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Deposition and Properties of Zn_3N_2 Thin Films by Atmospheric Pressure Chemical Vapor Deposition

Hisao Suzuki, Yuki Matsuyama, Takato Nakamura, Naonori Sakamoto, Naoki Wakiya and Naoyuki Takahashi*

Graduate School of Science and Technology, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka, Japan 432-8561 Fax: 81-53-478-1157, e-mail: tchsuzu@ipc.shizuoka.ac.jp

* Environmental and Biotechnological Frontier Engineering, Fukui University of Technology 3-6-1, Gakuen, Fukui, Japan 910-8505

Fax: 81-776-29-2686, e-mail: takanao@fukui-ut.ac.jp

Nitrogen doped ZnO is promising for the p-type semiconductor, however, little research work has been done about zinc nitride (Zn_3N_2) materials. In this study, Zn_3N_2 films were prepared by Atmospheric Pressure Chemical Vapor Deposition (AP-CVD). XRD patterns showed that Zn_3N_2 films are polycrystalline if the deposition temperatures were in the range from 500 to 700°C. SEM images exhibited that the Zn_3N_2 films were consisted of granular grains, and their diameter increased with deposition temperature. We determined that optimal deposition temperature was 600°C since dense microstructure was obtained at this temperature. UV-Vis-NIR measurement showed that optical band gap energy was 1.23eV.

Key words: Zn_3N_2 , thin film , AP-CVD , Structural properties

1. INTRODUCTION

Zinc nitride (Zn_3N_2) powders were firstly synthesized by Juda and Hahn in 1940 by direct reaction between ammonia and zinc powders [1]. This Zn_3N_2 powders is black or green in color and has the cubic anti-scandium oxide (Sc_2O_3) structure. However, little work has been done about Zn_3N_2 materials and seems that the preparation of the Zn_3N_2 is difficult. The preparation of the Zn_3N_2 has been reported, so far, by the several methods such as direct reaction [2], rf-magnetron sputtering [3], and MO-CVD. [4-5]. However, the properties of Zn_3N_2 are not well understood yet. On the other hand, zinc oxide (ZnO) is well known and has many applications such as for sensors, a transparent conductor, a varistor, and SAW devices. In addition, nitrogen doped zinc oxides are promising as p-type semiconductors [6]. Therefore, we think Zn_3N_2 is also one of the candidate for a p-type semiconductor as well as the optical materials. Actually, it has been reported that the p-type ZnO thin films were prepared by oxidation of Zn_3N_2 thin films. ZnO is a semiconductor with a direct band gap of 3.37 eV, and exhibits large exciton binding energy of 60 meV, showing the strong exciton emission of about 3.3eV at room temperature by ultraviolet and the electron beam excitation. The light-emitting devices by the exciton shows a low threshold and are highly effective compared with commonly used semiconductor light-emitting devices by the recombination transition of electrons and holes. Hence, the development of the high quality p-type ZnO is now strongly required to apply it to a high performance light-emitting device. It is easy to prepare n-type ZnO, whereas the preparation of p-type ZnO is very difficult. If the p-type ZnO is prepared from Zn3N2, the development of a novel light-emitting device is expected.

In this study, Zn_3N_2 films were prepared by Atmospheric Pressure Chemical Vapor Deposition (AP-CVD). In this method, films are deposited under the atmospheric pressure, preventing the adsorptions of the nitrogen during the deposition to obtain good quality films. Moreover, the composition control is easy by this method and the source materials are relatively cheap than those of the MO-CVD. In this study, Zn_3N_2 films were deposited and characterized by using X-ray diffraction for the structural analysis, SEM for a morphological observation, and some of the spectroscopies for the optical properties measurements.

2. EXPERIMENTAL

Zn_3N_2 films were prepared by AP-CVD, using horizontal hot-wall type quartz reactor. Zn powder and NH3 were used as the source materials, and a SiO_2 / Si (100) or fused silica was used as a substrate. Zn3N2 films were deposited in the temperature range from 500 to 700 °C for 60 min., with Zn partial pressure of 1.952×10^{-3} atm to determine the optimum conditions for the Zn3N2 film growth. Structural properties of Zn_3N_2 films were characterized using X-ray diffraction (XRD) with Cu-Kα radiation as X-ray source. X-ray tube voltage and the tube current were 40 kV and 20 mA, respectively. Morphological properties of Zn3N2 films were characterized using scanning electron microscope (SEM) with accelerating voltage of 10 kV. Optical properties of Zn_3N_2 films were measured using ultraviolet-visible-near infrared spectroscopy (UV-Vis-NIR) in 300-2300 cm-1 to determine the band gap energy.

3. RESULTS AND DISCUSSION

3.1 Structural properties and morphological properties of Zn_3N_2 films on SiO_2 / Si (100) substrate

Fig.1 shows XRD patterns for Zn_3N_2 films on a SiO_2 / Si (100) substrate deposited at different temperatures. Zn_3N_2 films deposited in the temperature range from 575 to 675 °C exhibited many peaks corresponding to the

Zn_3N_2, showing the polycrystalline Zn_3N_2 at this temperature range. At growth temperature of 550, as deposited film was amorphous. On the other hand, as deposited film at 700 °C exhibited weak or different peaks from Zn_3N_2, provably due to the desorption of source gas or decomposition of Zn_3N_2 during growth process because a growth temperature was too high.

Fig.2 shows SEM images of Zn_3N_2 deposited at temperatures of 575, 600, 625, 650, and 675 °C. The surface morphologies of the deposited Zn_3N_2 films are granular independent of the growth temperature. The average diameter of the grains in the Zn_3N_2 films deposited at temperatures of 575, 600, 625, 650, and 675 °C was 0.15, 0.20, 0.80, 0.50, and 0.60□m, respectively, showing the little effect of temperature on the grain size. We determined that optimal deposition temperature is 600 °C because dense morphology was obtained at this temperature.

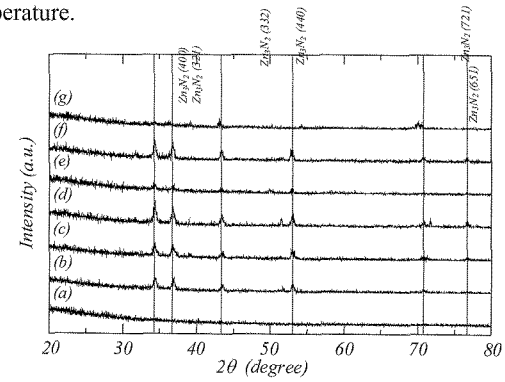
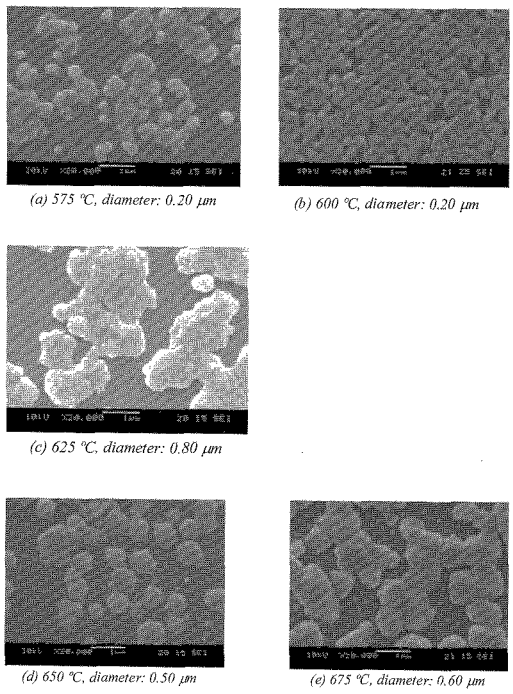


Fig. 1. *XRD patterns of Zn_3N_2 / Si (100) obtained at various growth temperatures*

(a) 550, (b) 575, (c) 600, (d) 625, (e) 650, (f) 675, (g) 700 °C



(a) 575 °C, diameter: 0.20 μm *(b) 600 °C, diameter: 0.20 μm*

(c) 625 °C, diameter: 0.80 μm

(d) 650 °C, diameter: 0.50 μm *(e) 675 °C, diameter: 0.60 μm*

Fig. 2. SEM images of Zn_3N_2 / SiO_2 / Si (100) obtained at various temperatures. (x 20000)
(a) 575, (b) 600, (c) 625, (d) 650, (e) 675 °C

3.2 Properties of Zn_3N_2 films prepared on fused silica substrate

In general, the substrate used is very important because the substrate of the surface strongly affect the growth of the film such as the film orientation, crystal structure, surface morphorogy and so on. If the single crystal substrate with good lattice matching were used, the epitaxial growth could be expected. In this study, a SiO_2/Si(100) substrate, commonly used in the semiconductor industries, was used for the experiment, whereas the appreciable deposits on the wall of the quartz tube. In fact, it has been reported the deposition of the Zn_3N_2 on the fused silica substrate [7]. Therefore, a fused silica substrate was also used in this study to elucidate the effect of the substrate. Zn3N2 film was deposited at temperature of 625 °C to compare the properties of the Zn_3N_2 films deposited on a SiO_2/Si (100).

Fig.3 shows XRD patterns of Zn_3N_2 films deposited on a SiO_2/Si(100) substrate and a fused silica substrate at growth temperature of 625 °C. From these XRD patterns, it was concluded that there was no effect of the substrate on the crystal structure of the resulting Zn_3N_2 films because almost same diffraction peaks were observed from the deposited Zn_3N_2 films.

Fig.4 shows SEM images of the Zn_3N_2 films deposited on a SiO_2/Si(100) substrate and a fused silica substrate. The grain size of the Zn_3N_2 film deposited on a fused silica substrate was relatively small but the morphology of the films did not show the significant change. The average diameter of the grains in the film deposited on a fused silica substrate was about 0.25 μm.

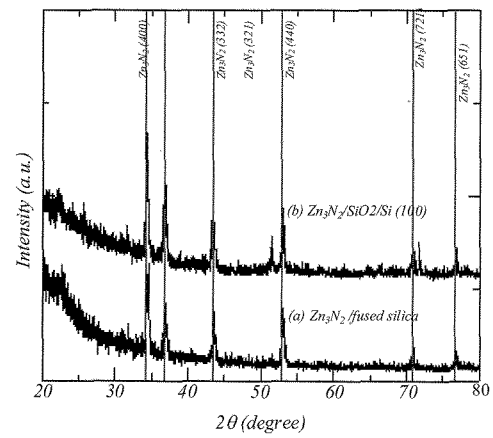
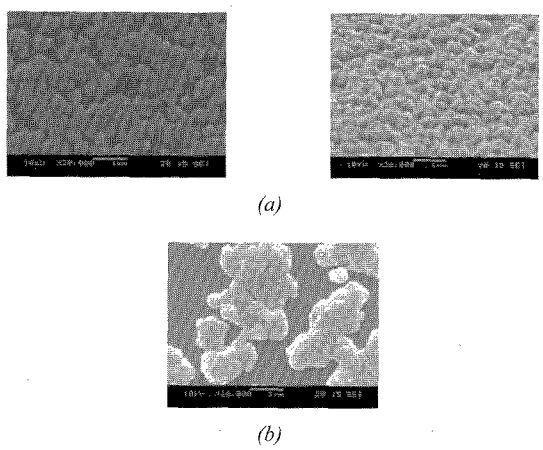


Fig. 3. *XRD pattern of Zn_3N_2 on different substrates*

(a) Zn_3N_2 / fused silica (b) Zn_3N_2 / SiO_2 / Si (100)



(a)

(b)

Fig. 4. *SEM images of Zn_3N_2 on different substrates*

(a) Zn_3N_2 / fused silica (b) Zn_3N_2 / SiO_2 / Si (100)

3.3 Optical properties of Zn_3N_2 films deposited on a fused silica substrate

The relation among absorption constant, transmittance, and reflectance is represented by the following equation;

$$a = -\log\frac{T}{1-R}\Big/d \qquad (1)$$

a : Absorption constant (cm^{-1})

T : Transmittance (-)

R : Reflectance (-)

d : Film thickness (cm)

In addition, the relation between absorption constant and the optical band gap is represented by the following equation for the case of direct transition [5];

$$a(h\upsilon) = A^*(h\upsilon - E_g)^{1/2} \qquad (2)$$

That is,

$$a^2(h\upsilon)^2 = A^*(h\upsilon - E_g) \qquad (3)$$

$a(h\upsilon)$: Absorption constant at energy (cm^{-1})

$h\upsilon$: Measurement wavelength (eV)

A^* : Constant (-)

E_g : The optical band gap (eV)

From these relations, is plotted as the function of $h\upsilon$ to obtain the E_g by the extrapolation of the tangential line of obtained curve.

To measure the optical properties of the Zn_3N_2 films deposited on a fused silica substrate, transmittance and reflectance were measured by UV-Vis-NIR, and the optical properties were evaluatedby using Eq. (1), (2), and (3). The result is shown in fig. 5. The result showed that the optical band gap of the Zn_3N_2 was 1.247eV. This value was larger than the reported theoretical value of 1.06eV [5]. The larger band gap energy suggests that the Zn_3N_2 is partially oxidized.

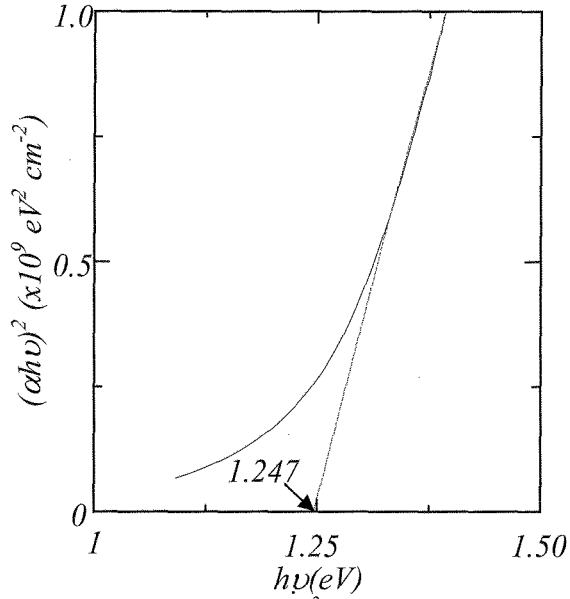


Fig. 5. *$(\alpha h\upsilon)^2$ versus $h\upsilon$ for*

4. CONCLUSIONS

In this study, Zn_3N_2 films were deposited on a SiO_2/ Si(100) substrate and a fused silica substrate by AP-CVD. It was found that the morphology of Zn_3N_2 films on both substrates were granular. There was little effect of the deposition temperature and the substrate on the morphology and the crystal structure of the resulting Zn_3N_2 films. We determined that the optimal deposition temperature was about 600 °C. The optical band gap of the resulting Zn_3N_2 film was 1.247 eV by UV-Vis-NIR measurement, showing the slightly larger value. Therefore, we concluded that the resultant Zn_3N_2 film could be partially oxidized. Further investigation is essential to elucidate the properties of the Zn_3N_2 and partially oxidized Zn_3N_2 films.

5. REFERENCES

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