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High resolution X-ray photoelectron spectroscopy of beta gallium oxide films deposited by ultra high vacuum radio frequency magnetron sputtering

Toshio Takeuchi [a,*], Hiroki Ishikawa [b], Norikazu Takeuchi [b], Yoshiji Horikoshi [a,b]

[a] *Kagami Memorial Laboratory for Materials Science and Technology, Waseda University 2-8-26 Nishi-Waseda, Shinjuku-ku, Tokyo, Japan 169-0051*
[b] *School of Science and Engineering, Department of Electrical Engineering and Bioscience, Waseda University 3-4-1 Okubo Shinjuku-ku, Tokyo, Japan 169-8555*

Abstract

The gallium oxide thin films with amorphous, crystalline, and nanostructure morphologies were deposited by a radio frequency magnetron sputtering system in ultra high vacuum conditions. High resolution X-ray photoelectron spectroscopy spectra of films were analyzed relating on the preparation conditions. On the amorphous films, the density of states at valence band region is dependent on the sputtering gas compositions. Beta gallium oxide (100) films are epitaxially deposited on magnesium oxide (100) crystalline substrate. The high resolution X-ray photoelectron spectra suggest the presence of the density of states valence band region with oxygen deficiency out of the stoichiometry on the epitaxial crystalline beta gallium oxide films.

Keywords: High resolution XPS; Gallium oxide; Oxygen deficiency; Valence band structure; UHV RF magnetron sputtering

1. Introduction original

Beta gallium oxide has the characteristics of being a chemically stable semiconductor oxide in air and of having larger band gap energy [1,2] than other transparent conductive oxides (TCOs) such as ITO and SnO2 [3–5]. Intensive research and development is being carried out into applications that take advantage of the special properties of beta gallium oxide including oxygen gas sensors [6–8], photo-catalysts [9,10] and ultraviolet TCOs. In the future, it is hoped to extend these applications to ultraviolet sensors, ultraviolet solar cells, human body detection systems, ultraviolet light emitting diodes, and ultraviolet laser diodes. Development of devices which combine several of these special features are also being considered; such combinations include a combined photo-catalyst and a solar cell, a combined TCO and photo-catalyst [9], and a combined light emitting diode and TCO. Development of technology for producing high quality beta gallium oxide is indispensable for advancing the above mentioned applications. Molecular beam epitaxy method [11,12], metal organic chemical vapour deposition method [13] and the pulsed laser deposition method [14] have been reported as methods for depositing beta gallium oxide films. One of the other methods which have succeeded in producing high quality beta gallium oxide films is a method involving ultra high vacuum (UHV: under the pressure of 4×10^{-7} Pa) radio frequency (RF: 13.56 MHz) magnetron sputtering [15]. This method has the potential to be used in industry since it allows high-speed large-area production of a quality film. Beta gallium oxide has a monoclinic crystal structure; its space group is C2/m and it has lattice parameters $a=12.23$ A, $b=3.04$, $c=5.80$, beta = 103.7° according to JCPDS 43–1012 [16]. Epitaxially grown beta gallium oxide films have been successfully deposited on crystalline substrates using UHV RF magnetron sputtering. Beta gallium oxide films have been grown having various surface orientations on substrates at elevated temperatures; examples include an epitaxial (100) surface deposited on MgO (100), *a* (020) surface on MgO (110), (−201) surface on MgO (111), (−201) surface on sapphire C and *a* (201) surface on sapphire R surface.

In this paper, we report on high resolution X-ray photoelectron spectroscopic study of epitaxial beta gallium oxide (100) deposited on the MgO (100) surface. Sputter deposition is the most widely used non-thermal technique for the commercial fabrication of oxide semiconductor films [1]. It is mainly used to deposit materials that are difficult to grow using chemical vapour deposition or metal organic chemical vapour deposition due to the lack of a suitable precursor. This includes metallic

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* Corresponding author.
E-mail address: takeuchi-toshio@nifty.com (T. Takeuchi).

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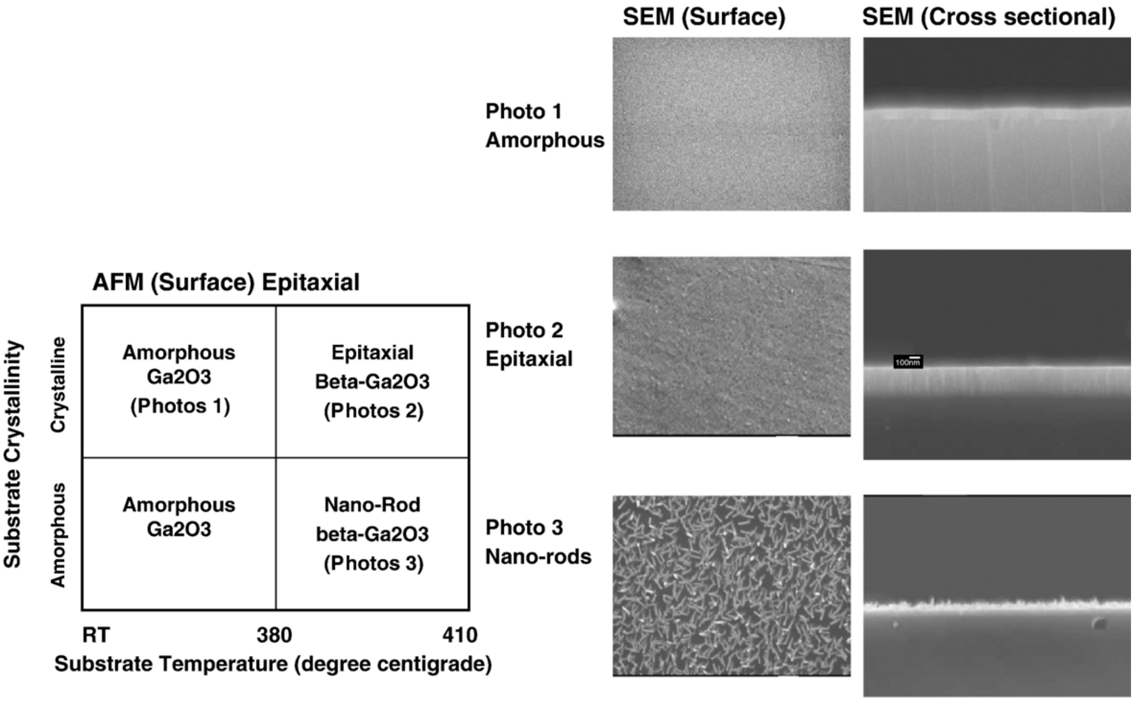
ohmic connections (e.g. aluminum, copper, gold, and tungsten), diffusion barriers such as TiN, and electrical insulators such as SiO_2 and Ga_2O_3. For the research purposes, however, sputtering is used to deposit a broad range of chemically complex materials and nano-structures.

2. Experimental

2.1. UHV RF magnetron sputtering method

In this study, gallium oxide thin films were deposited using an UHV RF magnetron sputtering system. The magnetron sputtering method has essential advantages of dry processes and plasma assisted presences. The depositions in the ultra high vacuum can add the advantages to avoid the inclusion of the impurities those which owe to low vacuum like processes molecular beam epitaxy and pulsed laser deposition technology. The sputter depositions of Ga_2O_3 films were carried out using an UHV RF magnetron sputtering system (Universal Systems, MS model, Japan). The deposition chamber was connected to a pumping system consisting of a turbo molecular pump, having a rotary pump as the fore pump and a pumping speed of 430 L/S. A circular Ga_2O_3 target having a purity of 99.999% with dimensions of $\varphi 50.8 \times 4.35$ (thickness) (Techno Fine Co., Japan) was sputtered from the magnetron sputtering cathode of a sputtering system (A320 A3V & CTM, AJA International USA). The films were deposited on two kinds of substrates, namely amorphous substrates (fused quartz glass substrates) and crystalline substrates (single-crystal sapphire and MgO substrates). Prior to deposition, all substrates were ultrasonically cleaned in acetone and ethanol; while the sapphire substrates were additionally treated with 10% HF and water solution and then rapidly dried with nitrogen gas. Transmission measurements were performed on the films deposited on fused quartz substrates, while X-ray diffraction patterns were obtained for the films deposited on crystalline substrates for the purposes of analyzing their nano-rod structures. Just before deposition, the chamber was evacuated to a base pressure of 4×10^{-7} Pa using a turbo-molecular pump. For planar magnetron discharge, high-purity argon and oxygen gas (99.9999% purity) were then introduced into the chamber at a constant flow rate of total 15 sccm of argon plus oxygen gases. The ratio of oxygen to argon was controlled precisely using mass flow controllers. Substrates were placed at a distance of 225 mm from the target. The substrate holder was rotated during sputtering to improve the film thickness uniformity. The working pressure was approximately 1×10^{-2} Pa. The applied RF power was maintained at 100 W and the range of substrate temperatures investigated was room temperature to 600 °C. The deposition speeds are spread from 0.06 to 0.4 angstrom per second depending on the gas compositions. A conventional stylus surface profiler (Alpha-step 500, Tencor) was used to measure the film thickness and this measurement was checked using a spectroscopic ellipsometer (HORIBA JOBIN YVON, UVISEL FUV-model). The phases of the deposited films were investigated by X-ray diffraction (XRD) using Phillips X'pert diffractometer with high intensity monochromatic Cu Kα-radiation ($\lambda = 1.51418$ A). The chemical state, structure, and composition



(a) (b)

Fig. 1. The unified crystallinity and surface morphologies of the Ga_2O_3 films deposited by UHV RF magnetron sputtering system as a function of substrate crystallinity and deposition temperature. (a): crystallinity acquired XRD X-ray theta–2theta plot spectra and (b): surface morphologies obtained by FE-SEM with that of interfaces of surface.