Photoelectric characterization of the β - Ga_2O_3 film with ZnO nano-interlayer compared to the β- Ga_2O_3 films

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High-quality β - Ga_2O_3 film and β - Ga_2O_3/ ZnO/ β - Ga_2O_3 film have been prepared by laser molecular beam epitaxy (LMBE) without annealing and their photoelectric characterization has been investigated. These semiconducting films were deposited on sapphire <002> substrate with 700□ for photoelectric and microstucture characterization. X-ray diffraction (XRD) showed that β - Ga_2O_3 and ZnO peak intensity, peak position and Full Width at Half-Maximum (FWHM). X-ray photoelectron spectroscopy (XPS) illustrated the atomic composition (Ga/O) and concentration (2/1.048) of β - Ga_2O_3/ ZnO/ β - Ga_2O_3 film surface. Ultraviolet transmittance spectrum (UV) indicated the different transmittance in the same region. Additionally, the bandgap of β - Ga_2O_3 film and β - Ga_2O_3/ ZnO/ β - Ga_2O_3 film were calculated by Tauc'plot method, the bandgap of β - Ga_2O_3 film was 5.1ev, but the one of β - Ga_2O_3/ ZnO/ β - Ga_2O_3 film was 4.8 ev. Room-temperature photoluminescence spectrum (PL) of the as-synthesized β - Ga_2O_3 film and β - Ga_2O_3/ ZnO/ β - Ga_2O_3 film revealed blue (419 nm) and UV (385 nm) emission, respectively. In addition, electrical properties of the films were investigated by Hall Effect investigations.

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1. Introduction

In recent years, with the rapid progress of micro-electronic and photoelectronic devices, the transparent conducting oxide (TCO) presents multi-variant developing and more extensive applications. TCO is important component in flat-panel displays and photovoltaic cells [1]. In order to satisfy the increasing demands of modern technology, we have an intensity tendency to exploit various kinds of TCO. The intention for this work is to search high-quality and novelty TCO film.

ZnO material has attracted considerable attention because of its potential application in short wavelength light emitting and detecting devices in the UV-blue spectral region [2], so it is applied to transparent electrode [3], surface acoustic wave filter material [4], and so on. Monoclinic structured gallium oxide β - Ga_2O_3 is a chemically and thermally stable material with a wide band gap 4.9 eV） material. Therefore, β - Ga_2O_3 has already been widely used in various fields, such as applications in transparent conductors, phosphors, gas sensors, transparent electronic devices, and ultraviolet (UV) photodetector [5] - [8]. A number of studies on the ZnO films and Ga_2O_3 films have been done. ZnO + Ga_2O_3 functionally graded thin films which were fabricated by combinatorial RF magnetron sputtering were used as organic light emitting diodes (OLEDs) [9]. In order to satisfy the demands of emerging technology, new TCOs were searching all the time, the zinc oxide-gallium oxide phase space by plasma enhanced chemical vapor deposition was a research [10]. K. Zheng et al reported an indium-free transparent resistive switching random access memory device based on GZO-Ga_2O_3-ZnO- Ga_2O_3-GZO structure by metal-organic chemical vapor deposition [11]. Combining different metal oxides may dramatically change the photoelectronic properties of films. No detailed research on the photoelectric characterization of β - Ga_2O_3/ ZnO/ β - Ga_2O_3 film has been conducted so far. In this paper, ultraviolet transparent conductive β - Ga_2O_3 films and that of β - Ga_2O_3 film with ZnO nano-interlayer were synthesized by laser molecular beam epitaxy (LMBE) on sapphire substrates without annealing.

2. Experimental

2.1 Thin film preparation

β - Ga_2O_3 film and GZG film were fabricated on sapphire substrates by L-MBE (450) without annealing. Ga_2O_3 ceramic target (99.99%) and ZnO ceramic target (99.999%) were used as material source. An excimer laser was used as the laser source, which has a wavelength of 248 nm, repetition rate of 1 Hz and pulse energy of 200 mJ. The sapphire <002> was used as a substrate and it was ultrasonically cleaned in acetone, alcohol and deionized water in turn.

The fabrication process was carried out at a pressure of 2×10^{-2} Pa in a pure oxygen atmosphere with target-to-substrate distance of 50 mm. The vacuum

chamber was pumped down to 10^{-5} Pa before introduing the oxygen gas. The rotation speeds of the substrate and the target were all 30 rpm. The substrate temperature (700□) was measured using thermocouple gauge. The hetero-epitaxy time of β - Ga_2O_3 film was 7500 s. The GZG film was fabricated by sputtering Ga_2O_3 ceramic target (3500 s), ZnO ceramic target (1500 s) and Ga_2O_3 ceramic target (3500 s) successively. The Reflection high energy electron diffraction (RHEED) could synchronously monitor epitaxial layer and analyze fresh surface. From the Fig. 1, it was the instant screenshot in the process of fabrication. The clear stripes indicated that it was high qulity crystal.

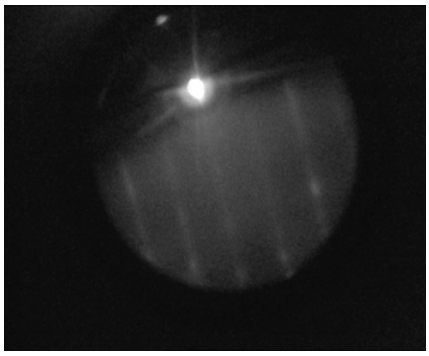

Fig. 1. The RHEED instant screenshot of the surface of fillm.

2.2 Properties characterization

In this paper, Rigaku D/max-rB X-ray diffraction (XRD) spectroscopy with a Cu Kα line radiation source was utilized to examine the crystallinity of the thin films. The composition of the GZG film surface was analyzed by X-ray photoelectron spectra (XPS) recorded on a PHI 5300 X-ray photoelectron spectrometer. The transmittance spectrum was detected by UV-visible spectrophotometer (U-4100), the photoluminescence and electrical properties were measured by Edinburgh Instruments FLS920 Steady-state fluorescence spectrometer (U.K.) with Xe lamp and Hall Effect investigation (HL5500), respectively. All of the above examinations were operated in room temperature.

3. Results and discussion

3.1 X-ray diffraction measurements

X-ray diffraction (XRD) patterns of β - Ga_2O_3 film and GZG film fabricated at 700℃ with sapphire substrate was shown in Fig. 2. The same diffraction peaks ($\bar{3}11$) and ($\bar{6}03$) of the β phase of Ga_2O_3 which were found at 38.26° and 58.96° were identified in XRD patterns of the two kinds of films, the intensity of the two peaks decreased when ZnO nano-interlayer existed in the β - Ga_2O_3 film. A possible reason is that there is a lattice mismatch problem which is caused by mixing the hexagon in wurzite crystal systems and rectangle in monoclinic crystal systems between the ZnO nano-interlayer and the up and down two β - Ga_2O_3 layers. There is an evident ZnO (002) diffraction peak at 34.22°. ZnO nano-interlayer shows a monocrystalline structure with mainly c -axis orientation. The peak which is signed 'S' is attributed to the sapphire substrate. We don't observe other peaks except these peaks. So we conclude that $ZnGa_2O_4$ and any zinc gallium oxides are not appearing in the interface between the ZnO layer and β - Ga_2O_3 layer. According to Scherrer Equation

$$D = k\lambda / \Delta\theta \cos\theta \quad (1)$$

(k is Scherrer constant, λ is X-ray wavelength (1.54178 Å), $\Delta\theta$ is The Full Width at Half-Maximum (FWHM), θ is the Bragg diffraction angle), the FWHM of the ZnO nano-interlayer is 0.31 according to Jade 5 software. Then, we calculate that the mean crystallite size of the ZnO nano-interlayer is around 4 Å using the diffraction peak (002). The quality of the as-deposited ZnO nano-interlayer still needs optimization. The mean crystallite size of the β - Ga_2O_3 layer are 3 Å using the diffraction peak ($\bar{3}11$) and 5 Å using the diffraction peak ($\bar{6}03$). The mean crystallite size of β - Ga_2O_3 film is consistent with the one of β - Ga_2O_3 layer.

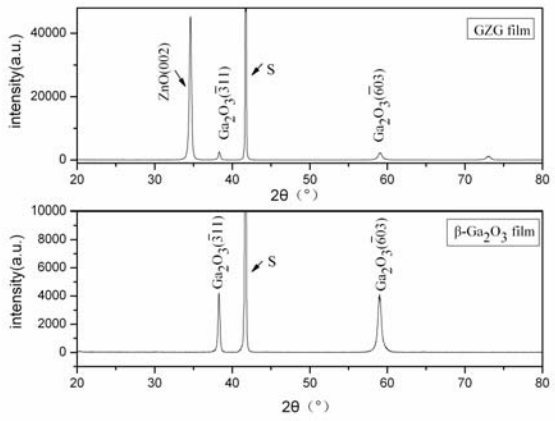

Fig. 2. X-ray diffraction (XRD) pictures of GZG film and β - Ga_2O_3 film.

3.2 X-ray photoelectron spectra

The composition of the GZG film surface can be futher determined by X-ray photoelectron spectra (XPS) measurements within a range of binding energies of 0-1200 eV for confirming without ZnO on the surface. Fig.

3 shows a typical survey spectrum of Ga_2O_3 film, clearly revealing the core levels of O1s and Ga2p. Therefore, it verifies that ZnO layer is among the two Ga_2O_3 layers, ZnO layer forming the nano-interlayer which influences the photoelectric and microstucture characterization of β - Ga_2O_3 film. The appearance of C1s peak is due to the absorption of C contamination. Quantification of the Ga2p and O1s peaks gives an average Ga/O atomic ratio of 2/1.048, which indicates that more oxygen vacancies exist in the GZG film surface. The cross section figure is shown in Fig. 4. It is measured by Zeiss supra55 field emission scanning electron microscope (FE-SEM). The thickness of GZG film is 225 nm via electronic caliper measurement. The ZnO nano-interlayer of GZG film is tens of nanometer thick.

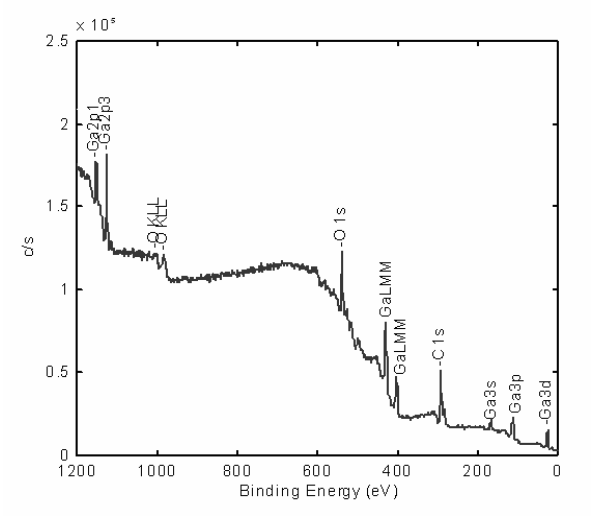

Fig. 3. X-ray photoelectron spectra (XPS) of surface of the GZG film.

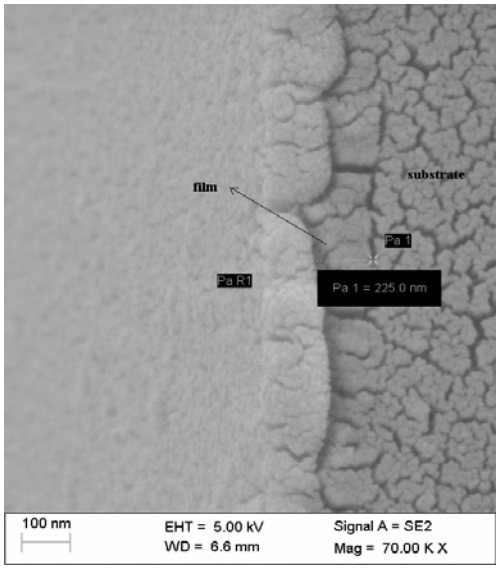

Fig. 4. Cross section SEM of the GZG film.

3.3 Ultraviolet transmittance spectrum

The transmittance spectrum of β - Ga_2O_3 film and GZG film have been tested by UV-visible spectrophotometer at room temperature, shown in Fig. 5. The sapphire substrate acted as a reference. We can see that the device exhibits high transparence. The transmittance of β - Ga_2O_3 film is approximately 95% on average in the visible region and around 97% - 98% on the deep ultraviolet range. While the transmittance of GZG film is almost close to 100% at shallow ultraviolet and visible region. Therefore the GZG film is a kind of ultraviolet anti-reflection film which has wide application prospect in ultraviolet and other optoelectronic devices and so on. Because the refractive index of air and sapphire substrate are 1.0 and 1.77, so the refractive index of GZG film should be among the refractive index of two former, but the refractive index Ga_2O_3 crystal and ZnO crystal are around 1.9 and 2.2, the possible reason are the minisize effect and the quantum confinement effect of nanomaterial due to Ga_2O_3 and ZnO is nanostucture in the GZG film. The direct band-gap material has the relationship

$$(\alpha h\nu)^2 \propto h\nu - Eg \tag{2}$$

According to

$$I = AI_0E^{-\alpha d} \tag{3}$$

The absorption coefficient $\alpha \propto -\ln T$. Shown in Fig. 6, we gain the two plots of $(\alpha h\nu)^2$ against the photo energy $h\nu$ by above formula. The optical band-gap of β - Ga_2O_3 film and GZG film are 5.1 ev and 4.8 ev respectively, which indicated that the optical band-gap decreases owing to ZnO nano-interlayer.

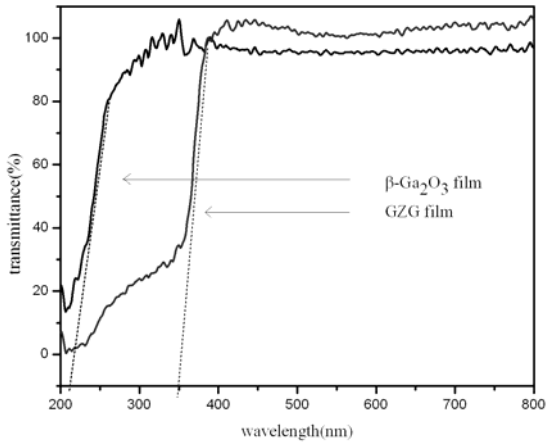

Fig. 5. Transmittance spectrum of β - Ga_2O_3 film and GZG film.

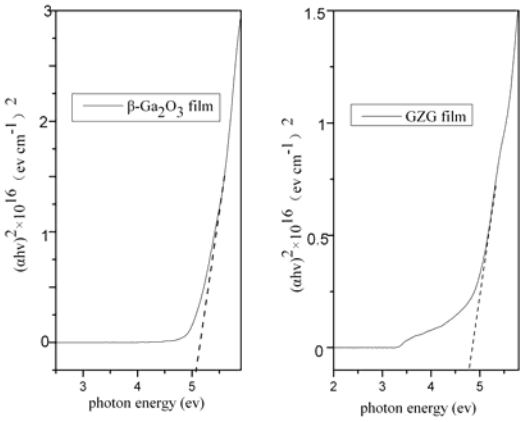

Fig. 6. The optical band-gap of β - Ga_2O_3 film and GZG film.

3.4 Photoluminescence measurement

Fig. 7 shows the measurement of PL spectra at room temperature of the as-deposited films and their Gaussian fitting plots. It can be observed that β - Ga_2O_3 film shows a strong blue emission band located at 427 nm. The PL spectra of GZG film consists of a strong ultraviolet (UV) emission band located at 384 nm and a red emission band centered at 660 nm. According to the following equation:

$$Ev(ev) = \hbar\omega = 1240/\lambda \quad (4)$$

The peak at 427 nm corresponds to Ev = 2.90 eV, the value of Ev is close to the blue luminescence of PL spectrum of gallium vacancies [12] β - Ga_2O_3 film contained. The UV emission (384 nm) is originated from the exitonic recombination corresponding to the near band-edge emission of band gap in ZnO nano-interlayer [13]. The peak at 384 nm corresponds to Ev = 3.22 eV, this red shift to the free exciton emission peak in bulk ZnO crystal (corresponding to Ev = 3.24 eV) indicates that binding energy of the exciton has a little enhancement owning to the Coulomb attraction between the electron and hole inside the ZnO nano-interlayer [14]. Furthermore, we observed a weak red lightemission peak at 660 nm from the Fig. 7(b), commonly referred to a deep-level or trap-state emission. It is appropriate to conclude that there are a number of oxygen vacancies in GZG film, because the films are fabricated at 700□, a quantity of oxygen vacancies can also easily be produced in our experiment. But their Gaussian fitting plots show the β - Ga_2O_3 film with strengthened blue light emission and GZG film with strengthened UV emission would be the promising material for applications in optoelectronic nanodevices.

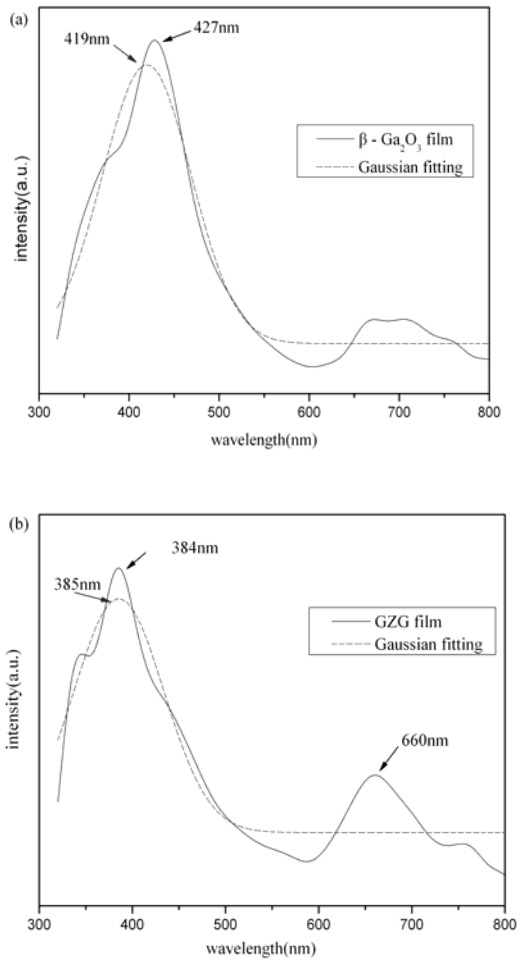

Fig. 7. PL spectra and Gaussian fitting plots of β - Ga_2O_3 film and GZG film.

3.5 Hall effect investigations

The electrical properties of β - Ga_2O_3 film and GZG film were measured by Hall Effect investigations. Resistivity, carrier mobility, carrier concentration and Hall coefficient have been measured by the Van Der Pauw method. The resistivity of the film is decided by carrier concentration and carrier mobility. A relatively low resistivity which was obtained for β - Ga_2O_3 film was too low to beyond the measuring range of Hall-effect instrument. This is accordance with previous result. However, GZG film is n type, super-low resistance (0.0144 Ωcm) semiconductor films, carrier mobility is 15.18 $cm^2/V^{-1}s^{-1}$, carrier concentration is over 2.86E19 cm^{-3}, Hall coefficient is -0.2185 cm^3/C. The electrical properties of GZG film are dominated by free electrons generated from Vo and Zni of ZnO nano-interlayer. The electrical conductivity in the GZG film is higher than that in β - Ga_2O_3 film due to the contribution of other defects

(Zn^{2+} iron, Vo and Zni). Some defects and interstitial atoms are expected to enhance the conductivity of GZG film [15]. Besides, we investigated whether grain-boundary scattering mechanism or formation of trapping states fit well with to the mean free path (MFP) of the carrier are factors affecting the mobility of the GZG film. By using the MFP equation

$$l = (\hbar / e)(3N / \pi)^{1/3} \mu \quad (4)$$

where $\hbar$ is Plank's constant, e is the electron charge, N is the carrier concentration, μ is the mobility. The MFP is around 1 nm by calculating. The average crystallite size of GZG film is calculated to be 3-5 nm, which is larger than the MFP of the free electron. Therefore, grain-boundary scattering mechanism and formation of trapping states fit well with to the mean free path (MFP) of the carrier are not important factors affecting the mobility of the GZG film.

4. Conclusions

We have investigated the optical and electrcial properties of β - Ga_2O_3 film and GZG film which had been fabricated by the LMBE method without annealing. The β - Ga_2O_3 film and GZG film were fabricated at 700 ^oC, especially, tens of nanometer thick ZnO nano-interlayer was formed in our experiment**.** In addition, GZG film has high transmittance in the shallow ultraviolet region and visible region. GZG film is a kind of ultraviolet anti-reflection film. The PL spectra of the as-deposited β - Ga_2O_3 film and GZG film reveal the dominant emission in the blue and UV regions. GZG film has even super-low resistance, which could be useful for the fundamental studies and many technological applications.

Acknowledgements

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