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Electrical characteristics of β-Ga_2O_3 thin films grown by PEALD

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In this work, 7.5 nm Ga_2O_3 dielectric thin films have been deposited on *p*-type (1 1 1) silicon wafer using plasma enhanced atomic layer deposition (PEALD) technique. After the deposition, Ga_2O_3 thin films were annealed under N_2 ambient at 600, 700, and 800 °C to obtain β-phase. The structure and microstructure of the β-Ga_2O_3 thin films was carried out by using grazing-incidence X-ray diffraction (GIXRD). To show effect of annealing temperature on the microstructure of β-Ga_2O_3 thin films, average crystallite size was obtained from the full width at half maximum (FWHM) of Bragg lines using the Scherrer formula. It was found that crystallite size increased with increasing annealing temperature and changed from 0.8 nm to 9.1 nm with annealing. In order to perform electrical characterization on the deposited films, Al/β-Ga_2O_3/*p*-Si metal–oxide–semiconductor (MOS) type Schottky barrier diodes (SBDs) were fabricated using the β-Ga_2O_3 thin films were annealed at 800 °C. The main electrical parameters such as leakage current level, reverse breakdown voltage, series resistance (R_S), ideality factor (n), zero-bias barrier height (ϕ_{Bo}), and interface states (N_{SS}) were obtained from the current–voltage (I–V) and capacitance–voltage (C–V) measurements at room temperature. The R_S values were calculated by using Cheung methods. The energy density distribution profile of the interface states as a function of (E_{SS}–E_V) was obtained from the forward bias I–V measurements by taking bias dependence of ideality factor, effective barrier height (ϕ_e), and R_S into account. Also using the Norde function and C–V technique, ϕ_e values were calculated and cross-checked. Results show that β-Ga_2O_3 thin films deposited by PEALD technique at low temperatures can be used as oxide layer for MOS devices and electrical properties of these devices are influenced by some important parameters such as N_{SS}, R_S, and β-Ga_2O_3 oxide layer.

1. Introduction

Monoclinic Gallium oxide (β-Ga_2O_3) is one of the large band gap semiconductor materials and it has a direct band gap about 5 eV [1]. Since β-Ga_2O_3 features a higher dielectric constant (∼10–14) than SiO_2 (∼4) and has a unique transparency from the visible into the ultraviolet (UV) region, this material is very good candidate for industrial applications such as solar cells and optoelectronic devices operating at short wavelength, gate dielectric materials for complementary metal–oxide–semiconductor (CMOS) devices, next-generation high power devices, etc. [2,3]. In addition, metal/β-Ga_2O_3/semiconductor (MOS) type hydrogen sensor diodes with β-Ga_2O_3 reactive oxide films are very useful for hydrogen gas sensing since the reactive oxide intermediate layer between metal and semiconductor Schottky barrier diodes could improve the hydrogen gas sensing performance [4–6]. Ga_2O_3 has five crystalline modifications (α, β, γ, δ, ε) but β-form is the most stable crystalline modifications from room temperature to melting point of about 1800 °C. Also, β-Ga_2O_3 has a chemically stable even if it is exposed to concentrated acids such as hydrofluoric acid [7].

Because of these beneficial material properties, β-Ga_2O_3 thin films require the careful structural and electrical analysis. As known, growth techniques are crucial to obtain quality thin films. Variety of thin film deposition methods such as sol–gel method [8], metal–organic chemical vapour deposition (MOCVD) [9], sputtering, pulsed laser depositon [10], molecular beam epitaxy [11,12], and atomic layer deposition technique (ALD) [13–18] have been used to achieve better quality of β-Ga_2O_3 thin films. Unlike other physical vapor deposition (PVD) or chemical vapour deposition (CVD) methods, ALD is based on the saturative surface reactions, which results in a self-limiting growth mechanism. As a result, excellent conformality and large-area uniformity in addition to accurately controlled film thickness are inherently obtained. With the help of remote plasma, the processing temperatures can also be kept relatively low, which makes ALD attractive for a wide range of low-temperature compatible substrates including transparent and flexible polymers. At low deposition temperatures, to enable exchange reactions between the atoms or molecules, activation energy is required which might be provided via plasma activation

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Plasma-enhanced ALD (PEALD) technique is widely used as an alternative to conventional ALD. Thus, plasma source creates ions and radicals, enhance the chemical reactions and provide a wider range of materials which can be deposited at low temperatures.

In this study, we report on the growth of ~7.5 nm Ga_2O_3 thin films on *p*-type Si substrate using trimethylgallium (TMG) and O_2 plasma as the Ga source and oxidant, respectively and extraction of the main electrical parameters of Al/β-Ga_2O_3/*p*-Si (MOS) type SBDs using the *I*–*V* and *C*–*V* characteristics at room temperature. Also, annealing effect on the structural and microstructural properties of β-Ga_2O_3 thin films was discussed. To the best of our knowledge, such a study is not yet carried out on PEALD-grown β-Ga_2O_3 thin films.

2. Experimental method

Ga_2O_3 thin films were deposited by a Fiji F200 PEALD reactor (Ultratech/Cambridge Nanotech Inc.) using TMG as the Ga precursor and O_2 plasma as the oxidant with a base pressure of 0.20–0.25 Torr. Firstly, cleaning procedures were performed to *p*-type Si (1 1 1) wafers with 5 min sequential ultrasonic agitation in isopropanol, acetone, methanol, and de-ionized (DI) water. Afterwards, the wafers were treated in (1:19) HF: H_2O mixture for 1 min to remove native oxide on substrate surface. As the last step of the cleaning procedure, Si (1 1 1) wafer pieces were rinsed with DI water and dried by using N_2. After the cleaning procedure, wafers were loaded into the ALD reactor through a load lock. As mentioned in our previous group paper [18], in order to optimize growth parameters needed for the self-limiting deposition of Ga_2O_3 thin films, the effect of TMG dose, O_2 plasma duration, and Ar purge time were studied. Firstly, 500 cycles Ga_2O_3 films were deposited on a wafer to obtain thickness parameters with High Resolution Transmission Electron Microscope (HRTEM). After thickness calibration, 120 cycles were deposited at 250 °C, where one cycle consisted of 0.015 s TMG (precursor bottle temperature 6 °C)/5 s Ar purge/2–60 s (25 sccm, 300 W) O_2 plasma/5 s Ar purge. Postgrowth annealing of 120 cycles Ga_2O_3 films was performed in a rapid thermal annealing system (ATV-Unitem, RTP-1000–150) under 100 sccm N_2 flow at 600, 700, and 800 °C.

For structural characterization, HRTEM (FEI Tecnai G2 F30 transmission electron microscope) at an operating voltage of 300 kV was used for the imaging of Ga_2O_3 thin films. Also, to provide crystallographic information, Selected Area Electron Diffraction (SAED) measurement was carried out. Grazing-incidence X-ray diffraction (GIXRD) measurements were performed in a PANanalytical X'Pert PRO MRD diffractometer operating at 45 kV and 40 mA, using Cu K-α radiation. Initial scans were performed within the range of 10–90° by using 0.1° step size and 0.5 s counting time. For the crystalline samples, additional data were obtained within the same 2θ range by the summation of eight scans, which were performed by using 0.1° step size and 10 s counting time. Surface roughness and root-mean square (RMS) values were obtained by using Asylum Research, MFP-3D Atomic Force Microscope. In order to investigate electrical properties of β-Ga_2O_3 thin films, Al/β-Ga_2O_3/*p*-Si metal–oxide–semiconductor (MOS) type Schottky barrier diodes (SBDs) were fabricated using the β-Ga_2O_3 thin films which annealed at 800 °C with standard lithography process. All of the fabrication processes were conducted at class 100 and 1000 UNAM cleanroom facility. Back ohmic contact and top rectifier contact metallization was carried out by the thermal evaporation of a ~80 nm-thick aluminum (Al) layer using VAKSIS Thermal Evaporation system (PVD Vapor – 3S Thermal). Samples were annealed in ATV RTA system at 450 °C for 2 min under N_2 atmosphere for back-ohmic contact.

3. Results and discussion

For thickness controlling, firstly 500 cycles Ga_2O_3 film deposited on Si (1 1 1) at 250 °C and cross-sectional High Resolution Transmission Electron Microscope (HRTEM) image was carried out as in Fig. 1(a). Film thickness was measured as 26.7 nm from this image, which is in good agreement with the results obtained by ellipsometry.

Also, to provide crystallographic information, Selected Area Electron Diffraction (SAED) measurement was carried out and shown in Fig. 1(b). As can be seen from Fig. 1(b), as-deposited Ga_2O_3 film shows amorphous nature. In our sample, 120 cycles Ga_2O_3 film was deposited on Si (1 1 1) at 250 °C and thickness was also is in good agreement with ellipsometry measurements.

Fig. 2(a) and (b) show GIXRD patterns of as-deposited and annealed Ga_2O_3 thin films at different temperatures, respectively. As-deposited Ga_2O_3 thin films were found as amorphous structure. After annealing at 600 °C under N_2 atmosphere, β-phase Ga_2O_3 peaks began to appear and peak intensity increased and became sharper with increasing annealing temperatures. In Fig. 2(b), all of the main diffraction peaks in the GIXRD pattern can be indexed to a monoclinic β-Ga_2O_3 (ICDD reference code: 00–011-0370). This GIXRD pattern reveals that β-Ga_2O_3 has been synthesized successfully by using low-temperature PEALD and subsequent thermal annealing. In order to investigate the effect of annealing temperature on the microstructure of the Ga_2O_3 thin films, average crystallite size values were calculated according to Scherrer formula [19]

$$d = \frac{0.9\lambda}{\Delta\theta_B cos\theta_B} \tag{1}$$

where, d is the average crystallite size, λ is the wavelength of the X-ray beam (0.15418 nm), $\Delta\theta_B$ is the full width at half maximum (FWHM) that was calculated from the XRD spectra, and θ_B is the Bragg angle.

As can be seen in Fig. 3, average crystallite size of the films was changed rapidly after annealing and increased with increasing annealing temperature. On the other hand, FWHM values for the most intense peak ($2\theta_B = 30.5$) is decreasing after annealing rapidly. The average crystallite size varied from 0.8 nm to 9.1 nm. This was evidence of improvement of crystal quality with increasing of annealing temperature. Also, 3D-AFM topographies were carried out to obtain idea about the surface morphologies and the root mean-square (RMS) values. 3D-AFM images were inserted in Fig. 2(a) and (b) for the as-deposited and annealed Ga_2O_3 thin films, respectively. RMS roughness values which was measured from 1 μm × 1 μm scan area were found as 0.16 and 0.37 nm for as-deposited and annealed thin films, respectively. It can be seen

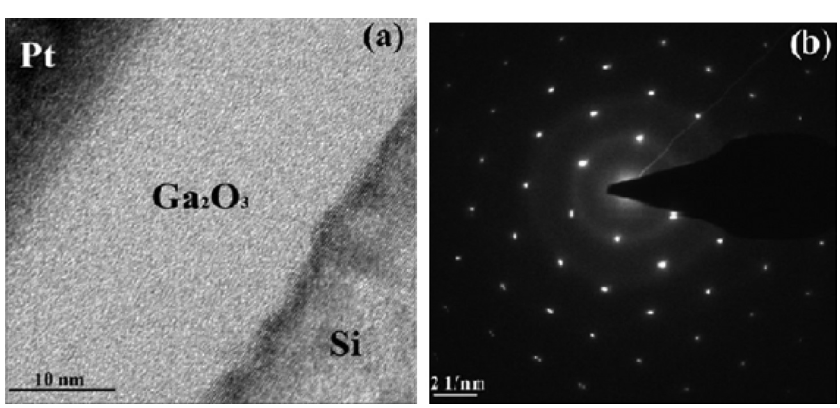

Fig. 1. (a) Cross-sectional HRTEM image of the Ga_2O_3 thin film deposited on Si (1 1 1) at 250 °C for thickness controlling. (b) SAED pattern of the same sample.