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DEGRADATION OF Zn₃N₂ FILMS PREPARED BY REACTIVE RF MAGNETRON SPUTTERING

Masanobu Futsuhara^{1,2}, Katsuaki Yoshioka² and osamu Takai¹

1 Department of Materials Processing Engineering, School of Engineering, Nagoya University Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

2 Paint Design Institute, Nippon Paint Co., Ltd. 1-15, 4-chome, Minami-Shinagawa, Shinagawa-ku, Tokyo 140, Japan

ABSTRACT

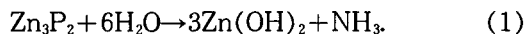
Degradation of Zn₃N₂ films is studied by using several analytical techniques. Polycrystalline Zn₃N₂ films prepared by reactive rf magnetron sputtering are kept in the air. Electrical and optical properties are measured by using van der Pauw technique and double-beam spectrometry. Structure and chemical bonding states are studied by X-ray diffraction (XRD), Fourier transfer infrared ray spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS). Significant differences are observed in optical properties between the degraded film and the ZnO film. XRD analysis reveals that the degraded film contains very small ZnO grains because very weak and broad ZnO peaks are observed. XPS and FT-IR measurements reveal the formation of Zn(OH)₂ in the degraded film. The existence of N-H bonds in degraded films is exhibited from the N 1s spectra. Zn₃N₂ change into the mixture of ZnO, Zn(OH)₂ and an ammonium salt.

INTRODUCTION

Zinc compounds have been actively investigated because of their significant properties. For example, zinc oxide (ZnO), which is an n-type semiconductor with a large optical gap of 3.2 eV, is important material for transparent conductive films because Al-doped Zn₃N₂ films shows high conductivity around 5×10^{-4} Ωcm and high optical transparency above 85% in the visible range^[1,2]. Zinc phosphide (Zn₃P₂) is a promising material for solar cells because Zn₃P₂ is a p-type semiconductor with direct gap of about 1.5eV^[3]. However zinc nitride has been scarcely studied. Juza et al sy-

nthesized a Zn₃P₂ powder sample^[4]. The Zn₃P₂ powder is blackish in color. The structure of Zn₃P₂ is anti-scandium oxide structure^[5]. Zinc atoms locate at the fluorine positions in CaF₂ structure, and nitrogen atoms occupy the calcium positions and is surrounded by the four closest zinc atoms. We first prepared a Zn₃P₂ thin film using reactive rf ion plating^[6]. The Zn₃P₂ film is near stoichiometric, and its structure is determined to be amorphous by X-ray diffraction. Recently, we have prepared the polycrystalline Zn₃P₂ films using reactive rf magnetron sputtering^[7,8]. The Zn₃P₂ film is determined to be n-type semiconductor with a direct gap of 1.23 ± 0.02 eV,

and shows large electron mobility around $100\text{cm}^2/\text{Vs}$. Therefore, the Zn_3P_2 film is a promising material for solar cells. However, Zn_3P_2 is rather unstable in the ambience with oxygen species. It is thought that Zn_3P_2 converts to zinc hydroxide ($\text{Zn}(\text{OH})_2$) by the reaction with H_2O molecules,



On the other hand, we observe the degradation of the Zn_3P_2 films prepared by reactive rf magnetron sputtering, and the formation of Zn_3P_2 in the air. Polycrystalline Zn_3P_2 films, which are prepared by reactive rf magnetron sputtering, are used as samples. Several analytical techniques are used to elucidate the degradation process.

EXPERIMENTAL

Zn_3P_2 films were prepared on substrates by reactive rf magnetron sputtering. Borosilicate glass and p-type(100) Si wafer were used for substrates. A metallic zinc disc ($100\text{mm}\phi$) was used as a target. The substrate was attached to a substrate holder and the target mounted on a cathode electrode. A sputtering chamber was evacuated below 5×10^{-4} Pa with a rotary pump and a diffusion pump. Ar- N_2 mixtures are used as sputtering gases. Ar and N_2 gases were introduced into the chamber through each mass flow controller, and the N_2 concentration was controlled from 20 to 100%. The Zn_3P_2 films prepared at 20, 50, 90 and 100% N_2 were used for the samples. The total gas pressure was kept at 1.0 Pa. The substrate temperature was maintained at 423 K during deposition by a heater set behind the substrate holder. The distance be-

tween the substrate and the target was 70mm. The rf power was maintained at 25 W. Film thickness was measured with a stylus profilometer and was 300–600 nm with 60–120 minutes deposition. The Zn_3P_2 films were kept in the air (humidity : 50–80%).

Optical properties were studied by measuring transmission and absorbance spectra with a double beam spectrometry. A clean borosilicate glass was used as a reference. The optical properties of a ZnO film were also measured for the comparison. The ZnO film was prepared on a borosilicate glass substrate by reactive rf magnetron sputtering using a sintered ZnO target. Electrical properties were investigated by van der Pauw technique^[9].

Electrical resistivity, carrier concentration and mobility were measured. Structure was measured by X-ray diffraction with $\text{CuK}\alpha$ radiation. Chemical bonding states were measured both by Fourier transform infrared spectroscopy (FT-IR) X-ray photoelectron spectroscopy (XPS). In the FT-IR measurement, a clean Si wafer was used as a reference. During as XPS measurement, the pressure of the analytical chamber was kept below 10^{-7} Pa order. A Mg anode was used as a X-ray source, and was operated at the voltage of 12 kV and the current of 10 mA. Chemical composition of the degraded film was estimated from the estimated from the peak area ratio with sensitive factors.

RESULTS AND DISCUSSION

Optical and electrical properties

As-deposited Zn_3P_2 films were blackish in color and had a smooth surface. During exposure to the air, the appearance of the Zn_3P_2

films gradually varied to transparent and colorless. Figure 1 shows the transmission and absorbance spectra of the as-deposited Zn₃P₂ film and the degraded Zn₃P₂ films. The Zn₃P₂ film prepared at 90% N₂ was used for the sample. The as-deposited Zn₃P₂ film shows transparency around 70% in the near infrared region, whereas the degraded film shows high optical transparency in the visible and infrared regions. The transmission and absorbance spectra of a ZnO film are also shown in Fig. 1. The wavelength of the absorption edge for the degraded film is shorter than that for the ZnO. From the transmission spectrum, absorption coefficient (α) was calculated and the dependence of α on photon energy ($h\nu$) was examined to determine the band

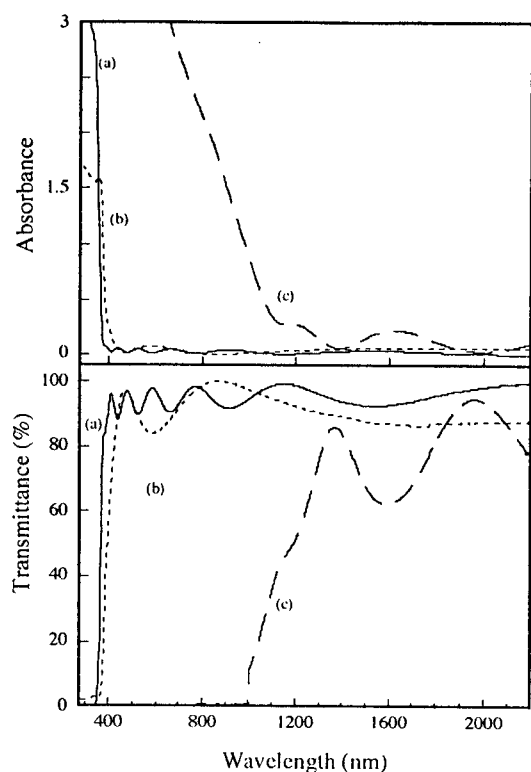


Fig. 1 Transmittance and absorbance spectra of (a) the degraded Zn₃N₂ film, (b) the ZnO film and (c) the degraded Zn₃P₂ film.

structure and optical band gap (E_g) by using two equations,

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

for direct electron transition from valence to conduction bands, and

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

for indirect electron transition. Here β and β are the edge width parameters. If the better linear relation is observed for the equation (1) rather than the equation (2), the transition of the electron is direct from the valence to conduction bands. Figure 2 indicates relationships between $h\nu$ and $(h\nu\alpha)^2$. The degraded film shows higher absorption than the ZnO film in the ultra violet region. The E_g value is determined by extrapolating the linear portion to $h\nu\alpha=0$. The E_g value is determined to be 3.26 eV for the ZnO film, whereas that is determined to be 3.45 eV for the degraded film. The E_g value of the degraded film is little larger than that of ZnO. This difference relate to the difference in structure and chemical bonding states between ZnO and the degraded film.

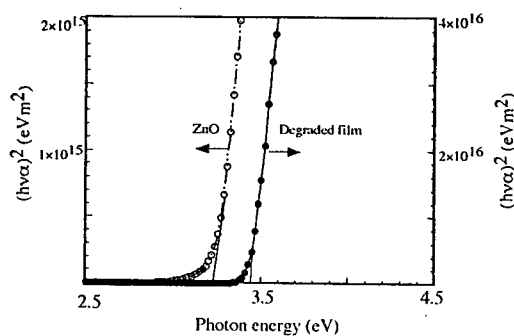


Fig. 2 Dependence of absorption coefficient on photon energy. The open circle shows the ZnO film, and the closed circle corresponds to the degraded Zn₃N₂ film.

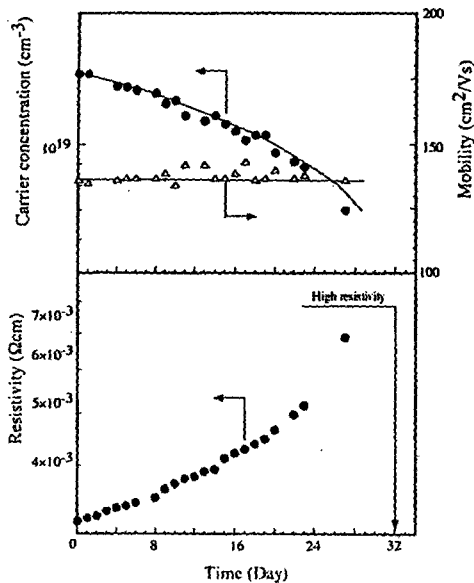


Fig. 3 Changes of electrical properties of the Zn_3N_2 film with exposure time in the air.

As-deposited Zn_3N_2 films indicate an n-type conduction with resistivity (ρ) of 10^{-3} to $10^{-2} \Omega\text{cm}$ which depends on the N_2 concentration in the sputtering gas^[7, 8]. Figure 3 shows the changes in electrical properties with exposure time of a Zn_3N_2 film in air. In this measurement, the sample is a Zn_3N_2 film prepared at 50% N_2 . The initial ρ of the Zn_3N_2 film is about $3.2 \times 10^{-3} \Omega\text{cm}$. ρ gradually increases with time up to 28 days, and at the 32 days ρ can not be measured by our equipment because of its high electrical resistivity. The degraded film shows high electrical resistivity. Carrier concentration (N) and mobility (μ) are also shown in Fig. 3. N slightly decreases with time up to 28 days, while μ is essentially constant. The slight increase in ρ is attributed to decrease in N . Nitrogen vacancies and/or excess zinc atoms can act as electron donors in Zn_3N_2 . The electron donors disappear by the degradation of Zn_3N_2 . This means that an insulating compound formed in the degraded Zn_3N_2 film.

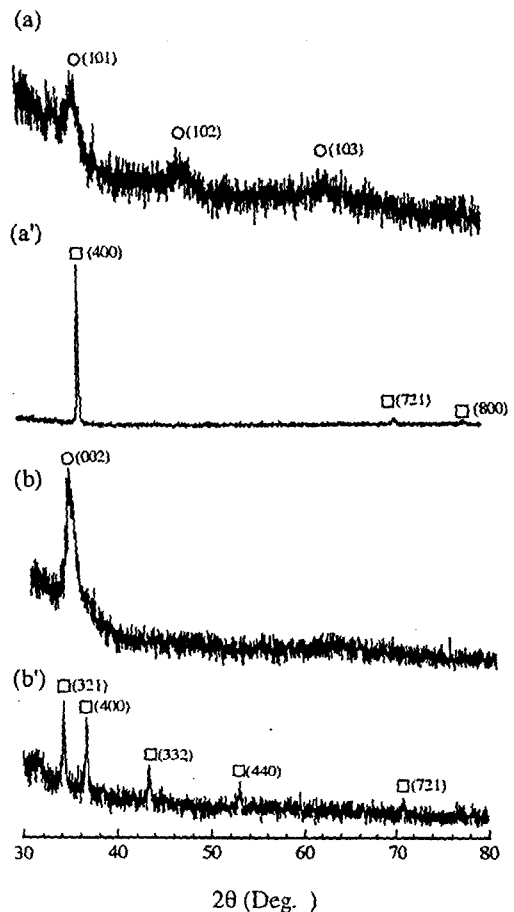


Fig. 4 X-ray diffraction patterns of the as-deposited Zn_3N_2 films and degraded films; (a) for the Zn_3N_2 film prepared at 20% N_2 (b) for the Zn_3N_2 film prepared 100% N_2

Structure

As-deposited Zn_3N_2 films are characterized to be polycrystalline, and the crystal orientation strongly depends on the N_2 concentration in the sputtering gas. Figure 4(a') and 4(b') indicate the X-ray diffraction patterns of the Zn_3N_2 films prepared at 20 and 100% N_2 , respectively. At 100% N_2 , all the peaks observed correspond to Zn_3N_2 peaks^[5]. This obviously shows the formation of the polycrystalline Zn_3N_2 film. On the other hand, a strong and sharp 400 peak and weak 800 and

721 peaks are observed for the film prepared at 20% N_2 , which means that the Zn_3N_2 grains preferentially grew. No ZnO peaks are observed in the diffraction patterns. Figures 4 (a) and 4 (b) show the X-ray diffraction patterns of the degraded films. The Zn_3N_2 peaks disappear in both diffraction patterns, 002 peak of ZnO is observed at 100% N_2 , and 101, 102 and 103 peaks of ZnO appear at 20% N_2 . No $Zn(OH)_2$ and $Zn(OH)_2 \cdot 0.5H_2O$ peaks are observed^[11,12]. The ZnO peaks observed are very weak and broad, which indicates that the size of the ZnO grains is very small and amorphous parts exist in the degraded film. XRD analysis reveals the formation of ZnO in the degraded films.

Chemical bonding states

In the FT-IR measurement, we used the Zn_3N_2 film prepared on a Si substrate at the N_2 concentration of 20%. Figures 5(a) and 5 (b) corresponds the FT-IR spectrum of the as-deposited Zn_3N_2 film and the degraded film. A peak due to stretching vibration of -OH peak is clearly seen at $3437cm^{-1}$ in the spectrum of the degraded film. This peak come both from adsorbed H_2O molecules and $Zn(OH)_2$ formed.

XPS measurement was performed immediately after taking out the sample from the sputtering chamber. The N 1s and O 1s spectra of the as-deposited Zn_3N_2 film are shown in Fig. 6(a). The sample in a Zn_3N_2 film prepared at 90% N_2 . No Ar etching is performed to avoid the change in the surface state by Ar ion bombardment. Both O 1s and N 1s peaks can be divided into two peaks. The main N 1s peak indicates a larger chemical shift. The binding energy of the main peak

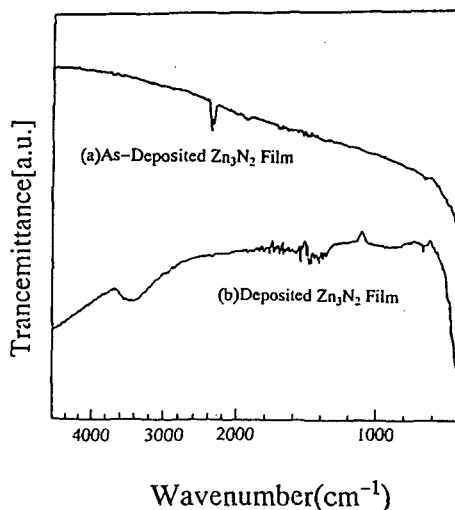
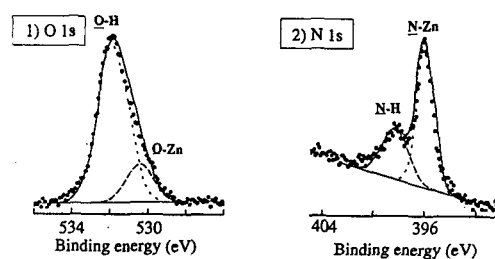


Fig. 5 FT-IR spectra of (a) as-deposited Zn_3N_2 film and (b) the degraded Zn_3N_2 film.

a) As-deposited Zn_3N_2 film



b) Degraded film

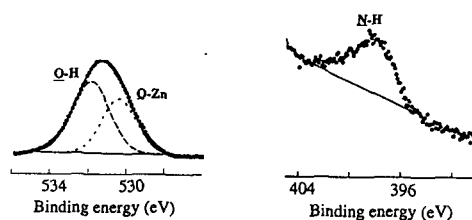


Fig. 6 O 1s and N 1s spectra of the as-deposited Zn_3N_2 film and degraded Zn_3N_2 films prepared at 90% N_2

shifts 3.0 eV from the binding energy for free_{1,2} amine(-NH₂). This obviously shows the formation of N-Zn bonds originated from Zn_3N_2 . The small peak in the N 1s peak is attributed to the N-H bonding. The main O 1s

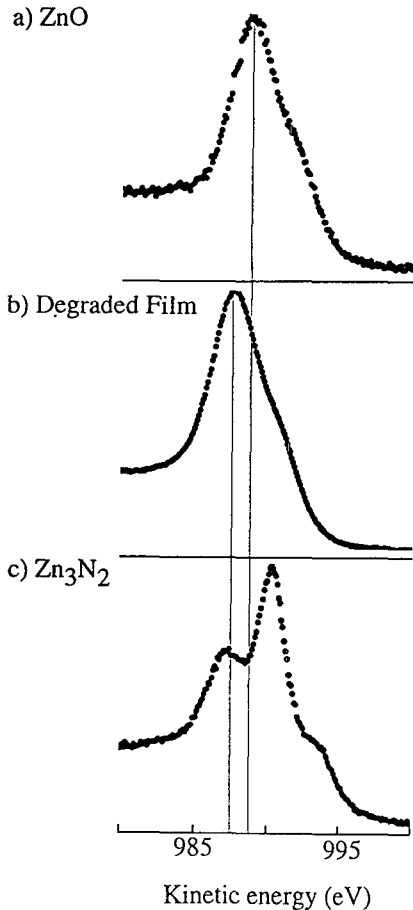
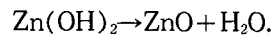


Fig. 7 Auger $L_{3M_{4,5}M_{4,5}}$ spectra of (a) the ZnO film, (b) the degraded Zn_3N_2 film and (c) the as-deposited Zn_3N_2 film.

peak results from O-H bonds and the small O 1s peak indicates the formation of Zn-O bonds. Figure 6(b) indicates the O 1s and N 1s spectra of the degraded film. In the N 1s spectrum, no N-Zn peak is observed and only the N-H peak is observed. The O 1s peak also can be divided into two peaks, but the ratio of the O-Zn peak to O-H peak for the degraded film is higher than that for the as-deposited film.

A large amount of H_2O molecules immedi-

ately adsorbs on the as-deposited Zn_3N_2 film after taking out it to air. Thus, the O-H and N-H bonds are observed for the as-deposited Zn_3N_2 films. The H_2O molecules react with Zn_3N_2 as eq. (1). Therefore the -OH stretching vibration peak in the FT-IR spectrum is attributed to the $Zn(OH)_2$, and XRD analysis reveals the existence of ZnO in degraded films. Therefore, the Zn-O peak in XPS O 1s spectra originates both from ZnO and $Zn(OH)_2$. The ZnO is formed according to the reaction,



The film composition was estimated from the peak area ratio with sensitive factors. Oxygen, nitrogen and zinc contents are about 82.6 and 12 atomic %, respectively. The large amount of excess oxygen resulted from adsorbed H_2O molecules because of the small amount of Zn. Hence, the O-H peak mainly originated from the H_2O adsorbed on Zn_3N_2 . The N-H peak shows the formation of an ammonium salt.

Figure 7 shows the Auger $L_{3M_{4,5}M_{4,5}}$ spectra. In this figure, Fig. 7(a), 7(b) and 7(c) correspond to the ZnO, the degraded and the Zn_3N_2 films, respectively. A shoulder peak is observed at 987.8 eV in the $L_{3M_{4,5}M_{4,5}}$ peak for Zn_3N_2 . The shoulder peak becomes a main peak in the $L_{3M_{4,5}M_{4,5}}$ peak for the degraded film. This means that the peak is attributed to the formation of O-Zn bonding that formed by the reaction between Zn_3N_2 and H_2O molecules adsorbed. Compared with the spectrum of the ZnO film, the band shape of $L_{3M_{4,5}M_{4,5}}$ peak for the degraded film is very similar to the band for ZnO, but the kinetic energy is little smaller than that for

ZnO. The chemical shift for an Auger peak relates to the change in valence electron density around an element; the decrease in valence electron density causes the decrease in kinetic energy of Auger electrons. Therefore the degraded compound probably has little higher ionicity rather than ZnO.

CONCLUSION

Degradation process of Zn_3N_2 in the air has been elucidated. Polycrystalline Zn_3N_2 films were used for samples and were kept in air. The appearance of the Zn_3N_2 film gradually changed from blackish in color to transparent and colorless. X-ray diffraction analysis revealed the formation of very fine ZnO grains because very weak and broad ZnO peaks were observed. XPS analysis revealed that a large amount of H_2O molecules adsorbed on the as-deposited Zn_3N_2 and degraded films. FT-IR and XRS measurements showed the formation of $Zn(OH)_2$ formed by the reaction between Zn_3N_2 and H_2O . The N-H bonding was observed in N 1s spectra of the degraded film, which came from a small amount of ammonium salt. From these results, Zn_3N_2 changed into a mixture of ZnO, $Zn(OH)_2$ and an ammonium salt by the reaction with H_2O molecules adsorbed.

REFERENCES

1. T. Minami, H. Nanto and S. Takata, J. Appl. Phys. Lett. **41**, 958(1982)
2. H. Sato, T. Minami and S. Takata, J. Vac. Sci. Tech. **11**, 2975(1993)
3. M. Pawlikowski, Infrared Phys. **21**, 181 (1981)
4. Juza and H. Hahn, Z. Anorg. Allg. Chem. **224**, 125(1940)
5. Powder Diffraction File compiled by the Joint Committee on Powder Diffraction, Card No. 35-0762
6. O. Takai, J. Surf. Finish Soc. Japn, **40**, 88 (1989)
7. M. Futsuhara, K. Yoshioka and O. Takai, Symp. Plasma Sci. Mater, **9** 33(1996)
8. M. Futsuhara, K. Yoshioka and O. Takai, Proc. 3 rd Asia-Pacific Conf. Plasma Sci. & Technol, p511(1996)
9. L. J. van der Pauw, Philips Res. Repts. **13**, 1(1958)
10. Powder Diffraction File compiled by the Joint Committee on Powder Diffraction, Card No. 36-1451
11. Powder Diffraction File compiled by the Joint Committee on Powder Diffraction, Card No. 20-1437
12. Powder Diffraction File compiled by the Joint Committee on Powder Diffraction, Card No. 20-1436