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Growth and Characterization of SnSe₂ by selenization of sputtered metallic precursors

P.A. Fernandes^{a,b}, M.G.Sousa^a, P.M.P. Salomé^c, J.P. Teixeira^a, J.P.Leitão^a, A.F. da Cunha^a

^aI3N and Departamento de Física, Universidade de Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal ^bDepartamento de Física, Instituto Superior de Engenharia do Porto, Instituto Politécnico do Porto, Rua Dr. António Bernardino de Almeida, 431, 4200-072 Porto, Portugal ^cInternational Iberian Nanotechnology Laboratory, Av. Mestre José Veiga s/n, 4715-330 Braga, Portugal

ABSTRACT

In the present work, we present a process to grow tin diselenide thin films by selenization at a maximum temperature of 470 °C, of tin metallic precursor layers deposited by dc magnetron sputtering.

For this maximum temperature, disklike grain morphologies were observed. Prominent XRD reflections at 20= 30.75°, 40.10° and 47.72° and vibration modes located at 119 cm⁻¹ and 185 cm⁻¹ were observed.

These results allowed concluding that the dominant phase is SnSe₂. The composition analysis, done by energy dispersive spectroscopy (EDS), showed that the films were close to being stoichiometric SnSe₂ with a Se to Sn ratio of 1.95.

Photoluminescence characterization was performed and revealed a dominant band at 0.874 eV and two other bands at ~0.74 and 1.08 eV with a lower relative intensities. The observed radiative transitions depend critically on the temperature.

MORPHOLOGICAL ...



SEM analysis reveals disk-like grains morphologies.

This feature is well explained by the SnSe₂ layered structure.

SEM/EDS Hitach SU-70 equipped with a Rontec EDS system operated at an acceleration voltage of 4.0 KV

... STRUCTURAL



The films are composed of the hexagonal-SnSe₂ phase. The peaks are sharp which suggests that the samples have good crystalline quality.

The peak located at a diffraction angle,

 $2\theta = 14.44^{\circ}$, corresponds to the (001) plane.

The formation of this phase from metallic

Sn precursors and Se vapour may be

interpreted as the result of the association

 $Sn(s) + 2Se(g) \longrightarrow SnSe_2(s)$

reaction defined:

GROWTH METHOD

The growth method used in this work is constituted by two stages:

- 1) Deposition of the metallic precursor layer, Sn, by DC magnetron sputtering;
- 2) Chalcogen incorporation, Se, and the annealing process, which allow the crystalline phase formation.

Selenezation system:

- Tubular furnace;
- Graphite box with 240 mg of high purity Se pellets;
- N_2 + 5% H_2 atmosphere at an operating pressure of 600 mbar;
- Heating rate: 10 Kmin⁻¹;
- Maximum selenization temperature: 470 °C.



GROWTH Reaction schematics of the formation of SnSe₂

XRD X'Pert MPD Philips PW 3710 system equipped with a CuK source



Raman scattering analysis allowed the assignment of peaks at 119 cm⁻¹ and 185 cm⁻¹ to the hexagonal-SnSe₂ phase and at 108 cm⁻¹ corresponding to the orthorhombic-SnSe phase.

Traces of condensed amorphous Se with a characteristic Raman peak located at 255 cm⁻¹ were observed.

RAMAN LabRam Horiba, HR800 UV spectometer, 532 nm excitation laser

... AND OPTICAL PROPERTIES OF TIN DISELENIDE THIN FILMS

At 7 K, three bands are +0.135observed: ~0.74, ~0.874 and . - 0.108 (îs ~1.08 eV. As temperature (T) is - 0.03 r 0.081 increased non-radiative deexcitation channels are 0.02 S . 0.054 ຫຼັ thermally activated: the Inte <u>ء</u> ر 0.027 dominant band at 0.874 eV 0.01 disappears for $T \sim 130$ K, whereas the intensity of the band at 0.74 eV increases; that band extinguish for T~170 K. 3

1.1

1.2

CONCLUSIONS



At low excitation power (P) values just the dominant band at 0.874 eV is observed; as P is increased, no saturation is present and the other two bands start to be observed

Two-step method can be used to grow SnSe₂ films. This method is based on the deposition of tin metallic layer and a post annealing process in a selenium atmosphere.

Selenization temperatures at 470 °C leads to films where SnSe₂ is the dominant phase.

Morphological analysis confirms the SnSe₂ disk-like grain morphology.

Optical analysis, at 7K, showed three bands located at 0.74, 0.874 and 1.08 eV.

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Bruker IFS 66v FTIR spectometer, equipped with a Ge diode detector