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PREPARATION OF THIN FILMS BISMUTH SULFIDE BY CHEMICAL BATH DEPOSITION TECHNIQUE, A SIMPLIFIED FORMULATION

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In this work where obtained bismuth sulfide thin films, by a simplified formulation, the method used for the synthesis of bismuth sulfide thin films, is denominated chemical bath deposition. It was determined the optical absorption characterization showed a direct bandgap between 1.3eV and 1.6eV. Scanning electron microscopy images are also reported, which shows homogeneity in the morphology of the obtained films, as function of the deposition time. When analyzing the material by transmission electron microscopy technique, it was obtained an interplanar distance of 3.11Å, also characterized by X-ray diffraction obtaining a main signal in $2\theta = 27.3°$.

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1. Introduction

Since several decades the study of bismuth sulfide thin films has been interesting, P. K. Nair *et.al* in 1998 [1], show a published a study concerning to the comparison of the properties of bismuth sulfide thin films prepared by thermal evaporation and chemical bath deposition. Different authors have reported optical band gap between the ranges 1.2 to 1.82 eV, and 1.52 to 1.9 eV [1, 2, 3]. There exists different ways to elaborate the bismuth sulfide thin films, among which are the silar method, pulsed laser deposition, spray pyrolysis, RF sputtering, vacuum thermal evaporation and chemical bath deposition, among other [3], [4].

One of the early research's concerning to bismuth sulfide films, elaborated by the chemical bath deposition method was in the year of 1980 by Pramanik P and Bhattacharya RN, previously in 1978, Miller B, Menezes S and Heller A, elaborated bismuth sulfide films by the anodic method, however there are documented studies about the properties of bismuth sulfide that date back in the 20's and 1917 by Case concerning with a study of the bismuthinite ore [1].

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The main applications of bismuth sulfide films is in photoelectrochemistry, particularly in solar cells. Applications such as optoelectronic, thermoelectric and photovoltaic devices are referred in [2], bismuth sulfide has also been used to prepare photodiodic arrays, sensors and infrared spectroscopy [3], in 2012 A.K. Rath et.al developed a bismuth sulfide composite with P-type PbS nanocrystals, applying to solar cells with efficiencies of 5% [4]. Panmand R.P, et.al in 2010 reported potential applications for bismuth sulfide in thermoelectric conversion [5].

There are other interesting applications of the material bismuth sulfide that can be consulted in several research papers as the listed in [6-17], the present research is focused into develop a new chemical formulation to grow bismuth sulfide thin films by the chemical bath deposition method. The found procedure used easy handled precursors and reaction conditions were determined for aqueous solutions. To characterize the Bi_2S_3 thin films were realized UV-vis spectroscopy, SEM, TEM, XRD and XPS.

2. Experimental

In this section we will explain the developed recipe to elaborate the thin films of bismuth sulfide (Bi_2S_3), using the chemical bath deposition technique. The Bi_2S_3 thin films were deposited on soda-lime glass substrates, these substrates were firstly cleaned with soap and water, after dried, and were located in a petri box and immersed in isopropanol, and was applied ultrasonic vibration, during 5 minutes.

The precursor agent of metal ions is bismuth nitrate pentahydrate, dissolved in water, two complexing agents, ammonium hydroxide and ethylenediamine were used, whose purpose is to gradually release the bismuth ions were used, because the ions in the salt are of polarity different from the metallic ones, they bond To obtain the sulfur ions thiourea was used. The formulation was as follows: 10 ml of bismuth nitrate pentahydrate, 5 ml of ammonium hydroxide, 10 ml of thiourea and 5 ml of ethylenediamine.

This formulation is innovative because it allows to control the chemical reaction dynamically, allowing the bismuth sulfide to gradually form. Manipulating the temperature and the reaction time. In many other works, thioacetamide is used as a precursor for sulfur, to obtain bismuth sulfide. Thioacetamide reacts rapidly with bismuth salt compared to thiourea which is slower. The temperature and reaction time are factors that affect the formation of thin films.

The realized characterization was carry on by using the next equipment: For the UV-vis measurements, Jenway 6850 with 0.1nm resolution in the 190 - 1100 nm range, to obtain the SEM images was used a JEOL 7000F JSM with a resolution between 0.8 to 1.0 nm, using and acceleration voltage of 0.1 to 30KV, producing magnifications from 25 until 1,000,000x.

Transmission Electron Microscope JEOL, model JEM 2010F Field Emission Electron Microscopy with an acceleration of electrons to 200kV.

3. Optical Characterization.

From the UV-vis obtained data, were determined the absorption plots and the energy band gap for direct transitions. The bismuth sulfide thin films show absorption spectra with an edge into 954nm which correspond to 1.3 eV, reported in other research's works for the bismuth sulfide, however, depending of temperature can vary between 1 to 1.4 eV. The obtained values at this work were 1.33, 1.38, 1.49, 1.57 eV, depending of deposition time, 4, 4.5, 5 and 6 h, respectively. For this information see figure 1. The graphics 1, 2, 3 and 4, correspond with deposition times of 4, 4.5,5 and 6 h, respectively. In the range from 790 to 1000 nm the absorption intensity is according with the increase of the thickness.

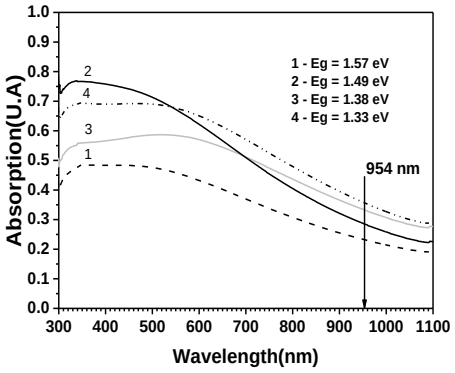

Fig. 1. Absorption UV-vis spectra of four Bi_2S_3 thin films to deposition times 1) 4h, 2) 4.5h, 3) 5h and 4) 6h

The next process consists into calculate the direct band gap for each Bi_2S_3 film, from the Tauc method. In figure 2, can be observed the geometric behavior of the direct Tauc variable $[(Abs)\ (E)]^2$ vs Energy, also the linear performance due to electronic transitions from valence band until conduction band. The parts a), b), c), and d) of figure 2, are corresponding with the reaction times of 4, 4.5, 5, and 6h.

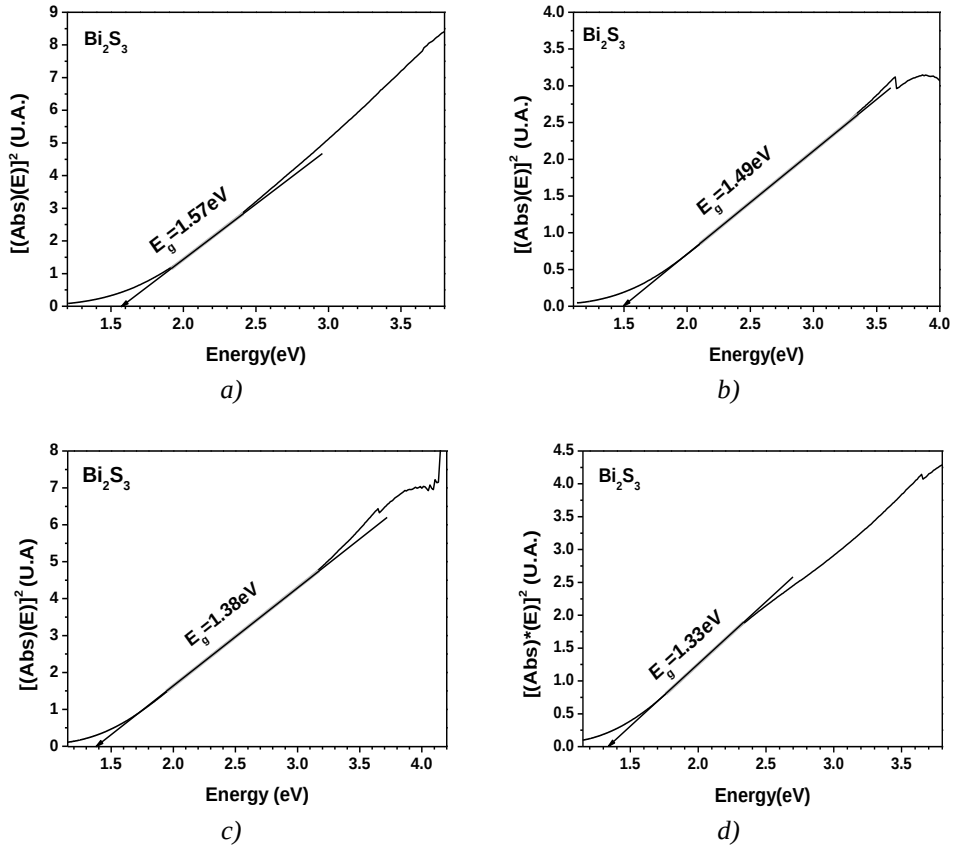

Fig.2. Tauc variables vs Energies for bismuth sulfide films deposited by CBD, band gap energies a) 4 h, b) 4.5 h, c) 5 h and d) 6 h.

4. SEM Characterization

Other realized characterization is the one corresponding to scanning electron microscopy, in figure 3 are shown four composed images for the different reaction times, a) 4, b) 4.5, c) 5, and d) 6h. The image in a) has two magnifications, the background is for 1000x and the in inset 70000x. Has can be observed at the scale of 1000x the material start with a granular morphology presenting empty edges, those empty edges are going filling trough a smooth background for reaction times of b) 4.5 and c) 5, diminishing the roughness, while for 6h, d), the morphology look more ordered with a few pin holes.

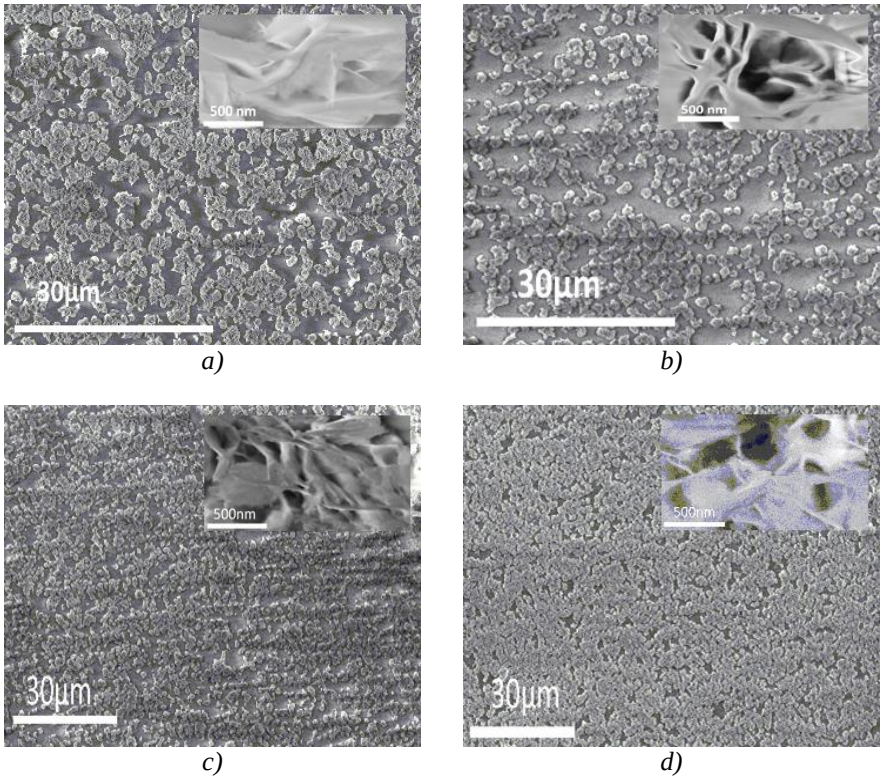

Fig.3. Morphologies of bismuth sulfide thin films with scanning electron microscopy, for reactions times of a) 4 h, b) 4.5 h, c) 5 h and d) 6 h

5. TEM Characterization

The next characterization depicts the results obtained by TEM, in figure 4a is shown contrast micrograph with a work scale of 5 nm for the bismuth sulfide compound. From figure 4a was applied the Fast Fourier Transform (FFT) to obtain figure 4b, then was assigned a fitting coordinate system to applied a mask, expanding the periodicity give place to figure 4c. In that image (figure 4c) were measured interplanar distances of d1 = 2.712Å, d2 = 3.114 Å and d3 = 1.733 Å, which correspond to orthorhombic bismuth sulfide with the crystallographic sheet PDF # 17-0320, and corresponding Miller indices (301), (211), (351), respectively. Finally from applying the inverse FFT is obtained the figure 4d, displaying a treated image, more idealized than the original contrast micrograph.

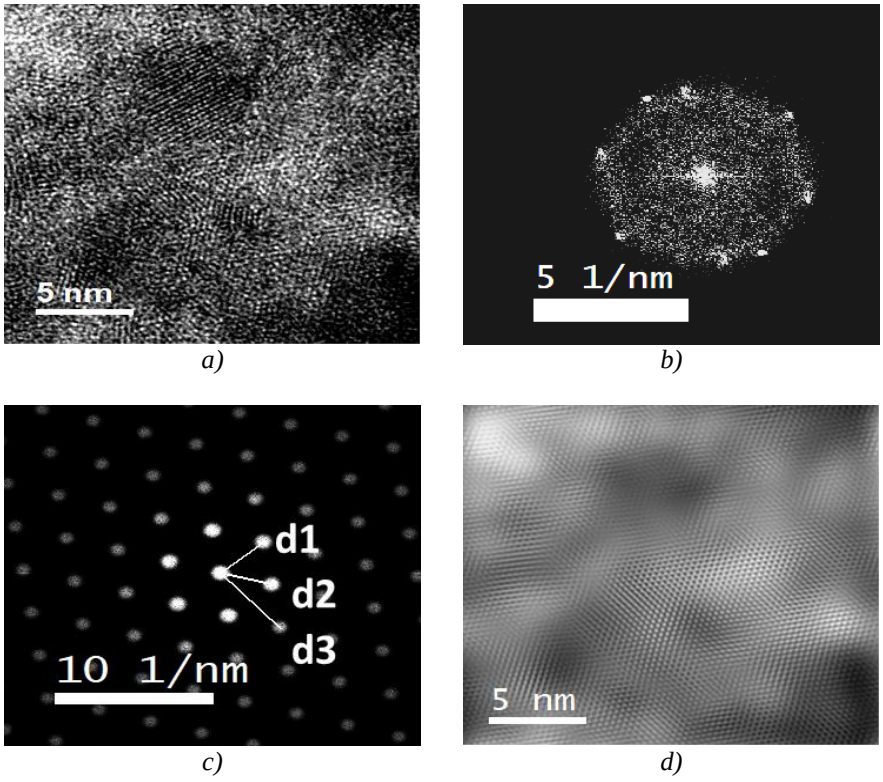

Fig.4. Contrast micrograph image for bismuth sulfide thin films with transmission electron microscopy, a) original image, b) FFT image, c) masking extrapolation and d) processed inverse FFT image or idealized.

The TEM is equipped with the EDS peripherical, EDS measurements were carry on Bi_2S_3 thin films obtaining the next pattern of energies, where could be identified the elements sulfur, bismuth, cooper (from the grid), silicon and oxygen (from the substrate), and carbon (as environmental contaminant). This preliminar composition characterization proof only the presence of the hope elements in our material. See figure 5.

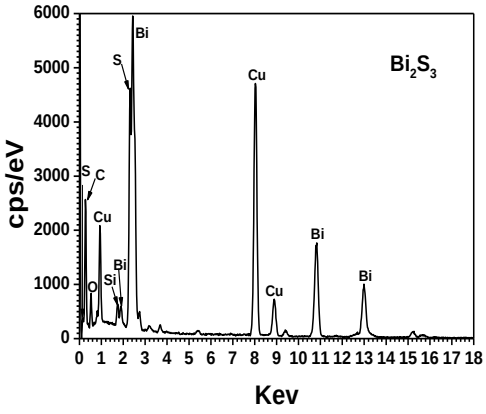

Fig.5. Plot that show the Energy Dispersive Spectroscopy (EDS) of a $B_{i2}S_3$ thin film elaborated by chemical bath deposition.

6. XRD Characterization

One more characterization was the XRD pattern in order to reforce the structural identification of our material. In figure 6a (4h), the material only shows one signal of diffraction corresponding with monoclinic bismuth in 2θ= 30.074°, in figure 6b (4.5h) the material shows furthermore a slight signal for orthorhombic Bi_2S_3 in 2θ=27.32°. While that for reaction time of 5h, see figure 6c, it arised another peak for orthorhombic Bi_2S_3 in 2θ=33.37°. Finally in figure 6d all the peaks fit with the orthorhombic phase of Bi_2S_3. The figure 6e is of the glass substrate, in order to justify the amorphous band.

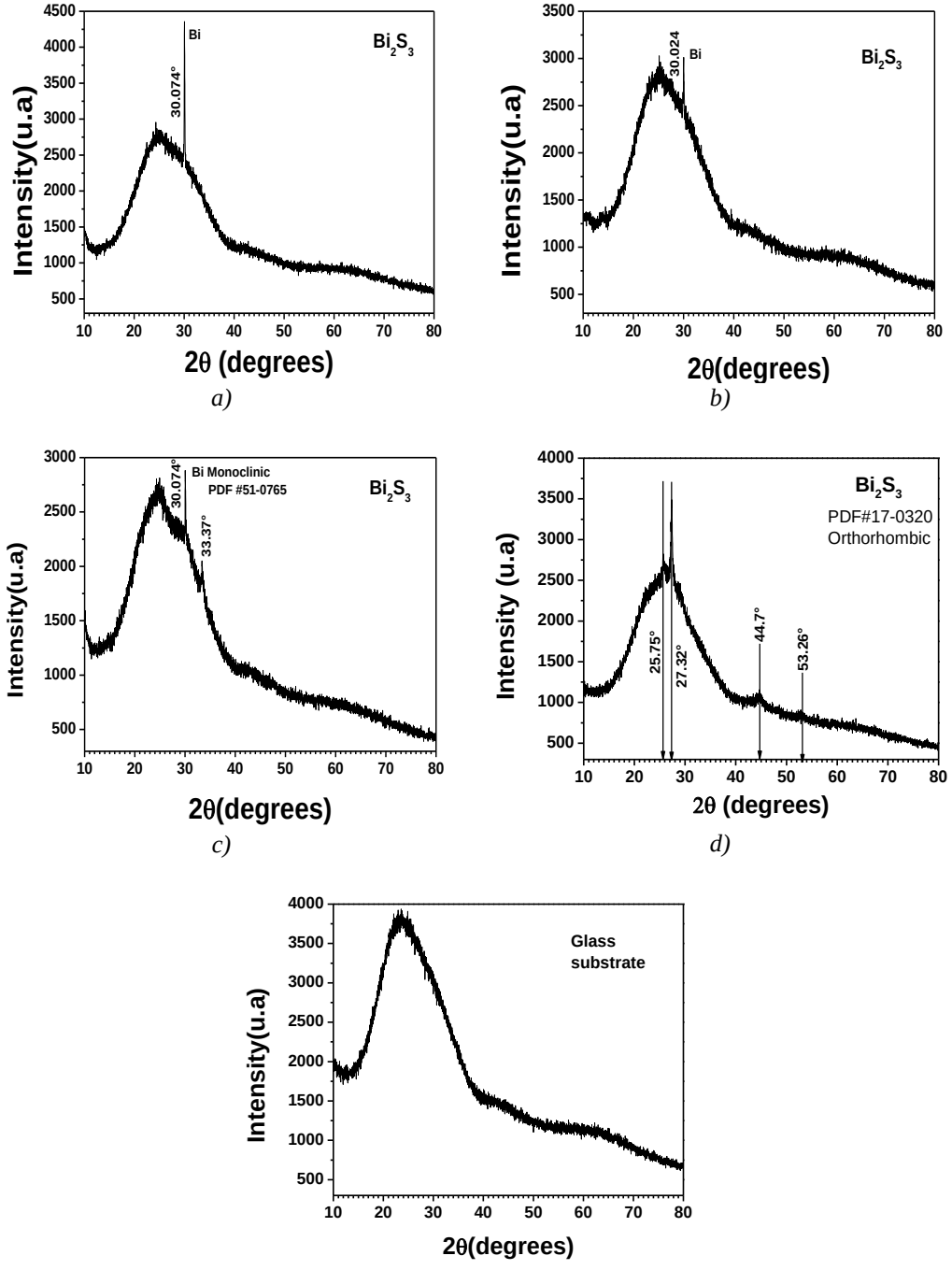

Fig.6. Set of XRD patterns corresponding to Bi_2S_3 thin film deposited on glass substrate, the plots a), b) c), and d) are for reaction times of 4, 4.5, 5 and 6h, respectively, and the plot e) is the pattern of the amorphous glass substrate.

7. Characterization XPS

By using a XPS equipment, we measure a survey type spectrum, where could be observe basically the hoped elements in our material. Were used several references standard sources to identified the binding energies. The improper elements as sodium, oxygen, silicon and carbon, come from the substrate or environmental contaminants. In figure 7 are shown all the elements contained on synthetized samples, this spectrum was took as guide to measure high resolution XPS, for the main chemical elements.

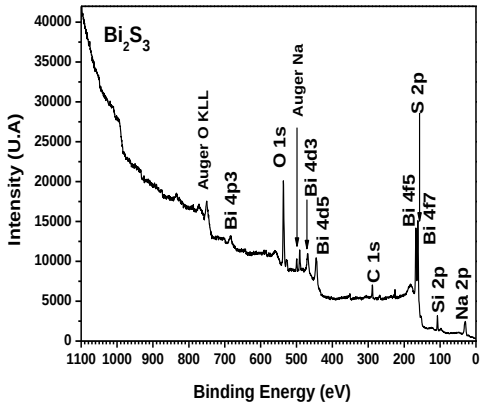

Fig.7. Spectrum of binding energies from X-rays photoelectrons spectroscopy for bismuth sulfide thin film synthetized by a new formulation of chemical bath deposition, that corroborate a certain purity of the elaboration method.

From the high resolution XPS measurements made for the bismuth sulfide film, realized for each of the main elements assumed to contain the thin film material (Bi, S, C and O), the carbon was analyzed individually because it is an environmental pollutant what is located very much on the surface of the Bi_2S_3 film and is generally analyzed for reasons of calibration of the XPS equipment, while oxygen is also an environmental contaminant contained in the atmosphere. Figure 8a shows the carbon signal located at an experimental value of 288.95 eV which is compared with respect to the standard value of the manuals (C 1s = 284.5 eV), the increment is indicated with a value of $\Delta C = 4.45$ eV. Figure 8b locate us the oxygen 1s, at a value 536.8 eV; Figure 8c shows a characteristic doublet type signal of the bismuth element with its maximum values at Bi 4f5 = 167.7 eV and Bi 4f7 = 162.5 eV; finally in figure 8d the signal for sulfur 2s is shown, centered around 229.6 eV. The presence of bismuth and sulfur is sufficient to validate the identity of the compound, complementing with the others characterizations.

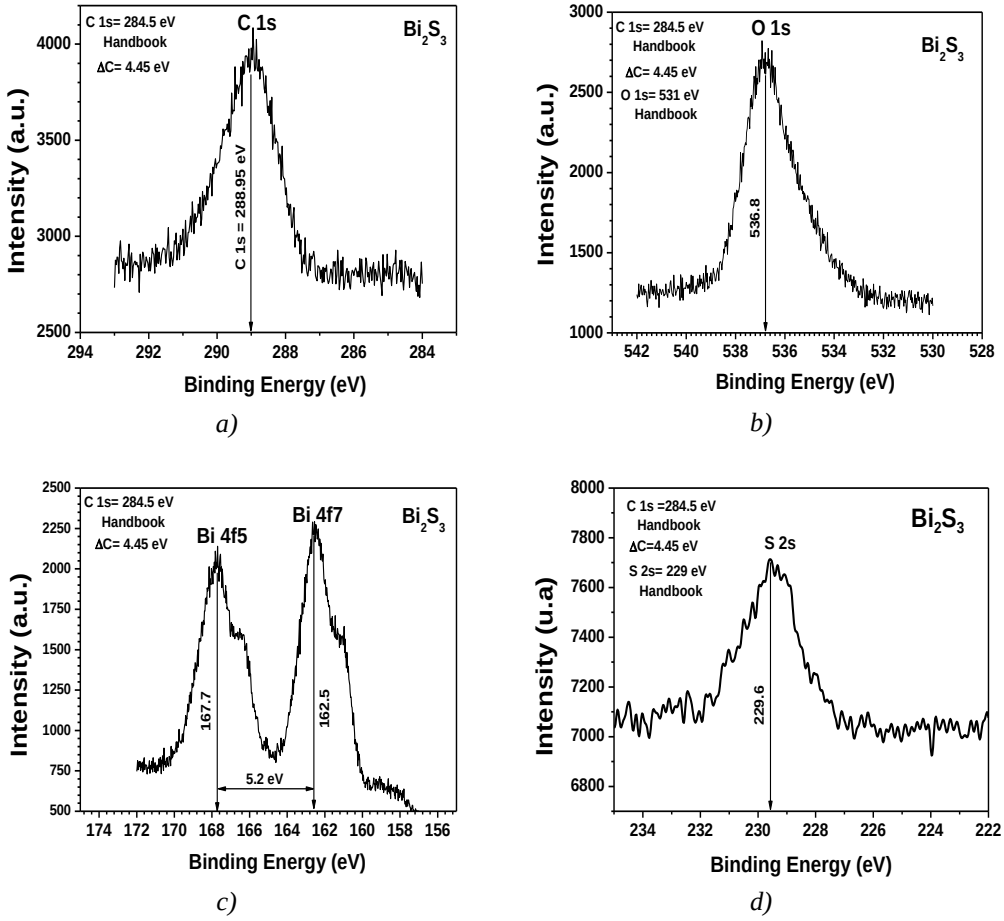

Fig.8. High resolution XPS for the main elements contained at the surface of Bi_2S_3 thin film, showing the presence of bismuth and sulfur, plus carbon and oxygen as environmental contaminants.

8. Conclusions

The main conclusion consist into the elaboration of a new formulation to grow thin films bismuth sulfide by chemical bath deposition technique. The used reagents were easy handled and the arrange of the grown system was in open atmosphere. The only solvent used was water and the reaction temperature was 36°C, relatively close to room temperature.

The adherence of the film to the substrate was very good and also its uniformity. We are sure that this simplified method will have very good applications.

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