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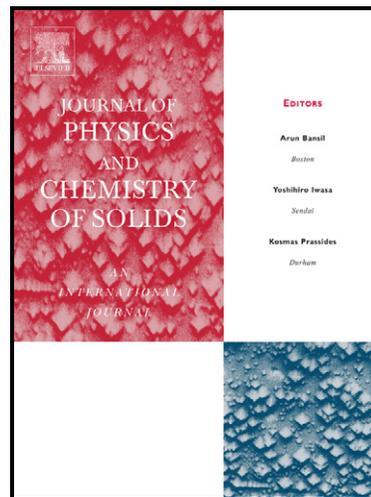
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Properties of In₂S₃ thin films deposited onto ITO/glass substrates by chemical bath deposition.

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ABSTRACT

In₂S₃ films have been chemically deposited on ITO coated glass substrates by chemical bath deposition, using different deposition times and precursors concentrations. The bilayers are intended for photovoltaic applications. Different characterization methods have been employed: optical properties of the films were investigated from transmittance measurements, structural properties by XRD and micro-Raman, and surface morphology by SEM microscopy analysis. Also, the direct and indirect band-gaps and the surface gap states were studied with Surface Photovoltage Spectroscopy (SPS). We proposed that electronic properties of the In₂S₃ samples are controlled by two features: shallow tail states and a broad band centered at 1.5 eV approximately. Their relation with the structure is discussed, suggesting that their origin is related to defects created on the S sub-lattice, and then both defects are intrinsic to the material.

KEYWORDS

In₂S₃, ITO, Chemical deposition, Raman spectroscopy, Surface Photovoltage Spectroscopy

1. INTRODUCTION

Indium sulphide buffer layers, prepared by Chemical Bath Deposition (CBD) have demonstrated their potential to obtain high efficiencies solar cells [1, 2]; their band gap energy values between 2 and 3.7 eV [3], their transparency, etc, are suitable characteristics for application in solar energy conversion. For obtaining In_2S_3 with the adequate properties for such application, we must to take into account several considerations about the material.

These properties of the In_2S_3 obtained by CBD method depend on different factors as precursors concentration, deposition time, and reaction temperature. But, the effect of the different conditions on the final layers properties is still not well understood and is one of the key points for the further development of this material. In particular for example, the presence of surface states is very important because their effect on the junction formation in solar cells; being then mandatory to know their origin and properties [4]. Commonly, this type of surface defects are possible recombination centres which strongly deteriorates the interface between the absorber and the buffer layers, and in consequence the final device performance.

In this work, a combination of optical, morphological and structural characterization, are used to explore the In_2S_3 layers, together with Surface photovoltage spectroscopy (SPS) in order to characterize the surface defect structure. The attention is mostly concentrated to study the effect of the different growth conditions on the formation, origin (intrinsic, extrinsic) and properties of the surface states, and their possible impact on the electronic properties of the buffer layer. Samples were prepared using different precursors concentration and growth time with the aim to identify the effect of both parameters.

EXPERIMENTAL

ITO thin films have been prepared by rf magnetron sputtering from an oxide ceramic target 90 wt.% In_2O_3 and 10 wt.% SnO_2 . The substrates were soda lime glasses (2 mm thick) that were placed in equivalent positions in an adjustable vertical frame and moved in front of the target to obtain simultaneous ITO deposition, without intentional heating. High purity Ar and O_2 were introduced through independent mass flow controllers after the vacuum chamber was evacuated below 1×10^{-4} Pa. The oxygen content in the sputter gas, as determined by the oxygen to argon partial pressure ratio, was adjusted in order to optimize the ITO properties according to previous studies [5, 6]. The process total pressure was kept at 4×10^{-1} Pa and the sputtering power density employed was below 1.5 W/cm^2 . The samples were after annealed at $350 \text{ }^\circ\text{C}$ in vacuum in order to improve their optical and electrical characteristics [7], achieving visible transmittance near 90 % and sheet resistance of $7 \text{ } \Omega/\text{sq}$ for the present ITO layers with about 350 nm thickness.

The deposition of In_2S_3 has been carried from an acidic solution of thioacetamide concentration (TA) (CH_3CSNH_2 , Fluka), and indium (III) chloride (InCl_3 , Fluka) 0.01 M at $70 \text{ }^\circ\text{C}$, for different deposition times (Table I). Other additives necessary to obtain films with photovoltaic quality are hydrochloric acid and acetic acid. Some of the samples were annealed at $200 \text{ }^\circ\text{C}$ in a tubular furnace under flowing nitrogen.

The thickness of the In_2S_3 films obtained was carried out with a profilometer (Dektak 3030).

Raman microprobe measurements were made on In_2S_3 layers before and after the thermal treatment using a HR800-UV Horiba-Jobin Yvon spectrometer coupled with an Olympus metallographic microscope. The spectra were obtained using as excitation the green line of an Ar^+ laser ($\lambda = 514 \text{ nm}$) and were fitted using the LabSpec software defining the peaks as Gaussian-Lorentzian.

Surface photo voltage spectroscopy (SPS) was carried out using a home-made equipment consisting in an isolated camera with a gold grid (Kelvin probe S, Besocke Delta Phi GmbH), controlled by a Kelvin Control 07. Ar pressure of 1 atm was imposed and the measurements were carried out at room temperature. Excitation was made with the light of a monochromator Spectra Pro 2300i 0.3m (350-1400 nm) with an ARC Model TS-428 250 W Tungsten-Halogen lamp. The surface photovoltage signal was monitored with an oscilloscope Iso-Tech ISR635 35MHz and measured with a Keithley 2010 Multimeter. The collected signal was corrected using the dark contact potential difference (CPDD) and the wavelength dependence of the lamp emission spectra, on the studied energy region. The indirect and direct band-gaps and the energy of the exponential defect tails were obtained means the analysis of the SPS spectra.

Optical transmission measurements of the samples referred to the air have been done with unpolarised light at normal incidence in the wavelength range from 300 to 2500nm, with a double beam spectrophotometer Perkin Elmer lambda 9.

X-ray diffraction (Philips X'pert-MPD diffractometer) was used to determine the crystallographic structure of the films, phase identification has been carried out by comparison of the observed d-spacing with the powder diffraction standards card files and SEM microscopic analysis (Hitachi S-2500) to study the surface morphology.

3. RESULTS AND DISCUSSION

The optical transmittance spectra corresponding to the different indium sulfide films are shown in Fig. 1. The transmittance of samples (Fig 1a) in the visible spectral range (400-800 nm) is above 70-80 %, being lower the transmittance for the films with high time deposition (and then thicker), whereas transmittance in the near-infrared region decreases owing to interaction with free-carriers in the ITO coating [5- 7], suggesting the presence of high shallow state density as will be confirmed after by SPS.

The X-ray diffractograms corresponding to the samples are shown in Figure 2. The $\text{In}_2\text{S}_3/\text{ITO}$ films have been annealed at 200 °C in nitrogen atmosphere due to the low crystallinity exhibited by the In_2S_3 films. The diffraction peaks of 2θ associated with ITO are at 21.5, 30.5, 35.5, 41.7, 45.7, 50.7, 60.6, 62.0 and 63.6° (JCPDS card no. 06-0416) corresponding to a cubic structure with (222) preferential orientation. The diffraction peaks of 2θ at 33.10, 43.6 and 47.6° corresponding to In_2S_3 (JCPDS card no. 32-0456) appear with small intensity in the F1, F2 and F4 samples. This is not surprising because of the very low samples thickness, their nanocrystalline structure and their poor quality.

The optical transmittance spectra corresponding to these samples (Fig 1b) show an increase in transmittance between 5 and 10% in the range 400-800nm being lower the transmittance for the films with high time deposition, as the samples without heat treatment.

The Raman spectra of as grown In_2S_3 is shown in Fig. 3a for samples F1 to F4. Raman modes are observed in the energy region between 200-500 cm^{-1} , but all of them are broad and with very low intensity, confirming the nanocrystalline or amorphous nature of these samples. Bands observed between 200-400 cm^{-1} can be assigned to $\beta\text{-In}_2\text{S}_3$ [8, 9], but the band at 460 cm^{-1} could be related to the S-S mode of elemental S [10], being an indication that free S is present on the samples. From Figure 3a it is evident that, the lower the growth time (F1 and F3), the higher the intensity of the band at 460 cm^{-1} , suggesting that for higher growth times there is a lack of S in the bath. After the thermal treatment at 200 °C spectra changes as is clearly observed in Figure 3b. The band at 460 cm^{-1} assigned to the S-S vibrational mode of elemental S vanishes to disappear, presumably due to S evaporation and/or reaction with the as grown layers, suggesting that high quantity of free S atoms can not form the In-S bonds before the thermal treatment. Also, several peaks and bands are enhanced in the whole frequency region. The active modes of $\beta\text{-In}_2\text{S}_3$ are present at 105, 117, 250, 305 and 363 cm^{-1} [7,8], confirming the composition and structure of the layers. Their nanocrystalline or quasi-amorphous nature is reflected in the broadening of the bands (mostly in the high frequency

bands), indicating that, although some crystallization happens after the thermal treatment, the layers still remains polycrystallines and/or nanocrystallines, difficulting a deeper study of the spectra. In any case, the Raman bands do not show any tendency, nor with the deposition time, neither with the bath concentration. This means that both conditions seems do not affect considerably the sample's structure after the thermal treatment (almost at large scale), being present in all the cases the active Raman modes corresponding to β - In_2S_3 phase.

Concerning to the SPS measurements, the first important point is that all the samples have n-type conductivity as was expected. In the Figure 4a the squared ($W - \text{CPD}$) difference is plotted for the as grown samples, where W is the maximum contact potential which is obtained at high energies (the value was taken nominally at 3.5 eV in all the cases) and CPD is the contact potential difference [11,12]. Note that before the thermal treatment, the surface photo voltage signal is very low. Due to this, it is not possible to accurately determine the direct and indirect band-gaps and then, these spectra will be only qualitatively discussed tacking into account two important features: the broad onset at high energies and the broad band centred at 1.5 eV approximately. The broad onset can be attributed to the presence of shallow states, extending from their corresponding band up to the band-gap (tail states) [11]. In such case, there is a high density of shallow states in the samples (specialy in the samples grown from low concentration solutions), in agreement with their poor crystallinity confirmed by XRD and Raman spectroscopy. Observing the Figure 4a, it is possible to establish two important correlations: the lower the concentration and growth time, the higher the broad onset. In any case, the bath concentration seems to affect more than the growth time. Then, almost in the as grown samples, this band could be related to the first growth steps where surface instabilities are largely expected, due to not satisfied bonds, for example. Further growth steps lead to a lower density of tails states on the surface, probably because the last growth steps are under more stable regimen.

In addition, when the growth time exceeds 25 min and/or the precursor concentration 0.3 M, a broad band centred at 1.5 eV starts to dominate the spectra. There are few reports on defect levels on In_2S_3 in general and about this energy region in particular [13], but with a simple reasoning we can try to obtain more information about it. Being the material n-type (holes are minority carriers), the increasing on the photovoltage implies the generation of minority carriers, i.e. holes. Then, in the spectra of the Figure 4a at 1.5 eV we are observing the excitation of holes from a hole-trap centre (probably positively charged and with donor character), in agreement with the observation in Ref. 13. Although it is not possible to establish the actual origin of this centre, their hole-trap properties could be related for example with positive charged centres, formed by anion vacancy in the In_2S_3 lattice: V_S (the charge of the centre could be +1 or +2, in agreement with their hole-trap properties). This is also in agreement with the Raman measurements, where free S was observed indicating that some S atoms were not included on the In_2S_3 structure, being the origin of the V_S . And also with the conductivity type of the samples, because this intrinsic defect (V_S) can explain the n-type conductivity. This band seems to be more dependent on the growth time.

After the thermal treatment the surface photovoltage spectra dramatically change as is clearly observed in the Figure 4b. The photovoltage markedly increase and the SPS spectra exhibit a well defined band edge. In order to analyse the spectra, numerical fitting using sigmoidal logistic functions were employed. Means these fittings we obtain both band gaps which are summarized in Table II. Also, with the slope of the plot of the difference ($W - \text{CPD}$) as a function of the photon excitation energy in semi-log scale, we obtain the exponential defect tails below the band-gap (E_t), or Urbach-energy which is directly related with the disorder on the surface [12], and is also summarized in Table II.

The results are in agreement with the reported values for In_2S_3 layers [14-17] and, as can be observed in the Table II, the direct band-gap tends to decrease with the bath concentration. No special correlations of the indirect band-gap is observed, neither with the

bath concentration, nor with the growth time. It is evident that samples F1 and F2 presents similar spectra and although the signal is considerably improved after heating, the presence of the band onset is also clear. Being both samples grown at low bath concentration, this is an indication that the deposition regime in the two cases was the same. Conversely, sample F3 strongly increase their signal after the crystallization and is very different that sample F4. It is worth to notice that shallows states for sample F3 are the major contribution to the photovoltage at high energies, indicating a disordered system in agreement with the XRD spectrum. To explain this phenomenon, we can take into account the growth conditions. At higher bath concentration, the first steps on the growth hapens at high deposition rates (as is the case of sample F3), and the layer becomes of low crystallinity. After certain time, the bath concentration fall-down and the growth rate starts to decrease explaining the better crystalline quality of the sample F4. In fact, the sample F4 behaves different to the others as is clearly observed in the proper Figure 4b. The broad onset diminish to vanish implying the minimization of the tail states density [11], and is accompanied by a low signal.

These tendencies are confirmed by the value of the Urbach-energy (E_t) presented in the same Table II. While samples F1 and F2 are comparables, the value of E_t for sample F3 is considerably higher and for F4 considerably lower. In such a case, the disorder on the systems is related to the shallow surface states (tail states) and in consequence the lower the Urbach-energy, the lower the band onset. Finally, the broad band centred at 1.5 eV for the precursors strongly decrease and shift to higher energies after the thermal treatment. The rearrangement of the atoms after thermal process can explain this behaviour and seems to be effective to eliminate this undesirable band absorption, probably for the difussion of S in order to compensate the V_s .

SEM images (Fig. 5) show the surface morphology of the films. For F1 layer the surface is very compact and homogeneous microstructure compared with the other samples, but

all of the samples shown nanocrystalline structure as is expected, with grain sizes lower than 100 nm.

4. CONCLUSIONS

β - In_2S_3 layers were prepared by CBD method with nanocrystalline and/or amorphous structure, confirmed by XRD and Raman spectroscopy. As grown samples exhibit poor crystalline quality with free S as the main secondary phase. The crystalline quality of the layers is enhanced after a thermal treatment at 200 °C, observing the elimination of the free S by evaporation and/or diffusion onto the layer. The surface photovoltage spectra of as grown CBD In_2S_3 shows two distinct features: a broad onset at high energies related to the tail states and a broad band at 1.5 eV with donor character and presumably related to anion vacancies. The contribution of both bands to the total surface photovoltage depends on the growth conditions, seems to be responsible of the control of the optical and electrical properties of the layers. With a bath concentration of 0.5M and a growth time of 35 min and after the crystallization process at 200 °C (sample F4), the surface tail states are minimized and the Urbach-energy is also considerably reduced, obtaining In_2S_3 layers with electronic and structural properties suitable for their application as buffer layers in photovoltaic devices. Unfortunately, the transparency of the film is reduced due to their thicker nature at undesirable values. Future works will be focussed on the optimization of the optical parameters without deteriorate the electronic and structural ones.

6. Acknowledgements

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REFERENCES

1. N. Naghavi, S. Spiering, M. Powalla, B. Canava and D. Lincot, *Prog. Photovolt.: Res. Appl.* 11 (2003) 437.
2. S. Spiering, A. Eicke, D. Hariskos, M. Powala, N. Naghavi and D. Lincot, *Thin Solid Films* 451–452 (2004) 562.
3. R. Bayón, C. Guillén, M. A. Martínez, M. T. Gutiérrez, and J. Herrero., *Electrochem. Soc.*, 145 (1998) 2775.
4. S. Gall, N. Barreau, S. Harel, J.C. Bernède and J. Kessler, *Thin Solid Films* 480-481 (2004) 138.
5. C. Guillén and J. Herrero, *Vacuum* 80 (2006) 615
6. C. Guillén and J. Herrero, *J. Appl. Phys.* 101 (2007) 073514
7. C. Guillén and J. Herrero, *Thin Solid Films* 510 (2006) 260
8. J. Alvarez-Garcia, A. Perez-Rodriguez, A. Romano-Rodriguez, T. Jawhari, J.R. Morante, R. Scheer, W. Calvet, *Thin Solid Films* 387 (2001) 216.
9. Y. Xiong, Y. Xie, G. Du, X. Tian, Y. Qian, *J. Solid State Chem.* 166 (2002) 336.
10. G. Parker, R. Woods, G. Hope, *Colloids Surf. A: Physicochem. Eng. Aspects* 318 (2008) 160.
11. L. Kronik, Y. Shapira, *Surf. Sci. Rep.* 37 (1999) 1.
12. J. Mwabora, K. Ellmer, A. Belaidi, J. Rappich, W. Bohne, J. Föhrich, Th. Dittrich, *Thin Solid Films* 516 (2008) 3841.
13. A. Timoumi, H. Bouzouita, M. Kanzari, B. Rezig, *Thin Solid Films* 480-481 (2005) 124.
14. B. Asenjo, A.M. Chaparro, M.T. Butierrez, J. Herrero, C. Maffiotte, *Electrochimica Acta* 49 (2004) 737.
15. N. Naghavi, R. Henriquez, V. Laptev, D. Lincot, *Appl. Surf. Scie.* 222 (2004) 65.
16. S. Gorai, A. Datta, S. Chaudhuri, *Mat. Lett.* 59 (2005) 3050.
17. R. Yoosuf, M.K. Jayaraj, *Sol. Energy Mat. & Sol. Cel.* 89 (2005) 85.

TABLE I

In₂S₃ films prepared on glass/ITO substrate.

Sample	[TA] (M)	Deposition time (min)	Thickness (nm)
F1	0.3	25	55
F2	0.3	35	70
F3	0.5	25	80
F4	0.5	35	85

Other growth conditions: 70 °C bath temperature, InCl₃, 0.01M HCl, 0.3M CH₃COOH.

TABLE II

Summary of the values extracted from SPS measurements (room temperature) of samples whit the thermal treatment at 200 °C under nitrogen atmosphere.

Sample	E_g dir. (eV)	E_g ind. (eV)	E_t (meV)
F1	2.57 ± 0.01	1.69 ± 0.06	61 ± 2
F2	2.61 ± 0.01	1.75 ± 0.10	69 ± 1
F3	2.51 ± 0.02	1.77 ± 0.05	141 ± 2
F4	2.48 ± 0.03	---	42 ± 1

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KEY TO FIGURES

Fig.1 Optical transmittance spectra for indium sulfides films on ITO/glass substrates (a) and (b) after the thermal treatment at 200 °C under nitrogen atmosphere.

Fig.2. XRD of samples F1 to F4 after the thermal treatment at 200 °C under nitrogen atmosphere. (* = corresponding In_2S_3 CJCPDS card n° 32-0456).

Fig.3. Raman spectra of samples F1 to F4 before (a) and after (b) the thermal treatment at 200 °C under nitrogen atmosphere.

Fig.4. SPS spectra of samples F1 to F4 before (a) and after (b) the thermal treatment at 200 °C under nitrogen atmosphere.

Fig.5. SEM images of In_2S_3 films: F1 (a), F2 (b), F3 (c) and F4 (c) deposited at 70 °C on glass and annealing at 200°C under nitrogen atmosphere.

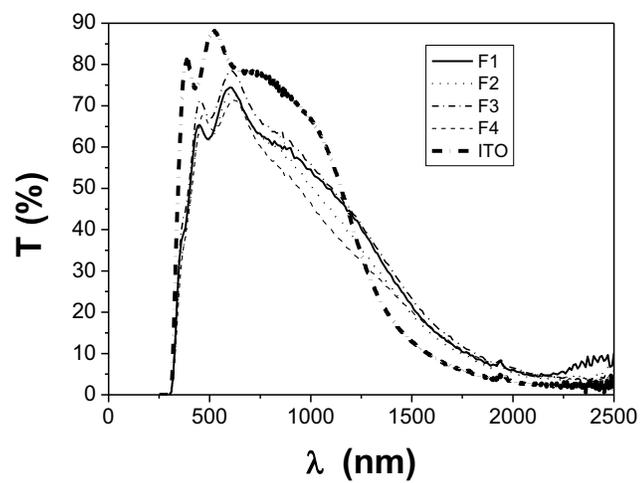


Figure 1a

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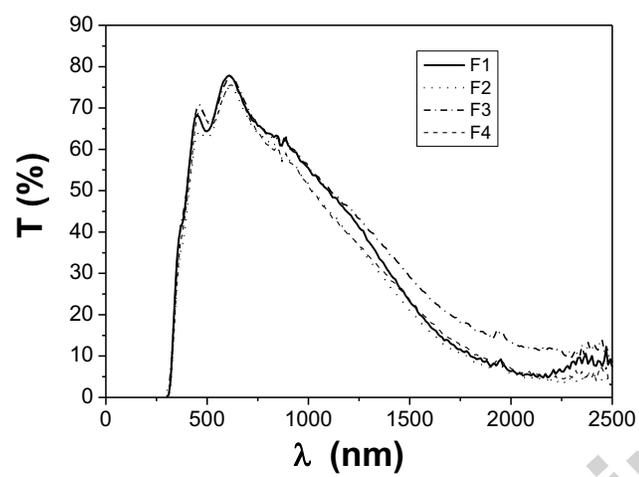


Figure 1b

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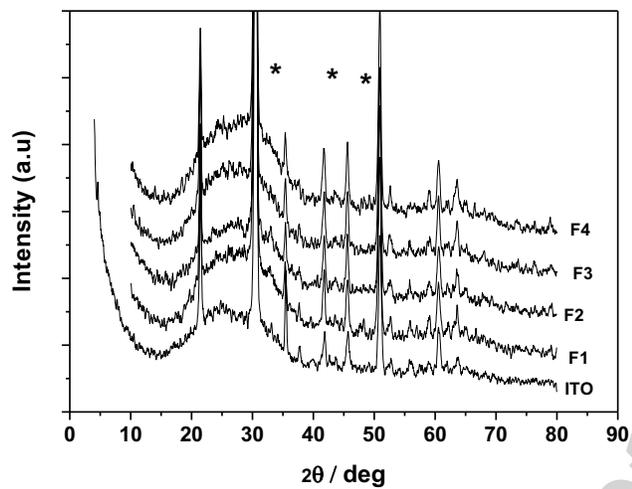


Figure 2

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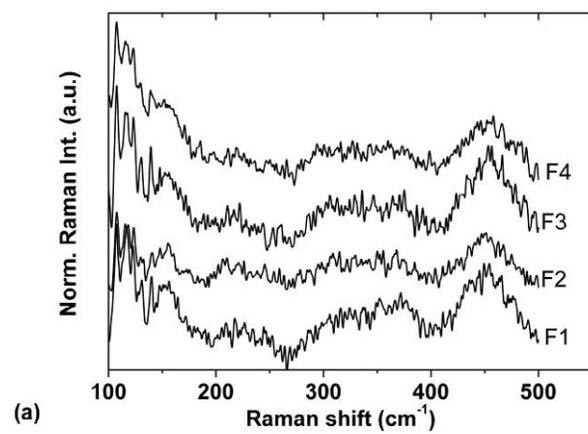


Figure 3a

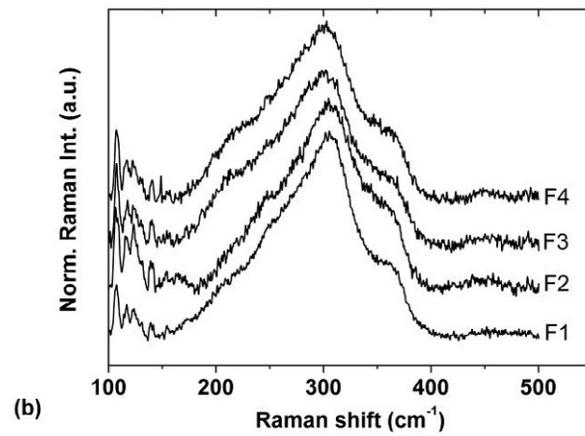


Figure 3b

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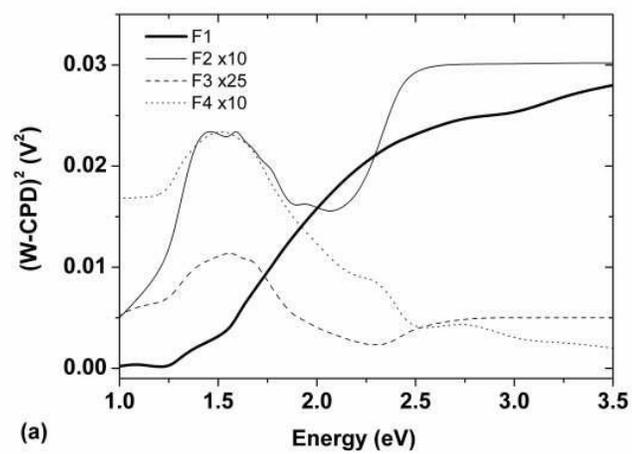


Figure 4a

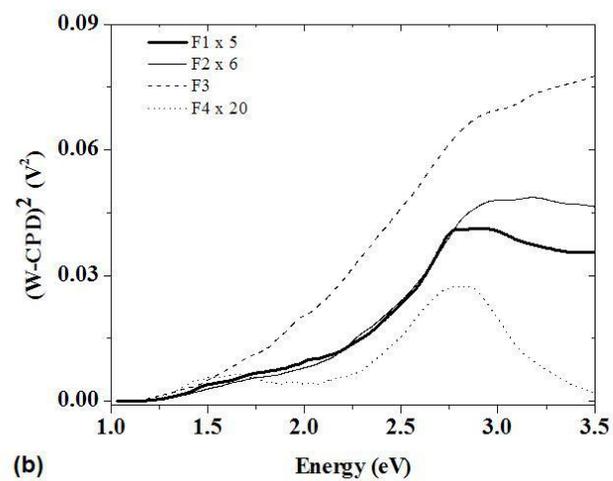


Figure 4b

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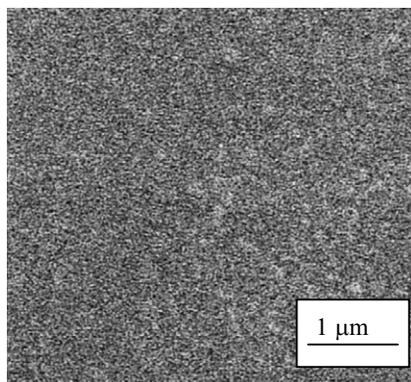


Figure 5a

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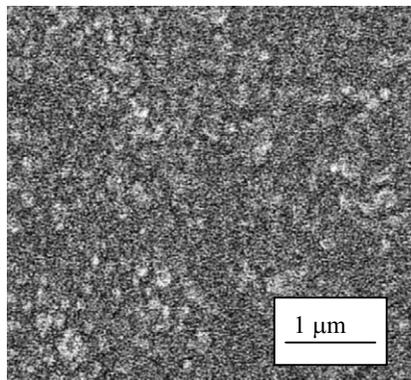


Figure 5b

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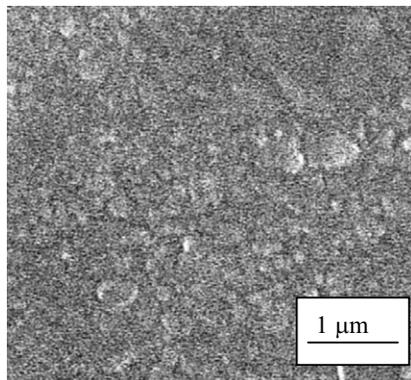


Figure 5c

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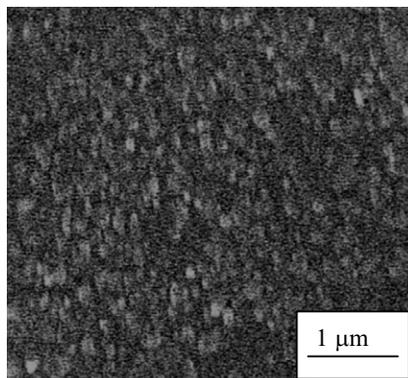


Figure 5d

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