



# Chemical environment and functional properties of highly crystalline ZnSnN<sub>2</sub> thin films deposited by reactive sputtering at room temperature

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## ABSTRACT

Zinc tin nitride (ZnSnN<sub>2</sub>) thin films have been deposited on glass and silicon substrates using a reactive co-sputtering process. Although the deposition temperature was limited to the room temperature, the films show a highly crystallization level and a strong preferred orientation in the [001] direction. The film composition, measured using energy dispersive X-ray spectroscopy and electron probe microanalysis, indicates a possible tin understoichiometry (or a zinc and a nitrogen overstoichiometry). As confirmed by transmission electron microscopy, the main oxygen contamination of the films results from oxidation of the grains boundaries after air exposure of the samples. X-ray photoelectron spectroscopy and Mössbauer spectrometry have been used to determine the chemical environment of atoms in the ZnSnN<sub>2</sub> crystals. Both methods confirm that Sn<sup>4+</sup> ions are bonded to nitrogen atoms and that the oxygen contamination results in the formation of Sn<sup>2+</sup> ions. Zinc tin nitride exhibit an electron mobility at room temperature close to 3.8 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an optical band gap of 1.8 eV as measured independently from UV–visible spectrometry and ellipsometry. The results obtained in the present study confirm the suitability of ZnSnN<sub>2</sub> thin films as an Earth abundant material for absorber layer in photovoltaic devices.

## 1. Introduction

The tracking of new photovoltaic (PV) absorbers is an activity under real development [1,2]. The need of terawatt scale generation requires to find new Earth abundant, non-toxic, easily recyclable materials that can be grown using up-scalable process to complete or to overcome and improve the current technologies. Under the proposed new materials, nitride semiconductors have attracted considerable interest because of their predicted suitable properties for solar energy applications. Those new III-nitride semiconductors also have excellent potential for various optoelectronic applications [3]. More especially, the ZnSnN<sub>2</sub> compound seems to be a semiconductor family of prime interest in the range of this new class of PV absorbers [4] due to its high absorption coefficient in the solar spectrum [5]. A study suggested the use of such wide bandgap absorber for tandem technologies [6].

As reported by Chen et al., ZnSnN<sub>2</sub> has a very small formation enthalpy and a narrow stable region in the element chemical potential space, so its single-phase synthesis is a challenge [7]. Few studies have been reported in literature in which ZnSnN<sub>2</sub> thin films have been grown

by plasma assisted molecular beam epitaxy (PAMBE) [8,9], RF sputtering [10], plasma-assisted vapor–liquid–solid technique [11], DC sputtering [12], by combinatorial approach [13] or using a high-pressure-metathesis reaction [14]. Beyond those different approaches, one of the main challenges around the study of ZnSnN<sub>2</sub> compound is the ability to reach carrier density as low as 10<sup>17</sup>–10<sup>18</sup> cm<sup>-3</sup> together with maximizing the mobility [15]. Another challenge also lies in the possibility to tailor the bandgap energy to fit the PV required standards. The modification of the crystallographic organization in heterovalent ternary compounds (HTC) give the possibility to tune their electrical and optical properties. A bandgap tuning in HTC such as GaInP<sub>2</sub> or ZnSnP<sub>2</sub> can be obtained by disordering Ga–In and Zn–Sn sublattices, respectively. The same behaviour has been observed in ZnSnN<sub>2</sub> but the variations in the influence of the cation-sublattice ordering of ZnSnN<sub>2</sub> structure on optoelectronic properties suffer from a lack of consensus [10,16,17]. It is so of an utmost importance to obtain a detailed characterization of the physico-chemical properties of ZnSnN<sub>2</sub> thin film to make its bandgap suitable for PV applications. Javaid et al. have deposited thin film solar cell based on n-ZnSnN<sub>2</sub> / p-SnO [18]. The low

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efficiency of the cell has been attributed to the large dark saturation current. In addition to PV applications, mono and bilayer ZnSnN<sub>2</sub> can be also considered as new material for photocatalysis [19].

This is the approach we followed here by analyzing ZnSnN<sub>2</sub> grown by sputtering. After optimization of the growth process, a nitride sample has been analyzed using X-ray diffraction, photoelectron spectroscopy, high resolution microscopy, electron probe microanalysis. In addition, we used here for the first time the Mössbauer spectroscopy to characterize zinc tin nitride thin films. Finally, the spectroscopic ellipsometry analysis gives information about the nature of the band gap.

## 2. Experimental details

The ZnSnN<sub>2</sub> thin films have been grown at room temperature by reactive magnetron co-sputtering using two metallic targets (Zn and Sn) in a pure nitrogen atmosphere. The target diameter was 50 mm and the distance between the targets and the substrate holder was fixed to 60 mm. Prior to their introduction in the chamber, the substrates have been cleaned by ethanol. Before the film deposition, an etching step using a radiofrequency plasma (13,56 MHz, – 200 V, 5 min) has been performed to clean the surface substrates. During the growth process the total pressure was kept at 1 Pa using a throttle valve using a nitrogen flow rate of 60 sccm. To obtain highly reproducible films, the targets were sputtered by fixing the voltage at – 250 V for Zn and – 460 V for Sn. The growth rate for ZnSnN<sub>2</sub> was approx. 1.0 μm/h and the samples were grown on glass and silicon substrates (2 × 2 cm<sup>2</sup>). The deposition procedure used for the ZnSnN<sub>2</sub> film growth is highly reproducible. A series of 10 deposition run has been performed and all the deposited films exhibit the same structure, the same composition and the same optical properties.

The atomic Zn / Sn ratio in the film was estimated by energy dispersive X-ray spectroscopy (EDS) using a Philips XL30.S FEG scanning electron microscope. The film composition was measured using a JEOL 8530-F electron probe microanalyser (EPMA). Quantitative measurements were performed at 15 kV and 40 nA, using pure standards for Zn and Sn, a standard of Fe<sub>4</sub>N for N and MgO compound as standard for O. The film structure was characterized by  $\theta$ – $2\theta$  X-ray diffraction (XRD) measurements with a Bruker D8 Advance diffractometer using a Cu anode ( $\lambda_{\text{Cu}}$   $K\alpha_1$  = 1.5406 Å). The film microstructure was characterized by transmission electronic microscopy (TEM) using a JEM – ARM 200 F Cold FEG TEM/STEM operating at 200 kV and equipped with a spherical aberration (Cs) probe corrector (point resolution 0.19 nm in TEM mode and 0.078 nm in STEM mode). The cross section of the sample was prepared by using a Focused Ion Beam (FIB) apparatus. The thickness of the films was measured with a tactile profilometer and the data were in good agreement with those obtained from TEM cross-section observations. XPS analysis have been performed to record N1s, Sn 3d and Zn 2p and core level spectra, on a K-Alpha Thermo Scientific spectrometer using Al K $\alpha$  radiation (1486.68 eV) with a spot size of 250 μm. Before analysis, the sample surface is cleaned using a mild Ar etching, allowing the removing of the main contaminants. Survey spectra were acquired at a pass energy of 200 eV and high-resolution spectra at 50 eV. The scan number was adjusted (between 10 and 25 scans) to the specific element to get similar signal-to-noise ratios. A flood gun was used for charge compensation and spectra were calibrated by fixing the C 1s main peak at 284.8 eV. Peak-fitting was performed with the Advantage© software (Thermo). <sup>119</sup>Sn conversion electron Mössbauer spectrometry (CEMS) spectra were recorded by a conventional Mössbauer spectrometer (Wissel) with a flowing gas (96% He, 4% CH<sub>4</sub>) proportional counter (Rikon-5) at room temperature. The velocity scale was calibrated with a <sup>57</sup>CoRh source and a metallic iron foil. The evaluation of Mössbauer spectra was performed by least square fitting of lines using the Winnormos (Wissel) program. The error on all of the <sup>119</sup>Sn Mössbauer spectra was ± 0.1 mm s<sup>–1</sup>.

Optical properties were deduced from transmittance and reflectance measurements in the 200–3300 nm range using a Varian Cary 5000

apparatus. Additional optical characterization was performed by *ex-situ* spectroscopic ellipsometry (SE) using a Horiba-Jobin Yvon UVISEL instrument in the spectral range 0.6–6.5 eV (2067–191 nm) at an angle of incidence of 70°. Finally, the electrical resistivity at room temperature was measured using the four-point probe method. The carrier density and the mobility were deduced from Hall measurements in the van der Pauw geometry (Ecopia, HMS-5000).

## 3. Results

### 3.1. Film structure and chemical environment in ZnSnN<sub>2</sub>

The film composition has been investigated by EDS (see Supporting information). Since this method is not accurate to determine the concentration of light elements (nitrogen and oxygen), only the atomic ratio Zn / Sn has been measured. Within the deposition conditions used for this study, this ratio is approx. 1.22. To have more details about the films composition, electron probe microanalysis has been also used. Using this method, the following atomic contents have been measured: 25.1% for Zn, 22.1% for Sn, 49.5% for N and 3.3% for O. From these values, the metal atomic ratio Zn / Sn is 1.14, i.e. very close to that estimated from EDS method. Furthermore, the atomic ratio N / (Zn + Sn) is 1.05. Thus, neglecting the oxygen content, the chemical composition of the zinc tin nitride thin film deposited on silicon substrate that can be expressed as: Zn<sub>1.01</sub>Sn<sub>0.88</sub>N<sub>2</sub>, indicating a possible tin understoichiometry (or a zinc and a nitrogen overstoichiometry). Although the film composition differs slightly from the expected one, the film deposited at room temperature on glass substrate is highly crystallized (Fig. 1). Lahourcade *et al.* also obtained highly crystallized films using RF sputtering on sapphire or GaN substrates at a deposition temperature of 250 °C [10]. On the other hand, Qin *et al.* obtained poorly crystallized ZnSnN<sub>2</sub> films on quartz and p-Si substrates using room temperature DC reactive sputtering of an alloyed Zn/Sn target [20]. Compared to the results reported in literature, reactive co-sputtering at room temperature is a suitable method for depositing highly crystallized ZnSnN<sub>2</sub> films on unmatched substrates (glass and silicon). In addition to the high crystallinity level, the diffractogram presented in Fig. 1 also shows that the ZnSnN<sub>2</sub> film grows with a strong preferred orientation. Since this diffractogram only contains two main peaks (at approx. 32.7 and 68.2°) the precise unit cells cannot be determined. According to the literature data, ZnSnN<sub>2</sub> may crystallize in several structures: orthorhombic *Pna*2<sub>1</sub>, orthorhombic *Pmc*2<sub>1</sub>, hexagonal *P6*<sub>3</sub>*mc*, or monoclinic. The determination the crystallographic structure is a key point in the study of the ZnSnN<sub>2</sub>. Theoretically, the most stable space group for ZnSnN<sub>2</sub> is predicted to be the orthorhombic *Pna*2<sub>1</sub> one (in comparison to orthorhombic *Pmc*2<sub>1</sub>) [10]. According to DFT predictions [8] it corresponds to the fully-cation-ordered ZnSnN<sub>2</sub>, while a fully disordered cation sub-lattice leads to a wurtzite ZnSnN<sub>2</sub> structure.

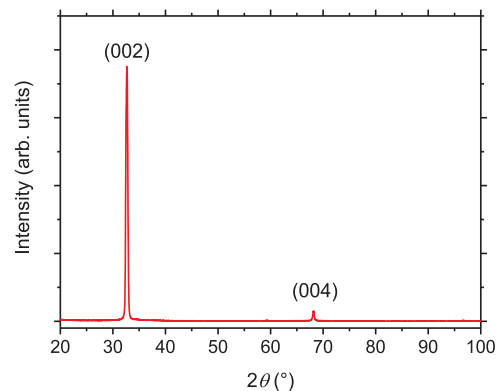


Fig. 1. X-ray diffractogram of a 1.6 μm thick film deposited on glass substrate. The two indexations correspond to the orthorhombic structure type (*Pna*2<sub>1</sub>) with *c* = 0.548(1) nm.

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