

Physical properties of carbon nanotubes deposited on aluminum-doped zinc oxide substrates for photovoltaic devices.

M5052-Nanomaterials-Characterization

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Objective

- ▶ This work is focused on proposing a characterization procedure for a composite of single-walled carbon nanotubes (SWCNTs) over aluminum-doped zinc oxide (ZnO: Al, AZO) thin films, towards evaluating its possible application such as a front-contact to reduce the charge recombination rate and to enhance the current density in photovoltaic devices.

The proposed characterization procedure includes different characterization techniques to obtain information about the vibrational and electronic properties of the material, its structure and morphology, its size, as well as its chemical composition and crystallography.

Sample preparation

- ▶ The AZO transparent conducting thin films were deposited by a radio-frequency (RF) magnetron sputtering system at room temperature in pure argon ambient chamber and a high vacuum level.
- ▶ The SWCNTs were deposited by spray-coating technique as the top layer over the ZnO: Al (AZO) substrates.

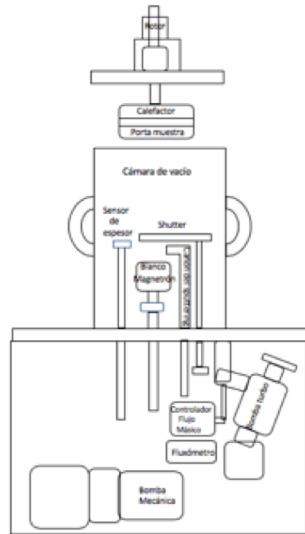


Fig. 1. Experimental set-up to deposit the AZO transparent conducting film



Fig. 2 Experimental set-up to deposit the SWCNTs/SDS suspension over the AZO substrates by the spray-painting technique.

Types of samples

- ▶ SWCNTs powder
- ▶ AZO transparent conductive films (samples of 2.5 cm x 2.5 cm)
- ▶ SWCNTs deposited on AZO transparent conductive films (samples of 2.5 cm x 2.5 cm)

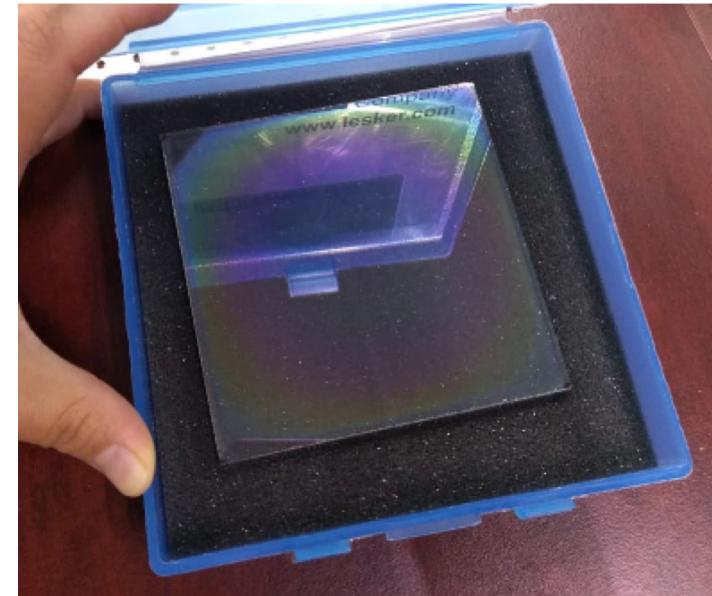


Fig. 3. Sample of AZO transparent conductive films deposited on non-conductive glass (size 10 cm x 10 cm)

RAMAN SPECTROSCOPY

- **Information provided by this technique.**

SWCNTs powder.

Diameter, chirality, vibrational and electronic properties and crystallinity.

AZO sputtered films.

Microstructure, crystallinity, vibrational properties and disorder degree (defects).

- **Sample preparation for analysis.**

For Raman studies, the samples will analyze ‘as grown’ with no special preparation, which is one of the advantages when performing analysis of samples with this technique.

- **Conditions to perform the test.**

SWCNTs & SWCNTs+AZO samples

Measuring range: 50-4000 cm⁻¹

Acquisition time: 10 seconds

Accumulations: 2

Hole: 100

Laser: 633 nm (wavelength excitation)

AZO sputtered films.

Measuring range: 50-1000 cm⁻¹

Acquisition time: 60 seconds

Accumulations: 5

Hole: 70

Laser: 633 nm (wavelength excitation)

RAMAN SPECTROSCOPY

What results do I expect with this analysis?

Through the Raman spectrum of the SWCNT's samples, I hope to identify the D (1320 cm^{-1}), G (1590cm^{-1}) and the G' (2700cm^{-1}) bands as well as the presence of bands below 300cm^{-1} that are named the radial breathing modes (RBM).

In the Raman spectrum of the AZO samples, I hope to identify the main Raman-active modes located at 438 cm^{-1} , 574 cm^{-1} , and 583 cm^{-1} , corresponding to the E^2_{high} ; $A1(\text{LO})$ and $E1(\text{LO})$ modes respectively.

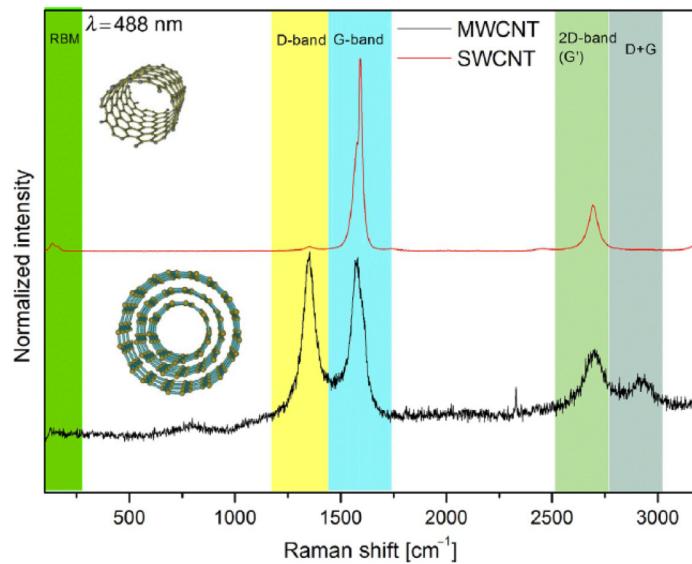


Fig. 4 Raman spectra of SWCNT and MWCNT with their structures.
Image taken from reference number¹, p. 12, without modifications to the original

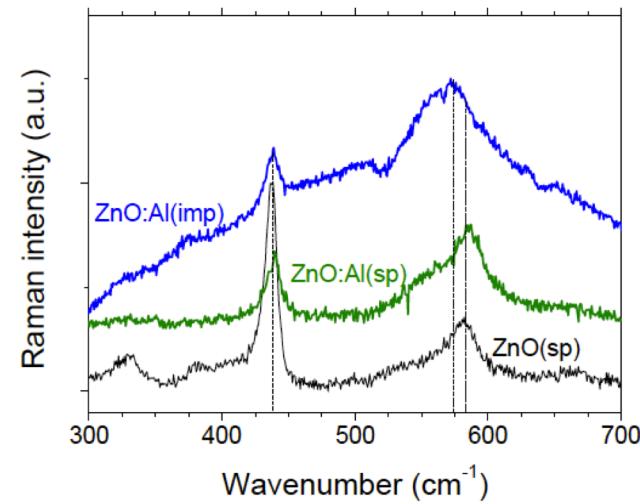


Fig. 5 Raman spectra of ZnO thin films doped with Al (≈ 0.5 at. %) by co-sputtering (sp) and by ion implantation (imp). The Raman spectrum of the pure ZnO thin film (black curve) deposited by sputtering (sp) is also shown for comparison.

Image taken from reference number3, p. 11, without modifications to the original

RAMAN SPECTROSCOPY

Preliminary results

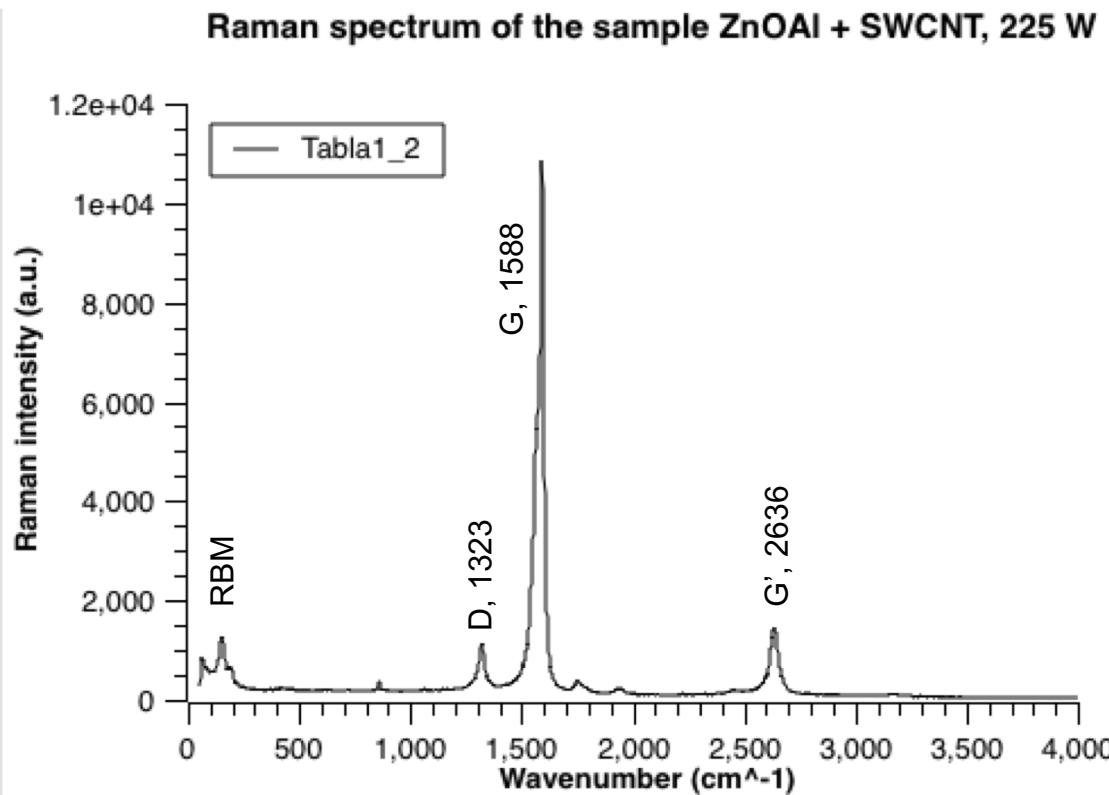


Fig. 6 Raman spectrum of the sample ZnOAI + SWCNT's deposited at 225 W

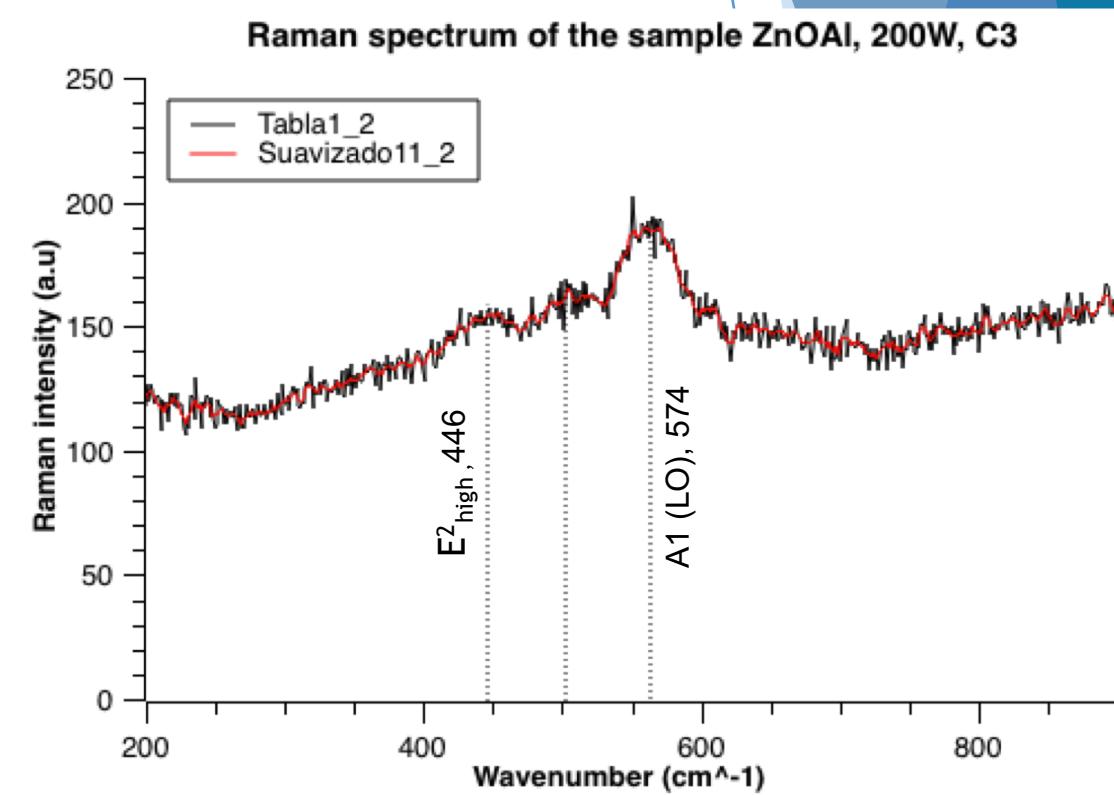


Fig. 7 Raman spectrum of the sample ZnOAI deposited by sputtering at 200 W

FIELD EMISSION SCANNING ELECTRON MICROSCOPY - EDS

- **Information provided by this technique.**

Structure, morphology, size, alignment, homogeneity and distribution of the SWCNTs and the crystals of AZO sputtered films. And also, with the EDS technique is possible to obtain a qualitative analysis about the chemical composition of the AZO substrates.

- **Sample preparation for analysis.**

SWCNTs powder.

Samples will analyze directly from the synthesis powder, which will set on carbon tape attached to the sample holder, without any special preparation

AZO films.

Samples will analyze directly from the synthesis films, which will set on on carbon tape attached to the sample holder, and then they will ground with a drop of metallic silver paint because the sample is a semiconductor.

- **Conditions to perform the test.**

AZO films

Voltage: 10 kV

WD: 4.0 mm

Detector: UED (upper electron detector)

SWCNTs samples

Voltage: 5 kV

WD: 2.9 mm

Detector: UED (upper electron detector)

SWCNTs over AZO sputtered films

Voltage: 1 kV

WD: 3.0 mm

Detector: UED (upper electron detector)

FIELD EMISSION SCANNING ELECTRON MICROSCOPY

What results do I expect with this analysis?

Through the field-emission scanning electron micrographs of the AZO films, I hope to observe their structure and morphology, taking as reference the wurtzite structure in hexagonal shapes.

And for the micrographs of the SWCNT's I hope to observe their alignment and dispersion over the AZO substrates. Also, to obtain specific characteristics, such as size, curvature, and entanglement of the carbon nanotubes.

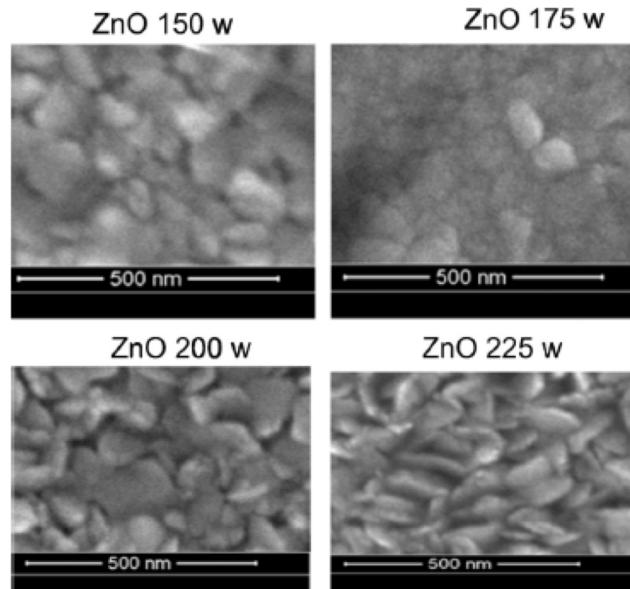


Fig. 8 FESEM images of ZnO films on Si substrates prepared at various RF powers.

Image taken from reference number⁵, p. 210, without modifications to the original.

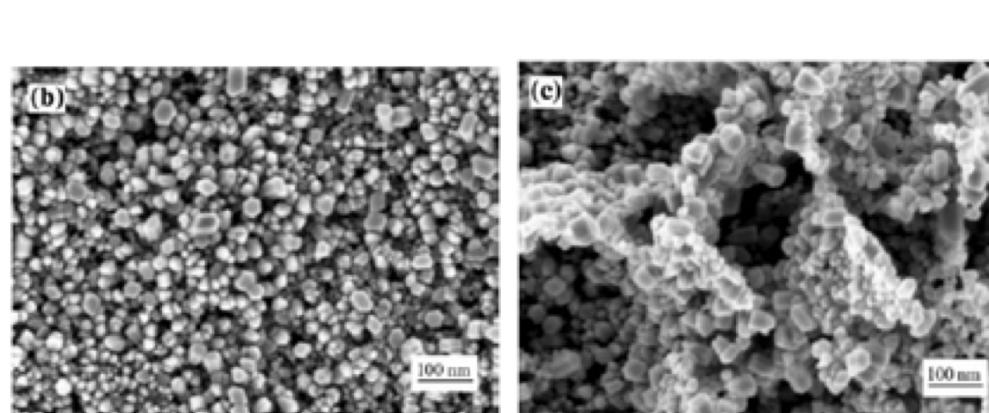


Fig. 9 FESEM micrographs of pure ZnO
Image taken from reference number⁶, p. 3605, without modifications to the original.

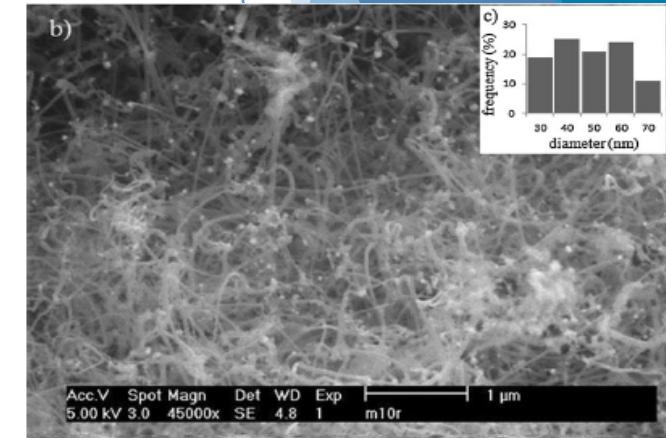


Fig. 10 SEM micrograph of
MWCNT's obtained by a
microwave technique
Image taken from reference
number⁷, p. 2837.

FIELD EMISSION SCANNING ELECTRON MICROSCOPY

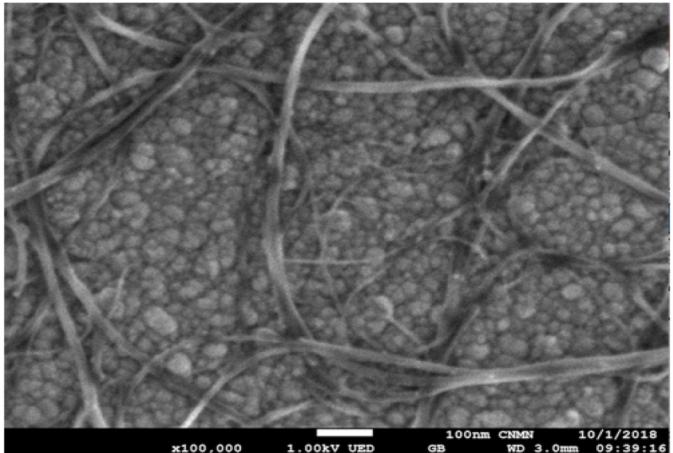


Fig. 11 FESEM image of the SWCNT sprayed film over the ZnO: Al (deposited at 225 W) substrate with magnification of 100,000 x.

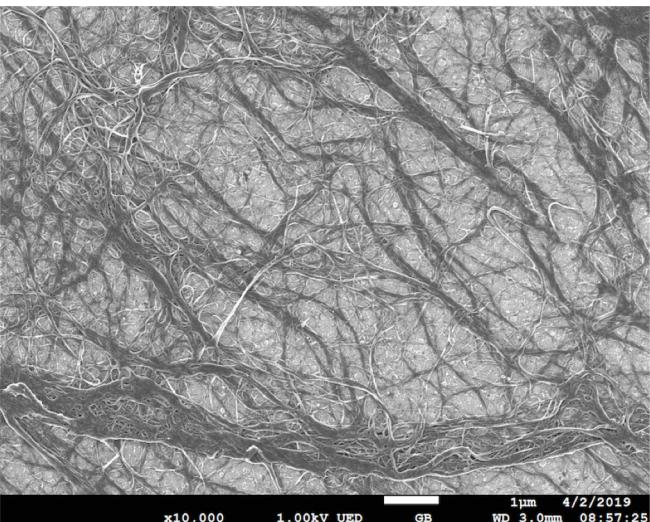


Fig. 12 FESEM image of the SWCNT sprayed film over the ZnO: Al (deposited at 225 W) substrate with magnification of 10,000 x.

Preliminary results

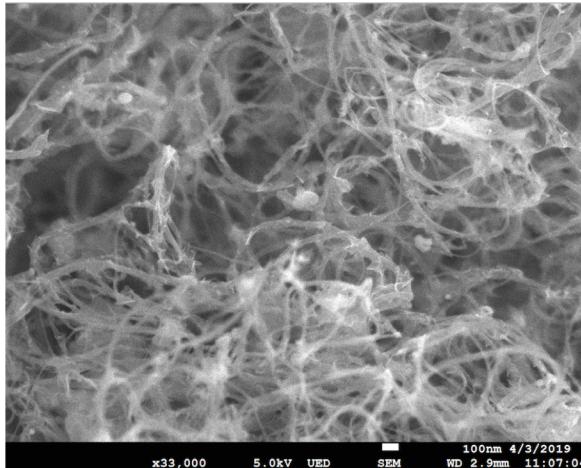


Fig. 13 FESEM image of the SWCNTs powder, with magnification of 33,000 x.

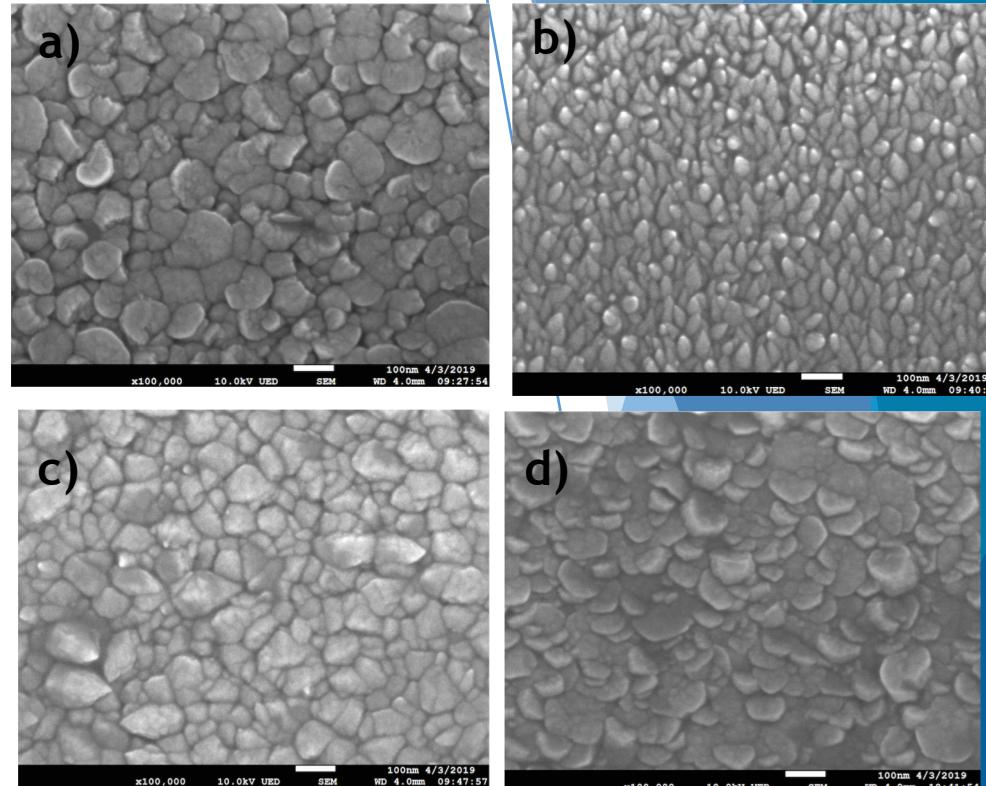


Fig. 14 FESEM micrographs of the ZnO:Al samples deposited by sputtering at various RF powers a) 150 W, b) 200 W, c) 225 W, d) 250W, with magnification of 100,000 x.

FIELD EMISSION SCANNING ELECTRON MICROSCOPY

Preliminary results-EDS

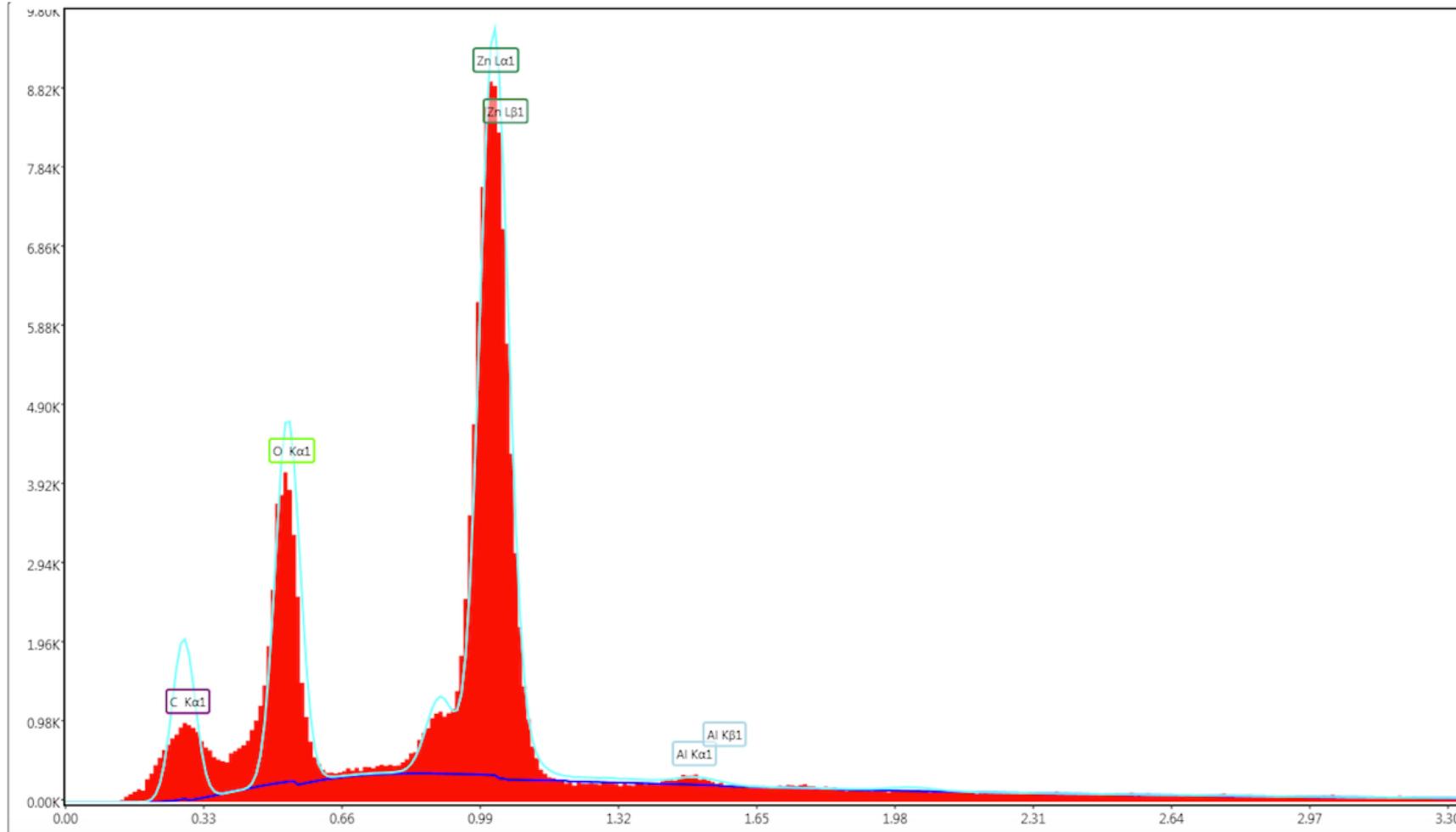


Fig. 15 Energy-dispersive X-ray spectroscopy (EDS) analysis confirming the presence of the C, O, Zn and Al in a sample of the composite SWCNT/ZnO: Al (deposited at 225 W by RF sputtering).

TRANSMISSION ELECTRON MICROSCOPY (TEM)

- **Information provided by this technique.**

TEM allows observing structural characteristics in the individual carbon nanotubes such as the diameter, curvature, length of the tubes, and the number of walls.

To analyze the ZnO: Al substrates and ZnO: A/SWCNT nanocomposites, TEM it's useful for determining their internal structure, size, and crystallinity.

- **Sample preparation for analysis.**

SWCNTs powder.

For TEM analysis of the SWCNT powder, a suspension will prepare in deionized water with 1 wt% SDS (sodium dodecyl sulfate). Then, the suspensions will sonicate in an ultrasonic bath for nine hours to optimize the particles dispersion. Next, a small drop of the suspension will deposit in a TEM copper grid for its observation.

AZO films.

Samples will not require special preparation to obtain plane-view TEM images.

- **Conditions to perform the test.**

Transmission Electron Micrographs of the ZnO: Al substrates and of the SWCNT/ZnO: Al samples will obtain at 300 kV using a Transmission Electron Microscope (TEM). Micrographs corresponding to the SWCNT powder will get at 200 kV acceleration voltage.

TRANSMISSION ELECTRON MICROSCOPY (TEM)

What results do I expect with this analysis?

Based on existing references in the literature, I would seek to obtain TEM images of powdered SWCNT samples (prepared in SDS solution) to determine the diameter of the carbon nanotubes, their length, and distribution.

Also, for the AZO films and the AZO / SWCNT composites, I would look for images of the cross-section and planar section of the sample to determine its internal structure and crystallinity.

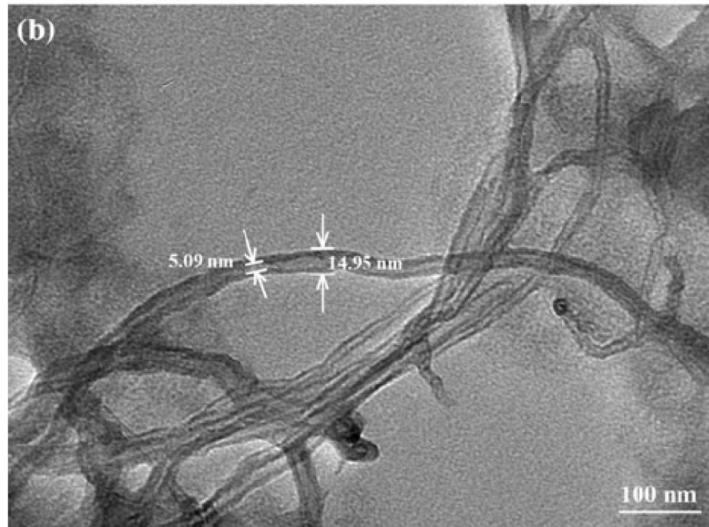


Fig. 16 TEM image of ZnO mixed with SWCNTs.

Image taken from reference number⁶, p. 3608, extracting only the subsection b).

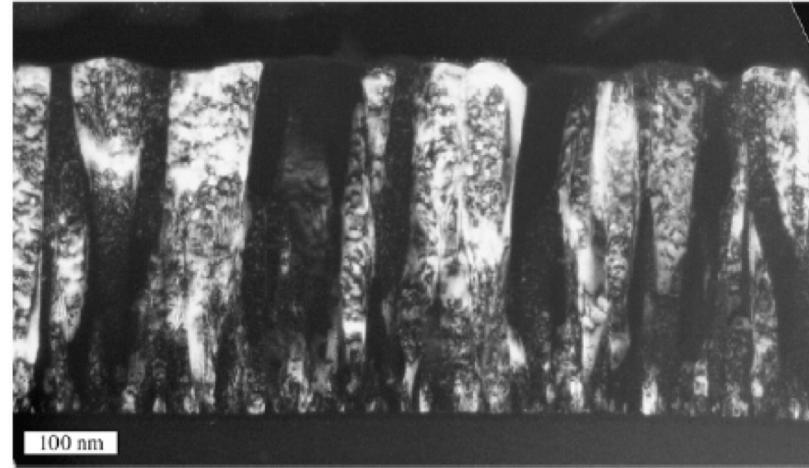


Fig. 17 TEM dark field image of a ZnO: Al film deposited at room temperature.

Image taken from reference number⁹, p. 7847, without modifications to the original.

X-RAY DIFFRACTION (XRD)

- **Information provided by this technique.**

It provides information about the chemical composition, crystallographic structure, and purity of the SWCNT, as well as to observe peaks related to metal catalyst particles.

Likewise, it's possible to determine the orientation and crystallinity of the ZnO: films.

- **Sample preparation for analysis.**

SWCNTs powder.

The powders of SWCNT's have to be dispersed in a small amount of pure ethanol to be able to disperse the sample in the sample holder and prevent it from agglutinating. Due to the nature of the material, it has to be placed in an area of 1 cm x 1 cm.

Fig. 18 Preparation of a suspension of a small amount of SWCNT in ethanol, to be able to disperse the sample on the sample holder in an area of 1 cm x 1 cm, for its X-ray analysis.



AZO films.

The AZO films and the composite of SWCNT and AZO film, do not require special preparation. They should only have the adequate size for its measurement (approximately, 2 cm x 2 cm).

X-RAY DIFFRACTION (XRD)

- **Conditions to perform the test.**

The diffraction pattern will measure in the interval 2θ between 10 and 100°. The X-Ray Diffraction (XRD) measurements will be carried out using an X-ray diffractometer system utilizing a wavelength $\lambda = 0.154$ nm as a source. The position, height, intensity and full-width at the half-maximum (FWHM) will be the main four parameters that will characterize the diffraction lines.

SWCNT's powder:

Conventional method

Current max: 15 mA

Current min: 2 mA

Voltage max: 40 kV

Voltage min: 20 kV

AZO films and AZO/SWCNT composite:

Grazing Incidence X-ray Diffraction (GIXRD)

Grazing incidence angle of 0.5

Current: 40 mA

Voltage: 45 kV

X-RAY DIFFRACTION (XRD)

What results do I expect with this analysis?

Through the X-ray diffractogram of the SWCNT's samples, I hope to observe the two dominant diffraction peaks corresponding to the hexagonal graphite structures, these peaks are located at $2\theta = 26.6^\circ$ and 43.45° and corresponding to the planes (002) and (001), respectively.

Also, for the AZO films I would look for the XRD patterns which confirm the hexagonal wurtzite phase of ZnO. The presence of zinc oxide should be traced at planes (100), (002), (102) and (110) which diffracted at diffraction angles of 31.75° , 34.38° , 47.55° and 56.63° respectively.

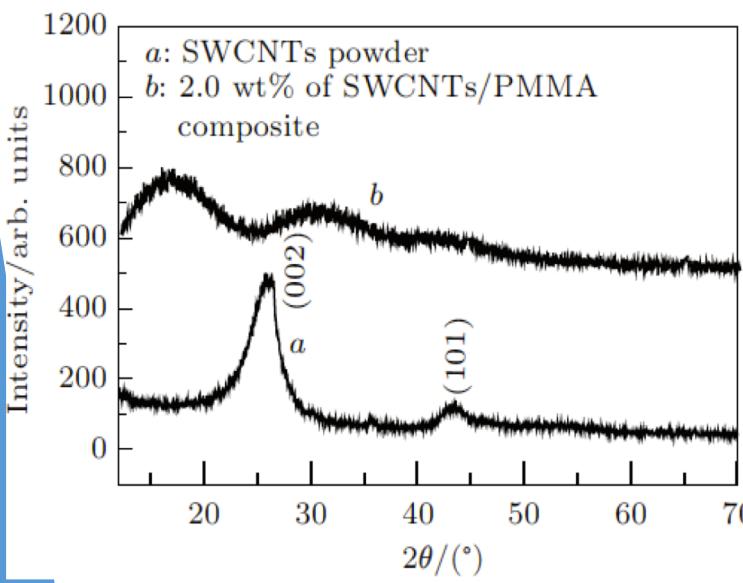


Fig. 19.- X-ray diffraction patterns of SWCNTs powder (curve a), and 2.0 wt% ratio (curve b) of SWCNTs/ polymethyl methacrylate nanocomposite films.
Image taken from reference number¹⁰, p. 105-101-1, without modifications to the original.

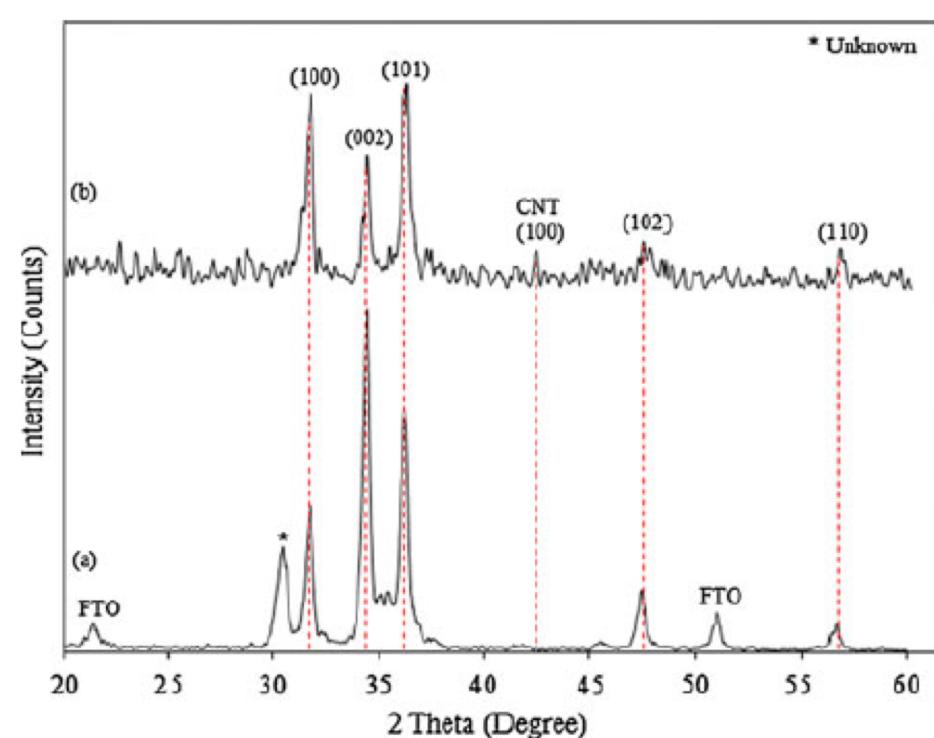


Fig. 20.- XRD patterns of a pure ZnO and b ZnO-SWCNTs
Image taken from reference number⁶, p. 3604, without modifications to the original

X-RAY DIFFRACTION (XRD)

Preliminary results

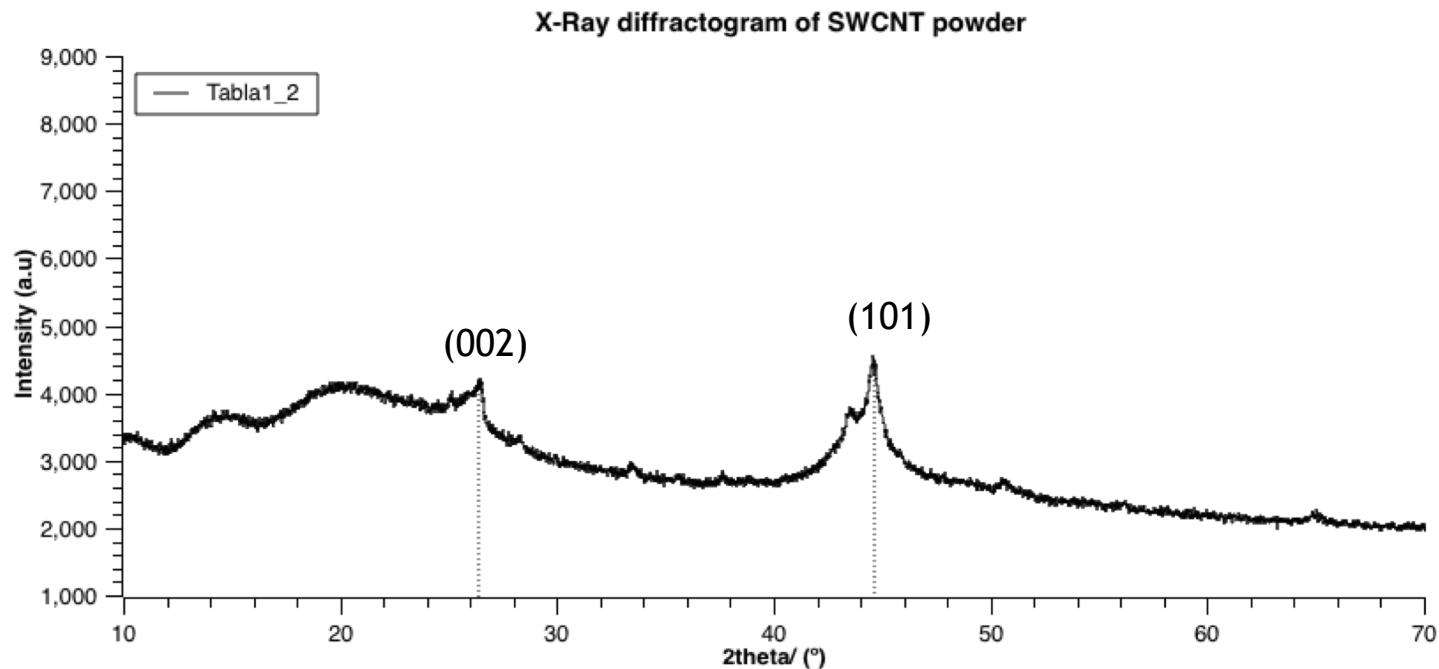


Fig. 21, X- Ray diffractogram of SWCNTs powder, this analysis was performed by a conventional X- Ray diffractometer.

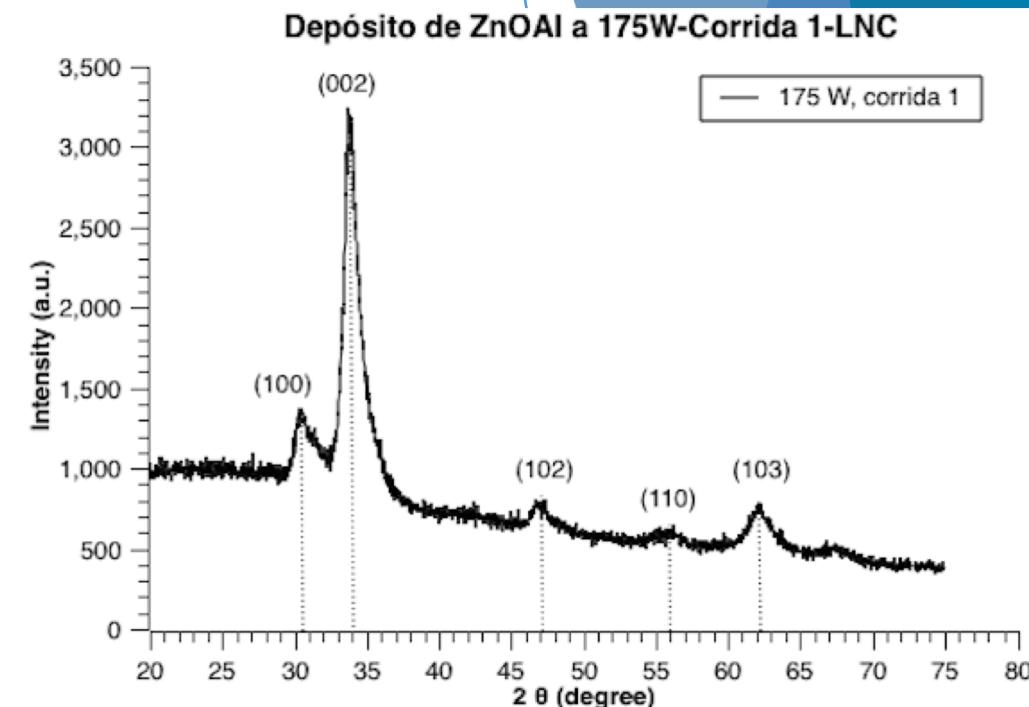


Fig. 22, X- Ray diffractogram of a ZnO:Al sample, this analysis was performed by Grazing Incidence X-ray Diffraction.

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