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Structural Characteristics and Photoluminescence Properties of Sputter-Deposition ZnGa_2O_4 Thin Films on Sapphire and Si(100) Substrates

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Abstract: In this paper, we report the growth and material characteristics of ZnGa_2O_4 thin films on *c*-plane sapphire and Si(100) substrates by a radio-frequency magnetron sputtering. When deposited on sapphire, the ZnGa_2O_4 film showed a polycrystalline nature and a less randomly oriented, primarily with the (111), (222) and (511) planes parallel to the substrate surface. On Si(100), the ZnGa_2O_4 thin film was randomly oriented with (311)- and (020)-plane polycrystalline properties. Transmission electron microscopy analysis revealed that an amorphous-layer interface was formed on the Si(100) substrate and the microstructure of ZnGa_2O_4 became disordered. The ZnGa_2O_4 /sapphire emitted ultraviolet photoluminescence and green emissions. The dominant optical transitions depended on the deposition temperature, oxygen and Zn contents, and nature of the substrate. The structural and optical properties of sputter-deposited ZnGa_2O_4 thin film on sapphire indicated that sapphire substrate is suitable for the growth of crystalline, high-quality ZnGa_2O_4 thin film.

Keywords: film; magnetron sputtering; microstructure

1. Introduction

Zinc gallate (ZnGa_2O_4) is a wide-band gap semiconductor oxide with a cubic spinel structure (Fd_{3m} , $a = b = c = 0.8335$ nm, and $\alpha = \beta = \gamma = 90^\circ$). The Ga^{3+} ion occupies the octahedral sites, and the Zn^{2+} ions occupy the tetrahedral sites, as schematically illustrated in Figure 1. ZnGa_2O_4 possesses an energy bandgap of approximately 5 eV and a conductivity of 30 Scm^{-1} [1]. Owing to its high transparency in the ultraviolet (UV) wavelength region, non-corrosive-gas emission under electron bombardment, and stability in high vacuum, ZnGa_2O_4 has been reported to be favorable for several optoelectronics applications in recent years, such as low-voltage vacuum fluorescent displays, field emission displays and UV photodetectors [2,3]. Moreover, UV light induces transitions of self-activated optical centers in the normal spinel structure of ZnGa_2O_4 , giving rise to an intense blue luminescence. When doped with Mn and Cr, the emission spectrum of ZnGa_2O_4 ranges from green to red [4,5]. Thus, ZnGa_2O_4 phosphor has been investigated for its unique and good luminescence characteristics.

ZnGa_2O_4 phosphor materials have been prepared by several methods, including radio-frequency (RF) magnetron sputtering [6], sol-gel processing [7], metal organic chemical vapor deposition (MOCVD) [8] and pulsed laser deposition [9]. However, they are mostly used to conduct synthesis of one-dimensional nanostructures (nanoparticles, nanowires and nanotubes) and are known to improve the emission characteristics of ZnGa_2O_4 phosphor powder [10–12]. In fact, thin film structures are more stable and reliable than one-dimensional nanostructures and better adhere to solid surfaces in practical devices. Wu et al. discussed the gas sensor properties based on epitaxial ZnGa_2O_4 thin

film grown on sapphire substrate by MOCVD [13]. Tsai et al. reported that the successful manufacture of deep-UV ZnGa_2O_4 photodetectors and investigate the effect of annealing temperature on the devices electrical properties [14]. Shen et al. showed that metal-oxide-semiconductor field-effect transistor films are a promising option in power device applications [15]. Among the various growth techniques, RF magnetron sputtering has been the most successful for wide area applications due to its easy controllability, strong adhesion, excellent film thickness uniformity and relatively low cost [16]. Few studies have analyzed the structural properties and luminescence characteristics of ZnGa_2O_4 films in terms of the strong demand for a UV light and laser source [17]. Therefore, UV-transparent and electroconductive ZnGa_2O_4 material is expected to be used in UV-photoelectronic devices. In this study, ZnGa_2O_4 thin films were prepared on sapphire and Si(100) substrates in a RF magnetron sputtering system. The crystalline qualities, surface morphologies, interface reactions, microstructure and optical properties of ZnGa_2O_4 on both the substrates were studied systematically.

Figure 1. Spinel structure of ZnGa_2O_4 .

2. Materials and Methods

ZnGa_2O_4 thin films were deposited on *c*-plane sapphire (thickness: 430 μm , surface roughness: <3 nm) and Si(100) (thickness: 300 μm , surface roughness: <2 nm) substrates by RF magnetron sputtering in a vacuum chamber. The sputter material was ZnGa_2O_4 ceramic target (ZnO and Ga_2O_3 powder, 99.99% purity, mixed in a 30:70 proportion, 2 inches in diameter, and 3 mm in thickness). Prior to deposition, the substrates were first cleaned in acetone and alcohol, followed by ultrasonic cleansing in de-ionized water for 30 min, and blow-dried in nitrogen gas. The working gas was high-purity argon (99.999%), maintained at a constant flow rate (~ 19 sccm). The reactant gas was oxygen, also supplied at a constant flow rate (~ 1 sccm). The sputtering process was performed under a base chamber pressure of approximately 5×10^{-6} torr, with turbo molecular and oil diffusion pumps. The plasma generation was activated by an RF power of 150 W at 13.56 MHz. The target-substrate distance was 15 cm. To ensure uniform film thickness, the substrate holder was rotated at 18 rpm during the deposition process. Substrates heating temperature were varied from 200 to 600 $^{\circ}\text{C}$ in steps of 100 $^{\circ}\text{C}$. Considering the low deposition rate of ZnGa_2O_4 , deposition times duration for 2 h with the thickness of 170 ± 3 nm. The surface morphologies, microstructures and elemental analyses of these coating samples were analyzed by scanning electron microscopy (SEM, S-3000H, Hitachi, Tokyo, Japan) and high-resolution transmission electron microscopy (HRTEM, H-600, Hitachi, Tokyo, Japan). The crystalline quality of the films was investigated by an X-ray diffractometer (XRD, XRD-6000, Shimadzu, Kyoto, Japan) with Cu $K\alpha$ X-ray source ($\lambda = 1.541874$ Å) radiation. The surface chemical compositions and bonding were examined by X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC-PHI, Kanagawa, Japan) using a monochromatic Cu $K\alpha$ X-ray source ($\lambda = 1.541874$ Å) at a passing energy of 20 eV with a spot size of 650 μm . After XPS, the sample surfaces were etched by focused argon-ion sputtering, and their chemical compositions were analyzed in the depth direction (Thermo Scientific K-Alpha). The binding energies were referenced to the adventitious carbon at 284.8 eV. The photoluminescence (PL) spectra were measured at room temperature (RT) under excitation by broadband incoherent UV light with a dominant wavelength of 266 nm.

3. Results and Discussion

Figure 2a,b depict typical XRD scan patterns of the ZnGa_2O_4 thin films deposited on sapphire and Si(100) substrates, respectively. In both the depositions, the substrate temperature was 600 °C. The diffraction peaks of the ZnGa_2O_4 samples confirmed a polycrystalline structure with a structural orientation dependent on the deposition conditions, substrate temperature, and the nature of the substrate. In Figure 2a, the preferred orientations were the cubic ZnGa_2O_4 crystal planes (111), (222) and (511), as indicated by the intense diffraction peaks at 18.54°, 37.4° and 57.72°, respectively, and referring to the reported data (Joint Committee on Powder Diffraction Standards (JCPDS) card file 38-1240) [18]. The diffraction peak about 42° was identified as the (0001) crystal plane of sapphire substrate. On the Si(100) substrate, the two principal diffraction peaks at 31° and 36° correspond to the preferred orientation (220) and the (311) reflections of ZnGa_2O_4 powder, respectively, as shown in Figure 2b. The crystallinity of the ZnGa_2O_4 film was evaluated by the full width at half maximum (FWHM) of the (111) peak. The FWHM values of ZnGa_2O_4 (111) grown on the sapphire and Si(100) substrates were measured as 0.29° and 0.49°, respectively. The lower FWHM on sapphire than on silicon is consistent with larger crystallites formed by aggregation of small grains or grain boundary movement during the film deposition process [19]. The grain sizes of ZnGa_2O_4 grown on the two substrates were calculated by the Debye-Scherrer equation [20]:

$$D = 0.9\lambda/\text{FWHM} \cos \theta \quad (1)$$

where D is the calculated grain size, λ is the X-ray wavelength (0.15418 nm), the FWHM is read from the XRD peaks, and θ is the diffraction angle. The grain sizes of ZnGa_2O_4 (111) deposited on sapphire and Si(100) were thus estimated as 27.43 and 16.43 nm, respectively. The FWHM of XRD diffraction peak is relative to the average grain size in the film [21]. Since the substrate temperature level of 600 °C showed a better crystalline quality as evidenced by XRD analysis, we only focused on the 600 °C samples in the following work (SEM, TEM, and PL). Plane-view SEM images of the ZnGa_2O_4 films grown on sapphire and Si(100) substrates are displayed in Figure 3a,b, respectively. The rod-shaped grains were observed in the both of ZnGa_2O_4 /sapphire and ZnGa_2O_4 /Si(100) samples. The difference can be attributed to the different lattice mismatches between the film and the substrates [22].

Figure 2. XRD patterns of ZnGa_2O_4 films grown on (a) sapphire and (b) Si(100) substrates.

Figure 3. Surface SEM images of ZnGa_2O_4 films on (a) sapphire and (b) Si(100) substrates.

The crystal structure of the ZnGa_2O_4 films was revealed by TEM. Figure 4a is a bright field cross-sectional TEM image of ZnGa_2O_4 on sapphire. On this substrate, the ZnGa_2O_4 film was approximately 171 nm thick. To investigate the detailed microstructure of ZnGa_2O_4 -on-sapphire, regions I and II in Figure 4a were further analyzed by HRTEM. The resulting magnified images are displayed in Figure 4b,c, respectively. In Figure 4b, no polycrystalline or amorphous layer is observed, and the substrate-film interface is clearly visible. The HRTEM image (Figure 4c) reveals d -spacing values of 2.51, 2.41 and 2.11 Å in region I. The crystallographic relationships in the ZnGa_2O_4 sample were derived from the selected area electron diffraction (SAED) patterns acquired in region II. The diffraction rings in the SAED clearly indicate the polycrystalline nature of the ZnGa_2O_4 /sapphire structure (Figure 4d). Both diffraction rings were indexed to orientations of the (111), (222) and (311) planes of the ZnGa_2O_4 phase.

Figure 4. (a) Cross-sectional TEM image of the ZnGa_2O_4 /sapphire sample. HRTEM images focused on (b) region I, (c) region II, and (d) region III.

For comparison, TEM images of the ZnGa_2O_4 film deposited on Si(100) are shown in Figure 5. The ZnGa_2O_4 film was noticeably thicker on Si(100) than on sapphire (Figure 5a), because the growth rate of ZnGa_2O_4 film deposition on amorphous layer is enhanced by amorphous layer with loose structure [23]. HRTEM images of the ZnGa_2O_4 film on Si(100) were acquired in the regions marked I and II in Figure 5a and are displayed in Figure 5b,c, respectively. In Figure 5b, the film-substrate interface (region I) appears as an amorphous layer with an approximate thickness of 2 nm. The native surface-oxide was removed from the Si(100) substrate before the deposition process. The newly produced amorphous silicon oxide layer might be attributable to deposition of the ZnGa_2O_4 film under

the oxygen working pressure of 9×10^{-3} torr [24]. Such an amorphous layer can interfere with the oriented growth, causing randomly oriented poly-crystallites in the ZnGa_2O_4 film. Multiple d -spacing values (2.49, 2.19 and 2.76 Å) were found in region I of this film (Figure 5c). Based on the ringed SAED patterns in region II (Figure 5d), the polycrystalline ZnGa_2O_4 phase was indexed to the orientation of (311), (400) and (220) planes, in good agreement with the XRD result.

Figure 5. (a) Cross-sectional TEM image of the $\text{ZnGa}_2\text{O}_4/\text{Si}(100)$ sample. HRTEM images focused on (b) region I, (c) region II, and (d) region III.

The chemical stoichiometries and surface electronic states of the ZnGa_2O_4 structures were derived from the XPS patterns. Figure 6a,b focus on the Zn 2p and Ga 2p peaks, respectively, in the core-level XPS spectra of the ZnGa_2O_4 films grown on each substrate. The estimated binding energies corresponding to each peak are listed in Table 1. As shown in Figure 6a, the Zn 2p XPS peaks of ZnGa_2O_4 appeared at approximately 1044.79 ± 0.5 eV (Zn 2p_{1/2}) and 1021.93 ± 0.5 eV (Zn 2p_{3/2}) on both substrates. Meanwhile, the Ga 2p XPS peaks of ZnGa_2O_4 were approximately located at 1044.67 ± 0.5 eV (Ga 2p_{1/2}) and 1117.75 ± 0.5 eV (Ga 2p_{3/2}) on both substrates (Figure 6b) [25–27]. These results indicate that the Zn and Ga atoms are bonded with O atoms to form the ZnGa_2O_4 spinel structure, rather than forming metallic clusters [28]. Figure 7 presents a compositional variation analysis of the stoichiometric Zn/Ga ratios in the ZnGa_2O_4 films deposited on sapphire and Si(100) with various the substrates temperature, respectively. The ratio of Zn/Ga decreased with increasing substrate temperature, whereas a ratio of Zn/Ga were estimated to be 0.2 and 0.12 for films deposited on sapphire and Si(100) at 600 °C, respectively. Hsieh et al. have reported that the loss of Zn in the ZnGa_2O_4 phosphor films at raise substrate temperature was observed by RF magnetron sputtering [29]. The different Zn/Ga atomic ratios in the two films can be attributed to Zn deficiency in the film during the high-temperature deposition processes, which depends on the substrate characteristics. As it is well known, the vapor pressure of ZnO is higher than that of Ga_2O_3 [30]. When the substrate temperature increases, the Zn atoms have more opportunities to diffuse from the film under the relatively high vapor pressure. Moreover, the Zn/Ga atomic ratio might respond to the changing scattering angle during the sputtering. Because Zn ions have a lower atomic mass than Ga ions, their path direction is more easily changed by collisions with other particles (gas ions, electrons, and natural and gas atoms) during the film deposition process [31]. Therefore, the ZnO loss in the films can be compensate by using different $\text{Ga}_2\text{O}_3/\text{ZnO}$ ratios of stoichiometric targets [32].

Figure 6. Binding energy spectra of (a) Zn 2p and (b) Ga 2p for the ZnGa_2O_4 thin films deposited on different substrates.

Table 1. Binding energies of Zn $2p_{3/2}$, Zn $2p_{1/2}$, Ga $2p_{3/2}$, and Ga $2p_{1/2}$ in ZnGa_2O_4 thin films deposited on sapphire and Si(100).

Substrate Type	Sapphire	Si(100)
Zn $2p_{1/2}$ Binding energy (eV)	1044.79	1045.20
Zn $2p_{3/2}$ Binding energy (eV)	1021.93	1022.42
Ga $2p_{1/2}$ Binding energy (eV)	1144.67	1145.17
Ga $2p_{3/2}$ Binding energy (eV)	1117.75	1118.37

Figure 7. Variation Zn/Ga ratio vs substrate temperature for the deposited of ZnGa_2O_4 /sapphire and ZnGa_2O_4 /Si(100).

Previously, it was reported that composition variations in the Ga/Zn stoichiometry and/or Ga–O ligand field cause changes in the PL intensity and shifts of the PL peak position [33]. Thus, we investigated the PL emission characteristics of the ZnGa_2O_4 thin films deposited on the two substrates. The RT PL emission spectra of ZnGa_2O_4 deposited on sapphire and Si(100) are displayed in Figure 8a,b, respectively. The PL intensity of the polycrystalline films was much higher on the sapphire substrate than on the Si(100) substrate, possibly because (consistent with the XRD results) ZnGa_2O_4 has a lower lattice mismatch with the oriented sapphire substrate than with the Si(100) substrate. The low defect density and high crystalline quality of the ZnGa_2O_4 films strengthen the oscillators and enhance their optical transitions [34].

Figure 8. RT PL spectra of the ZnGa_2O_4 films deposited on (a) sapphire and (b) Si(100).

The RT PL spectrum of ZnGa_2O_4 on sapphire exhibits a broad-band emission extending from 300 to 560 nm. This band is composed of several overlapping emission bands with peaks located at 340, 417 and 512 nm, which correlate with the results in Figure 8. The emission peak centered at 340 nm in the UV region is associated with excited excess Ga^{3+} ions of the Ga–O group [35], which is confirmed as the ${}^4\text{T}_{2\text{B}} \rightarrow {}^4\text{T}_{2\text{A}}$ transition. Another peak centered at 512 nm originates from the ${}^2\text{E}_\text{A} \rightarrow {}^4\text{T}_{2\text{A}}$ transition. This is because the Ga^{3+} ions are not located at the octahedral sites and remain on the tetrahedral sites in the spinel structure. The energy levels of the individual orbitals in the distorted octahedral structure are shifted by interactions between the p orbitals in the Ga^{3+} ion and the orbitals of the six oxygen ligands. Accordingly, they split into five $3d$ -orbital energy levels. The resultant energy-level transitions from the distorted octahedral structures are labeled ${}^4\text{T}_1$, ${}^4\text{T}_{2\text{A}}$, ${}^4\text{T}_{2\text{B}}$, ${}^2\text{E}_\text{B}$, ${}^2\text{E}_\text{A}$ and ${}^4\text{A}_2$. Transitions among the ${}^4\text{T}_1$, ${}^4\text{T}_{2\text{A}}$, ${}^4\text{T}_{2\text{B}}$, ${}^2\text{E}_\text{B}$ and ${}^2\text{E}_\text{A}$ energy levels are non-radiative processes, and the transition from ${}^2\text{E}_\text{A}$ to ${}^4\text{A}_2$ occurs by radiative photon emission [36]. The main emission bands of $\text{ZnGa}_2\text{O}_4/\text{Si}(100)$, peaking at 512 nm in Figure 8b, are the transition emissions between the lowest excited state ${}^2\text{E}_\text{A}$ and the ground state ${}^4\text{A}_2$. It is concluded that both the growth temperature and substrate type influence the dominant optical transitions. Similar experimental results were found by Assili et al. [37].

4. Conclusions

Polycrystalline ZnGa_2O_4 thin films were deposited on sapphire and Si(100) substrates by RF magnetron sputtering. The crystallites in the deposited ZnGa_2O_4 film showed a stronger orientation on the sapphire substrate than on Si(100), owing to the lower lattice mismatch between ZnGa_2O_4 and sapphire(0001) than between ZnGa_2O_4 and Si(100). The dominant emission peaks of ZnGa_2O_4 film deposited on sapphire, peaking at 340 and 512 nm, can be ascribed to ${}^4\text{T}_{2\text{B}} \rightarrow {}^4\text{T}_{2\text{A}}$ transitions. In contrast, the film deposited on Si(100) substrate emitted only an intrinsic green emission (${}^2\text{E}_\text{A} \rightarrow {}^4\text{T}_{2\text{A}}$ transition) with a peak at 512 nm in the PL spectrum. The different dominant emissions could be attributed to substitution of Ga^{3+} ions at Zn^{2+} sites during the high-temperature deposition process (which distorts the octahedral structure) and the nature of the substrate.

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