Superlattices and Microstructures 70 (2014) 117–130

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Influence of post-deposition annealing in air and vacuum on the properties of thermally evaporated gallium oxide films

Pritty Rao, Sanjiv Kumar *

National Centre for Compositional Characterization of Materials, Bhabha Atomic Research Centre, ECIL Post, Hyderabad 500062, India

ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 25 February 2014
Accepted 3 March 2014
Available online 19 March 2014

Keywords:
β-Ga_2O_3
Thermal evaporation
Annealing
RBS
Band gap
Semiconductor

ABSTRACT

Oxidative annealing in air or reductive annealing in vacuum around 773 K of thermally evaporated gallium oxide films produces monoclinic β-Ga_2O_3 films of distinctly different compositional, optical, morphological and electrical properties. The pristine films prepared by the evaporation of Ga_2O_3 powders are oxygen deficient, amorphous and absorbing in UV–visible region. The air annealed films are transparent (band gap ~4.9 eV), display nanometric granular morphology and are characterized by <1.0 eV extrinsic and 1.2–1.6 eV intrinsic activation energies in the Arrhenius plots of electrical conductivity. The growth of Ga_2O_3 phase on vacuum annealing takes place through the decomposition of Ga_2O, one of the constituents of the pristine films. The vacuum annealed films exhibit comparatively lower transparency (band gap <4.5 eV), comprise micron-sized dendrites or fibres and have <1.0 eV extrinsic and 1.7–2.0 eV intrinsic activation energies. The incorporation of these properties results from compositional changes in films induced by annealing in air or vacuum ambient.

1. Introduction

β-gallium oxide (Ga_2O_3) is an important semiconductor that has attractive applications in several fields such as optoelectronics, high temperature gas sensors, solar cells, spintronics etc. [1]. The

* Corresponding author. Tel.: +91 40 27121365; fax: +91 40 27125463.
E-mail address: sanjucccm@rediffmail.com (S. Kumar).

http://dx.doi.org/10.1016/j.spmi.2014.03.009
0749-6036/

versatility in applications stems from the unique physical, electrical and optical properties of the material. β-Ga_2O_3 is the only polymorph stable at ambient conditions among the five polymorphs of Ga_2O_3. It exists in monoclinic phase, has a high melting point (∼2073 K) and displays good chemical stability. Its band gap (E_g) is ∼4.8 eV which imparts it (a) transparency even in deep ultraviolet (UV) region and (b) good dielectric properties at room temperature. The specific resistivity of β-Ga_2O_3 can be as high as 10^{13} Ω cm while its dielectric constant and breakdown field are reported to be ∼10 and ∼2.1 MV/cm respectively [2]. The material, in fact, possesses interesting electrical properties. Although inherently an insulator at room temperature, it acquires n-type semiconducting properties at high temperatures or on doping with Ti^{+4} or Sn^{+4} [3,4]. The n-type conduction at high temperatures is often attributed to oxygen vacancies (V_O) which act as donors, though in a recent report Varley et al. have suggested that it may also arise due to unintentionally incorporated shallow impurities [5]. Due to the prevalence of electrical conductivity, β-Ga_2O_3 has been recognized as a material for high temperature gas (oxygen, hydrocarbons) sensors [6] and a UV transparent conducting oxide (UV-TCO) [4,7,8]. It is also regarded a promising material for solar blind detector [9] and single layer anti-reflecting coating for III-V semiconductors [10].

Though the properties of β-Ga_2O_3 are known for past few decades, studies on the material have been rather limited in comparison to other wide band gap semiconductors such as ZnO, SnO_2 or In_2O_3. However, recent years have witnessed a spurt in studies on both bulk single crystals and thin polycrystalline β-Ga_2O_3 films. Several techniques such as thermal evaporation [11], sputtering [12], pulsed laser deposition (PLD) [13–16], sol–gel process have been used to prepare Ga_2O_3 films with morphologies ranging from nanospheres [11] to nanorods [17] and nanowires [18,19]. In addition, in certain studies the formation of Ga_2O_3 dendrites has also been reported [20]. A feature common to the most of the methods is that high temperatures, often ranging from 873 K to 1273 K, are employed during the deposition or synthesis of the films. It is more hackneyed in methods based on the oxidation of GaSe or GaN films [21,22]. Such high temperatures are required not only to achieve chemical stoichiometry but also to induce crystallization and improve transmission characteristics of the films. For example, the films deposited by PLD at 1073 K or lower substrate temperatures (T_s) were black and acquired transparency in UV region only on increasing T_s to 1153 K [8]. Furthermore, there are instances wherein the films grown at an elevated substrate temperature have been subjected to *ex situ* annealing to obtain better quality films [23,24]. Such high deposition and or processing temperature are clearly a major limitation of these methods. Search of low temperature deposition methods producing Ga_2O_3 films possessing intrinsic properties of the material is, therefore, desirable.

Through this contribution we present the results of our studies on the formation of β-Ga_2O_3 films by the thermal evaporation of Ga_2O_3 powders at ambient substrate temperature followed by their *ex situ* oxidative annealing in air or reductive annealing in vacuum in 523–773 K temperature range. The structural, compositional, optical, electrical and morphological properties of thus prepared films have been investigated. Thermal evaporation is one of the simplest and the least expensive deposition techniques and yet is capable of producing good quality films. However, to the best of our knowledge, this method has been used only on a few occasions to deposit Ga_2O_3 thin films. These studies wherein the films were prepared either by the evaporation of Ga_2O_3 powder [11] or by rheotaxial growth and thermal oxidation (RGTO) method (a variant of thermal evaporation process that involved the oxidation of Ga metal films at ∼1173 K) dealt mainly with their morphological properties [25]. The paucity of details on the compositional and optical properties of thermally evaporated films prompted us to undertake the present studies. Herein we report that the method is well suited for the preparation of stoichiometric Ga_2O_3 films that exhibit good UV transparency at low (⩽773 K) processing temperatures.

2. Experimental details

2.1. Deposition of films

The films were deposited on Si, soda lime glass and fused silica substrates at a rate of 1–2 Å/s by resistively heating Ga_2O_3 powder (99.99%, Fluka AG) in a Mo-boat or a Ta-boat at $\sim 3 \times 10^{-4}$ Pa