

Nickel-Indium Sulphide Core-Shell Nanostructures obtained by Spray-ILGAR Deposition

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Ni nanowires (NWs) of different lengths were fabricated by pulsed potentiostatic deposition within pores of polycarbonate membranes. After template dissolution, substrates underwent sequential Spray-ILGAR[®] depositions of thin indium sulphide films. The effect of deposition temperature was also investigated. For low number of deposition cycles, results showed complete and uniform covering of metal over the entire length of NWs, with formation of Ni - In₂S₃ core-shell structures. However, with increasing number of deposition cycles films became uneven and crusty, especially at higher temperatures, owing to the simultaneous formation of nickel sulfide. This drawback was almost eliminated doubling the duration of the spray step.

1. Introduction

In the last years nanostructures fabrication has attracted spread attention owing to their special properties and high specific surface, important for several applications like catalysis and electric power generation (Eftekhar, 2008). Moreover, the possibility to build nanostructured thin film devices is one of the most challenging goals in different technological fields (Murray, 2008).

As for the first point, in the last years we have fabricated nanostructures of various materials (metals, oxides and semiconductors) using template electrodeposition (Inguanta et al., 2008, 2010a, 2010b) or galvanic deposition (Inguanta et al., 2011, 2012). However, in order to build a device an interface must be formed at the nanostructure surface; this can be achieved depositing a thin uniform film over the nanostructure, which requires a careful control of the process at a nanometric scale. For this purpose, the Spray-Ion Layer Gas Reaction (ILGAR[®]) (Allsop et al., 2006, 2009; Fischer et al., 2011; Gledhill et al., 2011) appears a very useful technique. In particular, Spray-ILGAR has been used for depositing layers on chalcopyrite (Cu(In,Ga)(S,Se)₂) solar cell absorbers. Among them, indium sulfide appears very interesting because it is a non-toxic material with a wide band gap (2–2.3 eV) and this has resulted in outstanding certified cell efficiencies of 16.1% (Sàez-Araoz et al. 2012).

However, it is not trivial to coat nanostructures homogeneously over their whole length. For this reason, we choose to test Spray-ILGAR deposition of In₂S₃ on a substrate of Ni NWs; the latter substrate was preferred as a model system, because of its metallic nature, ensuring fast heat transport along nanostructures, and due to the possibility of controlling carefully length and shape of nanostructures by changing the experimental parameters during template electrodeposition (Inguanta et al., 2008).

In the following we present the results of a systematic investigation on the deposition of thin In₂S₃ films on Ni NWs of different length; effort has been paid in finding suitable conditions for obtaining uniform coverage of the substrate. Thickness and morphology of the coatings were investigated as function of ILGAR parameters, like temperature and number of deposition cycles.

2. Experimental

Ni NWs were grown within pores of polycarbonate (PC) templates (Cyclopore, Whatman) having thickness of 15-20 μm and pore diameter of 180-230 nm. Initially, one side of the membrane was sputtered with gold and a Ni collector was deposited onto it by electrodeposition at -1.5 V(SCE); after lateral insulation, the front surface of the membrane was immersed in a Watt bath (300 g/l of $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$, 45 g/l of $\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}$, 45 g/l of H_3BO_3 , pH=4.5), and a unipolar pulsed bias was applied between -0.1 and -1.1 V(SCE) for variable times (60 to 180 cycles) using a potentiostat (Solartron 1470E), according to the procedure reported in (Inguanta et al., 2007, 2008, 2009). This procedure led to the growth of metallic Ni NWs having uniform diameter (about 250 nm) and length (variable from 4 to 10 μm , depending on deposition time). Morphology of a substrate after total template dissolution in dichloromethane is shown in Fig.1.

Before coating, substrates were cut in small pieces and fixed to glass holder by copper bi-adhesive tape. Edges of the substrates were sealed with a thermal resistant insulating tape.

Coating with In_2S_3 films was performed initially using the four steps "Standard Spray-ILGAR" process (Allsop et al., 2006, 2009; Gledhill et al., 2011; Fischer et al, 2011; Sáez-Araoz et al, 2012): a 10 mM InCl_3 ethanolic solution was sprayed using N_2 as carrier gas for 60 s (spray step); after 10 s purging, reactive H_2S , gas, mixed with the N_2 carrier, was blown on the substrate for 20 s (sulfurization step), followed by a final purging step of 10 s. To obtain better film properties, sometimes the spray step duration was doubled (120 s): we will name to this process as "Double Spray Time Spray-ILGAR".

Before and after deposition, samples were examined by Scanning electron microscopy, using a LEO-GEMINI 1530 field emission gun microscope, or a FEI field emission gun (FEG) environmental scanning electron microscope (ESEM, model QUANTA200), equipped with an X-ray energy dispersive spectrometer (EDS). XRF has been performed using a Philips MagiX Pro wavelength dispersive X-ray fluorescence spectrometer with Rh $K\alpha$ radiation.

X-ray analysis was performed using an Itai Structures (APD2000) diffractometer: diffraction patterns were obtained from 10° to 100° with a step of 0.04° and a measuring time of 2 sec per step, using the copper $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Identification of the compounds was carried out by comparison with the International Centre for Diffraction Data database (ICDD, 2007).

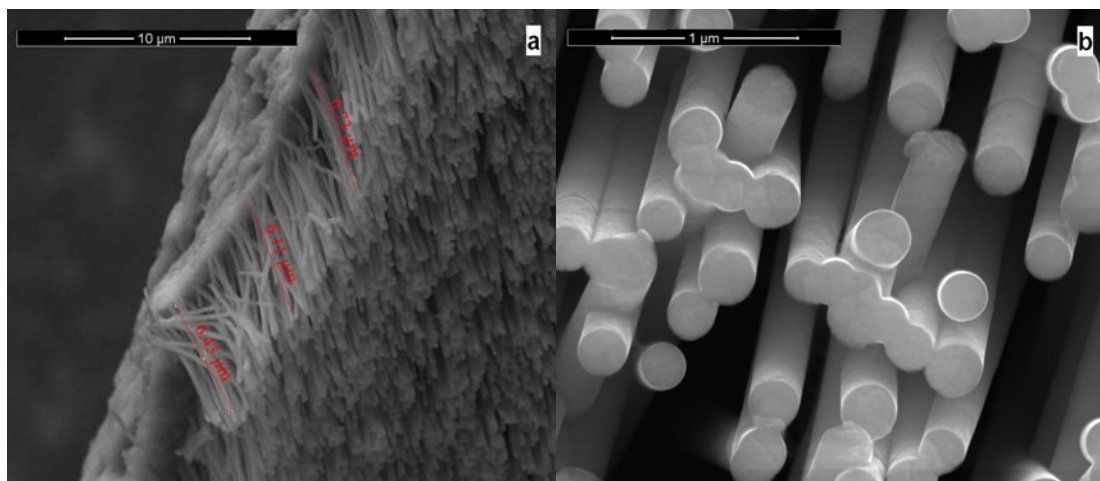


Figure 1: SEM images of a Ni nanowires substrate: (a) cross-section view and (b) top view.

3. Results and Discussion

3.1 Coating with different thickness at constant temperature

First we optimized the deposition conditions, reducing precursor concentration and deposition rate with respect to the standard depositions on flat substrates in order to minimize a preferred film growth at NWs heads. Then we performed a series of experiments with increasing number of In_2S_3 deposition cycles at the constant temperature of 175°C . In these experiments, we observed a progressive coating of the Ni NWs with increasing number of cycles, as shown in the SEM images of Fig.2.

Using the standard Spray-ILGAR deposition, the coating appears uniform and smooth after few deposition cycles (pictures a and b of Fig.2); for the first 25 cycles, an average deposition rate in the order of 1 nm/cycle was estimated at 175°C , with an almost linear increase of deposit thickness with number of cycles. It must be mentioned that film thickness was estimated from SEM pictures, whilst the XRF

technique, based on a previous calibration from In_2S_3 coatings on flat substrates, gave a sensible underestimation of the thickness, likely due to a considerable shadowing effect and therefore attenuation of exciting and fluorescing X-rays by the nanowires. For this reason, in the following we use XRF data only for relative comparison.

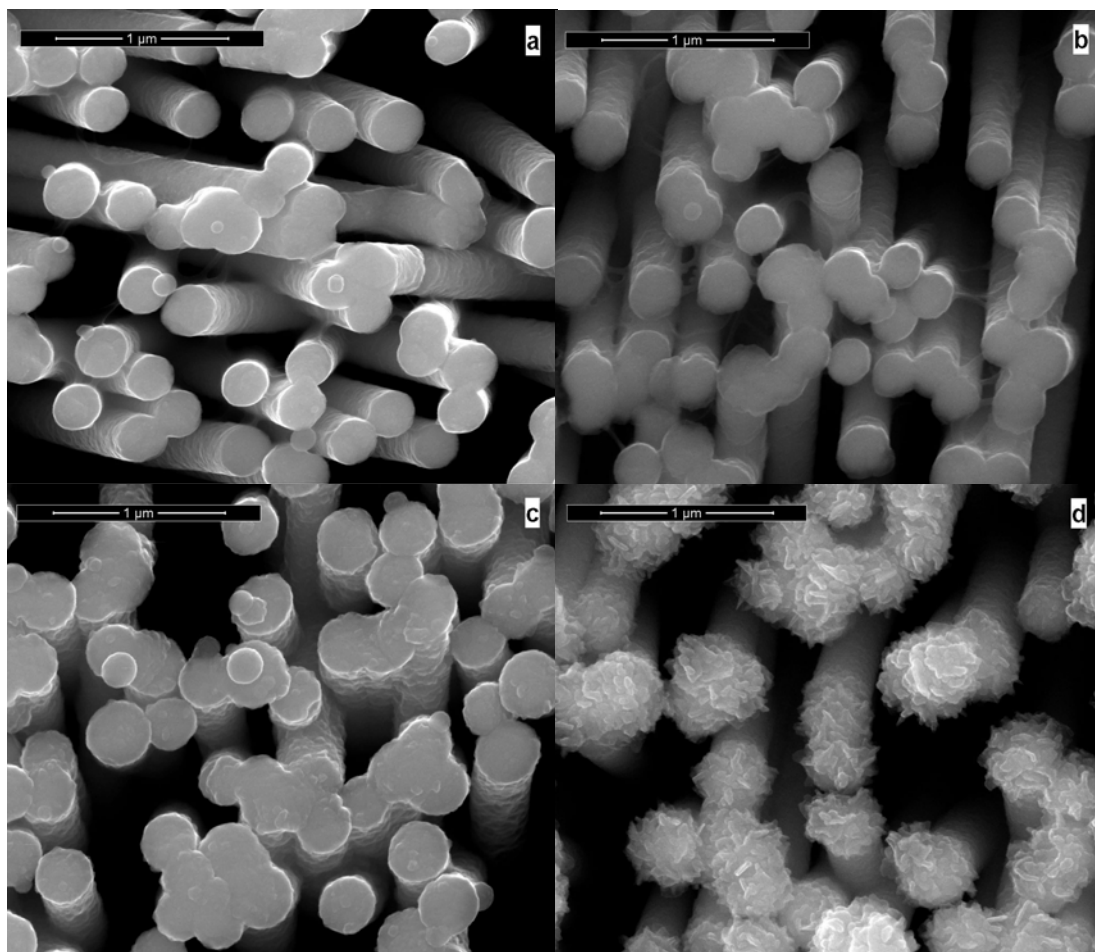


Figure 2: SEM images of Ni nanowires coated using the Standard Spray-ILGAR at 175°C after different deposition cycles: (a) 7 cycles; (b) 25 cycles; (c) 45 cycles; (d) 80 cycles.

For more cycles, coating becomes rough and crusty: micrographs c and d of Fig.2 display samples coated for 45 and 80 cycles, where a mushroom like coating and a lower homogeneity of the film is evident. This change of deposit morphology was attributed to a side reaction of incoming H_2S gas. In fact, during the deposition process, H_2S not only reacts with the $\text{In}(\text{O}_x, \text{Cl}_y, \text{OH}_z)$ precursor film at the NW surface, but it can also react with the Ni surface forming nickel sulphide. This is especially true during the first deposition cycles, where the precursor film is not yet compact and allows access to the metallic surface (Allsop et al., 2006, 2009; Gledhill et al., 2011; Fischer et al. 2011; Sáez-Araoz et al, 2012), but also during the final purging cooling step of the Spray-ILGAR coating process. In fact, according to our experimental results and unlike the situation with flat substrates, at the end of a Spray-ILGAR cycle H_2S is still present in the interspaces between NWs, and it can sulfurize the nickel surface by diffusion through the In_2S_3 layer.

Our explanation is supported by the XRF evaluation of sulphur content in the coating, which is sensibly higher with respect to stoichiometric In_2S_3 (see Table 1). In order to confirm further the formation of nickel sulphide during the standard Spray-ILGAR deposition and to investigate its structure, a substrate was exposed to H_2S at 225°C only for 7 cycles without the precursor spray step. SEM microscopy shows the presence of a rough and crusty layer, whose structure was identified by XRD as the trigonal Hazlewoodite, Ni_3S_2 (ICDD, 2007).

3.2 Effect of deposition temperature

In order to investigate the effect of deposition temperature, we performed depositions using the *Standard Spray-ILGAR* process at different temperatures (175 – 300 °C) and keeping the number of cycles constant (7 cycles). These present interesting features, summarized in Table 1, where the XRF intensities relative to indium and sulphur elements are shown.

The most striking finding is the different trend of the contents relative to In and S: while indium content first grows slowly, reaching maximum values between 250 and 260 °C, sulphur signal increases always in a supra-linear fashion. Consequently, the S to In count ratio diverges from the value foreseen for a pure In_2S_3 layer (determined in a separate experiment on stoichiometric In_2S_3 equal to about 1.9), in a larger amount as temperature grows (see last column of Table 1). This is a clear indication that using a *Standard Spray-ILGAR* deposition formation of Ni_3S_2 occurs on the metal surface: at higher temperatures Ni sulfuration reaction is strongly favoured, not only due to a higher reaction rate, but also because the deposited layer becomes crustier and a satisfying sealing of the metallic surface does not occur. Hence, diffusion of H_2S through the cracked layer is easier over 250°C, with formation of a mixed and even less compact film.

Table 1: Indium and sulphur content in the layer after 7 cycles of *Standard Spray-ILGAR* deposition at different temperatures

T [°C]	In [counts/s]	S [counts/s]	S/In count ratio
175	9.8	6.1	6.3
195	10.0	8.0	8.0
225	13.6	11.6	8.6
230	14.4	14.4	10.0
240	12.3	12.1	9,9
255	15.5	11.1	7.2
290	12.6	23.8	18.9
300	13.3	27.0	20.3

Based on the previous considerations, only In content is related to the In_2S_3 film deposited. Hence, data in Table 1 indicate that at high temperatures a decrease of deposition rate occurs, causing a saturation at about 250 °C; this is more evident for high number of cycles (not shown here). This finding is not completely new, because in (Allsop et al., 2009) it was shown that during In_2S_3 coating of inert flat substrates by the *Standard Spray-ILGAR* technique deposition rate approaches a saturation value for a temperature of about 280°C. It was hypothesized that at this temperature In_2S_3 particle formation occurs already in the flowing gas stream at a certain distance from substrate without sticking there. The lower saturation temperature with respect to the coating of flat substrates can be explained taking into account that in our case gas flows through nano-structured channels, which likely induce turbulence, with a much faster heat exchange and a more uniform temperature distribution.

3.3 Double Spray Time Spray-ILGAR

The undesired formation of Ni_3S_2 is greatly reduced adopting a double duration of the spray step (*Double Spray Time Spray-ILGAR*). This procedure results in a thicker sealing precursor film before the H_2S inlet, which causes a sensible reduction of Ni_3S_2 formation, i.e. an improvement of In_2S_3 layer homogeneity, and a smoother surface of the deposit. Another beneficial effect is the increase of deposition rate (1.6 nm/cycle).

Fig. 3 shows a 9 μm NWs substrate after a double spray time deposition at 175°C for 69 cycles; the resulting film (thickness >100 nm) is smooth and the formation of mushroom caps is strongly reduced.

Next step was to check the coating uniformity along the NWs length. For this aim, the sample of Fig.3 was scratched off and single NWs were transferred onto an aluminium foil to be analyzed by EDS spectroscopy. An Indium fluorescence line scan was performed over the whole length of single wires.

Fig.4 shows the result of the experiment: apart from the extremities, signals of both indium and sulphur appear almost constant throughout the length, confirming that NWs are completely coated over their full length by a uniform In_2S_3 layer. Bumps at the extremities can be explained by a small accumulation of deposit at NWs top, where exciting beam penetrates the whole head cover layer. Moreover, when the scan reaches NWs extremities EDS spectrometer detects additional quantities of In_2S_3 lying on the Al foil around the investigated wire.

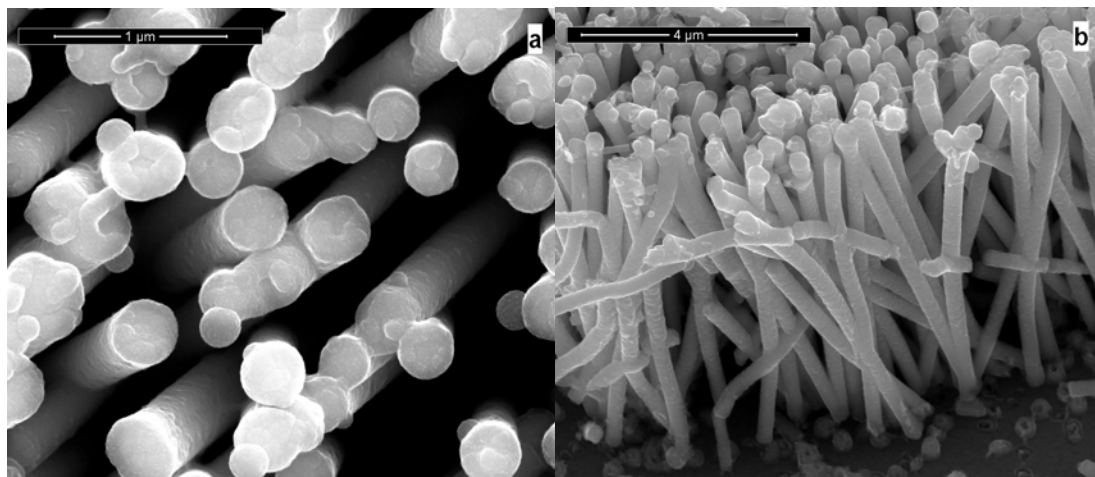


Figure 3: SEM images of In_2S_3 coated Ni nanowires by Double Spray Time Spray-ILGAR at 175°C for 69 cycles: (a) top-view and (b) cross-section view.

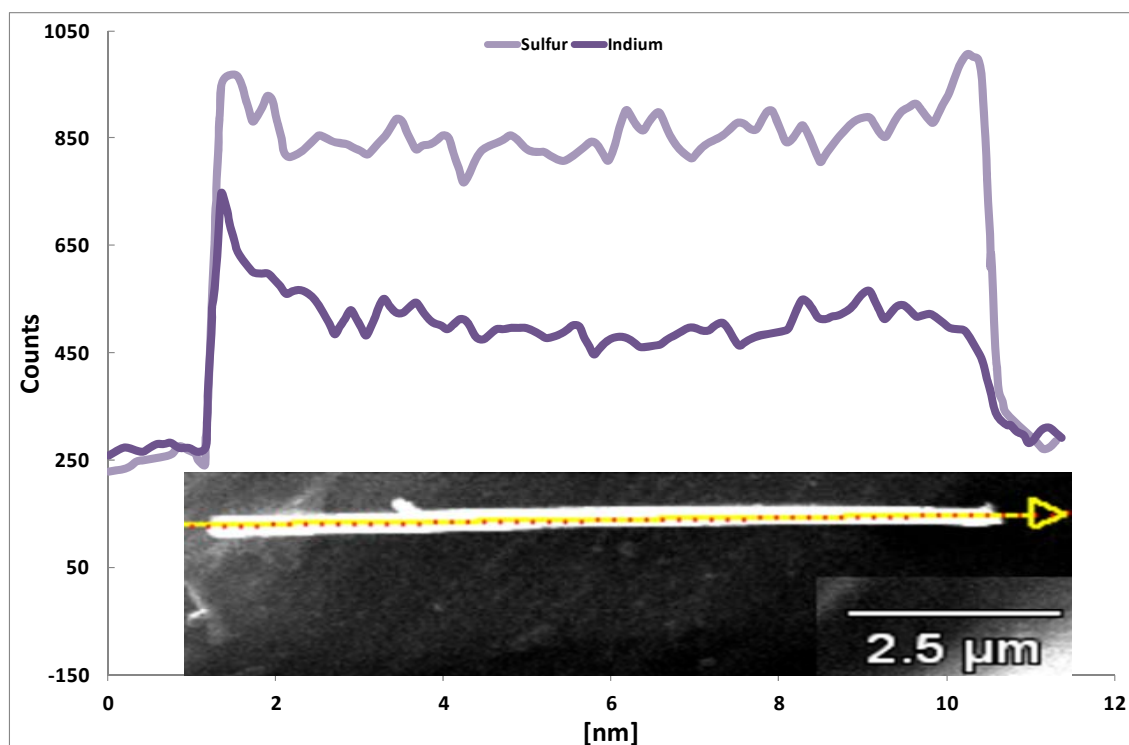


Figure 4: EDS line-scan of an In_2S_3 Ni nanowire coated Double Spray Time Spray-ILGAR at 175°C for 69 cycles.

4 Conclusions

Ni nanowires, having about 250 nm diameter and different lengths (4 to 9 μm) were uniformly coated with indium sulphide thin films using the vacuum-free Spray-ILGAR technique. Both deposit morphology and composition were analyzed as a function of the number of deposition cycles and for different operating temperatures.

Using the *Standard Spray-ILGAR* technique, deposited layers appear smooth and uniform only for few deposition cycles, whilst with increasing thickness they become crusty and less homogeneous, especially at higher deposition temperatures.

This drawback occurs because the standard In_2S_3 layer deposition by Spray-ILGAR is accompanied by the side reaction of metallic surface sulfurization to crusty Ni_3S_2 , whose formation depresses coating homogeneity and compactness. This undesired process is favoured at higher temperatures. Moreover,

with increasing temperature the In_2S_3 deposition rate undergoes saturation, probably due to increasing solid particle formation already in the gas phase.

The unwanted formation of Ni_3S_2 is sensibly reduced operating at the lowest deposition temperature of the explored range (175°C) and adopting a double duration of the spray step (*Double Spray time Spray-ILGAR* deposition). Using this improved procedure, EDS line scans have proven the deposition of smooth In_2S_3 films with a uniform coverage of nanowires up to 9 μm long over their full length.

In conclusion, we can state that the ILGAR process is so flexible that it allows adaptation also for the coating of quite extreme substrate geometries.

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