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Optical band gap of zinc nitride films prepared by reactive rf magnetron sputtering

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Polycrystalline Zn_3N_2 films are prepared on Si and quartz glass substrates by RF magnetron sputtering at room temperature. The structural and optical properties are studied by X-ray diffraction and double beam spectrophotometer, respectively. X-ray diffraction indicates that the Zn_3N_2 films deposited on Si and quartz glass substrates both have a preferred orientation in (321) and (442), also are cubic in structure with the lattice constant a=0.9847 and 0.9783 nm, respectively. The absorption coefficients as well as the film thickness are calculated from the transmission spectra, and their dependence on photon energy is examined to determine the optical band gap. Zn_3N_2 is determined to be an indirect-gap semiconductor with the band gap of 2.11(2) eV.

1 Introduction

Various zinc compounds are extensively studied because of their significant properties. For example, doped ZnO has been attracted considerable attention as a promising material for transparent, conductive films because its high transparency in the visible range and high electron conductivity [1-3]. Zn_3P_2 is determined to be a p-type semiconductor with direct gap of near 1.51 eV. It's a low cost material for solar cells because of its band structure [4].

Zn_3N_2 powders were first synthesized by Juza and Hahn [5] in 1940 and have remained a relatively unstudied material for 50 years. Zn_3N_2 is black in color and has the anti-scandium oxide (Sc_2O_3) structure. In 1993, a polycrystalline Zn_3N_2 film was prepared by Kuriyama [6] by a direct reaction between an evaporated metallic Zn film and NH_3 gas. The film had a large optical band gap of 3.2 eV. In 1997, Partin [7] reported the refinement of the structure of Zn_3N_2 by time-of-flight power neutron diffraction. In 1998, Futsuhara [8] investigated the optical properties of zinc oxynitride ($Zn_xO_yN_z$) films. $Zn_xO_yN_z$ films were deposited onto glass substrates from a ZnO target in N_2-Ar mixtures by reactive RF magnetron sputtering. Optical band gap (Eg) decreases from 3.26 to 2.30 eV with increasing nitrogen concentration in the films. In the same year, Futsuhara [9] also studied the structural, electrical and optical properties of Zn_3N_2 thin films prepared by reactive RF magnetron sputtering. The Zn_3N_2 films showed a high electron mobility of about 100 $cm^2V^{-1}s^{-1}$ at room temperature. Zn_3N_2 was determined to be an n-type semiconductor with direct gap of 1.23 eV.

This paper reports that Zn_3N_2 films were prepared on Si and quartz glass substrates by RF magnetron sputtering at room temperature. The structural and optical properties were studied by X-ray diffraction and double beam spectrophotometer, respectively. The transition of electrons from valence to conduction bands was investigated based on the transmission spectra. Kuriyama and Futsuhara have reported that Zn_3N_2 has a direct gap, however, we present here that Zn_3N_2 is indirect with a band gap to be around 2.11(2) eV.

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2 Experimental

The Zn_3N_2 films were fabricated on Si and quartz glass substrates by using a JPGF-450 RF magnetron sputtering system. A sputtering chamber was evacuated below 10^{-4} Pa. The sputtering RF power was 110 W and sputtering time was 90 min. N_2 (99.999%) was used as the sputtering gas. In this study the pressure of N_2 was maintained at 1 Pa. The Zn_3N_2 targets have been prepared by direct reaction between pure Zn powers and NH_3 gas with a flow of 500 ml/min at around 600°C for 3h. The separation between the substrates and the targets was 5 cm. The substrates were kept at room temperature.

Film structure was analyzed by X-ray diffraction using Cu Kα radiation. Optical transmission spectra were measured with a TU-1901 UV double beam spectrophotometer. A clean quartz glass was used for a reference. The absorption coefficients as well as the film thickness are calculated from the transmission spectra.

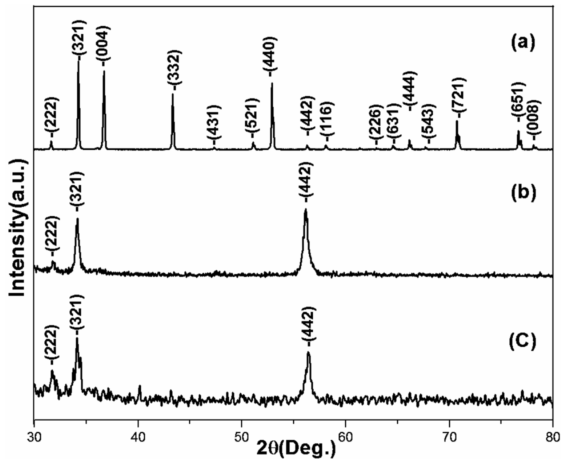

Fig. 1 X-ray diffraction patterns of the Zn_3N_2 target (a) and the Zn_3N_2 films deposited on Si (b) and the quartz glass substrate (c).

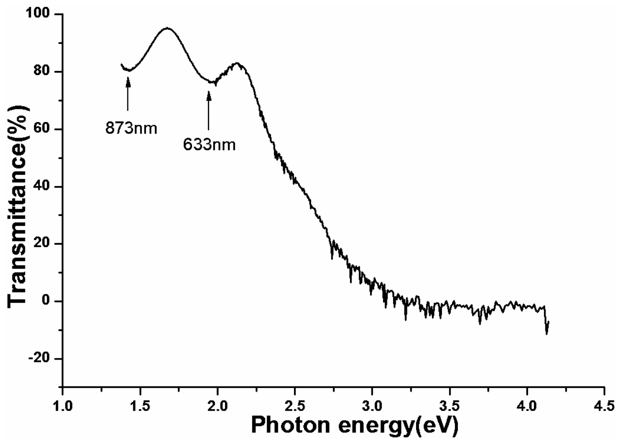

Fig. 2 Transmission spectrum of the Zn_3N_2 film deposited on quartz glass substrate.

3 Results and discussion

Figure 1 shows X-ray diffraction patterns of the Zn_3N_2 target (a) and the Zn_3N_2 films deposited on Si (b) and quartz glass substrates (c) by RF magnetron sputtering. The numbers above the peaks correspond to the values of crystal faces indices (hkl). In figure 1a, the crystal indices are fairly in agreement with the data of Zn_3N_2 powders recorded in the JCPDS document (Power Diffraction File Compiled by the Joint Committee on Power Diffraction, 1985, Card No. 35-0762). In figure b and figure c, it can be seen that the Zn_3N_2 films deposited on Si and quartz glass substrates both have a preferred orientation in (321) and (442), also are cubic in structure with the lattice constant a=0.9847 and 0.9783 nm, respectively, in good agreement with the value (0.9777 nm) published in the JCPDS document.

Figure 2 shows the absolute transmission spectrum of the Zn_3N_2 film deposited on quartz glass substrates. There are two dips at wavelength λ_1 =633 nm and λ_2 =873 nm respectively. The thickness of Zn_3N_2 film is calculated with the transmittance spectrum using the formula [10-11]:

$$x = \frac{1}{2n(\frac{1}{\lambda_1} - \frac{1}{\lambda_2})} \qquad (1)$$

Where x is the thickness of the Zn_3N_2 film, n is the refractive index, λ_1 and λ_2 are the wavelength of adjacent peaks in the transmittance spectrum. Let n = 2.0, we can have the film thickness x = 576 nm. Absorption coefficients (α) and photon energy ($h\nu$) were calculated from the transmission spectrum with film thickness 576 nm. Figure 3 shows that the $\ln(h\nu\alpha)$ plots of the Zn_3N_2 film as a function of photon energy $h\nu$ for the Zn_3N_2 film. As can be seen in figure 3, there is a nice linear relation between $n(h\nu\alpha)$ and the photon energy $h\nu$

from 2.40 to 2.86 eV. We can use the dependence of photon energy to determine the property of the band structure. Two fundamental equations are used for the analysis:

$$(\alpha h\nu)^2 = \beta(h\nu - Eg) \tag{2}$$

for direct electron transition from valence to conduction bands [12], and

$$(\alpha h\nu)^{1/2} = \beta'(h\nu - Eg) \tag{3}$$

for indirect electron transition. Here, $h\nu$ is the photon energy, Eg is the optical band gap, and β and β' are the edge width parameters.

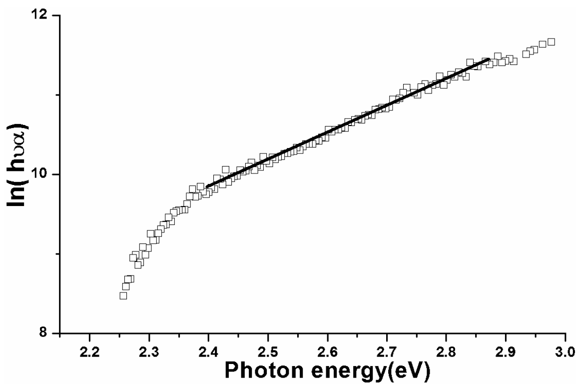

Fig. 3 Dependence of ln($h\nu\alpha$) on the photon energy for the Zn_3N_2 film.

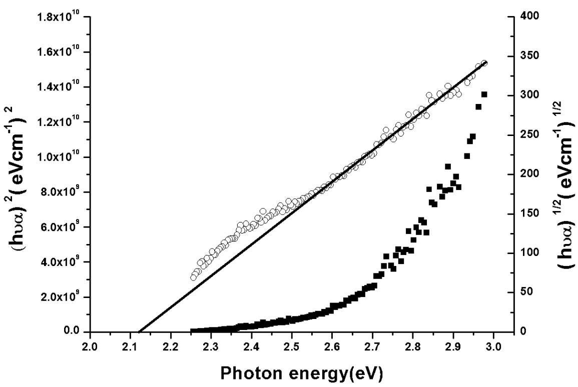

Fig. 4 Dependence of the absorption coefficient on the photon energy for the Zn_3N_2 film.

Figure 4 shows the absorption coefficients on the photon energy for the Zn_3N_2 film. As can be seen in figure 4, the absorption coefficients α obeys the indirect equation better than the direct equation. Eg is determined to be 2.11(2) eV by extrapolating the straight-line line portion to $\alpha h\nu = 0$.

Our study shows that Zn_3N_2 films have a indirect band bap of about 2.11(2) eV. It is in fair agreement with value in [8] (2.3 eV), but much larger than that of [9] (1.23 eV) and much smaller than that of [6] (3.2 eV). Different results could come from the different preparing methods or the different substrates. The film prepared in [6] has a band gap of 3.3 eV, which is very similar to that of ZnO, also its X-ray diffraction patterns is very similar to that of ZnO. Therefore the band gap value could be possible the band gap of ZnO rather than that of Zn_3N_2. We have different results with [9], both in the band gap value and the band gap character. Direct band gap was obtained in [9] but we reported a indirect one. So further investigation is needed to clear the controversy of the band gap value in Zn_3N_2 films.

4 Conclusion

Zn_3N_2 films were prepared on Si and quartz glass substrates by RF magnetron sputtering. X-ray diffraction indicates that the Zn_3N_2 films deposited on Si and quartz glass substrates both have a preferred orientation in (321) and (442), also are cubic in structure with the lattice constant a=0.9847 and 0.9783 nm, respectively. The absorption coefficients as well as the film thickness are calculated from the transmission spectra. According to the analysis of the photon energy dependence of absorption coefficients, an indirect optical band gap about 2.11(2) eV has been obtained.

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