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Optical Properties of *N*-doped *β*-Ga_2O_3 Films Deposited by RF Magnetron Sputtering

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Abstract: The *N*-doped *β*-Ga_2O_3 films were grown on Si and quartz substrates by RF magnetron sputtering in different ammonia partial pressure ratios (from 0% to 30%). The influence of ammonia partial pressure ratio and annealing treatment on the optical and structural properties were studied. The microstructure, optical transmittance, optical absorption and optical energy gap of the N-doped *β*-Ga_2O_3 films were significantly changed with the increasing of ammonia partial pressure. The green, blue and ultraviolet emission bands were observed and discussed.

Key words: RF magnetron sputtering; Transparent conductive oxide; Optical band gap; Post-annealed; *N*-doped *β*-Ga_2O_3

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0 Introduction

β-Ga_2O_3 is a transparent conductive oxide with the band gap E_g=4.9 eV [1]. Its unique ultraviolet (UV) transparency and thermal stability at high temperature attracted extensive attention for new UV optoelectronics[2]. It has been proposed as an alternative substrate to sapphire and SiC for the growth of GaN. The expitaxial growth of GaN on nitridized *β*-Ga_2O_3 substrates has been demonstrated[3]. Impurity doping is effective to improve the electrical and optical properties of *β*-Ga_2O_3[4]. For example, Masahiro Orita[5] used the floating zone method to grow Sn-doped *β*-Ga_2O_3 single crystals with (100) plane whose electrical conductivity is as high as 8.2 Scm^{-1}. Kiyoshi Shimamura [6] reported that the Si-doping can help to improve the photoluminescence of the *β*-Ga_2O_3. The Si-doped β-Ga_2O_3 and Sn-doped *β*-Ga_2O_3 behave as a n-type semiconductor because of donor impurity and oxygen deficiency [7]. Therefore, for development of short wavelength optoelectronic device based on *β*-Ga_2O_3, it is urgently need to obtain p-type *β*-Ga_2O_3 films. *N* is a potential P-type dopant for *β*-Ga_2O_3, because it is group V elements. In this study, ammonia was used as the N-doping source, which would result in hydrogen in the growth environment. It is theoretically suggested that the nitrogen substituting oxygen (N_O^-) and H^+ charged defects will combine to form the neutral N_O-H defect complexes in *β*-Ga_2O_3. The formation of N_O-H complexes could be expected to enhance the N solubility and suppress the interstitials atoms′ compensating [8]. When the film is annealed at appropriate temperatures, N_O-H complexes may be dissociated and the hydrogen is out of the film. By this way, the N solubility is improved. In this paper, the microstructure, surface morphology, transmittance and optical energy gap of N-doped *β*-Ga_2O_3 thin films are studied.

1 Experiment

The *β*-Ga_2O_3 films were grown on Si (111) and UV transparency quartz (JGS1) substrates by RF magnetron sputtering. The used target was 5N-sintered *β*-Ga_2O_3. The sputtering pressure was set to 1 Pa and the ammonia partial pressure ratios were varied from 0 to 30%. The thickness of the films is about 500 nm. The substrate temperature was fixed at room temperature (RT) during the deposition. The samples were post-annealed at 700 ℃ for 1h in nitrogen (99.99%) ambient. The crystal orientation, surface morphology, X-ray

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photo electron spectroscopy, luminescence spectrum, transmittance and absorption spectrum of the samples were characterized using X-ray diffraction (D/MAX2500V), scanning electron microscopy (JSM-5160V), X-ray photo electron spectroscopy (XSAM800), fluorescence spectrometer (RF-5301) and spectrometer (UV2550).

2 Results and discussion

2.1 Structural properties

The crystalline quality of N-doped β-Ga_2O_3 films deposited on the Si substrate is evaluated by XRD measurement shown in Fig. 1.

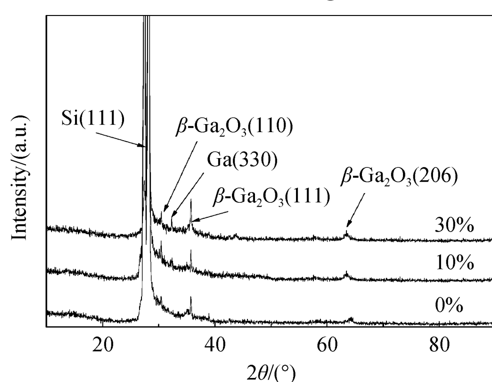
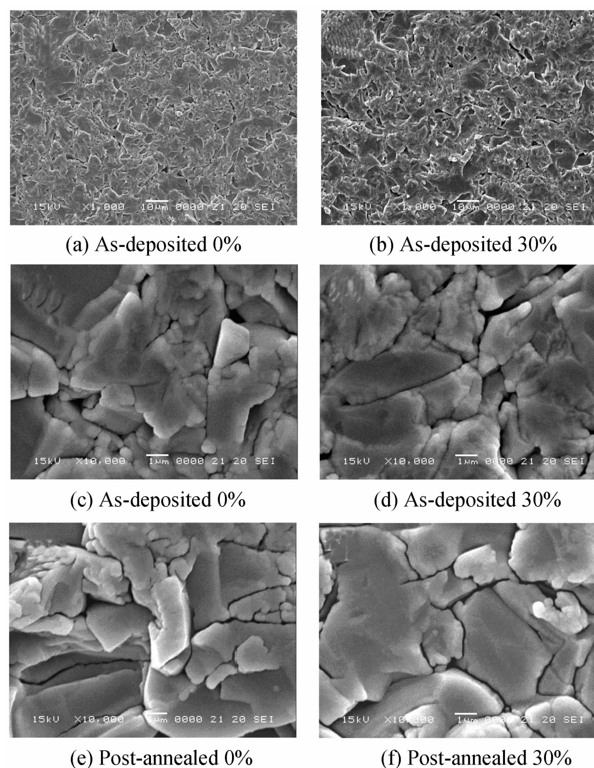


Fig. 1 XRD patterns of β-Ga_2O_3 films deposited on Si substrate with different ammonia partial pressure ratios and post-annealed in N_2 ambient at 700 ℃ for 1 h

After annealing, three β-Ga_2O_3 peaks of $(\bar{1}10)$, (111) and (206) plane appeare for all samples. The intensity of the peaks increases with increase of the ammonia partial pressure ratios. Diffraction peaks from other phases are not observed. As the ammonia partial pressure ratios increasing, the diffraction peak of Ga (330) appears [9]. We speculate that this is due to the chemical reduction of adsorption and interstitial hydrogen atoms. It indicates that the oxygen vacancies (V_O) increase with the ammonia partial pressure ratios. The (111) peak of the β-Ga_2O_3 slightly moves to the smaller degree with the increasing of the ammonia partial pressure ratios, which results from the N impurities in β-Ga_2O_3 films.

Fig. 2 shows the SEM images of β-Ga_2O_3 films deposited in 0 and 30% ammonia partial pressure ratios. Fig. 2(a) and (b) show that some projections are formed on the surface when sputtering is performed in 30% ammonia partial pressure. The projections disappear and the surface flatness is improved by reducing the sputtering ammonia partial pressure to 0. By comparing the high magnified SEM images (c)~(f), we can find that the microstructure of N-doped β-Ga_2O_3 films tends to change into the grain-like structures after thermal annealing process at 700 ℃ for 1 h in N_2 ambient.



(a) As-deposited 0% (b) As-deposited 30%
(c) As-deposited 0% (d) As-deposited 30%
(e) Post-annealed 0% (f) Post-annealed 30%

Fig. 2 SEM photographs of β-Ga_2O_3 films

The XRD patterns also show that the grain structure appears in β-Ga_2O_3 films after post annealing process. Furthermore, the size of the grain becomes larger with the ammonia partial pressure increasing. The surface of the post-annealed N-doped β-Ga_2O_3 films is rougher than the as-deposited one.

Fig. 3 shows the N 1s region of XPS spectra of the N-doped β-Ga_2O_3 films post-annealed in N_2 ambient at 700 ℃ for 1h. The intensity of the N

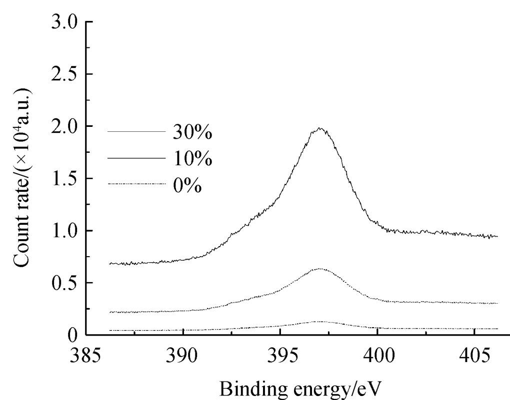


Fig. 3 N 1 s region of XPS spectra of N-doped β-Ga_2O_3 films

1 s peaks at 396.9 eV is observed to increase significantly with the ammonia partial pressure ratios. The peak is assigned to nitrogen atoms bound to Ga in β-Ga_2O_3. Notice that there is a weak peak at 396.9 eV for the sample prepared in 0 ammonia partial pressure ratios, which indicates that N was doped into the β-Ga_2O_3 films by post-annealed in N_2 ambient.

2.2 Optical properties

The optical band gaps of β-Ga_2O_3 films are estimated by extrapolating the linear portion of the square of absorption coefficient against photon energy using the equation.

$$(\alpha h\nu)^2 = B(h\nu - E_g) \tag{1}$$

Here B is a constant. Fig. 4(a) shows the $(\alpha h\nu)^2$ versus photon energy plots of the β-Ga_2O_3 films as-deposited. We can find that the β-Ga_2O_3 film deposited at 0 NH_3 ammonia partial pressure ratio has the smallest band gap of 4.86 eV. This value is in agreement with the reported values 4.9 eV for intrinsic β-Ga_2O_3[10]. The optical band gap of the β-Ga_2O_3 increases with the increasing of ammonia partial pressure ratios. The energy gap is up to 4.97 eV when the ammonia partial pressure is up to 30%. The increment of the band gap is 0.11 eV, which is caused by interval hydrogen and nitrogen in the β-Ga_2O_3. The interval hydrogen and nitrogen act as a donor and compensate the acceptor behavior of the substitute nitrogen[11]. These defects are increased by increasing of ammonia partial pressure ratios, which lead to increase of the donor electron in the β-Ga_2O_3 films. The increase of the optical band gap was explained by BM effect[12] due to the increased carrier concentration.

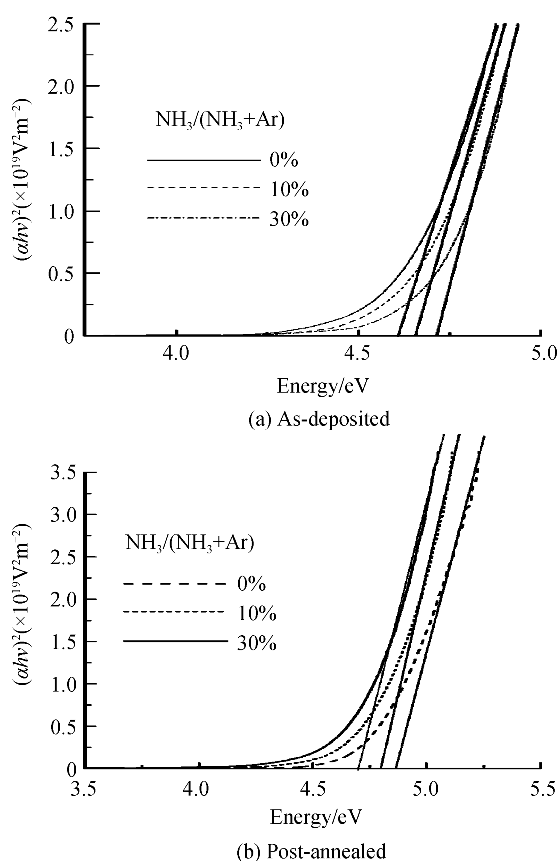
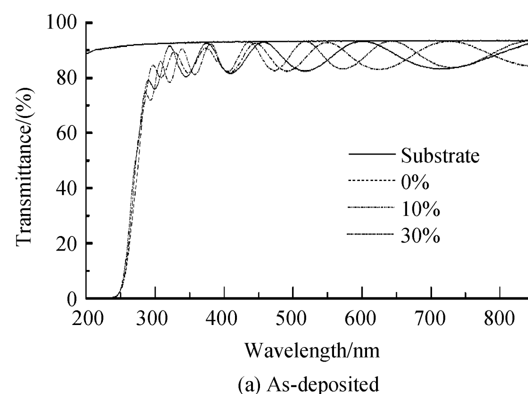


Fig. 4 $(\alpha h\nu)^2$ versus photon energy plots of the β-Ga_2O_3 films as-deposited and post-annealed in N_2 atmosphere at 700℃ for 1 h

Fig. 4(b) shows $(\alpha h\nu)^2$ versus photon energy plots of the β-Ga_2O_3 films post-annealed in nitrogen ambient. A dramatic change occurs after the annealing treatment, the optical band gap of the N-doped β-Ga_2O_3 shrinks with the increasing of the ammonia partial pressure. The largest and the smallest optical band gaps are 4.87 eV and 4.7 eV for 0 and 30% ammonia partial pressure ratios. XRD results show that the appearance of the Ga (330) due to the chemical reduction of adsorption and interstitial hydrogen atoms. It indicates that the V_O and N_O increase with the ammonia partial pressure ratios after annealing. So the shrinkage of the optical band gap might result from these defect related impurity levels and the crystal structure change.

The transmittance spectra of the as-deposited films are illustrated in Fig. 5(a). It shows that the average optical transmittance of the as-deposited films in visible region is almost not influenced by ammonia partial pressure ratio. All the films have transmittance more than 85% (including substrate) in the visible region and have an excellent transmittance more than 70% in the UV region (285~400 nm). A sharp absorption edge is observed around 270 nm. Fig. 5(b) shows transmittance spectra of the films post-annealed at 700 ℃ for 1 h in pure nitrogen ambient. The transmittance obviously deteriorates in the whole optical region and decreases with the increasing of ammonia partial pressure ratios.



(a) As-deposited

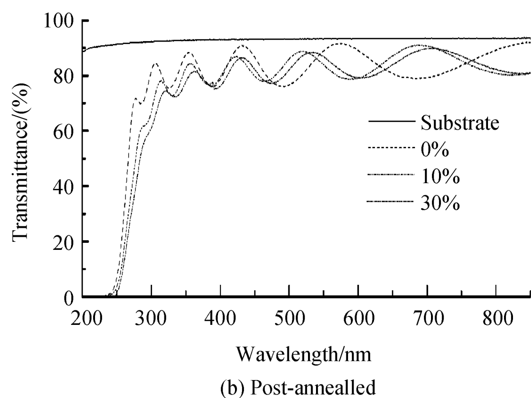
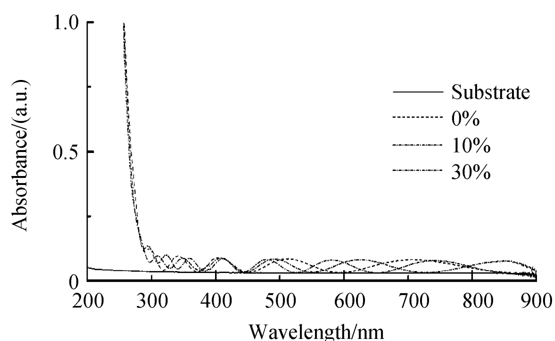


Fig. 5 Transmittance spectra of the as-deposited and post-annealed β-Ga_2O_3 films

Fig. 6 shows that the average absorption of the as-deposited β-Ga_2O_3 films is very low and don't show obvious difference in the visible region. All the films have a sharp absorption edge in the deep ultraviolet (DUV) region. However, the average absorption increases and becomes dispersion after annealing in the N_2 ambient. It is noteworthy that the optical absorption of the post-annealed films increases with the increasing of ammonia partial pressure ratios in the DUV region. Near-edge absorption appears in the post-annealed films. It indicates that the N atoms are dissociated from N_O-H complexes and serve as effective acceptors in the annealed films. Thus, the origin of this absorption is related to the N acceptor states in the



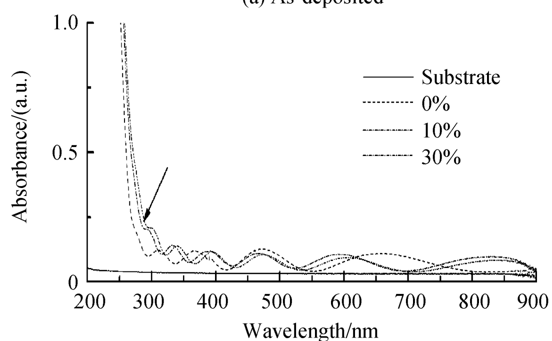


Fig. 6 Optical absorption spectra of the as-deposited and post-annealed β-Ga_2O_3 films prepared in the different ammonia partial pressure ratios

band gap of β-Ga_2O_3. The near-edge absorption indicates transitions from singly ionized N acceptors to shallow donors and the conduction band or from singly ionized N acceptors to deep level donors such as V_O or intrinsic defects. It implies that the activated N acceptors are present in the post-annealed N-doped films. The absence of near-edge absorption in the as-deposited films suggests that the N impurities are inactive, which results from the hydrogen passivation effect. The observations presented here further confirm our aforementioned analyses. Therefore, we conclude that the transmittance deterioration of the post-annealed N-doped β-Ga_2O_3 films is mainly due to the increase of the impurity band absorption.

2.3 Photoluminescence spectra

Fig. 7 shows the room temperature excitation spectra. The lower energy excitation band peaks at about 275 ~ 283 nm and corresponds to the absorption edge. The emission spectrum under UV excitation is in full agreement with the excitation spectra. Fig. 8 shows the Photoluminescence spectra of the β-Ga_2O_3 films prepared in different ammonia partial pressure ratios and post-annealed at 700 ℃ for 1h in N_2 ambient under 280 nm (4.4 eV)

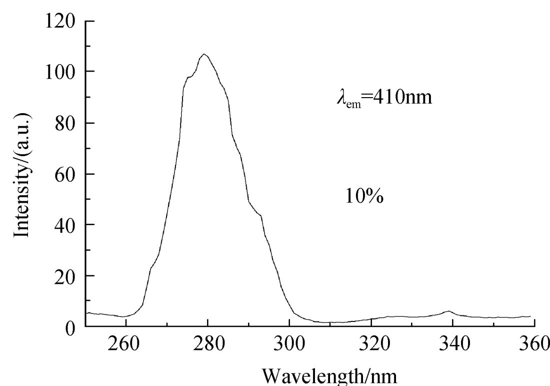


Fig. 7 Room temperature excitation spectra of the post-annealed N-doped β-Ga_2O_3 films

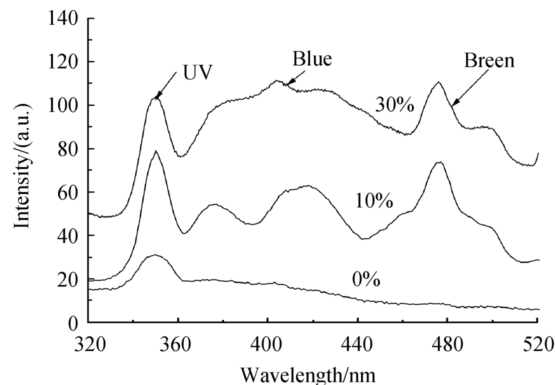


Fig. 8 Photoluminescence spectra of the β-Ga_2O_3 films prepared in different ammonia partial pressure ratios and post-annealed at 700 ℃ for 1 h in N_2 ambient

excitation at room temperature. One broad blue emission band centred at 410 nm (3.02 eV) is observed. According Fig. 7 and Fig. 8 we can find that an important Stokes shift of about 1.38 eV can be noticed, which indicates a strong electron - phonon coupling and means that these combining charges are strongly localized[13].

Moreover, the excitation of the blue luminescence with photon energy slightly below the band gap, which indicates that acceptor defects with ground state close to the valence band also participate in the blue emission. According to these models, the blue emission would originate from the recombination of an electron on a donor and a hole on an acceptor. After excitation of the acceptor, a hole on the acceptor and an electron on a donor are created. An electron in a donor band is captured via a tunnel transfer by a hole on the gallium - oxygen vacancy pair $(V_O, V_{Ga})'$ or nitrogen substituting oxygen (N_O') to form a trapped exciton, which emitting the blue photon. In our samples, the N_O' is increased with the ammonia partial pressure ratios. So the blue luminescence is largely enhanced when the $N_O'{}'$ concentration increases with ammonia partial pressure ratios. The electrons on donors are thermally detrapped to the conduction band and holes on acceptors are thermally detrapped to the valence band, they migrate through the conduction band or valence band, and recombine via a self-trapped exciton with emitting a UV photon. The broad green emission centred at 476 nm (2.48 eV) is generated by the radioactive recombination of photogenerated hole with the electron in ionized V_O[14].

3 Conclusion

The crystalline of the post-annealed β-Ga_2O_3 films is largely improved and the grain size becomes larger with increasing of ammonia partial pressure ratios. The surface of annealed *N*-doped β-Ga_2O_3 films is rougher than the as-deposited one. The optical band gap of the as-deposited *N*-doped β-Ga_2O_3 films increases with increasing of ammonia partial pressure ratios. However, after annealing, the optical band gap and transmittance decrease with increasing of ammonia partial pressure ratios. Three characteristic luminescence bands appear in UV (3.3 eV), blue (2.93 eV) and green (2.48 eV) spectral regions. The UV and blue emission are enhanced with increasing of ammonia partial pressure ratios.

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射频磁控溅射法制备N掺杂β-Ga_2O_3薄膜的光学特性

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摘 要:在不同氨分压比(0～30%)下,用射频磁控溅射法在玻璃和硅衬底上制备了*N*掺杂β-Ga_2O_3薄膜.研究了氨分压比和退火对薄膜光学和结构特性的影响.*N*掺杂β-Ga_2O_3薄膜的微结构、光学透过率、光学吸收和光学带隙随着氨分压比的增加发生了显著变化.观察到了绿光、蓝光和紫外发光带,并对每个发光带进行了讨论.

关键词:射频磁控溅射;透明导电氧化物;光学带隙 ;退火;*N*掺杂β-Ga_2O_3