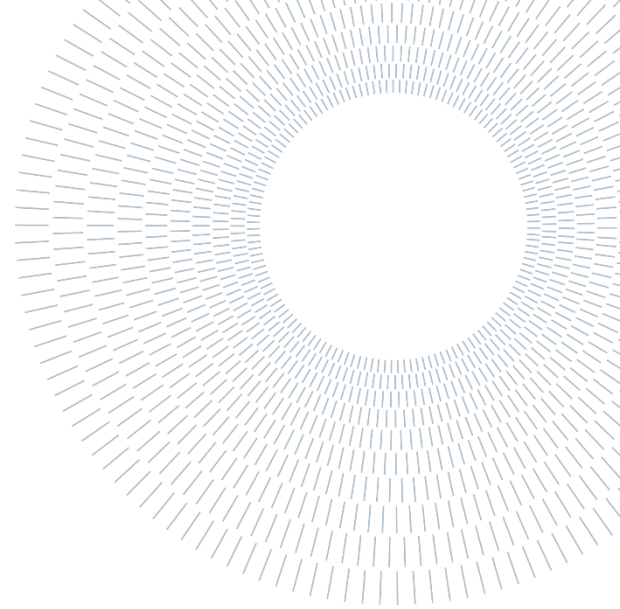




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EXECUTIVE SUMMARY OF THE THESIS

Synthesis and characterization of magnetron sputtered ZnSnN_2 thin films for novel photovoltaics

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLGIE

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1. Introduction

Currently, the demand for energy is increasing annually, and the most promising approach to meet global needs is harnessing solar energy. To exploit most of the solar spectra, engineered devices are needed, and tandem solar cells represent an innovative approach within the field of photovoltaics. However, achieving easy bandgap tuning is currently a significant challenge in photovoltaic research [1]. Compared to other classes of materials, binary and ternary nitrides of group III have gained significant attention from the scientific community. It has a potential to partially replace Si in p-n junction solar cells, so it has to exhibit excellent optoelectronic properties, hence, the study of Bandgap and carrier density is of paramount importance. As opposed to semiconductors based on In or Ga, identified as critical raw materials, ZnSnN_2 (ZTN) is instead

formed by inexpensive and earth-abundant and non-toxic elements [2].

It is the best candidate to be used in photovoltaic application since it has a high absorption coefficient in the solar radiation spectrum range [2]. From first principle's calculation it exhibits a wurtzite derived orthorhombic structure. ZnSnN_2 shows a direct bandgap varying from 1 to 2 eV depending on the arrangement of the cation sublattices [2]. The most stable and ordered structure is orthorhombic with Pna21 as space group, while the wurtzitic is disordered as the Zn and Sn are randomly positioned [3].

It is difficult to precisely determine the bandgap value since ZnSnN_2 is strongly affected by the Burstein Moss shift which increases the energy gap of the material due to the high carrier concentration (10^{20} cm^{-3}) shown on films independently of the crystal structure they belong to [3]. Since donor defects as Sn_{Zn} and O_{N} tends to form spontaneously in the material due to low energy formation, the main challenge is to reduce

the carrier concentration as low as 10^{15} cm^{-3} [4]. The main parameter that affects the properties of this novel semiconductor is found to be the ratio of $\text{Zn}/(\text{Zn}+\text{Sn})$ in the film composition; it modifies the structural, morphological, and electrical properties. It is proved that an off-stoichiometry of Zinc is beneficial to lower the carrier concentration to 10^{18} cm^{-3} . Increasing the content of Zinc will transmute in a higher concentration of Zn_{Sn} and O_{N} defects that passivate each other forming benign complex for lowering the carrier density [4]. Various techniques were exploited to synthesize the ZnSnN_2 thin films such as plasma-assisted vapor-liquid-solid deposition, RF and DC magnetron sputtering and Molecular Beam Epitaxy [3].

Therefore, the object of this thesis work is to investigate how the composition of ZnSnN_2 influences the structural, morphological, and optoelectronic properties. In particular, the thin films were deposited via magnetron sputtering with Direct Current (DC) applied toward two separate and cathodes, this configuration is relatively new for the synthesis of ZTN and only few research were done till now. Two independent cathodes were employed to precisely reach the desired composition in the film. Various analyses were performed to see the main modification of deposition parameters on the film, as the films were grown at different temperatures or with different gas pressure. Moreover, a study on the oxidation of Zn-Rich samples were performed. This work is intended to be an explorative investigation that will serve as solid base for future developments. In particular, the future goal is to implement the High Impulse power regime to Zn cathode to have a finely control of Zn content in the film which has been proven to have a substantial influence over the optoelectronic properties and structure of ZTN [4].

2. Experimental section

During this thesis work a total of 31 samples were synthesized with the magnetron sputtering in DC. Applied voltages were independently modified for the two separate cathodes made of high purity zinc and high purity tin. The magnetron sputter apparatus was produced by Kenosistec. A deposition time of 15 min with 5 rpm for the substrate and a vacuum level of $3 \times 10^{-6} \pm 0.3$ mbar was reached were used for all the depositions. The

voltage applied to Sn ranges from 421 to 466 V while from 329 to 611 V for Zinc. Different Nitrogen pressure of 0.5, 0.8, 1, 1.2 Pa were employed and also a sample was done with a mixture of Ar: N_2 of 1:1 for a total of 1Pa. Different substrate temperatures were employed; room temperature, 100, 200, 250, 300, 350, 380°C. Morphological analysis were performed in plane and in cross section with SEM apparatus. The microscope used in this thesis is a Field Emission Zeiss SEM Supra 40 based on a GEMINI column. The in plane and cross images were taken using 5,0 KeV with an aperture of 60 μm and a working distance of 5 mm. For EDXs analysis a working distance of 8.5 mm and an aperture of 120 μm was used for all the measurements.

To see the vibrational modes a Raman spectrometer was utilized, a Renishaw InVia micro-Raman spectrometer, equipped with an optical microscope (50x objective). The laser used is an argon ion laser, a monochromatic light source with wavelength $\lambda = 514 \text{ nm}$, with a power of 1 mW, with the real power on the sample of 0,39 mW to avoid any modification of the material. XRD analyses were performed by RSE in grazing mode. Optical and electrical properties have been investigated through UV/VIS/NIR spectroscopy (Lambda 1050 UV/VIS/NIR spectrophotometer equipped with a Perkin Elmer 150 mm integrating sphere, optical analyses were performed by Dr. Cristina Mancarella at IIT) and Van der Pauw method (Keythley 2400 SourceMeter, as current source, an Agilent 34970A voltage meter and a 0.57 T Ecopia permanent magnet, coupled with a Keysight 34972A LXI Data acquisition unit), respectively.

3. Results and discussion

During this thesis a multitude of sample featuring different composition of $\text{Zn}/(\text{Zn}+\text{Sn})$ were obtained by varying the power applied to the metal cathodes. A film thickness of 250-450 nm was reached in 15 min depending on the deposition condition. The $\text{Zn}/(\text{Zn}+\text{Sn})$ ranges from 0.38 to 0.78. The sample that features a $\text{Zn}/(\text{Zn}+\text{Sn})$ higher than 0.67 (Figure 1) tend to oxidize within days after the deposition.

It can be visibly evaluated due to a changing in the color of the surface ranging from green to blue. Cross-sectional measurements were performed on these oxidized samples and reveals a presence of a

thick oxide layer that grows in an uncontrolled way during time.

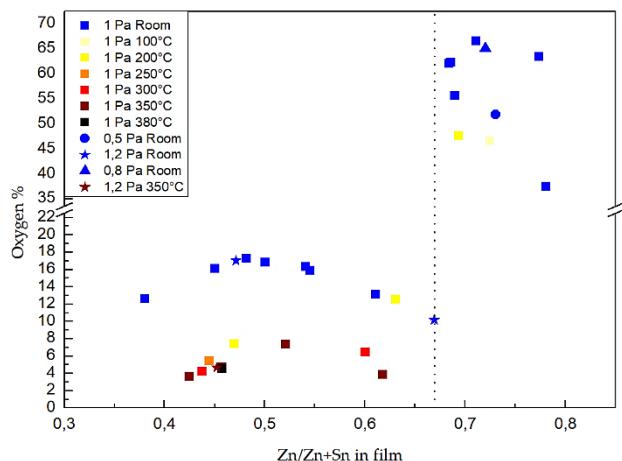


Figure 2: Concentration of oxygen in film at different Zn/(Zn+Sn) ratio. The dotted line indicates where the sample oxidize.

This oxygen intake is attributed to the exposure of ambient air of the samples and EDXs measurements shows that the oxide layer grows in the detriment of nitrogen present in the matrix.

This could be explained as the excess of zinc that cannot be incorporated into the lattice, will segregate, and react with oxygen present in the environment, since the as deposited Zn-Rich film shows oxygen value < 18%. All the samples with Zn/(Zn+Sn) lower than 0.67 remains stable during time and exhibits low oxygen content, the growth temperature is able to decrease the oxygen uptake in the chamber from a value of 15 to 6 ($\pm 2\%$). An interesting parabolic trend for the oxygen content is seen in Figure 1 and shows a peak when Zn/(Zn+Sn) is in the proximity of 0.5. This effect needs to be investigated in future research.

Moreover, for pressure of Nitrogen lower than 1Pa the formation of the correct ZnSnN₂ film is hindered due to the scarcity of Nitrogen present. The morphology of the films was investigated through in plane and in cross section measurements and is shown in Figure 2.

The surface is formed by homogenous grains with an irregular shape and for Zinc rich sample the grains are more defined and dispersed. A compact and big grains can be observed for film grown at 300°C with a Zn/(Zn+Sn) of 0.60. The SEM measurements were taken also in cross section and shows the typical columnar growth achieved by sputtering technique. Is interesting to note that as the Zn content increase, the columns became more defined and well resolved.

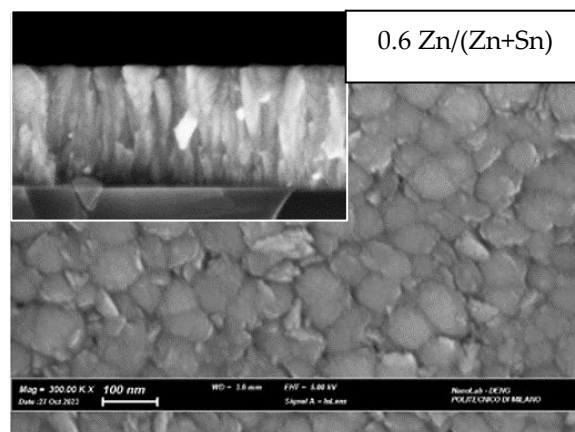


Figure 1: SEM images of the in plane and cross section morphology for a sample grown at 300°C.

The wurtzitic peaks and orthorhombic peaks are matching with except of additional peaks can be found in the proximity of 30.6° and 34.9° [5]. XRD analyses (Figure 3) shows a perfect matching of typical ZnSnN₂ structure and since the peak related to 30.6° and 34.9° present a large FWHM, it suggests the formation of an orthorhombic Pna21 structure [5].

As seen through XRD measurements the increasing in the growth temperature favor the crystallization among different planes and the increasing of Zn/(Zn+Sn) will lead to a correct formation of ZTN crystalline structure.

So, the combined effect of an over-stoichiometry in zinc and high substrate temperature promotes the crystallization of the film. The oxidized samples exhibit an amorphous structure.

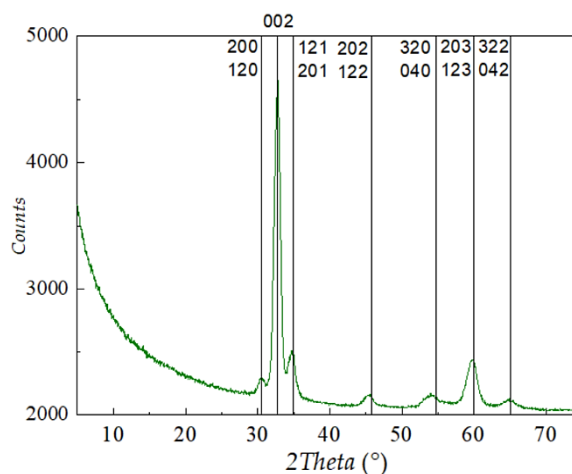


Figure 3: XRD spectra of the sample grown at 300°C with a Zn/(Zn+Sn) of 0,6. The reference lines indicates a wurtzite arrangement for ZnSnN₂ [5].

Later on, to fully characterize the structure, the vibrational modes were identified while performing Raman analyses (Figure 4). All the samples that feature a $Zn/(Zn+Sn)$ in the range of 0.45 to 0.67 shows typical vibrational modes of $ZnSnN_2$ [2].

As the Raman measurements reveals broad peaks that resemble the phonon density of states, and not well defined and sharp peaks, this means that the k-vector selection rule is broken, and this is typical of a glass-like phonon structure [2]. When the $Zn/(Zn+Sn)$ is higher than 0.67, only a broad band can be seen and is shifted from 660 to 625 cm^{-1} related to the high concentration of Zn [2], [4]. When the $Zn/(Zn+Sn)$ is close to 0.5 a band related to Zn-N at 660 cm^{-1} is slightly shifted to right, suggesting a modification of the bond.

Note that in Figure 4, the sharp peak located at 521 cm^{-1} is related to the Si substrate on which the film is deposited.

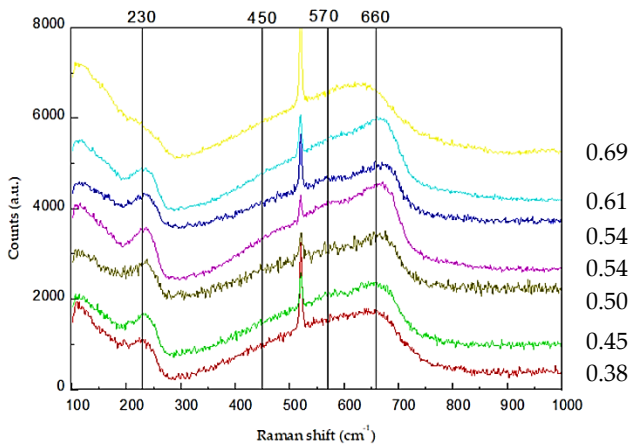


Figure 4: Raman modes of samples with different $Zn/(Zn+Sn)$ on the right, lines identify the position of the maximum found for each band.

Raman analysis performed on oxidized samples reveals only the peaks related to the Si substrate, in accordance with the fact that the oxygen replaced the nitrogen inside the film.

The growth temperature instead does not impact on the vibrational modes, this can be attributed due to the fact that the vibrational pattern of Zn, Sn and N does not varies, and the temperature influence only on the ordering of the cation sublattice.

Instead, an under-stoichiometry in zinc will show only a broad band, hindering the Zn-N related bonds [2]. The Raman bands as well as XRD crystalline structure of $ZnSnN_2$ are affected by the presence of oxygen. Note that the cation disorder determines the structure of ZTN that could be

wurtzite or orthorhombic, hence the bandgap of 1 and 2eV can be respectively achieved [3]. As said, the exact predicted values are difficult to reach since the Burstein Moss effect take place [3].

As the structure of these ZTN films is investigated, the focus will move toward electrical and optical properties (Figure 5).

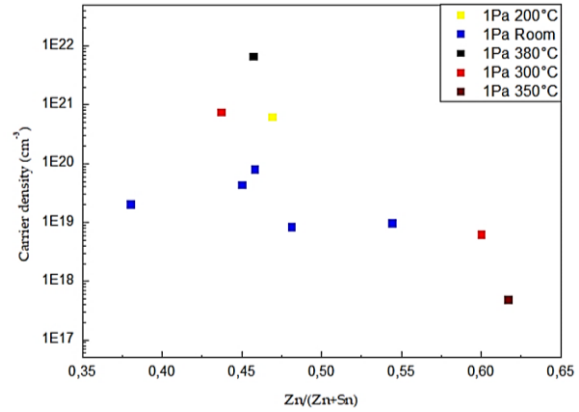


Figure 5: Carrier density as function of $Zn/(Zn+Sn)$. It decreases for Zn-rich film.

Despite the variability of the measurements performed, the trend is in accordance with what found in literature.

The carrier density decreases up to two orders of magnitudes (from 10^{22} to $10^{17} cm^{-3}$) when increasing the $Zn/(Zn+Sn)$ in the film from 0,45 to 0,62. This is attributed to the formation of the acceptor Zn_{Sn} defect that hinder the formation of donor defect Sn_{Zn} [2]. As observed, Zn-rich films led to a positive effect for lowering the carrier concentration [4].

The main reason that the electrical measurements are performed is for evaluating the carrier density that is correlated to the energy gap of the material. The $ZnSnN_2$ undergoes the Moss-Burstein effect for which the energy gap increase as the free electrons occupies the conduction band, with a consequent shifting of the Fermi energy level in the conduction band [3]. The energy gap values have been derived from optical measurements though the Tauc plot method. The Moss-Burstein effect is shown also by these deposited thin films where the energy gap increases from 2.4 to 2.9 eV when increasing the carrier density from 4.9×10^{17} to $6.6 \times 10^{21} cm^{-3}$. The most promising sample shows an energy gap of 2.15 eV and is deposited at ambient temperature with a pressure of 1.2Pa of pure nitrogen, featuring a $Zn/(Zn+Sn)$ of 0.67. The conductivity is then investigated and shows value that span from 1-100 $S cm^{-1}$. The conductivity is

improved when the film is grown at high temperatures [1].

This could be attributed to the fact that the grains coalesce with the help of the thermal energy and so, less grain boundaries, hence defects, are formed. For samples with $Zn/(Zn+Sn)$ lower than 0.5 the conductivity is increase by one order of magnitude, while is very low (1Scm^{-1}) for Zn-rich sample (Figure 6).

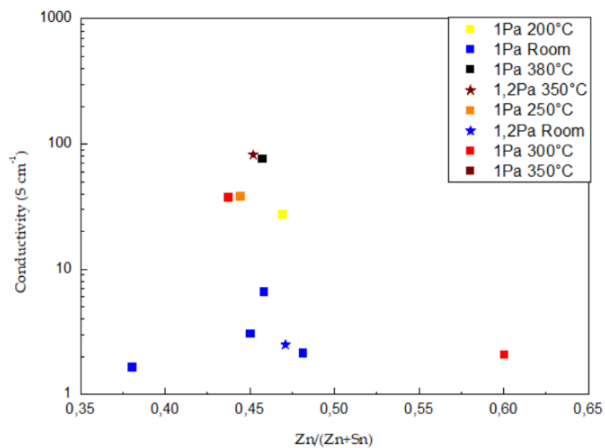


Figure 6: Conductivity as function of $Zn/(Zn+Sn)$, samples with different deposition condition are here shown.

4. Conclusion and perspectives

The key achievements of this work include:

Control over film composition: Exploiting two different cathodes allows the precise tailoring of all the films composition. A correlation between the cathode's power and the film composition is founded and is suitable for further research to know the film composition prior the deposition.

Oxidation study: A precise value of Zinc content of 0.67 $Zn/(Zn+Sn)$ will lead to an uncontrolled oxidation that will be detrimental for electrical application. Moreover, a peculiar parabolic trend in the oxygen uptake of the film is observed and need to be investigated in future research. Most interesting from EDXs measurements is that the nitrogen in the film will exchange with the oxygen present in the environment, as oxidized samples shown a little content of nitrogen. The temperature of the substrate during growth lead to a lowering in oxygen content in the film up to 10%.

Correlation of Composition and properties: A direct correlation between the film composition and the bandgap value is understood, essential for photovoltaics application, an over-stoichiometry

of zinc will lead to a decrease in carrier density up to four orders of magnitude due to the suppression of donor defects. In particular a bandgap value of 2.11 eV is reached.

Contribution to photovoltaics: An understanding of the correlation between the carrier density and the bandgap value is achieved, of paramount importance for specific solar cells applications as tandem solar cells.

During this thesis, more branches were open to investigate a plethora of ZTN properties and for future developments I will suggest performing electrical measurements on all the samples to better understand the exact trend of the carrier density as well as to precisely determine the way it affects the energy gap. Prior to the deposition a pre-sputter of the cathodes is suggested to avoid any nitrogen poisoning that will affect the film composition. Moreover, a High impulse power regime could be applied to the zinc cathode to see the effects of a high energy plasma toward the film. Also, a Bias could be applied to the anode to have an efficient intake of the charged atoms to form the film.

To conclude, the most promising path to follow based on this work is to move forward to Zn-rich films growth with pressure of nitrogen higher than 1Pa and with high substrate temperature. This would lead to a formation of a stable film with low concentration of oxygen, crystalline and with a low carrier concentration, hence a lower energy gap.

5. Reference

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