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## Study of amorphous Zinc Germanium Nitride thin films grown by reactive co-sputtering

Nicole Beddelem<sup>a,b,\*</sup>, Névine Rochat<sup>c,d</sup>, Christophe Licitra<sup>c,d</sup>, Bérange Hyot<sup>c,d</sup>, Patrice Miska<sup>a</sup><sup>a</sup> Institut Jean Lamour, CNRS - Université de Lorraine, Campus ARTEM, 2 allée André Guinier BP 50840, Nancy 54011, France<sup>b</sup> CEA Tech en Grand Est, 5 rue Marconi, Metz F-57075, France<sup>c</sup> Univ. Grenoble Alpes, Grenoble F-38000, France<sup>d</sup> CEA, LETI, MINATEC Campus, Grenoble F-38000, France

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## ABSTRACT

Under its crystalline form, the ZnGeN<sub>2</sub> alloy is promising for optoelectronic devices such as LEDs because of its large, direct and adjustable band gap. Nevertheless, data are scarce, more especially for the amorphous form. We report here on the study of zinc germanium nitride amorphous thin films obtained by reactive co-sputtering. The samples are elaborated by PVD and analyzed by physical and chemical methods to determine their composition, structure and optical properties. We observe a clear evolution of these properties with composition. The shape of the complex refractive index reveals changes in the electronic structure. Furthermore, the optical gap and Urbach energy decrease with increasing zinc content.

## 1. Introduction

The current generation of commercial LEDs exhibits a strong decrease in efficiency in the green-yellow-emission range known as the green-gap. The total efficiency of white light LEDs is therefore limited [1]. The ternary semiconductor ZnGeN<sub>2</sub> appears to be promising for improving the device efficiency in this regime [2]. This material is analogous to GaN where the column III element is periodically replaced by a column II (Zn) and a column IV (Ge) element and is particularly interesting due to a good lattice match with GaN as well as its similar energy band gap. This could enable the design of type-II InGaN-ZnGeN<sub>2</sub> quantum wells, used as active regions in the blue and green emission ranges [2]. The study of this material under crystalline and amorphous forms has therefore increased during the last years but data remain scarce.

We present here the study of amorphous zinc germanium nitride thin films grown by reactive co-sputtering. We analyze the evolution of the physical and chemical properties as a function of the zinc and germanium content. The composition is determined by microprobe analysis. Cross-sectional imaging by scanning electron microscopy (SEM) is used to determine the thickness and the structure of the films. X-ray diffraction (XRD) analysis indicates the amorphous form for the samples, even after thermal annealing and Fourier-transform infrared (FTIR) spectroscopy is used to determine and quantify the bond types. Ellipsometry and optical transmittance measurements are performed to

study the optical properties such as the complex refractive index  $\mathbf{n}$ , the optical band gap  $E_{04}$  and the Urbach energy  $E_U$ .

## 2. Sample elaboration and characterization

Zinc germanium nitride thin films are deposited by reactive co-sputtering. The starting vacuum is about 10<sup>-8</sup> mbar and the sputtering gas is 99.9999% pure ALPHAGAZ<sup>TM</sup> 2 nitrogen from *Air Liquide*. The cathode of the 99.95% pure germanium target from *A.M.P.E.R.E. Industrie S.A.S* is connected to a radio frequency (RF) source, the one of the 99.99% pure zinc target from *HMW Hauner GmbH & Co. KG* to a direct current (DC) source. The cathodes are confocal, with a target to substrate distance of approximately 10.5 cm. The substrate-holder is a rotating inconel molyblock on which a glass and a double-sided polished 500 μm thick silicon substrate are fixed. No thermal treatment or chemical etching is performed to remove the amorphous native oxide layer of the silicon. No differences are thus observed between the glass and the silicon substrate. A nitrogen flow of 18 sccm is used with a constant pressure of 1.3 Pa controlled by a gate regulation valve. The power on the germanium cathode is kept constant at 100 W and the current on the zinc cathode is gradually increased from 0.05 A to 0.1 A. The growths are done at room temperature and the growth-time is 45 min. This way, 6 transparent thin films with increasing zinc content and hence increasing thicknesses are obtained, whose colors range from pale yellow to dark orange.

\* Corresponding author at: Institut Jean Lamour, CNRS - Université de Lorraine, Campus ARTEM, 2 allée André Guinier BP 50840, Nancy 54011, France.  
E-mail address: [nicole.beddelem@univ-lorraine.fr](mailto:nicole.beddelem@univ-lorraine.fr) (N. Beddelem).

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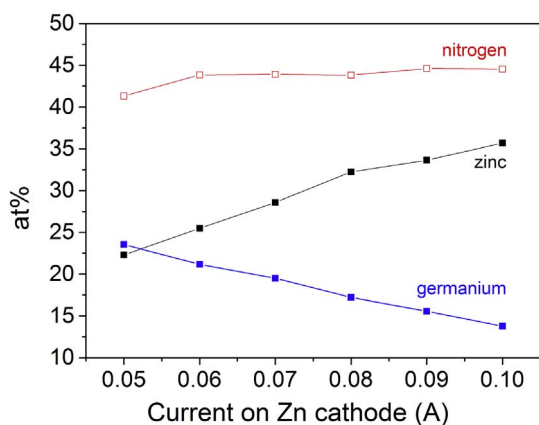


Fig. 1. Composition of the samples determined by microprobe analysis.

The composition is determined by microprobe analysis. The device used is a *JXA-8530F* from *Jeol*. The standards used are pure zinc, pure germanium,  $\text{Fe}_4\text{N}$  for nitrogen and  $\text{MgO}$  for oxygen. The quantification mode over the 100 averaged data points is Phi-Rho-Z. Cross-sectional imaging of the cleaved samples is done in a *HITACHI S-5500 SEM* for determination of the samples thicknesses and growth structure. X-ray analyses are done on a  $\theta - 2\theta$  diffractometer from *Bruker* with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ).

FTIR measurements are done on a *Bruker IFS55* and completed under nitrogen to avoid all atmospheric contributions. The orientation of the samples is chosen so that the incident P polarized beam is under Brewster's angle ( $65^\circ$  in this case). Using this configuration, all interference patterns disappear and no background-treatment is needed. A silicon sample is used as a reference.

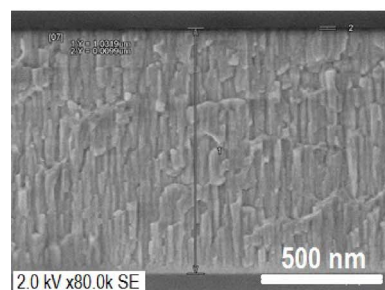
Ellipsometry measurements are performed using a *M2000* rotating compensator ellipsometer from *Woollam* with the films deposited on silicon substrates. The angle of incidence is varied from  $65^\circ$  to  $75^\circ$  every  $5^\circ$  and the data are acquired in the  $[0.73 - 6.48 \text{ eV}]$  range. The refractive index is modeled using a sum of 3 Tauc-Lorentz oscillators and the data fitted considering bi-layer system including surface roughness.

The optical transmittance  $T$  in the UV-visible-NIR range (300–3000 nm) is measured with the samples deposited on glass using a *Cary 5000* from *Agilent*.

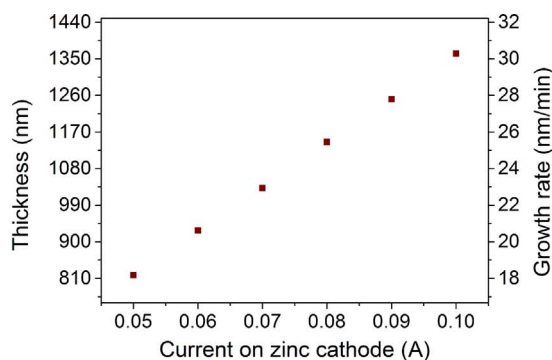
### 3. Results and discussion

#### 3.1. Composition and structure

The sample compositions determined by microprobe analysis are



(a)



(b)

Fig. 2. (a) Cross-sectional image of  $\text{Zn}_x\text{Ge}_{2-x}\text{N}_2$  thin film with  $x = 1.19$ . (b) Evolution of the thickness determined by cross-sectional imaging and associated growth rate.

reported in Fig. 1.

We see a linear variation of the  $\text{Zn}_x\text{Ge}_{2-x}\text{N}_2$  ranging from  $x = 0.97$  to  $x = 1.44$ . This behavior is in accordance with the change of the current on the zinc target. As the nitrogen content is constant, we see that the current modification enables us to modify the zinc and germanium content. The variation is linear with the applied current.

Cross-sectional imaging of the samples gives a view on the growth structure (Fig. 2 (a)). The films do not appear porous, large vertical ribbon-shaped domains can be observed.

The cross-sectional images also enable us to determine the sample thicknesses. As expected, a linear evolution of thickness from 800 nm to 1360 nm depending on the current on the zinc cathode is observed (Fig. 2 (b)). Indeed, a higher current corresponds to higher material quantity deposited on the substrates.

#### 3.2. X-ray diffraction

Samples grown at room temperature show no diffraction peaks apart from the silicon substrate (Fig. 3). Only a broad,  $10^\circ$  wide peak is seen around  $35^\circ$ . Growths done at a substrate temperature of  $70^\circ\text{C}$ ,  $140^\circ\text{C}$  and  $200^\circ\text{C}$  show the same diffractogram, as well as the samples successively thermally annealed at  $440^\circ\text{C}$ ,  $510^\circ\text{C}$  and  $545^\circ\text{C}$  (Fig. 3). We assume that the amorphous character of these zinc germanium nitride films may be due to the fact that RF-sputtered germanium nitride thin films are reported to crystallize very poorly, independently of the deposition parameters [3]. Their XRD response is a broad band between  $20^\circ$  and  $45^\circ$ , which is similar to the diffractograms obtained in this study, as well as to the diffractograms reported for amorphous GaN [4,5].

#### 3.3. FTIR

Absorbance spectra normalized to the layer thicknesses are reported in Fig. 4 (a).

An evolution of the peak areas is visible (Fig. 4 (b)). The peak around  $615 \text{ cm}^{-1}$  may be due to the presence of interstitial carbon atoms in the substrate. Only few studies report on the clear analysis of the FTIR peaks of  $\text{ZnGeN}_2$ . Shang et al. [6] reported 3 peak families used here to fit the spectra. The peak broadening may be due in our case to the amorphous structure of the films. The peak at  $\approx 500 \text{ cm}^{-1}$  can be attributed to the Zn-N bond [7], and the peak at  $\approx 750 \text{ cm}^{-1}$  to the Ge-N bond [8]. As shown in Fig. 4 (b), their area increase and decrease with the zinc content, respectively. This is in accordance with the composition evolution determined by the microprobe measurements. The peak at  $\approx 600 \text{ cm}^{-1}$  seems to remain constant and could be attributed to a Zn-N-Ge bond. Indeed, literature predicts IR peaks for  $\text{ZnGeN}_2$  at these wavenumbers [9].

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