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Structural and Optical Properties of Zn_3N_2 Films Prepared by Magnetron Sputtering in NH_3-Ar Mixture Gases

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Abstract: The Zn_3N_2 is a kind of wide band gap semiconductor and it can be converted into p-type ZnO:N after oxidation at temperatures higher than 400°C which has significant potential for electronic and optoelectronic applications. The Zn_3N_2 films were prepared by RF magnetron sputtering a metallic zinc target in NH_3-Ar mixture gases on glass substrate at room temperature. The optical transmission, optical absorption, structural property, chemical bonding states, photoluminescence were measured using a double beam spectrophotometer, X-ray diffractometer (XRD), X-ray Photoelectron Spectroscopy (XPS), fluorescence spectrometer. The effects of NH_3 ratio on the structural and optical properties of the films were examined. XRD analysis indicates that the films are polycrystalline and have a preferred orientation of (321). The intensity of the Zn_3N_2(321) peak increases with the NH_3 ratio. The films prepared with the NH_3 ratios of 5%～10% have low transmission values, the transparency of the films get better with the increase of the NH_3 ratio. The Zn_3N_2 films have an indirect band gap, the optical band gap increases from 2.33 to 2.70 eV when the NH_3 ratio varies from 5% to 25%. XPS analysis shows that the Zn_3N_2 film is easily hydrolyzed by air moisture. Photoluminescence spectrum shows two emission peaks, which are located at 437 nm and 459 nm.

Key words: Zinc nitride films; Magnetron sputtering; NH_3 ratios; Photoluminescence

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0 Introduction

During the past few years, zinc compounds have emerged as attractive materials owing to their significant properties[1-3]. 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 ℃[4-5]. 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[6-8]. 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[9], 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 zinc target in N_2 - Ar plasma on quartz substrates with the temperature of 473 K[10], and the 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 having 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 RF magnetron sputtering system using a metallic zinc target in NH_3-Ar mixture gases on glass

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substrate under room temperature. The structural and optical properties of zinc nitride films are discussed in detail.

1 Experiment

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, 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 the X-ray diffraction (XRD) technique using a Rigaku D/MAX 2500 V/PC diffractometer with Cu-Kα radiation source. PL spectrum was measured by fluorescence spectrometer (RF-5301).

2 Results and discussion

2.1 Structural properties

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 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) (2θ= 31.3°) and Zn_3N_2(321) (2θ= 33.7°), there is also another peak at 2θ=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)

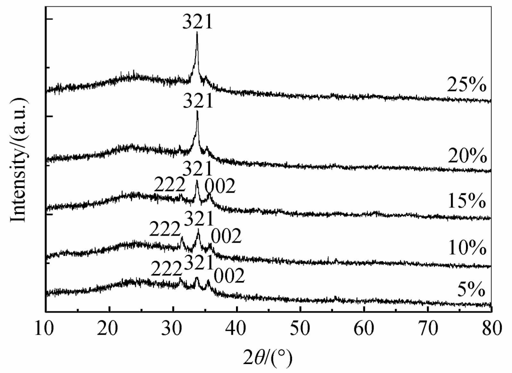

Fig. 1 XRD patterns of the films deposited with various NH_3 ratios

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 the (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.

2.2 Optical properties

Transmittance of Zn_3N_2 films deposited at room temperature and different NH_3 ratios is shown in Fig. 2. 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 great effect on the

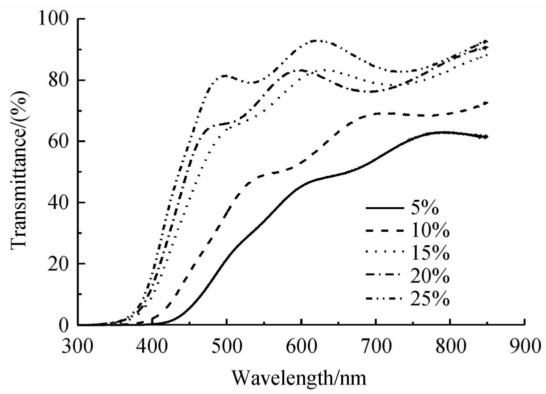

Fig. 2 Transmittance of the Zn_3N_2 films deposited with various NH_3 ratios

transmittance. The film deposited at 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 becomes better which leads to a better crystallinity and transparency.

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, Eq. (2) is used to calculate the optical band gap

$$(ahv)^2 = b(hv - E_g) \qquad (2)$$

And for indirect band gap semiconductors, Eq. (3) is used to calculate the optical band gap

$$(ahv)^{1/2} = b'(hv - E_g) \qquad (3)$$

where hv is the photon energy, E_g is the optical band gap, and b (b') is the constant. The value of optical band gap is determined through extrapolating the linear portion to $ahv = 0$. Fig. 3 represents the dependence of the absorption coefficient on the photon energy for the film prepared at the NH_3 ratio of 25% and room temperature. It can be seen that a good linear relation is fitted with Eq. (3), indicating 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. [11] (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 prepared methods.

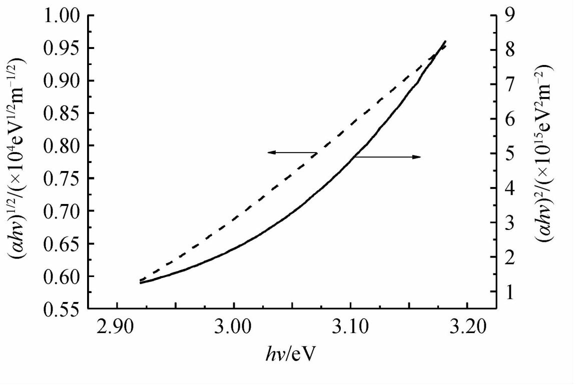

Fig. 3　The dependence of the absorption coefficient on the photon energy for the film prepared at 25% NH_3 ratio

Fig. 4 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 eV, 2.38 eV, 2.58 eV, 2.63 eV and 2.70 eV, respectively. The optical band gap of the films increases with NH_3 ratios, 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 optical material for transparent optoelectronic devices.

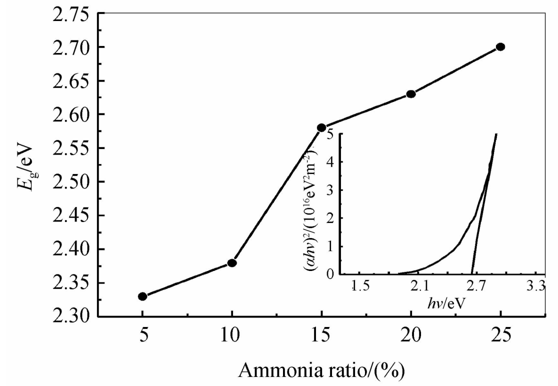

Fig. 4　Optical band gap of Zn_3N_2 films deposited with various NH_3 ratios

2.3　XPS spectra

In order to investigate the chemical bonding states of the Zn_3N_2 films, XPS experiments were carried out . Fig. 5 shows the full scan results of

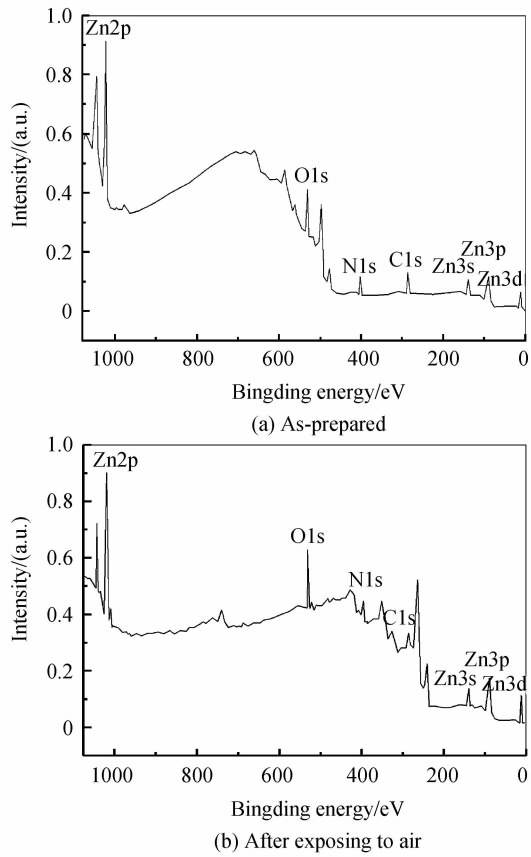

Fig. 5　XPS spectra of the Zn_3N_2 film prepared at NH_3 ratio of 25%

the Zn_3N_2 film prepared at the NH_3 ratio of 25% and room temperature. The peaks of Zn2p, 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 the Zn_3N_2 has been hydrolyzed by air moisture.

2.4 Photoluminescence spectra

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 Xe lamp source. As shown in Fig. 6, the emission band can be fitted with two Gaussian bands which are 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[10]. The PL peak located at 459 nm (2.69 eV) fits the optical band gap (2.70 eV) well and it is attributed to the intrinsic emission.

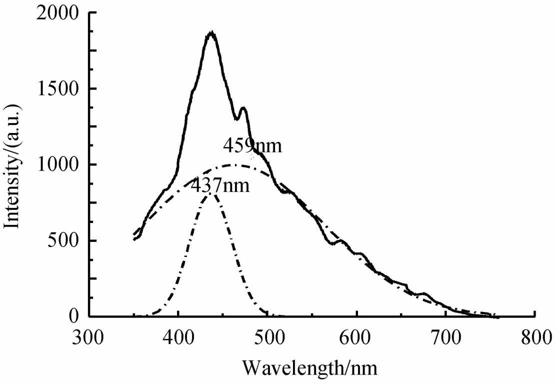

Fig. 6 Room temperature PL spectrum of the Zn_3N_2 film prepared with 25% NH_3 ratio

3 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 the 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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NH_3-Ar 气氛下制备的 Zn_3N_2 薄膜的结构和光学性能

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摘　要：Zn_3N_2 是一种宽带隙半导体材料，在温度高于 400°C 氧化可生成 p 型 ZnO:N，p 型 ZnO:N 在电子学和光电子学领域有广泛的应用. 在 NH_3-Ar 气氛下，用 RF 磁控溅射金属 Zn 靶在玻璃衬底上室温制备了 Zn_3N_2 薄膜. 用紫外-可见分光光度计、X 射线衍射仪、X 射线光电子谱分析仪、荧光分光光度计对 Zn_3N_2 薄膜的光学透过、光学吸收、结构、化学键态和光致发光进行了测量，研究了 NH_3 分压对 Zn_3N_2 薄膜的结构和光学特性的影响. XRD 分析表明 Zn_3N_2 薄膜呈现多晶结构，具有(321)择优取向，Zn_3N_2(321)衍射峰强度随 NH_3 分压增加而增强. 在 NH_3 分压 5%～10%制备的 Zn_3N_2 薄膜有较低透过率，透过率随 NH_3 分压增加而提高. Zn_3N_2 薄膜是间接带隙半导体，当 NH_3 分压从 5%变化到 25%时，光学带隙从 2.33 eV 升高到 2.70 eV. XPS 分析表明 Zn_3N_2 薄膜在潮湿空气中容易水解. 室温下 Zn_3N_2 薄膜在 437 nm 和 459 nm 波长出现了发光峰.

关键词：Zn_3N_2 薄膜；磁控溅射；NH_3 分压；光致发光