the spectrum. Carbon contaminations were reduced to a low level after 10 min. Ar^+ ion sputtering. High resolution spectra of Ga 2p and O 1s core level are shown in the Figure 4(b) and Figure 4(c) respectively. A chemical

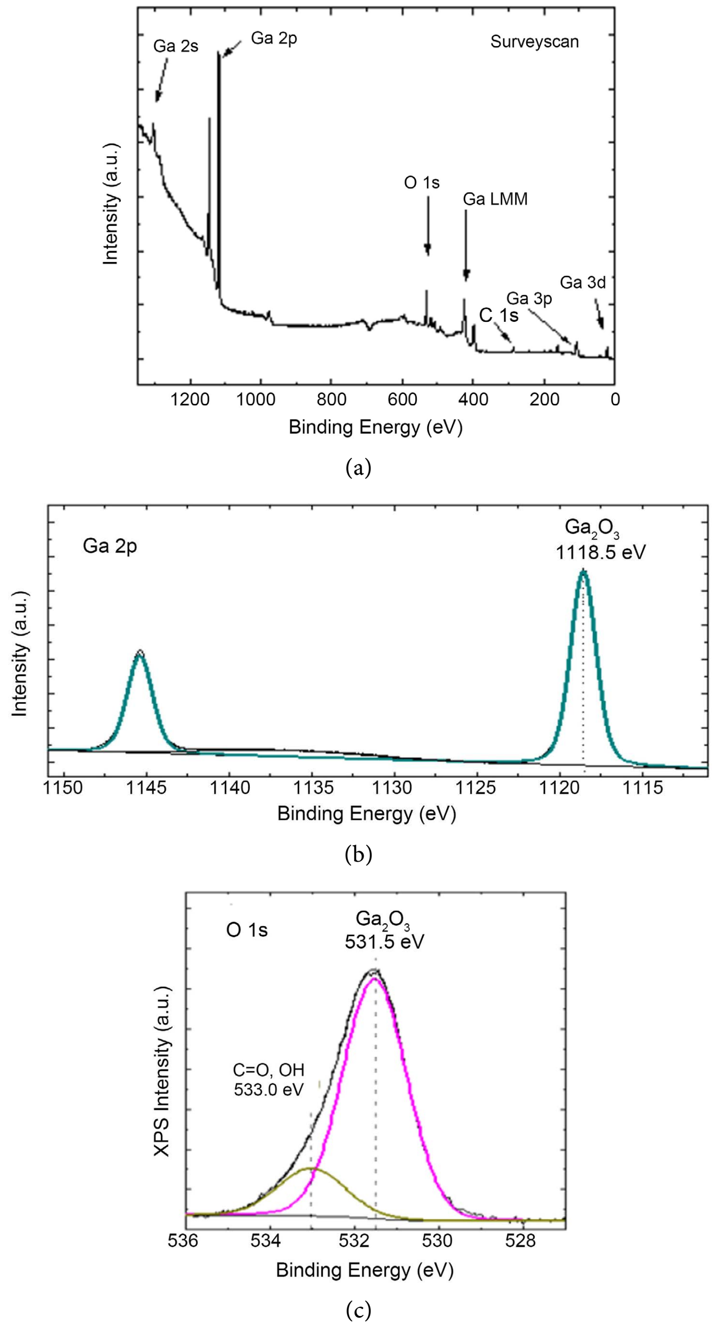


Figure 4. (a). XPS survey spectrum of annealed Ga_2O_3 film after 10 min. Ar^+ ion sputtering; (b). High resolution XPS spectra of the Ga 2p core level of annealed Ga_2O_3 film after 10 min. Ar^+ ion sputtering; (c). High resolution XPS spectra of the O 1s core level of annealed Ga_2O_3 film after 10 min. Ar^+ ion sputtering.

shift of 0.1 eV in Ga 2p and a shift of 0.2 eV in O 1s core level were observed in annealed Ga_2O_3 thin film compared to as deposited Ga_2O_3 thin film after 10 min. of Ar^+ ion sputtering. No chemical shift were observed in Ga 2p and O 1s core level in annealed Ga_2O_3 thin film after 10 min. of Ar^+ ion sputtering.

4. Conclusion

XPS analysis in this study reveals that composition of surface layers and the inner layers of Ga_2O_3 thin films is almost stoichiometric. The XPS results present that as-deposited and annealed film contains the elements gallium, oxygen, and carbon. Carbon contaminations were reduced to a low amount after 10 min. Ar^+ ion sputtering. No chemical shift was observed in Ga 2p in as-deposited and annealed Ga_2O_3 thin film after 10 min. of Ar^+ ion sputtering. Hence, it is concluded that there is no evidence of the formation of any other Ga-related compounds other than Ga_2O_3 on the surface and in the bulk. A small chemical shift is observed for O 1s core level binding energy for as-deposited film. So Ga_2O_3 thin films deposited by spray pyrolysis method can be used for harsh environment.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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