Influence of Substrate Temperature and Nitrogen Gas on Zinc Nitride Thin Films Prepared by RF Reactive Sputtering*

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Abstract: Zinc nitride (Zn_3N_2) thin films were prepared by radio frequency (RF) magnetron sputtering on quartz glass at different substrate temperatures. The structure and composition were characterized by X-ray diffraction and Raman-scattering measurements, respectively. The polycrystalline phase Zn_3N_2 films appeared when the ratio of the N_2 partial pressure to the total pressure reached 1/2. The effects of the substrate temperature on the electrical and optical properties of the Zn_3N_2 films were investigated by Hall measurements and optical transmission spectra. The electrical and optical properties of the films were highly dependent on the substrate temperature. With the substrate temperature increasing from 100 to 300℃, the resistivity of the Zn_3N_2 films decreased from 0.49 to 0.023Ω·cm, the carrier concentration increased from 2.7×10^{16} to $8.2\times10^{19}\,cm^{-3}$, and the electron mobility decreased from 115 to $32cm^2/(V\cdot s)$. The deposited Zn_3N_2 films were considered to be n-type semiconductors with a direct optical band gap, which was around 1.23eV when the substrate temperature was 200℃.

Key words: zinc nitride; thin film; magnetron sputtering; electrical and optical properties
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1 Introduction

Zinc compounds have been the subject of intensive research and development efforts during the last few decades because of their wide direct band gaps and potential applications in visible and UV optoelectronic technologies. Among them, zinc oxide (ZnO) has important application potential owing to its unique properties. Its wide band gap of 3.37eV and exciton binding energy of 60meV at room temperature make ZnO suitable for short wavelength opto-electronic devices, including light-emitting diodes (LEDs), laser diodes (LDs), and room-temperature UV laser devices[1,2]. Zinc phosphide (Zn_3P_2), with a direct gap of near 1.51eV, is a promising material for low cost solar cells[3]. Zinc sulphide (ZnS) is considered to be the key material for applications in light-emitting diodes (LEDs) and laser diodes (LDs) in the ultraviolet (UV) range of the spectrum because of its band gap of 3.73eV at room temperature[4~6]. Semiconductor nitrides such as aluminum nitride (AlN) and gallium nitride (GaN) can be considered as promising materials for their potential in optical devices or high speed and high-power electronic devices due to their characteristics of wide band gap, high electron saturation velocity, and high breakdown voltage[7,8]. As with the materials above, Zn_3N_2 is also a direct band gap and n-type semiconductor with cubic antibixbyite structure. Therefore, Zn_3N_2 also has important application potential due to its significant electrical and optical properties[9~13]. In addition, many groups have already succeeded in forming p-type ZnO films by thermal oxidation of Zn_3N_2 films[14,15]. However, different values of its physical properties and different preparation techniques of Zn_3N_2 have been reported. For instance, the band gap energy was reported to be 3.2eV by Kuriyama[10], 1.23eV by Futsuhara[11] and 1.01eV by Toyoura[12]. Among many prepara-

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tion techniques, reactive RF magnetron sputtering has been used to grow high quality stoichiometric nitrides because the plasma can provide sufficient active nitrogen species at low substrate temperature.

In this work, RF planar magnetron sputtering was employed to prepare polycrystalline Zn_3N_2 thin films on quartz glass. The crystal structure of the films investigated by X-ray diffraction (XRD) was dependent on the N_2 concentration in sputtering ambient and the substrate temperature. In addition, the effects of the substrate temperature on the electrical and optical properties of the Zn_3N_2 films were investigated.

2 Experiment

Zn_3N_2 films were prepared on quartz glass substrates by reactive magnetron sputtering with a conventional RF (13.56MHz) sputter setup. The background pressure of the sputtering chamber was evacuated below 1×10^{-4} Pa with a turbo molecular pump. The quartz glass substrates were ultrasonically cleaned in acetone, rinsed in alcohol, and then dried in hot air. A metallic zinc disc (purity of 99.999%) of 60mm in diameter was used as the target. The target-substrate distance was maintained at 60mm. The sputtering time was 30min and the RF power was kept at 50W. Before film deposition, the target was sputter-etched in Ar plasma for 30min to remove contamination. N_2-Ar mixtures were used as sputtering ambient. The N_2 and Ar gases were introduced into the sputtering chamber through the individual mass flow controllers. The total flow rate and total pressure were 40sccm and 1.2Pa, respectively. Meanwhile, the nitrogen partial pressure varied from 0.12 to 0.96Pa. The substrates can be heated up to 300℃, as measured by a thermocouple fixed beside the samples. In order to study the effects of the ratio of the N_2 partial pressure to the total pressure (P_N/P_T) and the substrate temperature, two series of experiments were performed. First, the substrate temperature was fixed at 200℃, while the ratio of the N_2 partial pressure to the total pressure (P_N/P_T) was varied from 1/10 to 4/5. Secondly, the P_N/P_T was fixed at 1/2, while the substrate temperature was varied and other growth parameters were held constant.

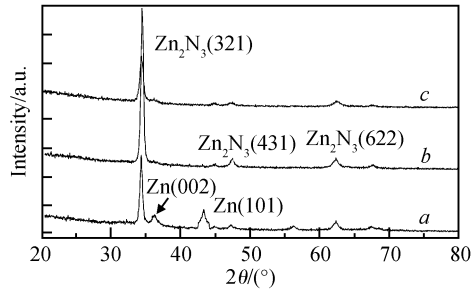

Fig. 1 X-ray diffraction patterns of the thin films deposited at the various ratios of the N_2 partial pressure to the total pressure P_N/P_T of 1/5 (*a*), 1/2 (*b*), and 4/5 (*c*) Substrate temperature was 200℃.

The crystallographic properties of the thin films were investigated by an X-ray diffraction system (Rigaku D/Max-IIIC, with a wavelength of 0.1542nm). The surface morphologies and thickness of the gold coated thin films were characterized by scanning electron microscopy (SEM Hitachi S-4800). Raman-scattering measurements (HORIBA Jobin Yvon HR800) were conducted in the wave number range of $100\sim1200cm^{-1}$. The 488nm line of an Ar^+ ion laser was used for excitation, and the incident laser power was 1mW. The electrical properties of the film were examined by Hall measurements using the van der Pauw configuration and hot-probe measurements. The ohmic contacts were fabricated by evaporating aluminum at the four symmetrical corners of the samples, which were then annealed at 350℃ in Ar flow for 2h. Optical transmission spectra were measured by a double beam spectrometer (Hitachi U-3500). A clean quartz glass was used for a reference sample. Absorption coefficient was calculated from the transmission spectrum with film thickness. All the above measurements were performed at room temperature.

3 Results and discussion

The crystal structure and orientation of the deposited thin films were investigated by XRD. Figure 1 shows the XRD patterns of the thin films prepared at different N_2 concentrations. It can be seen from Fig. 1 that, besides the diffraction peak of the Zn_3N_2 (321) ($2\theta=34.3^\circ$), there are also some other peaks at $2\theta=36.2^\circ$ and 43.2° arising from the metallic zinc with hexagonal close-packed crystal structure. This indicates that both

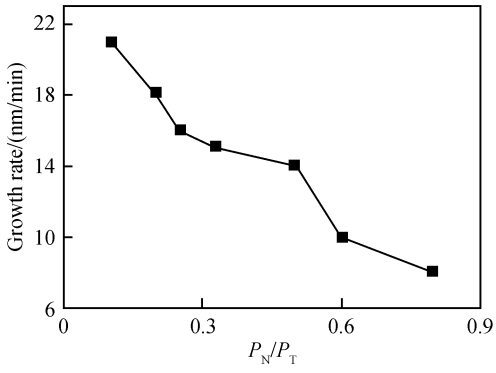

Fig. 2　Film growth rate versus the ratio of the N_2 partial pressure to the total pressure P_N/P_T

Zn_3N_2 and Zn co-exist when $P_N/P_T = 1/5$. When $P_N/P_T = 1/2$, the peaks were attributed to the metallic Zn disappearance, indicating that the thin films prepared in this N_2 concentration were in a polycrystalline phase. When the P_N/P_T is increased to 4/5, the intensity of the dominating Zn_3N_2(321) peak decreases, and the other peaks arising from the Zn_3N_2 (431) and (622) nearly disappear. But it should be pointed out that the (321) peak is still dominant, revealing a preferred orientation of the thin film. The results of the XRD analysis are different from the report of Futsuhara in Ref. [11], in which the dominating peak of $2\theta = 36.7^\circ$ was attributed to Zn_3N_2(400). We think that the differences in the deposited parameters may be the main reasons for this disagreement, such as the substrate temperature, the sputtering power, and the substrate species. The results of the XRD analysis show that the P_N/P_T ratio affects the thin film texture greatly. When P_N/P_T is less than 1/5, more sputtered zinc atoms reach the substrate than excited nitrogen species, so there are not enough excited nitrogen species reacting with the sputtered Zn atoms. Therefore, the deposited film showed two phases of Zn_3N_2 and Zn. Increasing P_N/P_T from 1/5 to 4/5, we get a single phase of Zn_3N_2 with the preferred orientation. But the growth rate measured by cross section SEM micrograph decreases with increasing P_N/P_T, as shown in Fig. 2. This can be explained as follows. At a fixed sputtering gas pressure, a higher P_N means a lower P_{Ar}, resulting in a lower sputtering yield from the zinc target, because the sputtering rate of Ar^+ is larger than that of N^{2+}.

In order to investigate the effects of the substrate temperature on the crystallizability and the

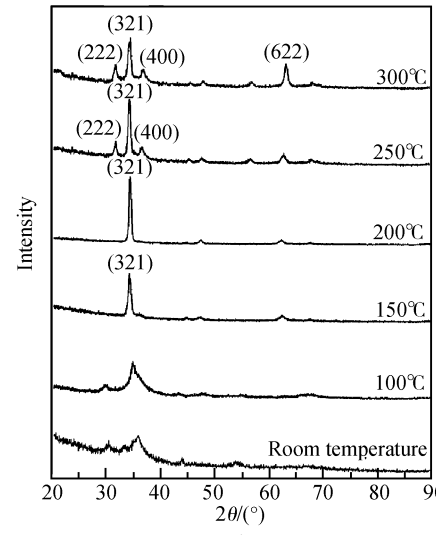

Fig. 3　X-ray diffraction patterns of thin films deposited at various substrate temperatures　P_N/P_T was 1/2.

orientation of the thin films, the films were deposited at various substrate temperatures when P_N/P_T was fixed at 1/2. Figure 3 shows the XRD patterns of the thin films prepared at various substrate temperatures. It can be seen that when the substrates were at room temperature or 100℃, the deposited thin films were amorphous Zn_3N_2. As the substrate temperature is increased from 100 to 200℃, the Zn_3N_2(321) peak at $2\theta = 34.3^\circ$ becomes dominant, and the film shows Zn_3N_2 (321) preferred orientation. When the substrate temperature is increased to 300℃, the Zn_3N_2(222), (400) and (622) peaks at $2\theta = 31.7^\circ$, 36.8° and 63.1° appear in the patterns, indicating that the deposited Zn_3N_2 thin films are polycrystalline films. The intensity and the full width at half-maximum (FWHM) of the Zn_3N_2(321) peak of the film deposited at 200℃ are the highest and narrowest, respectively. We can evaluate the mean grain sizes (GS) of the thin films by Scherer's formula[15]:

$$GS = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where λ, θ, and B are the X-ray wavelength (0.154nm), the Bragg diffraction angle, and the full width at half-maximum of the (321) peak, respectively. The calculated grain sizes of the samples are 76, 56, and 44nm for the samples deposited at 200, 250, and 300℃, respectively.

Figure 4 shows the Raman spectra of the thin films deposited at various substrate temperatures.

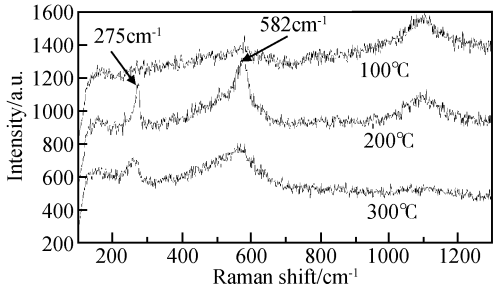

Fig. 4 Raman spectra of the thin films deposited at various substrate temperatures P_N/P_T was 1/2.

In the measurement range of 100～1200cm^{-1}, the deposited thin films show two vibration peaks around 275 and 582cm^{-1}. The predominant 582cm^{-1} mode and the 275cm^{-1} mode are local vibrational modes related with the vibrating nitrogen-related complexes[16,17]. As the substrate temperature is increased from 100 to 300℃, the intensity and shape of the peaks are changed noticeably. This indicates that the composition of the thin film is highly sensitive to the substrate temperature. The intensity of vibration peaks in the film deposited at 200℃ is strongest. The kinematicenergy of the sputtered species at 200℃ substrate temperature may be sufficient to make nitrogen species react with the Zn atoms on the quartz glass substrates.

Figure 5 shows typical SEM images of the surface morphology of the samples prepared at various substrate temperatures. The surface morphology of the films changes significantly with increasing substrate temperature. The grains curve and form dendrite-like structures which intersect each other in the sample deposited at a substrate temperature of 100℃. The Zn_3N_2 film was composed of uniform particles with 70nm in size, as the substrate temperature increased to 200℃. When the sample was deposited at 300℃, the sizes of the grains became smaller than that of the sample deposited at 200℃, and the surface of the film became more compact and flat. The insert (d) of Fig. 5 shows an SEM cross sectional image of the sample deposited at 200℃; there is no void between the film and the substrate. In addition, it was confirmed that the thickness of the film is about 420nm compared with the interposed marker.

The hot-probe measurements indicate that all of the fabricated thin films exhibited n-type conductivity. Table 1 shows the results of the Hall measurements. As the substrate temperatures increased from 100 to 300℃, the resistivity (ρ) of the Zn_3N_2 film decreased from 0.49 to 0.023Ω·cm, the carrier concentration (n_e) increased from 2.7×10^{16} to 8.2×10^{19} cm^{-3}, and the electron mobility (μ) decreased from 115 to 32cm^2/(V·s). Therefore, the decrease in resistivity is attributed

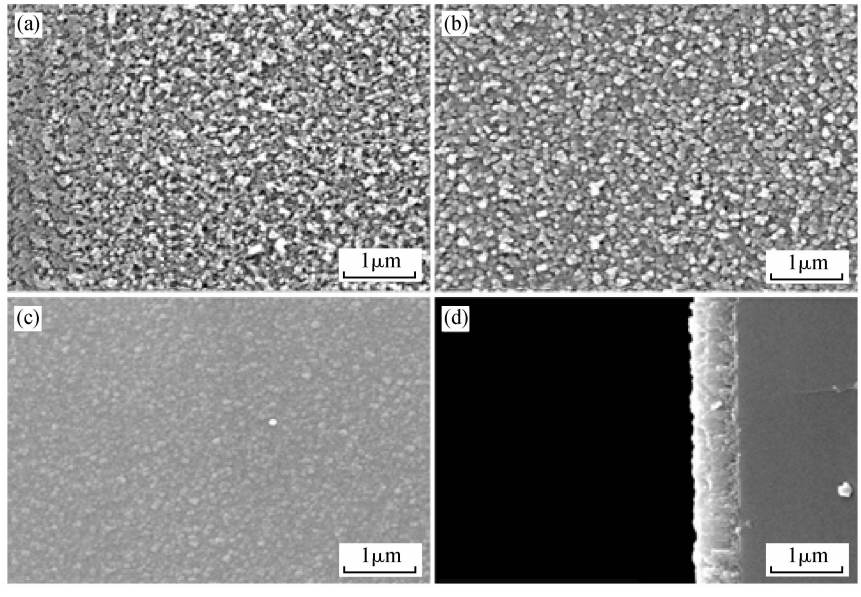

Fig. 5 Typical SEM images of the samples prepared at various substrate temperatures (a) 100℃; (b) 200℃; (c) 300℃; (d) Cross sectional image of (b)

Table 1　Results of the Hall effect measurements of the thin films deposited at various substrate temperatures　P_N/P_T was 1/2.

Substrate temperature /℃	Resistivity /(Ω·cm)	Mobility /(cm²/(V·s))	Carrier concentration /cm⁻³	Conductivity type
100	0.49	115	-2.7438×10^{16}	n
150	0.12	96	-4.127×10^{17}	n
200	0.056	83	-6.4947×10^{18}	n
250	0.042	45	-9.6537×10^{18}	n
300	0.023	32	-8.2012×10^{19}	n

to the increase in the carrier concentration. The electron mobility decreased monotonically with increasing carrier concentration. The electron mobility is dominated both by ionized impurity scattering and by grain boundary scattering in polycrystalline semiconductor. In the deposited Zn_3N_2 films, the electron mobility monotonically decreased with increasing carrier concentration. Furthermore, the results of the XRD analysis show that the sizes of the grains became smaller with increasing substrate temperature. It can be concluded that the electron mobility in the Zn_3N_2 films is mainly dominated by the ionized impurity scattering, while the grain boundary scattering has little influence on the electron mobility.

The optical properties of the fabricated samples were evaluated by measuring the transmission spectra in the wavelength range of 550～1100nm using the spectrophotometer. Typical transmission spectra of the films deposited at various substrate temperatures are shown in Fig. 6. The fundamental absorption edge was located at around 1000nm. The transmittance rate of the films in the near infrared range is about 65%. The absorption

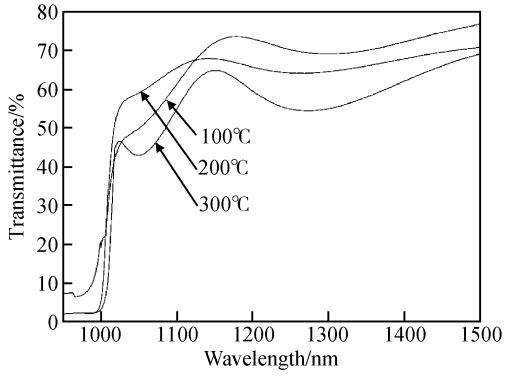

Fig. 6　Typical transmission spectra of films deposited at various substrate temperatures　P_N/P_T was 1/2.

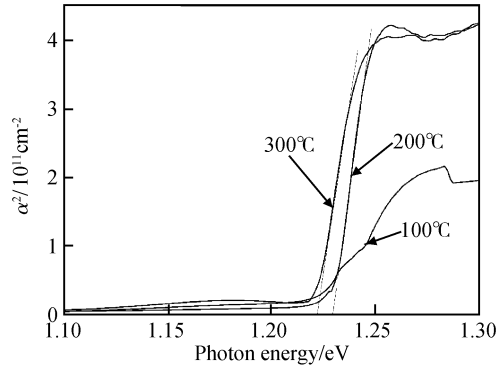

Fig. 7　Relation between squared absorption coefficient and photo energy of the films deposited at various substrate temperatures　P_N/P_T was 1/2.

coefficient of the films can be calculated from the transmission spectrum with the film thickness. In order to check the band structure of the Zn_3N_2 films, Figure 7 shows the absorption coefficient as a function of the photon energy. It can be seen that the relationship between the absorption coefficient and the photon energy the of the films deposited at 200 and 300℃ followed the equation

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (2)$$

As for the absorption edge of semiconductors, Equation (2) is valid for the direct electron transition from valence to conduction bands. Therefore E_g was determined by extrapolating the linear part of these plots to $\alpha = 0$. The E_g of the films deposited at 200 and 300℃ were calculated to be 1.23 and 1.22eV, respectively. In our work, the values of band gap energy agree well with the results reported by Futsuhara in Ref. [11] in spite of the differences in the deposited parameters such as the substrate temperature, the N_2 concentration, or the substrate species.

4　Conclusions

Zinc nitride (Zn_3N_2) thin films were prepared by radio frequency (RF) magnetron sputtering on quartz glass at various substrate temperatures. The polycrystalline single phase Zn_3N_2 thin films were fabricated when the P_N/P_T exceeded 1/2. The structural, electrical and optical properties of the Zn_3N_2 films were highly dependent on the substrate temperature. With the substrate temperature increasing from 100 to 300℃, the Zn_3N_2 film changed from amorphous to highly ordered films, and the mean grain size of the samples de-

posited at 200℃ was about 70nm. The resistivity of the Zn_3N_2 film decreased from 0.49 to 0.023 Ω·cm, and the carrier concentration (n_c) increased from 2.7×10^{16} to $8.2\times10^{19}cm^{-3}$, whereas the electron mobility (μ) decreased from 115 to $32cm^2/(V\cdot s)$, respectively. The E_g of the films deposited at 200 and 300℃ were determined to be 1.23 and 1.22eV, respectively.

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衬底温度和氮气分压对氮化锌薄膜的性能影响*

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摘要： 采用射频磁控溅射法在不同衬底温度和不同氮气分压下在石英玻璃衬底上制备氮化锌薄膜. 利用 XRD 和喇曼散射仪分析了样品的晶体结构和组成. 结果表明当氮气分压为 1/2 时可以生成多晶单一相的氮化锌薄膜. 利用霍尔效应和光学透过谱测量了样品的电学和光学性质. 结果表明衬底温度对样品的电学和光学性质有很大的影响. 衬底温度从 100℃ 上升到 300℃ 时，样品的电阻率从 0.49 降低到 0.023Ω·cm. 电子浓度从 2.7×10^{16} 升高到 $8.2\times10^{19}cm^{-3}$. 在衬底温度为 200℃，氮气分压为 1/2 时，样品的光学带隙为 1.23eV.

关键词： 氮化锌；薄膜；射频溅射；光电性质

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