Study of an organic-metallic SnO₂ ink for electronic printing applications.

Author: Edurne Máñez Gimeno.

Facultat de Física, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain*.

Abstract: This work shows a way of achieving a semiconductor SnO₂ film and its basic characterization. Two inks were prepared with dehydrated tin chloride diluted in 2-methoxyethanol, with and without acetic acid respectively. A third ink was also used, which had been previously prepared with dehydrated tin chloride with a different molar ratio without any other additive. These inks were annealed at 300, 370, 440, 530 and 600ºC, and were studied by the following techniques: TGA (Thermal gravimetric analysis), DSC (Differential scanning calorimetry), XRD (X-ray diffraction) and XPS (X-ray photoelectron spectroscopy). Having done the thermal treatments, we examined the results provide by all experiments. TGA and DSC show the rate of the reactions when we heat up the ink. The obtained result is consistent with the theoretical deduction but this experiment is not able to differentiate between SnO and SnO2. XRD shows that we obtain crystalline SnO₂, and with XPS results we conclude that we also have amorphous SnO.

I. INTRODUCTION

The aim of this work is to synthesize inks, from which SnO₂ is obtained by thermal treatment.

In the last years, SnO₂ has become an important n-type semiconductor with a forbidden energy band from 3.64eV at 57ºC. It has great properties to be applied in solid state gas detector devices, transparent conducting electrodes, rechargeable Li batteries, and optical electronic devices. [1]

The characteristics and performance of inks have been studied so they can be used with inkjet printing drop-on-demand technique.

This technique is a method of direct writing, whose patterns are made by selective deposition of materials in specific regions. By using drop-on-demand heads, it creates patterns by placing single drops. This additive pattern is made in one step, which reduces substantially both the processing time and the materials. Consequently, the manufacturing cost is decreased. It is an interesting technique for the manufacturing of devices such as TFT (thin film transistor), liquid crystal display color filters, organic light-emitting diodes, among others.

Inkjet printing is, therefore, characterized as a noncontact additive method, which is particularly advantageous for preparing integrated organic devices. Inkjet printing is particularly effective in fabricating devices involving functional organic materials, which are chemically and physically fragile. Very low cost FETs are now required for many applications such as those in electronic paper or electronic tags. This is due to its unique capability of additive and noncontact patterning. This differentiates inkjet printing from other additive patterning methods. [2]

Inkjet printing could become a key technology to reducing material and power consumption, industrial waste and CO₂ emission, and to realizing a sustainable microelectronics industry[3]. The technological advances made with this technique in the last few years have generated interest in the electronic industry.

The following techniques have been used to study the compounds:

Thermal Gravimetric Analysis, TGA: Technique that allows to study degradation processes in depth. It consists of determining the loss of mass experienced by a sample when it undergoes a thermal program. It is carried out in different atmospheres which are perfectly controlled. In this case, it was an air/oxygen atmosphere in oxidative conditions. A very sensitive weighing scale is used in order to obtain the weight variation depending on time and temperature.

This technique allows to get information from the sample, such as its purity, its ability of solvent retention, its atoms, its velocity of reaction and its energy of activation. [4]

Differential Scanning Calorimetry, DSC: This is an ideal characterization technique to describe the phase transitions, the heat emission-absorption. It is useful to detect very small heat content [mW] changes. It measures the difference between the heat flow supplied to the sample and that supplied to a reference, when both undergo the same thermal programme. It is significant for its high sensitivity.

X-Ray Diffraction, XRD: It consists on the scattering of *x-rays* by crystal atoms, producing a *diffraction* pattern that yields information about the structure of the crystal. X-ray diffraction is an experimental technique for solving crystal structures. Powder XRD is perhaps the most used technique for characterizing materials.

The term 'powder' really means that small crystalline domains are randomly oriented. Therefore when the 2-D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various "d" spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material. This phase identification is important because the material properties are highly dependent on its structure.

X-rays are electromagnetic radiation with typical photon energies in the range of 100eV - 100keV. For diffraction applications, only short wavelength x-rays, in the range of a few angstroms to 0.1 angstrom (1keV - 120keV) are used. Because the wavelength of x-rays is comparable to the size of atoms, they are suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic x-rays can penetrate deep into the materials and provide information about the bulk structure.

* Electronic address: edurnemg@hotmail.com

Today x-ray diffraction is widely used in materials and biological research. Structures of very large biological machinery (e.g. protein and DNA complexes, virus particles) have been solved using this method. [5]

X-Ray Photoelectron Spectroscopy, XPS: This technique is based on the photoelectric effect, which was first discovered by Albert Einstein in 1905.

The photoemission process from a solid sample takes place when a highly energetic photon interacts with matter, causing an electron to be removed from an atomic orbital or from a band and to reach the vacuum level.

The excitation energy must be large enough for the electrons to overcome the work function of the solid.

The initial state of the photoelectron can be either a valence band or a core level state. In this respect, soft x-rays, in the range 300-1000eV, are ideally suited to probe the core levels of a solid, which generally show no dispersion due to their highly localized atomic-like character.

Two strong points of photoemission spectroscopy are its chemical sensitivity and its suitability for solid surface investigation. The backscattered photoelectrons, in fact, convey information on the chemical composition of the sample. [6]

II.   EXPERIMENTAL PROCEDURE

Two inks (named Compounds 1 and 2) were prepared with dehydrated tin chloride diluted in 2-methoxyethanol, with and without acetic acid respectively. The solvent chosen for both solutions was 2-methoxyethanol because it fulfils all the necessary requirements to be used as ink in an inkjet equipment. It fulfils requirements such as superficial tension and boiling point [7]. Regarding viscosity, even if it does not fit to the recommendations of the machine, 8-12cP, a second more viscous solvent such as Glycerol can be added in the right measure. In case of infulfilment of these parameters, the printing would be of bad quality and consequently, this ink could not be used in any device.

A third ink (Compound 3) was also used, which had been previously prepared with dehydrated tin chloride with a different molar ratio without any other additive.

In compound 1, dehydrated tin chloride in 2-methoxyethanol and acetic acid in a molar ratio of 1 $SnCl_2$:2 $C_2H_4O_2$ were diluted. In compound 2 and 3, only dehydrated tin chloride in 2-methoxyethanol was diluted.

Compound 1: 8ml of 2-methoxyethanol, 2g of dehydrated tin chloride ($SnCl_2$-$2H_2O$) and 1 ml acetic acid ($C_2H_4O_2$). Molar ratio ($SnCl_2$) 1:2 ($C_2H_4O_2$).

Compound 2: 8ml of 2-Methoxyethanol and 2g of dehydrated tin chloride ($SnCl_2$-$2H_2O$). Molar ratio ($SnCl_2$) 1:0 ($C_2H_4O_2$).

Compound 3: 8ml of 2-Methoxyethanol and 1.8g of dehydrated tin chloride ($SnCl_2$-$2H_2O$). Molar ratio ($SnCl_2$) 1:0 ($C_2H_4O_2$).

These three samples were shaken during a minimum of 24 hours at 50ºC.

The aim of adding acetic acid to the ink is mainly to foster the ionization of tin chloride, because it eliminates the chlorines along with the solvent when thermal treatments are applied. In this way, any remaining impurity of chloride in the final SnO_2 compound is avoided.

The density of protons resulting from this weak acid in the sample has not been controlled, because the quantity of ionized acetic acid has not been taken into account, since it is only partially ionized. That is the reason why there is not a study on the pH of the sample, which would be of interest in order to quantify to which extent our ink is stable, but in this case a qualitative study is sufficient, bearing in mind the equilibrium constant of the dissociation reaction of $SnCl_2$ and the reaction of tin acetate formation

A.   DSC AND TGA EXPERIMENTS

Once the compounds were ready, TGA and DSC studies on compounds 1 and 3 were carried out, which allowed to calculate the changes in mass when the sample was heated, the temperature at which it ceases evaporation and the mass remaining when no other change happens.
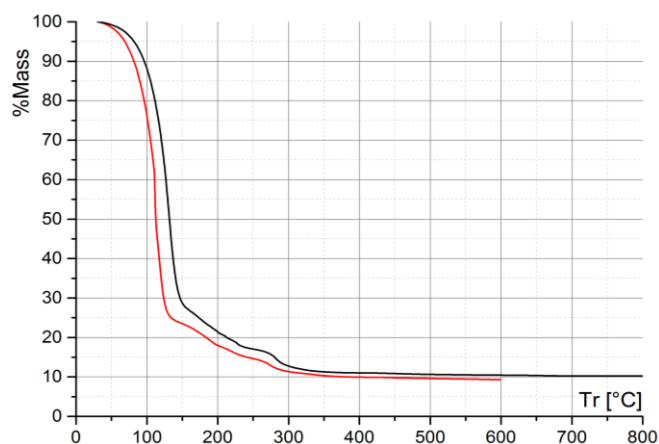

FIGURE I. Result of the TGA experiment for compound 1 and 3. Values are expressed in % to make them comparable. Compound 1(black) and compound 3 (red).

TGA graph for compound 1 shows a strong fall from the beginning of the experiment until 150ºC (from 100% to 28.72% of mass) due to the evaporation of the solvent and some chlorides. Right after that, there is change on the rate of evaporation, directly depending on the temperature, and there is a constant performance in the TGA derivative until 200ºC (leaving 21.39% of mass). The temperature keeps on rising and the mass keeps on evaporating with some slight changes in rhythm until 400ºC (when 11.02% of mass remains). At this point, the derivative becomes zero and consequently there is no more evaporation and the mass keeps constant around 10-11%m.

In the case of compound 3, the TGA performance is very similar, but it has to be noted that in the first big fall, the

solvent evaporates at lower temperatures. At 150ºC, there is a 23.5%m. Then the rhythm changes and the mass drops proportionally with the temperature until 400ºC (10%m).

This is where TGA graphs for both compounds coincide: there is no more evaporation and both samples remain with approximately the same mass concentration.

As we have seen in the chart, compound 1 requires a higher heat in order to make the same amount of mass evaporate under 300ºC, it showing that any sort of reaction that requires a higher energy has to be. Once reached 300ºC, it may be interpreted as a direct oxidation and both compounds match their masses for higher temperatures.

After this analysis, the temperatures of 300, 370, 440, 530 and 600ºC were chosen for the annealing treatment of the compounds.

As far as DSC is concerned, there is a clear difference between the two compounds. For temperatures from 180ºC until 600ºC, they keep a similar performance but compound 1 evolves at a higher power.

For compound 1, there is a peak which corresponds to an exothermic transformation with a maximum at 50ºC, followed by an endothermic process with a minimum at 90ºC. Then, it increases proportionally to temperature in the range from 120ºC until 220ºC, including another very narrow endothermic peak at 230ºC. At 300ºC there is an exothermic transformation that finishes at 380ºC, followed by a constant performance until 460ºC are reached, when another exothermic process leads to Sn oxidation.

For compound 3, two exothermic peaks are shown from the beginning of the experiment until 140ºC, with maxima at 65ºC and 115ºC. In the range between 140ºC and 290ºC, there is a slight increase in power, including the same endothermic peak shown in compound 1, with a minimum at 230ºC. At 300ºC the beginning of an exothermic transformation that finishes at 420ºC can be detected and then the power increases with a second peak at 600ºC, which causes the oxidation of tin.
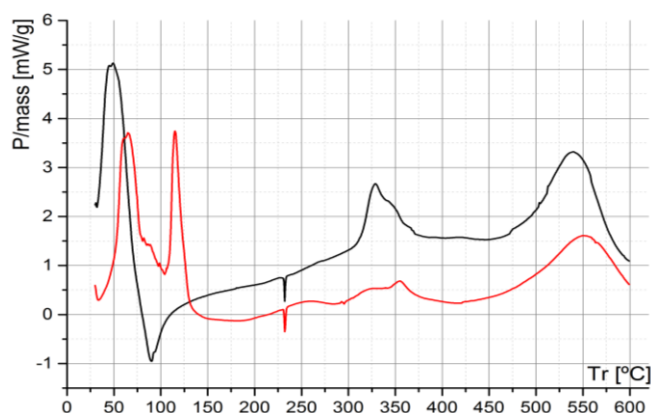

FIGURE II. DSC graph. The evolution of a normalized power regarding the temperature supplied on the samples is observed. Compound 1(black) and compound 3 (red).

By means of molar calculations, the percentage of mass has been obtained in case SnO, 11.09%, or SnO$_2$, 12.40% are

formed. These values correspond with the results obtained by TGA, where there is no more evaporation from 400ºC and there is a constant mass of approximately 10-12%.

Compound 1	TGA (13,81 mg)		
	mass (mg)	mol	mass (%)
2-ME	9,900	1,30E-04	71,69
AA	1,345	2,24E-05	9,74
SnCl$_2$	2,155	1,14E-05	15,61
2H$_2$O	0,410	1,14E-05	2,97
TOTAL			100
SnO	1,531	1,14E-05	11,09
SnO$_2$	1,713	1,14E-05	12,40

TABLE I. Mass, moles and percentage of mass in compound 1, and mass, moles and percentage of mass in case SnO or SnO$_2$ were formed. 2-ME means 2-methoxyethanol and AA means acetic acid.

Compound 3	TGA (5,82 mg)		
	mass (mg)	mol	mass (%)
2-ME	4,72	6,21E-05	81,09
SnCl$_2$	0,93	4,88E-06	15,89
2H$_2$O	0,18	4,88E-06	3,02
TOTAL			100
SnO	0,67	4,88E-06	11,54
SnO$_2$	0,74	4,88E-06	12,63

TABLE II. Mass, moles and percentage of mass in compound 3, and mass, moles and percentage of mass in case SnO or SnO$_2$ were formed. 2-ME means 2-methoxyethanol.

The percentage obtained in both oxides is so similar that with this technique it is impossible to ascertain whether SnO or SnO$_2$ are formed in the final sample.

B. XRD EXPERIMENTS

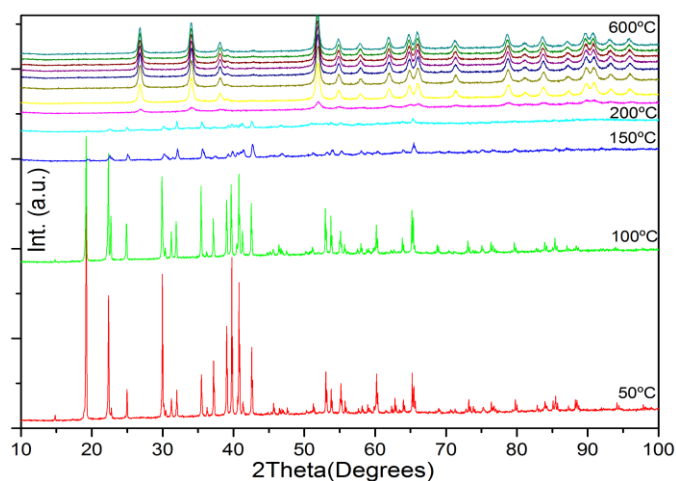The first XRD experiment has been conducted on a pure SnCl$_2$ powder at different temperatures.

FIGURE III. XRD spectra for SnCl$_2$ annealed in situ at temperatures from 50ºC to 600ºC.

For lower temperatures, $SnCl_2$ peaks can be seen. As temperature increases, a decrease in the intensity of peaks can be noticed until it reaches 200-250ºC, where the spectrum is almost flat. That indicates that the initial crystalline $SnCl_2$ has become amorphous. For temperatures higher than 300ºC there are diffraction peaks of SnO_2. [8]

In the graph below, the diffraction peaks for compounds 1 or 2 (with or without acetic acid) deposited and annealed at 530 and 600ºC are represented.
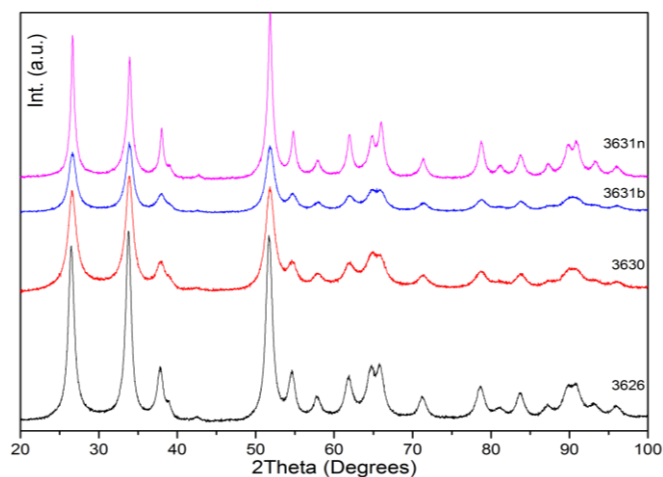

FIGURE IV. XRD graph for samples 3631n, 3631b, 3630 and 3626. Samples 3631n and 3631b belong to compound 2 annealed to 530ºC and relate to the black and white sides, accordingly. Samples 3630 and 3626 belong to compound 1 reheated to 530ºC and 600ºC respectively.

These peaks can be compared with the previous graph: for high temperatures peaks coincide, there is SnO_2 and, at these temperatures, chlorine is evaporated.

The diffraction spectrum at 600ºC shows more intense peaks, due to the fact that the increase in temperature provides more energy to the system and consequently the size of the crystal gets bigger. Each peak is associated to a Miller plane. When the intensity of peaks is high, it means that the crystal shows a higher arrangement in that direction, large crystal size whereas when the intensity is low it means that there is few arrangement. Therefore, when it is lighted up by x-ray, the detector receives less photons at this direction because they are scattered. Hence the intensity is lower.

Differences are shown between the white and the black areas of the sample at the same temperature. It is noticeable that the white area at 530ºC with acetic gives a spectrum similar to the one without acetic acid at the same temperature. However, the black area at 530ºC shows a crystal size quite similar to the sample with acetic acid annealed at 600ºC.

The fact that the sample is black implies that there are accessible states within the GAP with visible energy. When it is lightened up with wavelengths corresponding to that range of energies, the photons are absorbed. This indicates that it is not pure SnO_2. Otherwise there would be no states within the GAP. In the white area, all the photons sent are reflected as a result of the lack of states within the GAP.

The fact that the crystals in the black area are similar to the ones in the sample annealed at 600ºC, bigger than the white area, is not related to the accessible states of the GAP, but rather to the quantity of acetic acid accumulated in each region. Acetic acid helps chlorines to disappear, but once there is no more chlorine in the ink, there is no longer any difference between the presence or the absence of this acid.

There is no way to get information about the amorphous area in the sample with XRD experiments. To go further, XPS is needed.

C. XPS EXPERIMENTS

In this experiment we analyzed the compound 1 reheated to 530ºC and to 600ºC, where the last sample had a white side and a black side; and the compound 2, which was reheated to 530ºC, where we got the same black and white sides as a result.

So as to analyze the outcomes, it has been needed two peaks to make a fit of the tin peak, implying that Sn has two valences, one of these corresponding to SnO_2: an obtained result from the diffraction method. The other one is not trivial to indentify.
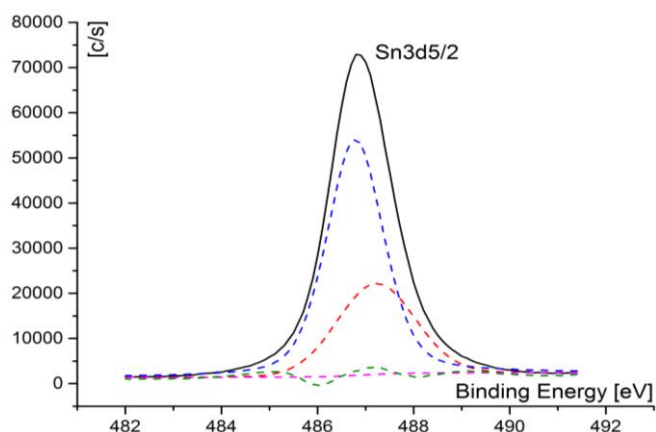

FIGURE V. The two peaks needed to make a fit of the tin peak in the white part of compound 1 reheated to 600°C.

We are going to calculate the Auger Parameter for each peak of Sn3d5 found. This parameter will help us to discern whether we have an oxide or a metal. The values obtained are 918.6 and 919.0eV.

The two peaks indicate two kinds of oxidation states of tin, we cannot rule out the Sn-metal option.

In these systems, it is very common to have regions with Sn-metal on the surface, where the XPS experiment is performed, meaning tin bonded to another tin but not bonded to oxygen. The Sn-Sn bond may break and merge with oxygen or ambient water, thus producing states within the GAP and giving the black color.

For this reason we might think on the surface of our sample have metallic tin, this would be reflected in the results of XPS as a second peak. According to the bibliography [9] [10]

[11], the two peaks are so close between them, therefore they cannot form a bond Sn-metal. The only option left is the second peak belongs to SnO amorphous. [12]

Although there are other combinations of peaks in the same amount, the two peaks we see in Fig. V are the ones that minimize the error. We have to consider that the peaks positions are the ones that give us the information from the sample's chemical composition. A peak just being more or less intense only means that we receive a more or less signal.

III. CONCLUSIONS

Inkjet printing technology is maturing as a patterning method in the microelectronic device industry.

▪ It has been proved after treatment of the information get from TGA y DSC, of the sample with or without acetic acid, that there are no important changes as far as the concentration of chlorine is concerned. The problem with this acid is that it does not ionize easily in 2-methoxyethanol because it is a weak acid and its quantity of protons is small. It is not possible to get rid of all chlorines, interesting to get SnO_2, which is our goal.

Discrepancy between the experimental non-evaporated mass and the theoretical one is reflected in these cases; either in the formation of SnO_2 or SnO, it does not guarantee all chlorines sublimate. The discrepancy may be linked to several reasons:

• At the beginning of the measurement, prior to the machine is stabilized at its initial temperature at 30ºC, some evaporation might not be measured at all. Therefore, the mass discrepancy can be resulting from an error of the TGA and DSC machinery measurement.

• However, it could also be that the ink was not completely homogeneous either and the drop used in the process was not concentrated in its entirety, assuming that when making calculations.

• Or it might be the case as well where the tin were to sublimate thus the initial and the final m% were not retained, even though this situation is exceptionally rare. What does mean adding acetic acid to our ink?

As the chlorine sublimates, there is not any significant change observed. It needs more heat in order to evaporate the same amount of mass as we add more acetic acid.

▪ From the results obtained by diffraction of $SnCl_2$, it has been proved that it does not become SnO, because it is crystalline and therefore would look in the diffraction pattern, but it becomes directly SnO_2, unless there is an amorphous part of SnO. That is to say, in our final compound there would only be SnO_2.

▪ From the results obtained by XPS see that there are two oxidation states, two peaks, one of which is crystalline SnO_2, obtained by XRD. The second peak cannot be crystalline SnO because would be reflected in the XRD experiments. We have also confirmed that it cannot be Sn-metal, so we opted for the option of amorphous SnO.

APPENDIX

In order to calculate the Auger Parameter we have used the following expression:

$$Kinetic\ energy \quad KE = h\nu - EB(M4N45N45) - WF \quad [1]$$
$$AP = KE + EB(Sn3d5) \quad [2]$$

[1] G.E. Patil, D.D. Kajale, V.B. Gaikwad, "Preparation and characterization of SnO_2 nanoparticles by hydrothermal route", *International Nano Letters*, 2012, p. 1-2.

[2] T. Kawase, S. Moriya, C.J.Newsome, "Inkjet Printer of polymeric field-Effect transistors and its applications", *The Japan Society of Applied Physics*, 2005, p. 3649-3650.

[3] T. Kawase, S. Moriya, C.J.Newsome, "Inkjet Printer of polymeric field-Effect transistors and its applications", *The Japan Society of Applied Physics*, p. 3657

[4] Georg Widmann. "Información TA: Interpretación de curvas TGA", Matter Toledo. Disponible en: http://es.mt.com/mt_ext_files/Editorial/Generic/3/ TA_UserCom13_0240929710242401_files/tausc13s.pdf

[5] Materials Research Laboratory at UCSB: an NFS MRSEC. "X-ray Basics". Disponible en: http://www.mrl.ucsb.edu/centralfacilities/x-ray/basics

[6] Elettra Sincrotrone Trieste S.C.p.A "X-ray Photoelectron Spectroscopy". Disponible en: http://www.elettra.trieste.it/lightsources/labs-and-services/surface-lab/x-ray-photoelectron-spectroscopy.html

[7] Luis Fco. Portilla, "Solution synthesized SnO_2 inkjet-printed thin- films transistors", 2012.

[8] H.Mahmoudi Chenari, L. Weinhardt, N.S. Rodriguez Lastra, M.A.Ernst, F.Reinert, "Structural properties and x-ray photoelectron spectroscopic study of SnO_2 nanoparticles", *Materials Letters*, 2012, p. 168-170.

[9] Perkin-Elmer Corporation. Physical Electronics Division. "Handbook of X-ray Photoelectron Spectroscopy". Appendix A. Auger Parameters. P.210

[10] Thermo Scientific XPS. Disponible en: http://xpssimplified.com/elements/tin.php

[11] NIST X-ray Photoelectron Spectroscopy.Database. Disponible en: http://srdata.nist.gov/xps/EnergyTypeValSrch.aspx

[12] F. A. Akgul, C. Gumus, Ali O. Er, A. H. Farha, G. Akgul, Y. Ufuktepe, Zhi Liu."Structural and electronic properties of SnO_2", *Journal of Alloys and Compounds*, 2013, p. 52-54