Structural and optical properties of Zn_3N_2 films prepared by magnetron sputtering in NH_3–Ar mixture gases*

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Abstract: Zinc nitride films were prepared by RF magnetron sputtering a metallic zinc target in NH_3–Ar mixture gases on glass substrate at room temperature. The effects of NH_3 ratio on the structural and optical properties of the films were examined. X-ray diffraction (XRD) analysis indicates that the films are polycrystalline and have a preferred orientation of (321). An indirect optical band gap increased from 2.33 to 2.70 eV when the NH_3 ratio varied from 5% to 25%. The photoluminescence (PL) spectrum shows two emission peaks; the peak located at 437 nm is attributed to the incorporation of oxygen, and the other at 459 nm corresponds to the intrinsic emission.

Key words: zinc nitride films; magnetron sputtering; NH_3 ratios; photoluminescence

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1. Introduction

During the past few years, zinc compounds have emerged as attractive materials owing to their significant properties[1, 2]. Zinc nitride (Zn_3N_2) has attracted the research interest in recent years since it can be converted into p-type ZnO:N after oxidation at temperatures higher than 400 ℃[3, 4]. It is known that the realization of reproducible and controllable p-ZnO will lead to the new era of cheap and reliable transparent optoelectronic devices. However, Zn_3N_2 is a relatively new material and its physical properties are not well understood. For example, the optical band gap of Zn_3N_2 has remained a controversial issue and the use of Zn_3N_2 films has not been extensively explored, so further research is needed. Up to now, some groups have successfully fabricated zinc nitride films. In 1998, polycrystalline zinc nitride films were deposited by reactive RF magnetron sputtering a metallic zinc disc in N_2–Ar mixture gases on glass substrate with the temperature of 423 K, and a direct band gap of 1.23 eV has been obtained[2]. In 2006, zinc nitride films were prepared onto quartz substrates from a zinc nitride target in nitrogen working gas by reactive RF magnetron sputtering at room temperature[5], the films were cubic in structure and had an indirect transition optical band gap of 2.12 eV. In 2009, zinc nitride films were prepared by RF magnetron sputtering a zinc target in N_2–Ar plasma on quartz substrates at a temperature of 473 K[6], and a polycrystalline zinc nitride film with only one diffraction peak was first reported.

The general issue in the growth of stoichiometric nitrides is the provision of nitrogen with high chemical reactivity. NH_3 gas can be used as a nitrogen source because NH_3 gas easily decomposes at low temperature. In this paper, polycrystalline zinc nitride films were prepared by using a RF magnetron sputtering system using a metallic zinc target in NH_3–Ar mixture gases on glass substrate at room temperature. The structural and optical properties of zinc nitride films are discussed in detail.

2. Experimental

Zinc nitride films were deposited onto glass substrates by RF magnetron sputtering a metal zinc target (purity of 99.99%) in the NH_3 (purity of 99.99%) and Ar (purity of 99.99%) mixture gases. The glass substrates were ultrasonically cleaned in acetone and alcohol, rinsed in deionized water and subsequently dried in flowing nitrogen gas. Prior to deposition, the sputtering chamber was pumped down to 6×10^{-4} Pa and the target was sputter-etched in pure Ar gas for 30 min to remove contamination, then pure ammonia gas was introduced into the chamber. NH_3 and Ar gases were introduced into the sputtering chamber through separate mass flow controllers, and the total flow rate was regulated to 20 sccm with NH_3 varying from 1 to 5 sccm. The working pressure was 1.0 Pa, the RF power was maintained at 50 W, the substrates were kept at room temperature and the distance between the substrate and the target was 60 mm. The thickness of all the films was around 400 nm.

Optical transmission was measured in the range of 300–850 nm using a double beam spectrophotometer (TU1901) by taking the glass substrates into consideration. The structural property was analyzed by X-ray diffraction (XRD) using a Rigaku D/MAX 2500 V/PC diffractometer with a Cu-Kα radiation source. The PL spectrum was measured by using fluorescence spectrometer (RF-5301).

3. Results and discussion

The analysis of XRD patterns for a series of films prepared at room temperature and different NH_3 ratios is shown in Fig. 1. The XRD analysis indicates that all the films are polycrystalline, and the crystallinity depends on the NH_3 ratios in

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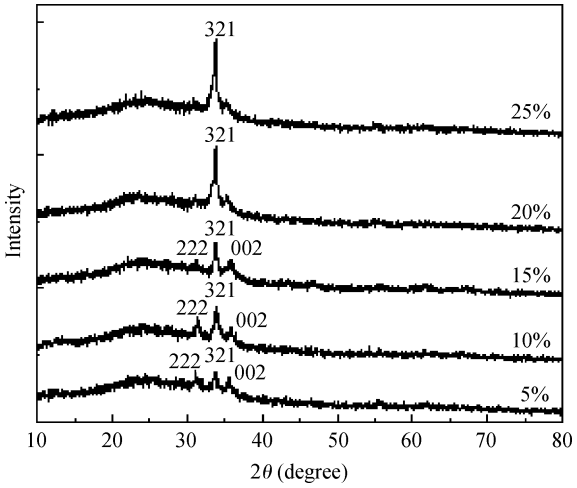

Fig. 1. XRD patterns of the films deposited with various NH_3 ratios.

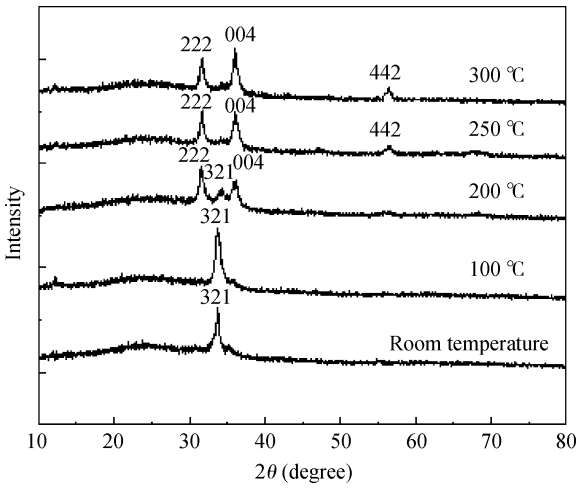

Fig. 2. XRD patterns of the films deposited at various substrate temperatures.

the sputtering ambient. It can be seen from Fig. 1 that for the film prepared at NH_3 ratio of 5%, besides the diffraction peaks of Zn_3N_2 (222) ($2\theta = 31.3°$) and Zn_3N_2 (321) ($2\theta = 33.7°$), there is also another peak at $2\theta = 35.7°$ arising from the metallic zinc. This indicates that both Zn_3N_2 and Zn co-exist when the NH_3 ratio is 5%. As the NH_3 ratio is increased from 5% to 15%, the Zn_3N_2 (321) peak becomes dominant, indicating that the crystallites of Zn_3N_2 grow preferentially with the increase of the NH_3 ratio. The nitride on the substrate is described by the following reaction:

$$3Zn(s) + 2NH_3(g) \rightarrow Zn_3N_2(s) + 3H_2(g). \quad (1)$$

When NH_3 ratio is less than 15%, more sputtered Zn atoms reach the substrate than excited nitrogen species, so there are not enough excited nitrogen species reacting with the sputtered Zn atoms. Single phase Zn_3N_2 thin films with (321) crystal orientation are formed at the NH_3 ratio over 20%. The intensity of the Zn_3N_2 (321) peak increases with the NH_3 ratio. XRD analysis shows that the NH_3 ratio affects the film textures.

In order to study the effect of the substrate temperature on the properties of the Zn_3N_2 films, the Zn_3N_2 films were deposited at various substrate temperatures and with a NH_3 ratio of 25%. Figure 2 shows XRD patterns of the Zn_3N_2 films deposited at various substrate temperatures. When the substrate temperature is lower than 100 ℃, the films are single phase polycrystalline. As the substrate temperature is increased from 100 to 200 ℃, Zn_3N_2 (222), (321) and (004) peaks at $2\theta = 31.38°$, $33.61°$ and $36.43°$ appear in the patterns. With the further increase of the substrate temperature, the intensity of the Zn_3N_2 (004) peak increases, the Zn_3N_2 (321) peak disappears and the Zn_3N_2 (442) peak at $2\theta = 56.42°$ appears.

Transmittance of Zn_3N_2 films deposited at room temperature and different NH_3 ratios is shown in Fig. 3. The film prepared with the NH_3 ratio of 5% has a very low transmission. The film deposited at the NH_3 ratio of 10% also has low transmission values. For the other films, the transmission can be as high as 80% (and even larger for some of them) in the visible region and the transparency of the films get better with the increase of the NH_3 ratio. It can be confirmed that the NH_3 ratio has a great effect on the transmittance. The film deposited at

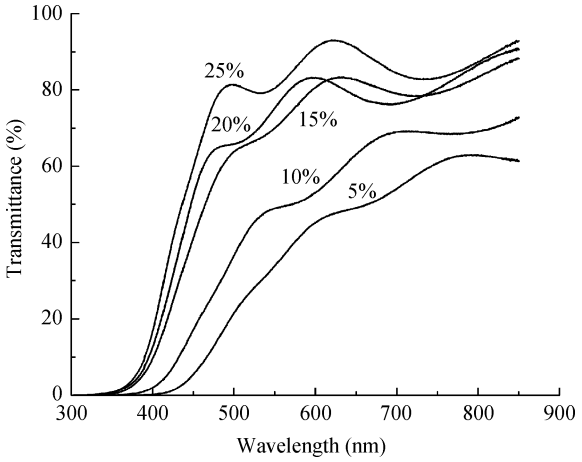

Fig. 3. Transmittance of the Zn_3N_2 films deposited with various NH_3 ratios.

5% NH_3 ratio is rich in Zn atoms, which deteriorate the crystallinity of the Zn_3N_2 films and has a low transmittance. With increasing the NH_3 ratio to 10%, more nitrogen species react with Zn atoms, the stoichiometric ratio of the films gets better, which results in an improved transparency. With the further increase of the NH_3 ratio, the stoichiometric ratio of the films improves, which leads to better crystallinity and transparency.

Transmission spectra of the films deposited at various substrate temperatures and NH_3 ratio of 25% are shown in Fig. 4. For all of the films, the transmission can be as high as 75% (and even larger for some of them) in the visible region, the absorption edge is located at around 400 nm. The film prepared at the substrate temperature of 100 ℃ has the maximum transmission in the violet region. The variation of the transmission is attributed to the variation of the crystallinity of the Zn_3N_2 films.

The dependence of the absorption coefficient on the photon energy is analyzed using the following expression for near-edge optical absorption of semiconductors. For direct band gap semiconductors, Equation (2) is used to calculate the optical band gap:

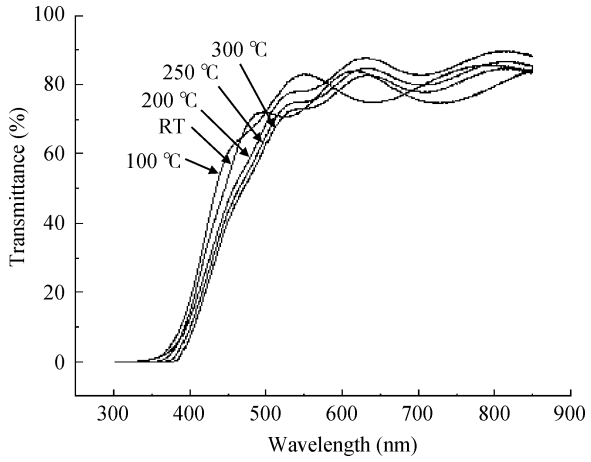

Fig. 4. Transmittance of the Zn_3N_2 films deposited at various substrate temperatures.

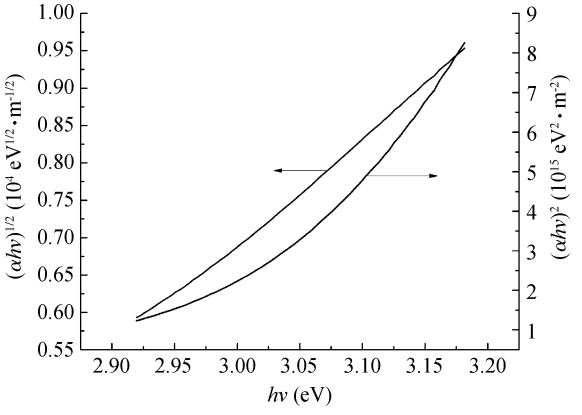

Fig. 5. Dependence of the absorption coefficient on the photon energy for the film prepared at 25% NH_3 ratio.

$$(\alpha h\nu)^2 = b(h\nu - E_g). \quad (2)$$

For indirect band gap semiconductors, Equation (3) is used to calculate the optical band gap:

$$(\alpha h\nu)^{1/2} = b'(h\nu - E_g), \quad (3)$$

where $h\nu$ is the photon energy, E_g is the optical band gap, and b (b') is the constant. The value of the optical band gap is determined through extrapolating the linear portion to $\alpha h\nu = 0$. Figure 5 represents the dependence of the absorption coefficient on the photon energy for film prepared at a NH_3 ratio of 25% and at room temperature. It can be seen that a good linear relation is fitted with Eq. (3), indicating that zinc nitride has an indirect band gap, and the optical band gap is determined to be about 2.70 eV. The optical band gap of zinc nitride films estimated in the present study is smaller than that of Ref. [7] (3.4 eV), much larger than that of Ref. [2] (1.23 eV). The difference of the optical band gap value could come from the different film preparation methods.

Figure 6 gives the optical band gap of the films deposited at room temperature and NH_3 ratios of 5%, 10%, 15%, 20% and 25%, and the values are 2.33, 2.38, 2.58, 2.63 and 2.70 eV, respectively. The optical band gap of the films increases

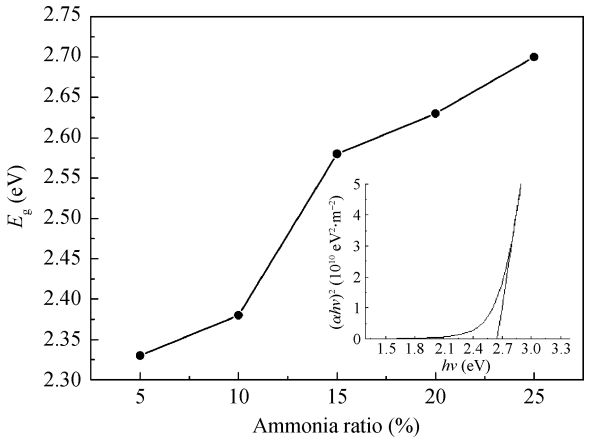

Fig. 6. Optical band gap of Zn_3N_2 films deposited with various NH_3 ratios.

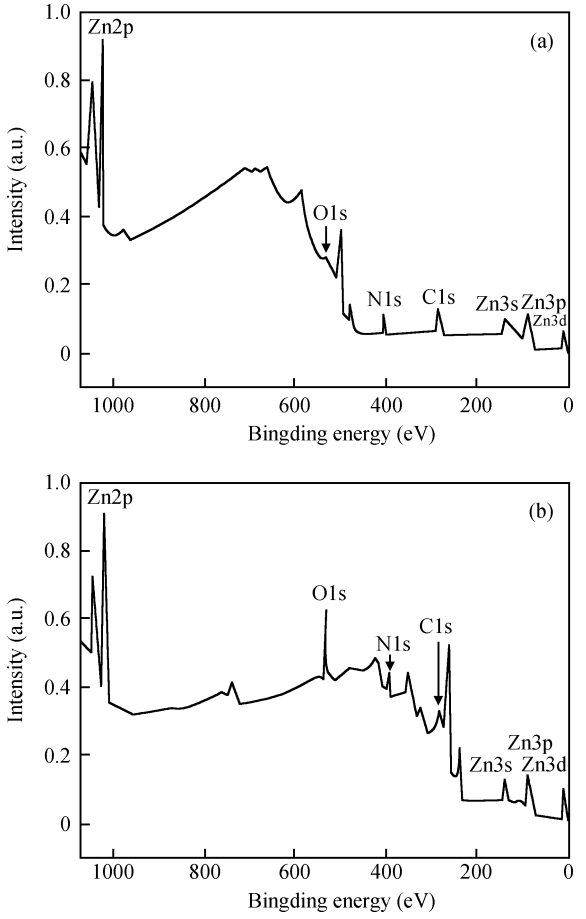

Fig. 7. XPS spectra of the Zn_3N_2 film prepared at NH_3 ratio of 25%. (a) As-prepared. (b) After exposure to air.

with NH_3 ratios, and this is attributed to the improved crystallinity of the films. The Zn_3N_2 is a kind of wide band gap semiconductor and could be a potential candidate as an optical material for transparent optoelectronic devices.

In order to investigate the chemical bonding states of the Zn_3N_2 films, XPS experiments were carried out. Figure 7 shows the full scan results of the Zn_3N_2 film prepared at the NH_3 ratio of 25% and room temperature. The peaks of Zn2p,

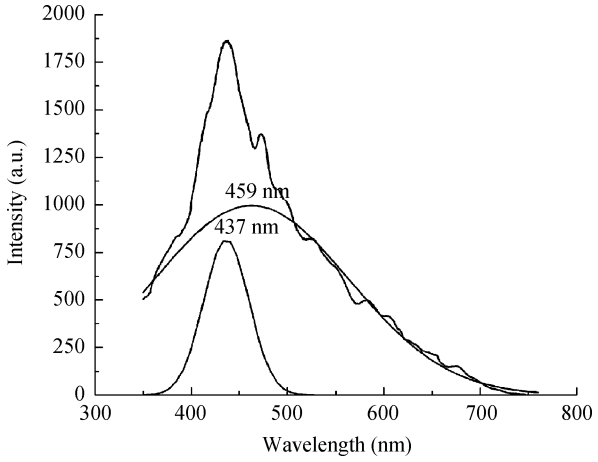

Fig. 8. Room temperature PL spectrum of the Zn_3N_2 film prepared with a 25% NH_3 ratio.

O1s, N1s and C1s are clearly shown in the XPS spectra. Zn_3N_2 is easily hydrolyzed by air moisture and the reaction can be written as:

$$Zn_3N_2 + 6H_2O \rightarrow 3Zn(OH)_2 + 2NH_3. \quad (4)$$

After exposing the samples to air, the intensity of the O1s peak becomes much higher compared with that of the as-prepared Zn_3N_2 films, indicating that the Zn_3N_2 has been hydrolyzed by air moisture.

The room temperature PL emission spectrum of Zn_3N_2 film deposited at 25% NH_3 ratio and room temperature was measured at an excitation wavelength of 325 nm using a Xe lamp source. As shown in Fig. 8, the emission band can be fitted with two Gaussian bands located at 437 nm (2.84 eV) and 459 nm (2.69 eV). It is obvious that the value of 2.84 eV is larger than the optical band gap of 2.70 eV. The samples have been exposed to the atmosphere before the PL measurement, from the XPS analysis, the peak of PL located at 437 nm (2.84 eV) should be attributed to the transition of photogenerated electrons from the conduction band to the valence band of $Zn_xO_yN_z$. According to the Pauling theory, ionicity in a single bond increases with the difference in the values of electron negativity between two elements formed the single bond. The electron negativity of O (3.5) is larger than that of N (3.0), which indicates that Zn–O bond has a larger ionicity than Zn–N bond. The increase in E_g is probably attributed to the increase in ionicity due to the formation of Zn–O bonds[6]. The PL peak located at 459 nm (2.69 eV) fits the optical band gap (2.70 eV) well and is attributed to intrinsic emission.

4. Conclusion

Zinc nitride films were prepared by RF magnetron sputtering a metallic zinc target in NH_3–Ar mixture gases at room temperature. The polycrystalline single phase Zn_3N_2 films were obtained at a NH_3 ratio over 20%. The structural and optical properties of the Zn_3N_2 films were highly dependent on the NH_3 ratios. With the NH_3 ratio increasing from 5% to 20%, the structure of Zn_3N_2 film changed from three phases to single phase. The optical band gap of the films varied from 2.33 to 2.70 eV and the transmittance was improved with increasing the NH_3 ratios from 5% to 25%. The PL spectrum exhibits a strong violet emission band at 437 nm and one weak band at 459 nm.

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