PERGAMON

Solid State Communications 112 (1999) 513–515

solid state communications

www.elsevier.com/locate/ssc

RF-sputter deposition of Zn–Ge nitride thin films

S. Kikkawa[1,*], H. Morisaka

ISIR, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan

Received 6 July 1999; accepted 4 August 1999 by F.J. DiSalvo

Abstract

Nitride Zn–Ge thin films were deposited by reaction sputtering. Black conducting $(Zn_{1-x}Ge_x)_3N_{2+\delta}$ with $x \leq 0.27$ was obtained in a compositional range below 29 wt% Ge against the total metal content. Greenish pale yellow $ZnGeN_2$ was observed in a range of 30–60 wt% Ge. This crystallized in a hexagonal lattice of a comparable size to the isoelectronic GaN. Its solid solution range seems to be very narrow and its band gap was estimated to be about 3.1 eV. Ge_3N_4, like amorphous $(Ge_{1-y}Zn_y)_3N_{4-\gamma}$ with $y \leq 0.43$ films, shows pale yellow color above the compositional range of 60 wt% Ge.

Keywords: A: Semiconductors; B: Chemical synthesis; C: Crystal structure and symmetry; D: Electronic transport; D: Optical properties

1. Introduction

Structural feature is important for a semiconductor thin film. Efforts have been made on homoepitaxial growth of GaN on the small bulk GaN crystals. Dislocation density was less than $10^6\,cm^{-2}$ with the residual doping level of $10^{17}\,cm^{-3}$ [1]. The reduction of dislocation density is very critical for a blue laser application. The range of substrates available for use in group III nitrides is limited. Growth of GaN bulk crystal is still in a preliminary research level and is not yet commercially available. The most commonly used substrate for the nitride devices has been a sapphire, which has a large lattice mismatch to the nitride resulting in a defect density of $10^{8\sim11}\,cm^{-2}$. ZnO did not show any improvement in the GaN quality from the films on sapphire or GaAs [2]. Low-temperature buffers were required to improve nucleation behavior of GaN on $LiGaO_2$ and InN on $LiAlO_2$ [2].

Crystal structure has been refined on the wurtzite GaN. The hexagonal lattice sizes were $a = 0.3190$ nm and $c = 0.5189$ nm [3]. Isoelectronic replacement is possible on the group III nitrides to II–IV analogues. It has advantages to control both crystal lattice size and electronic structure. $ZnGeN_2$ is a derived binary nitride from GaN substituted with its neighboring II and IV group elements. Its crystal structure originally assumed to be derived from wurtzite [4]. Neutron diffraction showed an ordering of Zn and Ge in a tetrahedral site in $ZnGeN_2$ with a monoclinic crystal lattice of $a = c = 0.3167$ nm, $b = 0.5194$ nm, $\beta = 118°53'$ [5]. The crystal structure is of the $NaFeO_2$ type with space group $Pna2_1$. $ZnGeN_2$ will be either a candidate material for a blue laser emitter itself substituting GaN or a substrate material for the GaN thin film growth when its defect density will be very low. Its preparation and properties have been studied less [4–6]. A brief report is available on the optical and electrical properties of $ZnGeN_2$ thin film grown in an open flow $HCl–N_2$ atmosphere on Zn and Ge elements [6]. Both Zn_3N_2 and Ge_3N_4 are end members of nitrides in a Zn–Ge binary system. Only their crystal structures have been reported [7–9].

In the present investigation, rf-sputter deposition was applied to obtain thin films of $ZnGeN_2$, zinc and germanium nitrides, respectively. Zn, Ge and their composite targets were sputtered in nitrogen atmosphere. The products were characterized in structure, electrical and optical properties.

2. Experimental

Films were grown on glass or Si wafer substrates without

* Corresponding author. Tel.: + 81-6-6879-8452; fax.: + 81-6-6879-8452.

E-mail address: kikkawa@sanken.osaka-u.ac.jp (S. Kikkawa)

[1] This research was partly supported by NEDO International Joint Research Program on Advanced Nitrides (97MB2).

0038-1098/99/$ - see front matter
PII: S0038-1098(99)00389-0

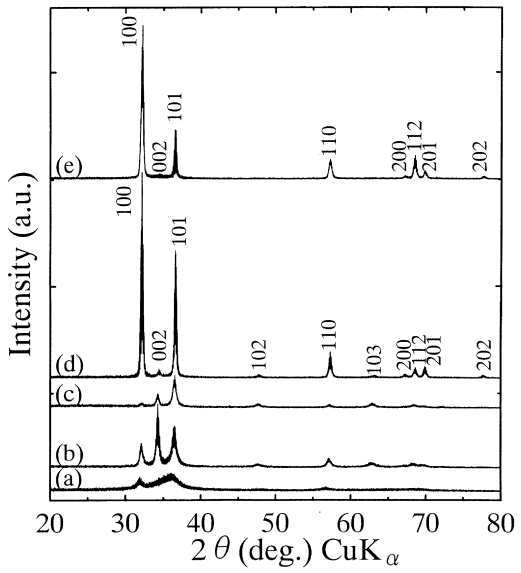

Fig. 1. X-ray diffraction pattern of $ZnGeN_2$ thin films prepared with various Ge wt% against total metal content: (a) 30; (b) 45; (c) 51; (d) 52; and (e) 57%.

their heating in a rf-magnetron sputter deposition equipment (Anelva SPF-210H). Sputter gas was nitrogen in a 6N purity. Target materials were Zn or Ge in a 5N purity of 100 and 76 mm in diameter, respectively. Zn/Ge compositional ratio was controlled by changing distribution of small Ge chips (5×5 mm^2) on the Zn target. X-ray diffraction was measured using Rigaku diffractometer both for powder and for thin film with a monochromatized CuK_α radiation generated with a rotary target. 2θ angle was scanned with an X-ray incident angle $\theta = 1°$ in the thin film diffractometry. Texture was observed by Hitachi scanning electron microscope S-2150 with Horiba EMAX-2770. Optical absorption was measured with a UV–visible spectrometer, Jasco 670 on the films deposited on silica glass substrate. Electrical properties were investigated on the films of 10×10 mm^2 using gold lead wire with indium electrodes applying ResiTest 8300.

3. Results and discussion

It is necessary to obtain preparation conditions of both end members in the use of the composite target. Both the applied rf-power and sputter gas pressure were adjusted for depositions of Zn and Ge nitrides, respectively. Zinc nitride was prepared in a region with 0.5 ~ 1.3 Pa of sputter gas pressure and 20 ~ 40 W of rf-power. Zn target itself was destroyed due to a severe nitridation in higher conditions. Metallic Zn deposited at 0.5 Pa in 30 W. A black Zn_3N_2 thin film was obtained at 1.3 Pa in the range of 20–40 W (JCPDS 35-762). It showed a preferred orientation in the ⟨100⟩ direction of anti-bixbyte type structure. The crystallinity was reduced both at 1.3 Pa in 40 W and at 0.5 Pa in 20 W. Film thickness was in the range of 0.6–1.4 μm in a 2 h deposition. A columnar texture was observed in its cross-section by SEM. Zn_3N_2 thin films were of the n-type semiconductors with an electrical resistivity of 0.44 Ω cm at room temperature. The carrier density was 1.98×10^{18} and its mobility was 72.1 cm^2/(V s). The films were easily oxidized to ZnO in an ambient atmosphere in a month.

Germanium nitride was prepared at 1.3 Pa in the range of 30–40 W for 3 h. Thin films of germanium nitride were electrically insulating and pale yellow in color. X-ray diffraction showed a hallow pattern in a 2θ range of 20–40° corresponding to Ge_3N_4 like amorphous. The amorphous patterns showed some similarity to the reported data for α- and β-Ge_3N_4 on the films deposited at 40 and 30 W, respectively (JCPDS 11-69, 38-1374). Local structures similar to the high temperature α- and low temperature β-phases are present in the respective films because of the different energy supply during the deposition. The former showed a smaller optical absorption gap than the latter: 2.6 and 2.7 eV for the films deposited at 40 and 30 W for 180 min, respectively. They were 3.0 and 3.2 eV for the respective films deposited for 90 min. The local structure may slightly change with the deposition duration as well as the applied rf-power. The film was stable at 500°C in an ammonia flow but decomposed to metallic Ge at 700°C.

Germanium content could be controlled in the film deposited using the composite target with various Zn/Ge area ratios, in which Ge chips were distributed on a Zn metal target. The composition control was difficult in an opposite configuration of the composite target, in which Zn chips were easily changed to nitride to reduce severely the deposition rate of zinc nitride. Films were deposited at 1.3 Pa in 30–40 W. Black $(Zn_{1-x}Ge_x)_3N_{2+\delta}$ solid solution was obtained in a range below 29 wt% Ge against the total metal content. The composition corresponds to $x = 0.27$. This gradually became X-ray amorphous with an increasing x and electrically resistive; 8.52×10^8 Ω cm at $x = 0.27$. $ZnGeN_2$ was observed on the films deposited in the range of 30 ~ 60 wt% Ge. Crystallinity was poor in the brown film obtained at 30 wt% Ge as shown in Fig. 1. Greenish pale yellow $ZnGeN_2$ crystallized well with an increase of Ge content changing the crystalline orientation. The X-ray diffraction patterns could be indexed in a hexagonal lattice. Solid solution range was assumed to be very narrow because the lattice parameters changed very little against the Ge content. $ZnGeN_2$ crystallized very well and showed the smallest unit cell volume of 4.64×10^{-2} nm^3 with $a = 0.3213$ nm and $c = 0.5191$ nm at the Ge content of 52 wt%. It corresponds to Zn/Ge = 1.0 in the molar ratio. The $ZnGeN_2$ crystal lattice has been reported as monoclinic with $a = c = 0.3167$ nm, $b = 0.5191$ nm, $\beta = 118°53'$ in neutron diffraction [5], and as hexagonal with $a = 0.3193$ nm, $c = 0.5187$ nm [4] Their unit cell volumes are 4.51×10^{-2} and 4.58×10^{-2} nm^{-3}, respectively. The

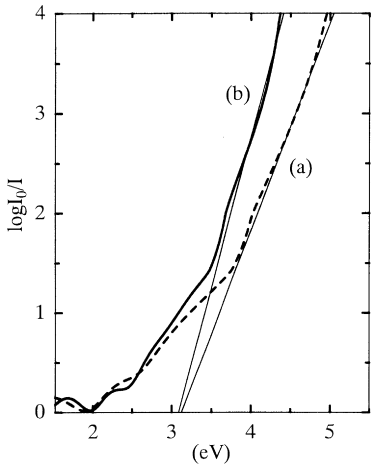

Fig. 2. Optical absorption spectra of $ZnGeN_2$ thin films deposited for (a) 20 and (b) 30 min.

present value is slightly larger than the previous ones probably due to the presence of excess nitrogen absorbed during the sputter deposition. The present product was an electrical insulator. Vapor-grown $ZnGeN_2$ film has been reported to be an n-type semiconductor with electrical resistivities between 0.3 and 0.4 Ω cm at room temperature [6]. Trace doping of chlorine from its preparation atmosphere might contribute for the electron doping. The present films showed optical absorption spectra in Fig. 2. They were slightly different with the film thickness but basically the same. The band gap can be estimated to be about 3.1 eV. They are comparable to a value of 3.26 eV for GaN [1]. The reported value of 2.67 eV for $ZnGeN_2$ might be related to its impurity level [6]. The lattice parameters shrunk after its annealing in ammonia for 1 h; $a = 0.3219$ nm, $c = 0.5226$ nm at 500°C and $a = 0.3214$ nm, $c = 0.5129$ nm at 700°C. They were also electrical insulators even after the annealing. Pale yellow Ge_3N_4 like amorphous $(Ge_{1-y}Zn_y)_3N_{4-\gamma}$ film was obtained in a range above the Ge content of 60 wt%. The composition corresponds to $y = 0.43$. It was also electrically insulating.

4. Conclusion

Isoelectronic replacement of GaN was performed by preparing $ZnGeN_2$ thin films applying the rf-sputter deposition. Use of a composite target where Ge chips were distributed on a Zn metal target was significant to control the film composition in the reaction sputtering in nitrogen atmosphere. The product showed a slightly larger crystal lattice with $a = 0.3213$ nm and $c = 0.5191$ nm than the previously reported values. The values are also larger than the $a = 0.3190$ nm and $c = 0.5189$ nm of GaN. The obtained product was an electrical insulator with a slightly smaller optical band gap of ca 3.1 eV than 3.26 eV of GaN.

Acknowledgements

Authors would like to thank Dr M. Takahashi and Ms K. Adachi for their assistance in a preliminary data acquisition.

References

[1] B. Monemar, J. Crystal Growth 189/190 (1989) 1.
[2] J.D. MacKenzie, S.M. Donovan, C.R. Abernathy, S.J. Pearton, P.H. Holloway, R. Linares, J. Zavada, B. Chai, J. Electrochem. Soc. 145 (1998) 2581.
[3] H. Schula, K.H. Thiemann, Solid State Commun. 23 (1977) 815.
[4] M. Maunaye, P. Haridon, Y. Laurent, J. Lang, Bull. Soc. Fr. Minéral. Crystallogr. 94 (1971) 3.
[5] M. Wintenberger, M. Maunaye, Y. Laurent, Mater. Res. Bull. 8 (1973) 1049.
[6] W.L. Larson, H.P. Maruska, D.A. Stevenson, J. Electrochem. Soc. 121 (1974) 1973.
[7] D.E. Partin, D.J. Williams, M. O'Keeffe, J. Solid State Chem. 132 (1997) 56.
[8] R. Juza, A. Neuber, H. Hahn, Z. Anorg. Allg. Chem. 239 (1938) 273.
[9] S. Wild, P. Grieveson, K.H. Jack, Spec. Ceram. (1977) 815.