Effect of annealing atmosphere on the structural and optical properties of the Nb-doped β-Ga_2O_3 films

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The Nb-doped β-Ga_2O_3 (β-Ga_2O_3:Nb) thin films have been deposited on the Si and quartz substrates by radio-frequency magnetron technique in argon ambient. The effects of annealing atmosphere on the structural and optical properties of β-Ga_2O_3:Nb thin films have been investigated. The crystallinity of β-Ga_2O_3:Nb film is improved obviously after annealing. An increase in surface roughness is observed on annealed films. The bandgap from 5.19 to 5.26 eV is obtained after annealing in different atmosphere, which is larger than the 5.09 eV before annealing. Moreover, the red-shift of photoluminescence emission peak is observed after annealing, and the annealing atmosphere has an influence on the peak intensity.

1. Introduction: Thin-film transparent conducting oxides β-Ga_2O_3, a wide bandgap semiconductor, show superior performance in ultraviolet (UV) photodetector [1, 2], gas sensors [3] and metal–semiconductor field-effect transistor [4]. Up to present, a large number of methods have been employed to prepare the β-Ga_2O_3 films, such as radio-frequency (RF) magnetron sputtering [5–7], pulsed laser deposition [8–10], molecular beam epitaxy [11–13], metal-organic chemical vapour deposition [14–16], low pressure chemical vapour deposition [17] and so on. RF magnetron sputtering has a wide applicability in laboratory researches because of the high deposition rates and the temperature of substrate has no relevant change during the sputtering. Additionally, this method has several other advantages of producing uniform, pure and cohesive films.

Doping is usually used to control the optical and electrical properties of Ga_2O_3 materials, and a large number of researches on doping have been reported. Recent studies indicate that the memory capacitor with lightly Nb-doped Ga_2O_3 shows better charge-trapping characteristics [18]. Nb-doped Ga_2O_3 has immensely applied prospects in high-performance memory applications. So, it is necessary to explore the appropriate fabrication conditions of β-Ga_2O_3:Nb thin films. In recent years, many works have done to investigate the effects of annealing on the structure and properties of Ga_2O_3 materials. In 2005, Hyoun Woo Kim prepared gallium oxide nanowires and investigated the effect of thermal annealing on the structural and optical properties [19]. In 2013, Sun Rui reported that the annealing atmosphere has an influence on the structure, morphology and transmittance of N-incorporated Ga_2O_3 films [20]. In 2016, Ma Jin reported the effect of annealing on the properties of Ga_2O_3:Mg films [21]. All the researches indicate that the annealing treatment has an important influence on the film quality.

In this Letter, Ga_2O_3:Nb thin films that prepared by RF magnetron sputtering method are annealed in different atmosphere, and the effects of annealing atmosphere on the structural and optical properties of Ga_2O_3:Nb thin films are investigated. The results indicate that the β-Ga_2O_3:Nb thin film shows excellent crystallinity, smooth surface and large bandgap after annealing in N_2.

2. Experiment: The β-Ga_2O_3:Nb thin films were deposited on the Si and quartz glass substrates by RF magnetron sputtering technique. All the substrates were cleaned in toluene, acetone, ethanol and deionised water ultrasonically for 15 min. Then, the substrates were dried with flowing nitrogen and placed in the sputtering chamber. A Ga_2O_3 disk embedded by a Nb_2O_5 tabletting was used as the target. Before each deposition, the Nb:Ga_2O_3 target was pre-sputtered for 10 min to remove the contaminants on their surface. The RF power applied to the target was set at ∼80 W. The base pressure in the sputtering chamber was 1×10^{-3} Pa; then, high purity argon gas (99.999%) was introduced into the chamber through a gas flow controller and the films were deposited at a working pressure of 0.6 Pa for 40 min. Subsequently, the β-Ga_2O_3:Nb thin films were subjected to annealing at 1000°C for 1 h in flowing N_2, O_2 and Ar, respectively.

The doping levels of Nb in samples were measured by energy-dispersive X-ray spectroscopy (EDS). The crystalline structure of the films was examined by X-ray diffraction (XRD) using Purkinje D3 diffractometer. Ultraviolet–visible absorption spectrums were carried out using a Shimadzu UV-3600 spectrophotometer. The surface morphology was characterised using scanning electron microscope (Supra 55). The root-mean-square (RMS) values were measured by a DI MULTIMODE atomic force microscopy (AFM). The photoluminescence (PL) spectra were measured at room temperature with an Edinburgh FLSP920 spectrophotometer. The excitation light was the monochromatic light from a xenon short arc lamp with a wavelength of $\lambda = 270$ nm.

3. Results and discussion: The elemental composition and concentration of the as-grown β-Ga_2O_3:Nb thin film are measured by EDS. As shown in Table 1, elements of oxygen, gallium, silicon and niobium are observed. It indicates that the Ga_2O_3:Nb thin films were successfully prepared by RF magnetron sputtering. The concentration of niobium element is 1.72 wt% in the β-Ga_2O_3:Nb thin film.

In order to investigate the influences of annealing atmosphere on the crystal structure and crystallinity of Ga_2O_3:Nb thin films, the XRD analysis on the as-grown and annealed samples was performed. As shown in Fig. 1, the diffraction peaks of (201), (110), (−111) and (710), which are all indexed to the β-Ga_2O_3, are observed in all the as-grown and annealed films. The crystal structure keeps stable after annealing in different atmosphere, but the crystallinity was greatly enhanced, especially annealing in N_2 atmosphere. The migration ability of the atoms is highly enhanced at high temperature, and the Ga, O and Nb atoms would incorporate on the lattice sites during the annealing treatments, contributing to the high crystallinity quality of β-Ga_2O_3:Nb films. The (−111) diffraction peak of β-Ga_2O_3:Nb thin film that annealed in N_2 is slightly stronger than those of others, indicating that trace amounts of

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Table 1 Elemental composition and concentration of the as-grown β-Ga_2O_3:Nb thin film

Element	wt%	wt% Sigma	Standard sample label
O	26.67	1.06	SiO_2
Ga	71.61	1.24	GaP
Nb	1.72	0.96	Nb
total	100.00	—	—

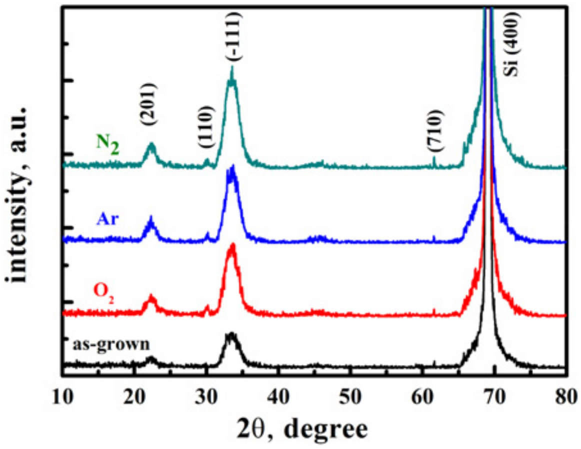

Fig. 1 *XRD spectra of the β-Ga_2O_3:Nb thin films after annealing in different atmosphere*

N atoms may be incorporated on the lattice sites. As reported by Liu *et al.* [22], Sun *et al.* [5] and Kim *et al.* [23], the incorporating of N atoms has an active effect on the crystalline quality of β-Ga_2O_3:Nb films. Therefore, the observed slightly stronger diffraction peak in film annealed in N_2 indicates that annealing in N_2 and incorporating N atoms can improve the crystalline quality of films.

Fig. 2 displays the top view scanning electron microscopy (SEM) images of as-grown and annealed β-Ga_2O_3:Nb thin films. Fig. 2*a* shows the SEM images of the as-grown film. The surface of as-grown film is continuous and flat. Figs. 2*b–d* show the SEM images of annealed films that were annealed in Ar, O_2 and N_2, respectively. After annealing at 1000°C, the surface morphology of β-Ga_2O_3:Nb films greatly changed. Vally-ridge like surface morphology formed in the O_2 and Ar annealing atmosphere.

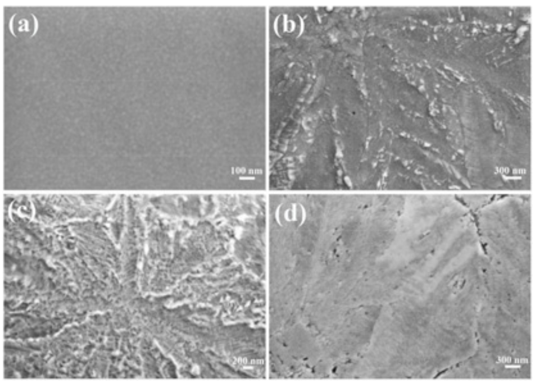

Fig. 2 *SEM images of the β-Ga_2O_3:Nb thin films annealed in various atmosphere*
a As-grown
b Ar
c O_2
d N_2

While the surface of the β-Ga_2O_3:Nb thin film annealed in N_2 is relatively flat except some hole-likes defects. Besides, the RMS for as-grown and annealed β-Ga_2O_3:Nb thin films analysed by AFM with a scanning area of 4 μm × 4 μm is shown in Fig. 3. The RMS for the as-grown β-Ga_2O_3:Nb film is close to 1.149 nm. While the RMS for the β-Ga_2O_3:Nb films that annealed in N_2, O_2 and Ar are 2.725, 6.75 and 3.789 nm, respectively. It indicates that the RMS for the β-Ga_2O_3:Nb films becomes larger after annealing treatments, especially annealing in O_2 atmosphere. This may be due to the annealing gas that can diffuse into the β-Ga_2O_3:Nb films, and because the absorption of O_2 is relatively more than the absorption of N_2 and Ar.

The optical transmittance spectra of the as-grown and annealed β-Ga_2O_3:Nb thin films deposited on the quartz substrates in the wavelength range of 200–800 nm are shown in Fig. 4. The average transmittance of all the films in visible range are over 70%. The spectrum of the as-grown shows a sharp intrinsic absorption edge at ~250 nm. After annealed in N_2, O_2 and Ar, the absorption edge of β-Ga_2O_3:Nb films display a clear blue-shift. For the direct bandgap transition semiconductors, the absorption coefficient α and optical bandgap (E_g) are related by the equation

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (1)$$

where A is a constant, ν is the frequency of the incident photon and h is the Planck's constant. Then the relation curve of $(\alpha h\nu)^2$ and $h\nu$

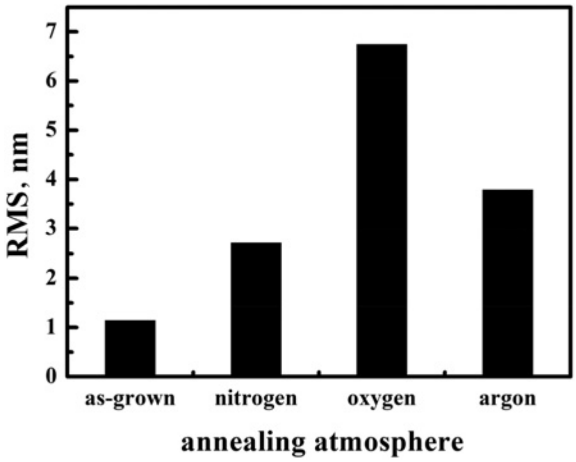

Fig. 3 *RMS versus the annealing atmosphere*

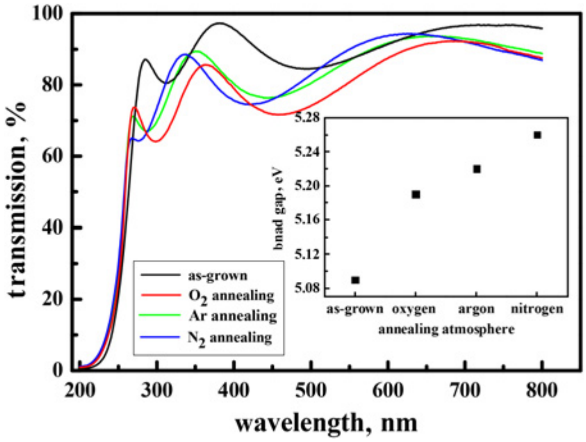

Fig. 4 *Transmittance spectra of the β-Ga_2O_3:Nb films as a function of the annealing atmosphere. The inset figure shows the optical bandgap of β-Ga_2O_3:Nb films under different annealing atmosphere*

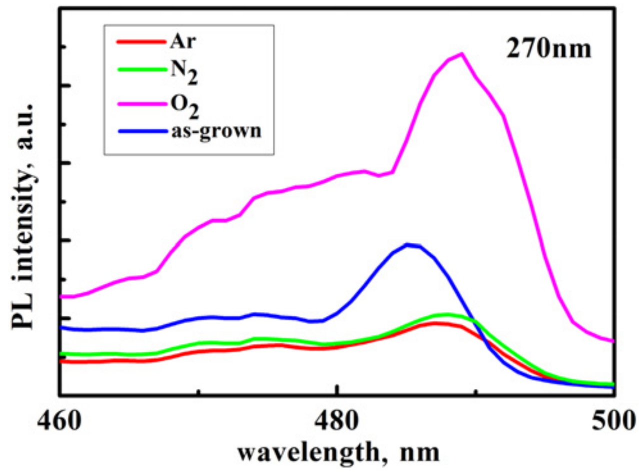

Fig. 5 *Room temperature PL spectra of as-grown and annealed β-Ga_2O_3: Nb films under different annealing atmosphere*

can be plotted, and E_g can be estimated by extrapolating the straight-line portion of this plot to the energy axis. The bandgap E_g for the as-grown film is close to 5.09 eV. The bandgap E_g shown in the insets of Fig. 4, annealed in O_2, Ar and N_2, was 5.19, 5.22 and 5.26 eV, respectively. The wider the bandgap is, the greater the advantages β-Ga_2O_3:Nb film possesses in solar-blind photo-detectors area. Considered from this angle, annealed in N_2 atmosphere is the best choice for β-Ga_2O_3:Nb thin films. The effect on annealing on the bandgap of Ga_2O_3 film has been reported by other researchers. The bandgap of the Ga_2O_3:Mg film decreases after annealing [21], while the N-incorporated Ga_2O_3 film increases [20] which is similar to our results.

It is speculated the doped substance may have an crucial effect on the bandgap of the Ga_2O_3 film after annealing, but how the annealing atmosphere influences the film is still unknown, and further researches are required.

Fig. 5 shows the PL spectra of the as-grown and annealed β-Ga_2O_3:Nb thin films deposited on the Si substrates in the wavelength range of 460–500 nm, which are recorded at room temperature (300 K) under excitation of a beam of light of 270 nm. The peak location and peak intensity are distinct difference between the PL spectra of the four samples. The emission from as-grown film is band located in blue spectral region, and the maximum of the band is located at 485 nm. While the maximum of the band that emission from the annealed films is located at 488 nm, presenting an obvious red-shift. It is also worth noting that the PL spectrum of β-Ga_2O_3:Nb thin film annealed in O_2 atmosphere possesses the highest peak intensity. It reveals that the annealing temperature is related to the peak location, and the annealing atmosphere has an influence on the peak intensity. Since the gallium vacancies enhance the green emission [24], we speculate that annealing in O_2 would increase the gallium vacancies of the β-Ga_2O_3:Nb thin film, while annealing in N_2 or Ar would decrease the gallium vacancies of the β-Ga_2O_3:Nb thin film. Besides, the red-shift may be attributed to the synergistic effect of various defects, oxygen vacancies and gallium–oxygen vacancy pairs [25], but the change of the β-Ga_2O_3:Nb thin films during the anneal process is still unknown. Further researches are required to investigate what factors contribute to the red-shift of PL spectra.

4. Conclusions: The β-Ga_2O_3:Nb thin films are prepared by RF magnetron sputtering method, and the effect of annealing atmosphere on the structural and optical properties of β-Ga_2O_3: Nb thin films are investigated. The annealing treatment improves the crystallinity, especially in N_2. After annealing at 1000°C, the surface morphology of β-Ga_2O_3:Nb films greatly changed, and an increase in surface roughness is observed on annealed films. The bandgap of the β-Ga_2O_3:Nb film increases after annealing, and the film annealed in N_2 possesses the largest bandgap. The annealing temperature is related to the location of PL emission peak, and the annealing atmosphere has an influence on the peak intensity.

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