Formation of $ZnGa_2O_4$ films by multilayer deposition and subsequent thermal annealing*

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The Ga_2O_3/ZnO multilayer films are deposited on quartz substrates by magnetron sputtering, the thickness values of Ga_2O_3 layers are in a range of 19 nm–2.5 nm and the thickness of ZnO layer is a constant of 1 nm. Formation of spinel $ZnGa_2O_4$ film is achieved via the annealing of the Ga_2O_3/ZnO multilayer film. The influences of original Ga_2O_3 sublayer thickness on the optical and structural properties of Ga_2O_3/ZnO multilayer films and annealed films are studied. With the decrease of the thickness of Ga_2O_3 sublayer, the optical band-gap of Ga_2O_3/ZnO multilayer film decreases, the intensity of UV emission diminishes and the intensity of violet emission increases. The annealed film displays the enlarged optical band gap and the quenched violet emission. UV fluorescence bands are observed from Ga_2O_3 and $ZnGa_2O_4$.

Keywords: multilayer films, optical band-gap, optical transmittance, photoluminescence

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1. Introduction

The $ZnGa_2O_4$ is a binary compound oxide, which consists of ZnO and Ga_2O_3. Like other wide band gap semiconductors, $ZnGa_2O_4$ has potential applications in optoelectronic devices operating at short wavelength.[1] Polycrystalline $ZnGa_2O_4$ thin film can be synthesized by various methods including sputtering,[2] sol–gel,[3] chemical vapor deposition,[4] and pulsed laser deposition.[5] The structural and optical properties of $ZnGa_2O_4$ film depend on the mixture molar ratio of ZnO and Ga_2O_3, thus allowing band-gap engineering of ternary $ZnGa_2O_4$ compound, which is undoubtedly vital for functional devices. Furthermore, the optical properties of multilayer films can be tailored to suit different applications by varying the thickness of each sublayer.[6] In the present work, Ga_2O_3/ZnO multilayer films are prepared at ambient temperature by varying the thickness values of Ga_2O_3 sublayers, and then a solid-state reaction was conducted to synthesize the $ZnGa_2O_4$ films. Single phase $ZnGa_2O_4$ films and $ZnGa_2O_4$ films inlaid with Ga_2O_3 are formed via annealing the Ga_2O_3/ZnO multilayer films with various Ga_2O_3 sublayer thickness values at 800 °C. The effects of Ga_2O_3 sublayer thickness on the structural and optical properties of Ga_2O_3/ZnO multilayer films and $ZnGa_2O_4$ films are investigated.

2. Experimental procedure

Multilayer Ga_2O_3/ZnO thin films are grown on UV transparency quartz (JGS1) substrates by alternate DC reactive magnetron sputtering of high purity Zn (99.99%) target and RF magnetron sputtering of sintered Ga_2O_3 (99.99%) target. After substrate cleaning, sputtering is performed in an ambient mixture of 20-sccm Ar and 6-sccm O_2 at 1.0 Pa. Table 1 shows the sample growth structures of the multilayer films. In detail, the total thickness values of all samples are about 200 nm. The thickness of the individual Ga_2O_3 layer varies from 19.0 nm to 2.5 nm, whereas the thickness of the ZnO layer is kept at 1.0 nm to obtain different Ga/Zn ratios. Single phase $ZnGa_2O_4$ films and $ZnGa_2O_4$ films inlaid with Ga_2O_3 are formed via annealing the Ga_2O_3/ZnO multilayer films with various Ga_2O_3 sublayer thickness values under vacuum condition at 800 °C for 1 h. The crystal orientations, surface morphologies, optical transmittances, and photoluminescences of the samples are characterized using x-ray diffraction (D/MAX 2500V), atomic force microscopy (Veeco DI AFM), double beam spectrophotometer (TU1901), and fluorescence spectrometer (RF-5301), respectively.

Table 1. Sample structural compositions of Ga_2O_3/ZnO multilayer films.

Sample ID	A1	B1	C1	D1	E1
Ga_2O_3 sublayer thickness/nm	200	19	7	5	2.5
ZnO sublayer thickness/nm	0	1	1	1	1
Repetition periods	1	10	25	33	57

3. Results and discussion

Much effort has been paid to the artificial engineering of oxides and semiconductors for functional device applications. In most cases, multilayer films have shown different physical properties from the conventional single layer thin films.[7] The variation of thickness of individual Ga_2O_3 sublayer has a

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significant influence on the optical properties of Ga_2O_3/ZnO multilayer film. The transmission spectra of Ga_2O_3/ZnO multilayer films with different Ga/Zn ratios grown by changing the sublayer Ga_2O_3 thickness values are depicted in Fig. 1. It is shown in the figure that the average optical transmittance of the as-deposited films in the visible region is almost not influenced by the variation of Ga_2O_3 sublayer thickness. All the films show 87% transparency in the visible region. The absorption edge shifts toward longer wavelength as the thickness of the Ga_2O_3 sublayer decreases from 19 nm to 2.5 nm. The transmittance in the UV region decreases successively with the decrease of Ga_2O_3 sublayer thickness. This behavior is due to the fact that ZnO has a lower band gap than Ga_2O_3.[8–10]

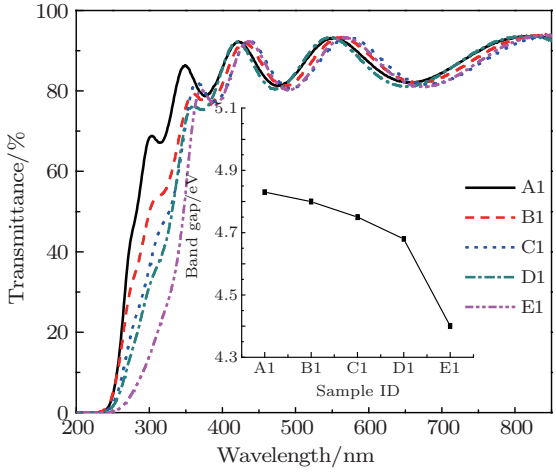


Fig. 1. (color online) Optical transmission spectra of Ga_2O_3/ZnO multilayer films with different Ga_2O_3 sublayer thickness values. The inset shows the corresponding band gap values determined from transmission spectra.

The band gap energy (E_g) is calculated from the α^2 versus E_g plot by assuming that $(\alpha h\nu)^2 = A(h\nu - -E_g)$, where α is the absorption coefficient, $h\nu$ is the photon energy, and A is a constant.[11] The absorption coefficient (α) can be calculated from the relation $T = B\exp(-\alpha d)$, where B is a constant, d is the thickness value of film, and T is the transmittance.[12] The inset in Fig. 1 shows the calculated band-gap energies for different Ga_2O_3 sublayer thickness values. The optical band gap of the as-deposited Ga_2O_3/ZnO multilayer film decreases from 4.8 eV to 4.4 eV with Ga_2O_3 sublayer thickness decreasing from 19 nm to 2.5 nm. The corresponding optical band gap of pure Ga_2O_3 film is 4.83 eV.

The room temperature emission spectra of intrinsic Ga_2O_3 film and as-prepared Ga_2O_3/ZnO multilayer films (under excitation at 250 nm) are shown in Fig. 2. The intrinsic Ga_2O_3 thin film shows a UV emission due to the recombination of a self-trapped exciton.[13] However, for the Ga_2O_3/ZnO multilayer films, there are broad emission ranging from UV region to violet light. It is observed that the intensity of the UV emission, originating from Ga_2O_3, decreases with the decrease of Ga_2O_3 sublayer thickness. Because the band gap value of ZnO is lower than the UV emission spectrum energy,[14,15] according to the quantum tunneling theory, ZnO sublayer will lower the UV spectrum transmittance progressively with the decreasing of Ga_2O_3 interlayer thickness and the increasing of the ZnO sublayer deposition period. Moreover, the violet emission is observed for the Ga_2O_3/ZnO multilayer film. On the one hand, in our experiment, the Zn ions cannot react fully with oxygen ions via DC reactive magnetron sputtering at ambient temperature, the Zn interstitial atoms (Zn_i) are formed inevitably. On the other hand, among the six types of point defects in ZnO lattice: V_o, Zn_i, Zn_O, V_{Zn}, O_i, and O_{Zn}, only the Zn_i is a shallow donor.[16–18] Bylander[19] reported experimentally that the Zn interstitial level is 0.22 eV below the bottom of the conduction band. According to Refs. [20] and [21], the defect level corresponding to Zn_i lies slightly below the bottom of the conduction band. Consequently, we propose that the violet emission is attributed to the transition from Zn_i states to the valence band of ZnO. Additionally, progressive enhancement of the violet emission can be explained by the increase of the ZnO content in Ga_2O_3/ZnO multilayer film because of reducing the Ga_2O_3 sublayer thickness value.

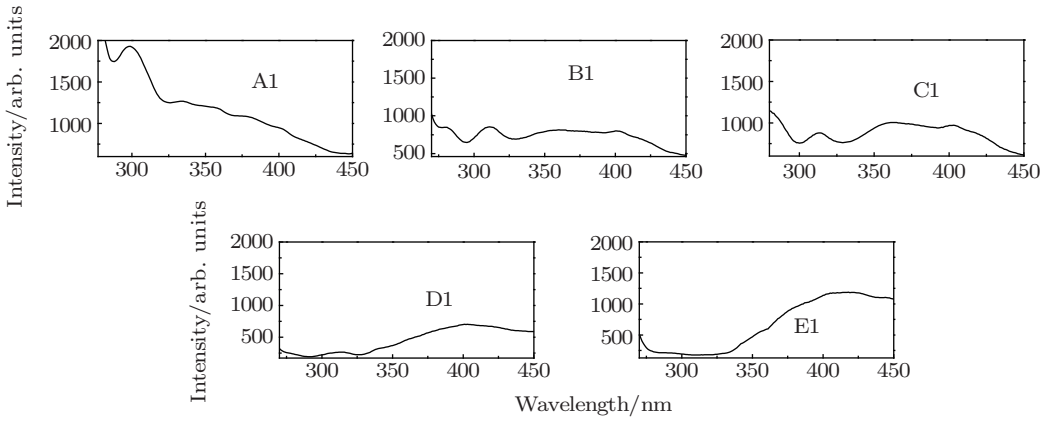


Fig. 2. Photoluminescence spectra of as-deposited Ga_2O_3/ZnO multilayer films with different Ga_2O_3 sublayer thickness values.

The Ga_2O_3/ZnO multilayer films are further annealed for the formation of $ZnGa_2O_4$ film. To obtain the stoichiometric $ZnGa_2O_4$ films, the Ga_2O_3/ZnO multilayer films with various Ga_2O_3 sublayer thickness values are annealed at 800 °C for 1 h. The XRD patterns of the films annealed at 800 °C are shown in Fig. 3. According to the XRD analyses, the spinel $ZnGa_2O_4$ phase is formed in all of the annealed films with various original Ga_2O_3 sublayers, which indicates the successful solid-state reaction between the Ga_2O_3 sublayer and ZnO sublayer. However, the Ga_2O_3 phase still remains in each of the annealed films of B1, C1, and D1. In addition to the (220) peak of $ZnGa_2O_4$ as shown in pattern B1, the Ga_2O_3 (004) and Ga_2O_3 (202) diffraction peaks appear in the XRD pattern of the annealed film with the original 19-nm Ga_2O_3 sublayer. It suggests that the 19-nm Ga_2O_3 sublayer is too thick to form uniform $ZnGa_2O_4$ film, resulting in the Ga_2O_3 film remaining within the annealed Ga_2O_3/ZnO multilayer film. In the case of pattern C1 and pattern D1, $ZnGa_2O_4$ (220), $ZnGa_2O_4$ (311), and Ga_2O_3 (202) diffraction peaks appear respectively, $ZnGa_2O_4$ and Ga_2O_3 structures coexist in the annealed film with the original 7-nm and 5-nm Ga_2O_3 sublayer, due to an inappropriate ZnO/Ga_2O_3 ratio in the Ga_2O_3/ZnO multilayer film. However, only diffraction peaks of the $ZnGa_2O_4$ phase appear in pattern E1, indicating the successful formation of the single-phase $ZnGa_2O_4$ film after annealing the Ga_2O_3/ZnO multilayer film with 2.5-nm Ga_2O_3 sublayer. In comparison with the $ZnGa_2O_4$ power diffraction, Joint Committee on Powder Diffraction Standards Card No. 38-1240, the XRD pattern E1 in Fig. 3 indeed reveals the (311) preferential orientation of the $ZnGa_2O_4$ film.

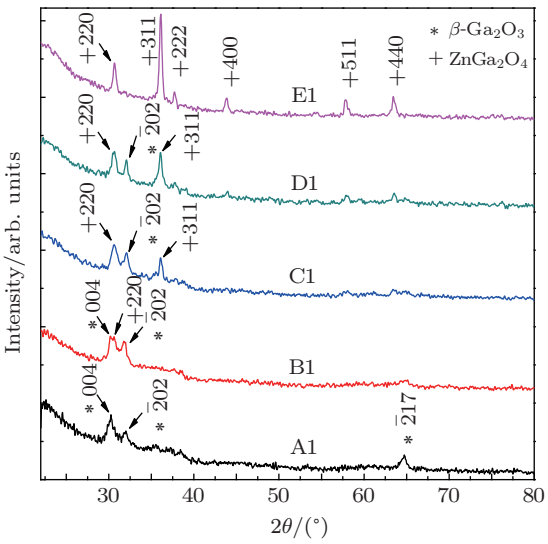


Fig. 3. (color online) XRD patterns of annealed films with various original Ga_2O_3 sublayer thickness values.

Figure 4 shows the surface morphologies measured by AFM over an area of 1 μm×1 μm of the Ga_2O_3/ZnO multilayer films (sample C1) deposited at ambient temperature and annealed at 800 °C, respectively. The film in Fig. 4(a) shows a root mean square (RMS) roughness value of 20 nm and rolling hills on the surface, while the film in Fig. 4(b) shows an RMS value of 18 nm and packed columnar topography. Thermal annealing causes a more compact layer with smooth surface. In addition, although it is impossible to perform a direct measure of the actual grain size from the AFM images, the results do exhibit the apparent crystallization evolution of thin film after annealing. It should relate to the fact that the ZnO sublayer has incorporated into the Ga_2O_3 sublayer to form the spinel $ZnGa_2O_4$ phase at high temperature.

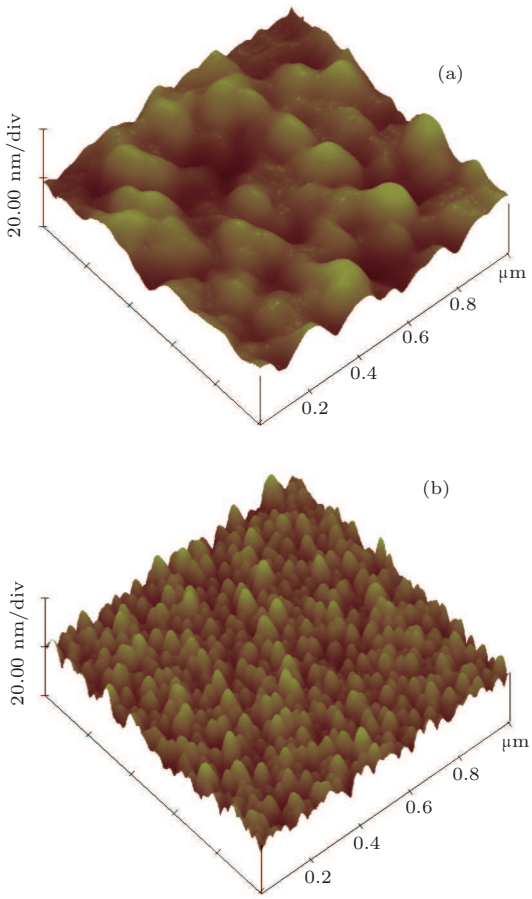


Fig. 4. (color online) Surface morphologies of the (a) as-prepared and (b) post-annealed Ga_2O_3/ZnO multilayer films (sample C1).

The transmittances of post-annealed samples are plotted in Fig. 5. It shows that the deep-UV transmittance of post-annealed Ga_2O_3 film is higher than that of as-deposited Ga_2O_3 film (plotted in Fig. 1), which demonstrates that annealing treatment is beneficial to the decrease of the intrinsic defects. However, unexpectedly, the transmittance of annealed Ga_2O_3/ZnO multilayer film in deep-UV region shows a notable enhancement successively with the decrease of Ga_2O_3 sublayer thickness value. The transmittance of annealed multilayer film is larger than that of annealed Ga_2O_3 film in deep-UV region. Besides, there is no more notable transmittance difference between the post-annealed film and as-prepared

film (plotted in Fig. 1) in the visible region. The inset of Fig. 5 shows the calculated optical band-gaps of annealed films. The optical band gap of annealed film is enlarged continuously from 4.92 eV to 5.09 eV with Ga_2O_3 sublayer thickness decreasing from 19 nm to 2.5 nm. The corresponding optical band gap of annealed Ga_2O_3 film is 4.89 eV. The freak optical phenomenon of annealed film is attributed mainly to the formation of the new compound $ZnGa_2O_4$ phase, which has a wide band gap of 5.2 eV.[22] The annealed films with β-Ga_2O_3 phase and spinel $ZnGa_2O_4$ phase exhibit variable effective optical band-gap with the variation of original Ga_2O_3 sublayer thickness value. It would be possible to design the materials having different concentrations of the two different phases, which will show a continuous tuning of the band gap of ternary alloy.

Figure 6 displays the room temperature photoluminescence spectra of the annealed films. It shows that the violet emission originating from the transition from Zn_i states to the valence band of ZnO is quenched, which implies that the defects Zn_i and ZnO layer are diminished after annealing. This is accordance with the XRD result. The intrinsic Ga_2O_3 thin film shows a UV emission due to the recombination of a self-trapped exciton.[13] In addition to the UV fluorescence band from Ga_2O_3, new UV fluorescence bands are observed. The $ZnGa_2O_4$ is known to be a normal spinel with all the Zn ions in tetrahedral sites and the Ga^{3+} ions in octahedral sites, and Ga^{3+} ions must be not only on the octahedral sites but also on the tetrahedral sites when the zinc gallate is synthesized under the excess gallium oxide environment. Therefore, the new UV bands are considered to originate from the self-activated optical centers due to the tetrahedral Ga–O groups in the spinel lattice.[23] The intensity of the UV emission band does not lower as the original Ga_2O_3 sublayer thickness value decreases. It demonstrates that the ZnO interlayer has been dissolved and ZnO has reacted with Ga_2O_3 to form the spinel $ZnGa_2O_4$ compound in the annealing process.

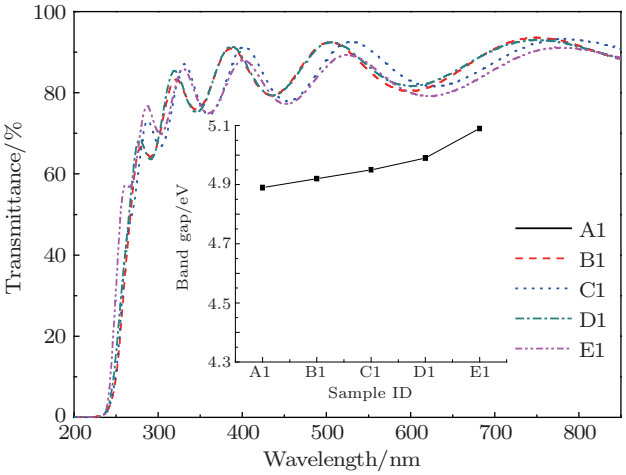


Fig. 5. (color online) Optical transmission spectra of annealed films with different original Ga_2O_3 sublayer thickness values. The inset shows the corresponding optical band-gap values.

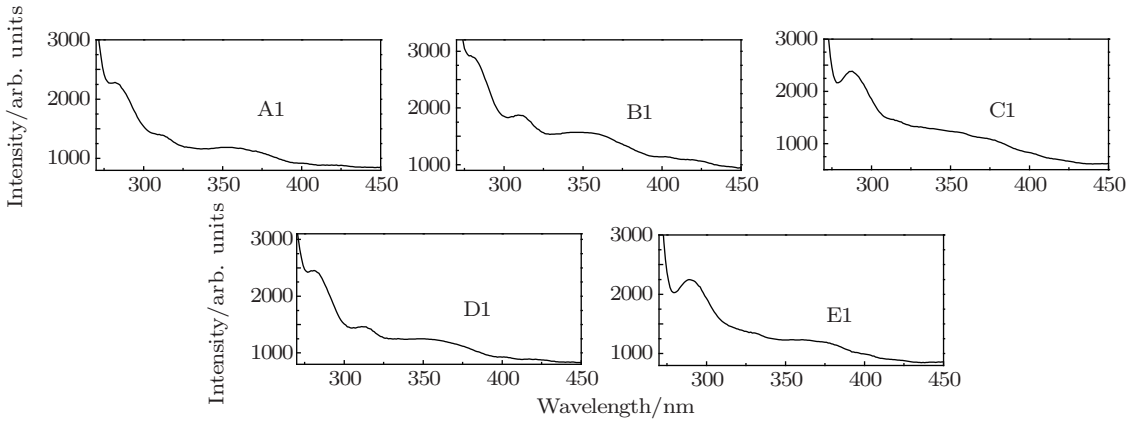


Fig. 6. Photoluminescence spectra of annealed films with different original Ga_2O_3 sublayer thickness values.

4. Conclusions

The Ga_2O_3/ZnO multilayer films are deposited on quartz substrates at ambient temperature, the absorption edge shifts toward longer wavelength and optical band-gap decreases with the decreasing of Ga_2O_3 sublayer thickness. Ga_2O_3/ZnO multilayer film shows broad emission band ranging from UV region to violet light, the intensity of the UV emission is reduced and the intensity of the violet emission is enhanced with the decreasing of Ga_2O_3 sublayer thickness value. The $ZnGa_2O_4$ compound is formed via annealing the Ga_2O_3/ZnO multilayer films. XRD results of annealed film display β-Ga_2O_3 phase and spinel $ZnGa_2O_4$ phase. The optical band gap of annealed film is enlarged, and the transmittance of annealed film in deep-UV region is enhanced with the decreasing of original Ga_2O_3 sublayer thickness value. The annealed film shows a broad UV emission band originating from the Ga_2O_3

recombination of a self-trapped exciton and the $ZnGa_2O_4$ self-activated optical centers due to the tetrahedral Ga–O groups in the spine1 lattice.

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