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“Wet Technique” Metal Deposition for SEM Observation

Guy Stremsdoerfer, Jean-Marc Krafft, Eric Queau and Jean-René Martin

Laboratoire de Physicochimie des Interfaces, URA CNRS 404, Ecole Centrale de Lyon, B.P. 163, 69131 Ecully Cedex, France

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Résumé. — La technique de métallisation chimique par voie liquide est une alternative aux méthodes classiques de métallisation pour l’observation d’échantillons non conducteurs. Simple, rapide, économique, cette technique apporte dans certains cas, en particulier pour les substrats tridimensionnels, la solution aux problèmes des charges parasites. Une première technique consiste à métalliser les échantillons en deux étapes ; une étape d’activation de la surface non conductrice suivie par un dépôt autocatalytique permettant d’obtenir un film continu et conducteur de 300 à 500 Å d’épaisseur. La deuxième technique qui met en œuvre une solution colloïdale Sn-Pd, permet en une seule étape d’obtenir des échantillons pouvant être observés au MEB dans d’excellentes conditions. Cet article décrit les conditions et propriétés de ces techniques “humides” de préparation.

Abstract. — “Wet technique” metal deposition for the metallization of non conducting surfaces and especially 3D substrates in order to perform SEM observation is an attractive method. The deposition of a 300–500 Å thin “wet” metallic film needs a two step procedure: an activation step followed by an electroless deposition step. This metallization technique gives good results nevertheless the authors show in this work that a one step process is sufficient to obtain a good SEM observation. The use of a Sn-Pd colloidal solution allows to prepare nonconductive surfaces in order to get SEM observation; this method is cheap and quick. This paper describes the conditions and properties of this “wet” preparation.

1. Introduction

Generally the surface of non conductive specimens examined in the Scanning Electron Microscope needs to be made conductive. Coating a specimen with a thin film of conducting material prevents charging phenomena which result in image distortion. Coating is also requires to reduce thermal and radiation damages in organic and biological materials. This damage can result in significant loss of material.

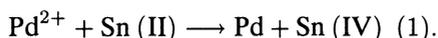
Thermal evaporation and sputtering techniques are commonly used for coating specimens for SEM. These dry techniques require high vacuum or low pressure of inert gas. “Wet” methods, less-known than the “dry” methods but more and more employed in coating, proceed in liquid

(aqueous) media. As compared to the “dry” methods they are simple, require cheap facilities and are easy to manage. In water, metals exist as cations and their deposition at the substrate-solution interface is the result of the capture of electrons. Several methods of “wet” metal deposition exist, depending on the kind of energy used to promote the reducing electrons to a level suitable for the reduction step. Among these “wet” methods, the electroless or autocatalytic technique is well adapted. In the “autocatalytic process” [1] the electrons are supplied by a reducing agent dissolved in the solution. This method is already widely used in the electronic industry, especially for the fabrication of printed circuit board [2] where it competes with electroplating and often completes it. The composition of the deposition baths must be such that the reduction reaction in the bulk solution is completely inhibited. Such inhibition is obtained by the addition of efficient cation masking (complexing) agents. When cations are in this way masked, their redox potential decreases in such a manner that their reduction can only proceed on surfaces enough catalytic to strongly enhance their reduction rate. A number of metals, the more noble: Au, Pd, Ni, Pt, Co, Ag, Cu can be deposited by this method in the range of 100 Å to few microns thickness. Autocatalytic deposition is possible when the substrate surfaces are rendered catalytically active to initiate the metal deposition. Two process are used to activate the non conductive surfaces. In the sensitization/activation process, the substrate is firstly sensitized in a solution of a reducing metallic salt such as tin salts (Sn(II)) or titanium salts (Ti(III)), then immersed in an aqueous solution of a noble metal salt such as palladium (PdCl₂) or gold (AuCl₃). During this step, it has been assumed that the redox reaction between adsorbed divalent Sn and the cations of the noble metal occurs. The other process, which supplanted the first, uses a mixed solution containing both the reducing agent and the catalytic metal salts. The advantages of this solution are the use of a single-step procedure and that it provides a highly catalytic surface.

We have studied since several years, in our laboratory, the electroless deposition process as a useful tool for microelectronics and microstructures [3-5]. We present in this paper two “wet” preparation for SEM observation, non conductive surfaces: the electroless bath for copper deposition and the Sn-Pd colloidal solution.

2. Experimental

2.1 PREPARATION OF Cu ELECTROLESS FILM. — In order to perform electroless metal deposition, samples were degreased in alcohol and dipped few minutes into a Sn (II) solution (SnCl₂ = 10 g.l⁻¹, HCl = 40 ml/l) then, after rinsed in water, dipped into a palladium solution (PdCl₂ = 0.5 g.l⁻¹, HCl = 10 ml/l). This activation step allowed to render the sample surfaces catalytic for the electroless deposition by the oxide-reduction mechanism :



The Cu electroless film was made at room temperature in a few minutes, dipping samples into a Cu basic bath deposition (CuSO₄, 5H₂O = 3.6 g.l⁻¹; HCHO 37% = 10 ml/l; KNaC₄H₄O₆, 2H₂O = 25 g.l⁻¹; NaOH = 3.8 g.l⁻¹). The deposition rate was 1.5 μm.h⁻¹ at room temperature.

2.2 PREPARATION OF Sn-Pd COLLOIDAL SOLUTION. — The mixed Pd-Sn solutions were prepared in concentrated acidic media (HCl 4.3M, pH < 0) according to references [6]. The formation mechanism of this solution have been recently presented [7]. Using Cryo-Transmission Electron Microscopy, it has been shown, without any doubt, that the mixed Pd-Sn solution was a colloidal system. The role of each step during the formation of the catalyst, the parameters that modify the colloid properties and the characteristics of the Pd-Sn solution (colloid size, stability, aging), were presented.

After each of these “wet technique” preparations, samples were rinsed in water, dried under nitrogen flow and observed with a Philips XL 20 SEM microscope type.

3. Results

3.1 ELECTROLESS BATH DEPOSITION. — We present here, the metallization of $2.3\ \mu\text{m}$ diameter latex particles. For these micro-tools, 3D “dry” metallization is very difficult. Particles are in solution with an emulsion agent avoiding their agglomeration. After the sensitization step with Sn(II) solution and activation step with Pd (II) solution, a thin copper film of around $200\ \text{\AA}$ to $500\ \text{\AA}$ thickness is deposited onto these latex particles. Photo 1 is obtained with a 30 kV beam energy and slow scan speed (60 ms/line) at X: 10000. We do not observe any dark effect and no charging phenomena. Under electron beam, charges are well evacuated between latex particles. Therefore, the metallization on the gap of the whole particles is possible and uniform. The Cu electroless film does not modify the latex surface morphology and a magnification of around X: 50000 can be reached, only limited by the nuclei size.

This example shows that electroless bath deposition is a low cost technique and an attractive way specially for 3D samples for SEM observation. Nevertheless, this method can be only used with samples which are not modified by aqueous media. We give here an electroless bath deposition example. If the bath formulation is not adequate for the substrate, it is possible to use other electroless baths deposition. However, by this “wet technique” metal deposition, a two step procedure is necessary (activation-deposition) and we have tried to reduce in one step the process to make it more attractive.

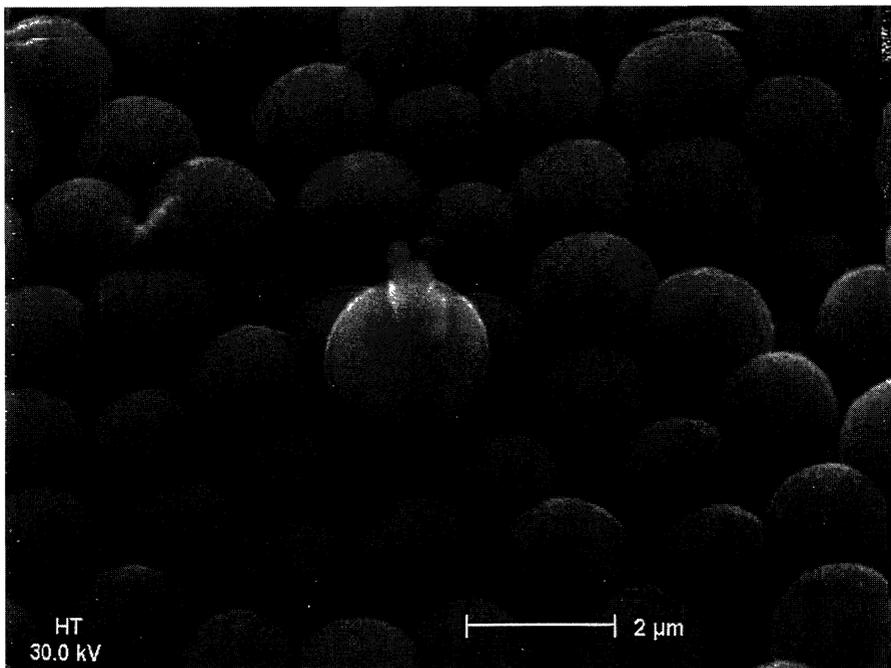
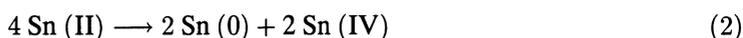
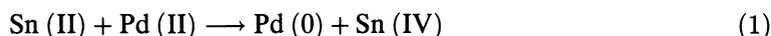


Photo 1. — Cu electroless metal deposition to SEM observation onto $2.3\ \mu\text{m}$ diameter latex particles. (Current probe: 0.01 nA).

3.2 SENSITIZATION AND ACTIVATION SOLUTIONS. — Non conductive samples have been observed just after sensitization and activation steps. In each case, SEM observations are impossible. During the sensitization step, Sn(II) mono or bi layers are adsorbed onto the substrate but it is well known that tin salts or oxides are not conductive. During the activation step, Pd²⁺ is reduced by Sn²⁺ and progressively catalytic nuclei are formed. If the nucleus density is sufficient to initiate an electroless deposition, it has been shown that there is no electrical conduction because the nucleus density is too low. It is due firstly to the partial Sn(II) desorption in the Pd solution as we can observe by the coloration changing of the activation solution and secondly, as described by us [8] and others [6, 9] the nuclei composition is not Pd(0) but almost PdSn₂ and then more Sn(II) are involved in the reactions:



So, sensitization and activation solutions, used individually or both, do not allow to obtain SEM observation preparation.

3.3 Sn-Pd COLLOIDAL SOLUTION.

3.3.1 The Coating Solution. — The advantages of this process is the use of a single-step procedure and the obtaining of a highly catalytic surface. A palladium and tin salt mixture in HCl solution leads to complex reactions which results in a colloidal solution. Formation mechanism of Pd-Sn colloidal solution have already been described [7]. This mechanism is strongly dependent on the initial tin to palladium concentration ratio and the stabilization depends on the process preparation. So, it is possible to synthesize colloidal solutions in which colloid size is chosen. The three step process can be summarized as following: i) the mixing of Pd and Sn solutions is made with a moderate tin concentration; results have shown that an initial Sn/Pd ratio equal to around 3 is well suitable (low complex stability and moderate growth rate of colloids). ii) A time is necessary to wait till the expected colloid size is obtained. On the cryo-TEM observation (Photo 2), it can be observed the colloidal nature of this coating solution and the presence of 3 nm diameter cores not agglomerated but at least separated from each other by 2–3 nm. The average core diameter can be chosen between 1 nm and 5 nm. Above 10 nm the solution is unstable. The temperature increases the growth rate of colloids and of course decreases the growth time. iii) A strong excess of Sn(II) ions must be added in the solution in order to obtain a final tin to palladium ratio equal to around 40. Then the colloidal Pd-Sn solutions can be used for coating non conductive substrates for the SEM observation. Under a nitrogen storage the colloidal solution is stable for more than one year.

The deposition process on non conductive surfaces dipped into the coating solution consists of adsorption of colloids. This adsorption process leads to a surface saturation (Fig. 3). The kinetics of colloid adsorption depends on the nature of the substrate. Generally the saturation of plastic surfaces needs about 10 min. Adsorbed colloids form a layer on immersed surface which do not require a special preparation. When the thin film is achieved, the specimen is rinsed in water and dried under nitrogen flow. This wet coating process, protected by a patent (10), is fast, simple and it does not require any specific apparatus.

3.3.2 Structural and Conductivity Features. — It has been shown [7, 8] by Rutherford Back Scattering analysis, EDX and HRTEM that the colloidal layer is essentially constituted of Pd and Sn with a Pd / Sn ratio equal to around 0.3–0.5. At saturation, the film is formed by a monolayer

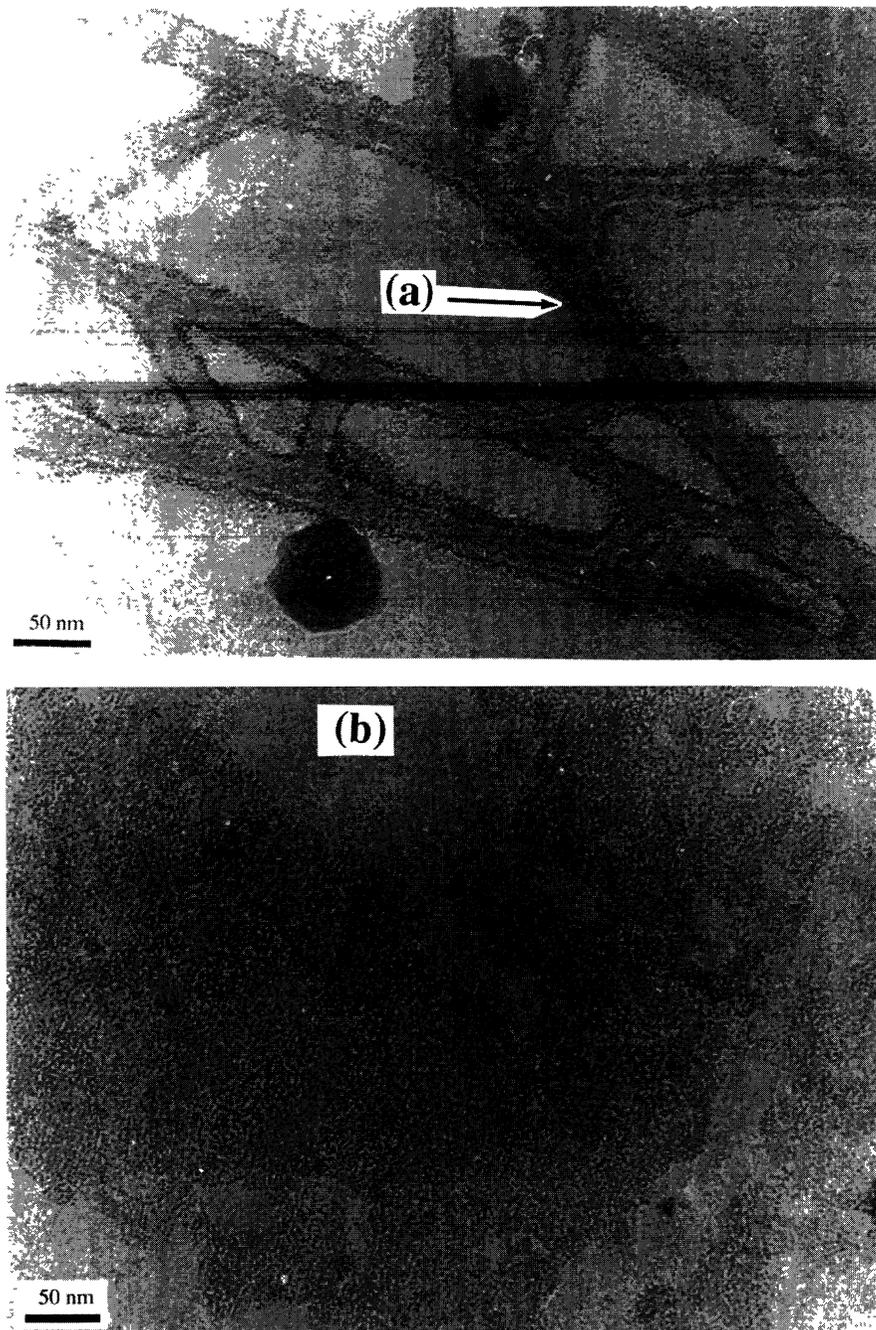


Photo 2. — Cryo-micrographs (X 330000) of colloids in solution near a) and far b) from the carbon sample.

of colloids. Nevertheless, some colloids can locally coalesce to form little islands. The island thickness is not beyond 3 or 4 colloids.

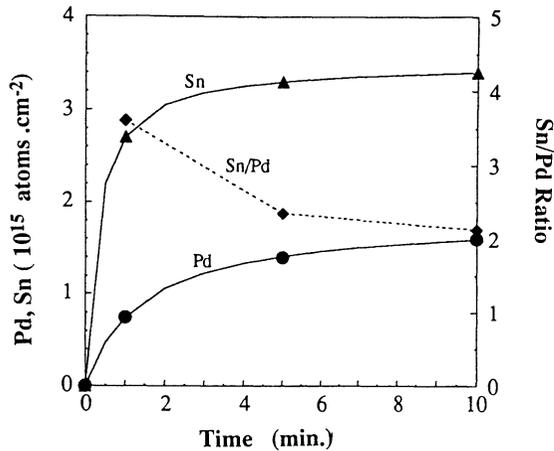


Fig. 3. — Kinetics of Pd-Sn colloid ($\Phi = 2$ nm) adsorption controlled by RBS analysis.

The electric resistance of the thin film obtained by liquid coating after a 10 mn adsorption of 2 nm colloid size is about $1 \Omega \text{ cm}$. It is more resistive than an equivalent layer of metallic Pd. T.E.M. observations (Photo 4) show that the adsorbed film do not constitute a real continuous metallic layer. Yet, the conductivity of this thin film is sufficient to ensure that the specimen current is drained to ground without the development of a significant surface potential. So, typical beam energy (10–30 kV) is used with a current probe which never reaches 0.5 nA. Classically slow scan speed (60 ms/line) can be used to examine a specimen which is coated with the colloidal solution.

3.3.3 Properties of the Colloidal Solution for SEM Observation.

3.3.3.1 Wide Range Substrate. — Sn-Pd colloidal solution can be used on a lot of non conductive substrates as: epoxy, A.B.S., kevlar fibers, polyamide, methyl-polymethacrylate (PMMA) ... The simultaneous observation of different materials treated by colloidal solution is possible on a same sample. Polymer, ceramic and metallic films can be well observed on a cross section of a ceramic sample (Photo 5). Biological (Photo 6) or natural material can also be prepared by this technique for SEM observation without any damage. Nevertheless, substrates which do not resist to aqueous and HCl media cannot be treated by this “wet” technique. At low beam energy, plastics and polymers which are organic compounds, present a poor secondary electron emission. So, at low voltage, the Pd/Sn layer would improve the secondary electron emission of these materials.

3.3.3.2 3D Observation. — When a sample is dipped into liquid coating solution, the solution wets all immersed surfaces which can consequently adsorb colloids. So, the thin film coats evenly all sample surfaces. Photo 7 shows SEM image of glass fiber tissue which are treated with colloidal solution. With usual coating technique, the observation of these types of specimen is generally difficult because after coating, fibers can move and expose uncoated surfaces. As the solution wet all fibers, there is not any uncoated surface and therefore no problem associated with charging under electron beam appears. Solution infiltrates also into porosity and complex structures of substrates. So, in order to examine hidden surfaces of complex samples, we can exploit completely the movement range that the SEM allows without any charging phenomena. This liquid coating technique is a real tridimensionnal coating method.

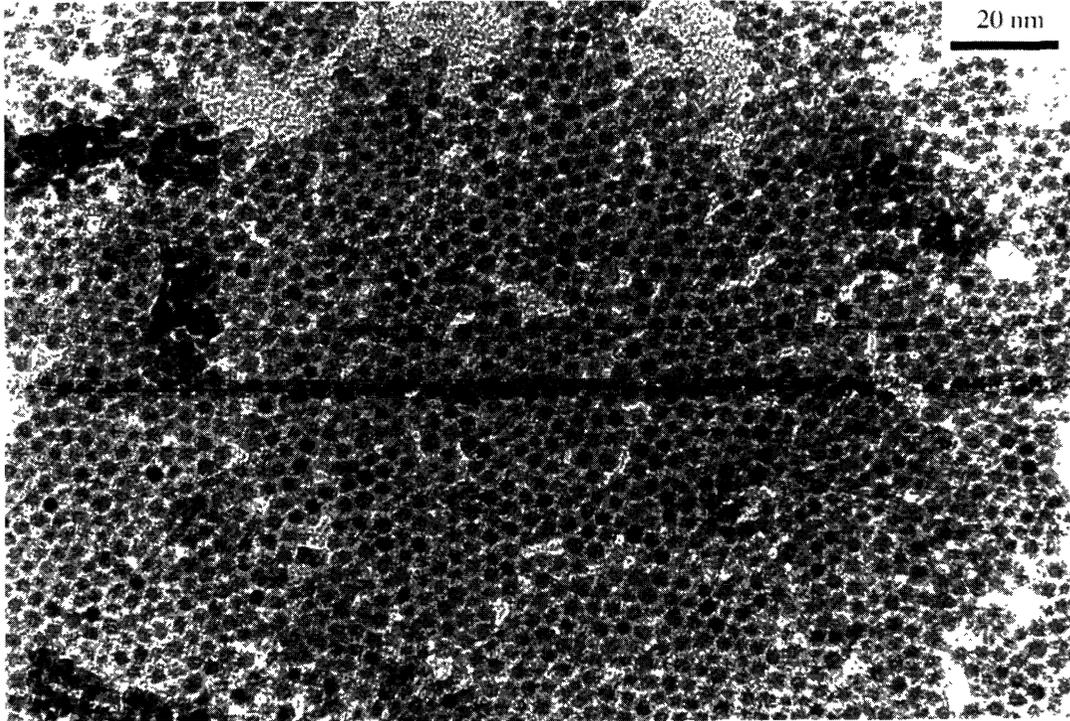


Photo 4. — TEM micrograph of the adsorbed 2 nm colloid particles after 10 mn adsorption.

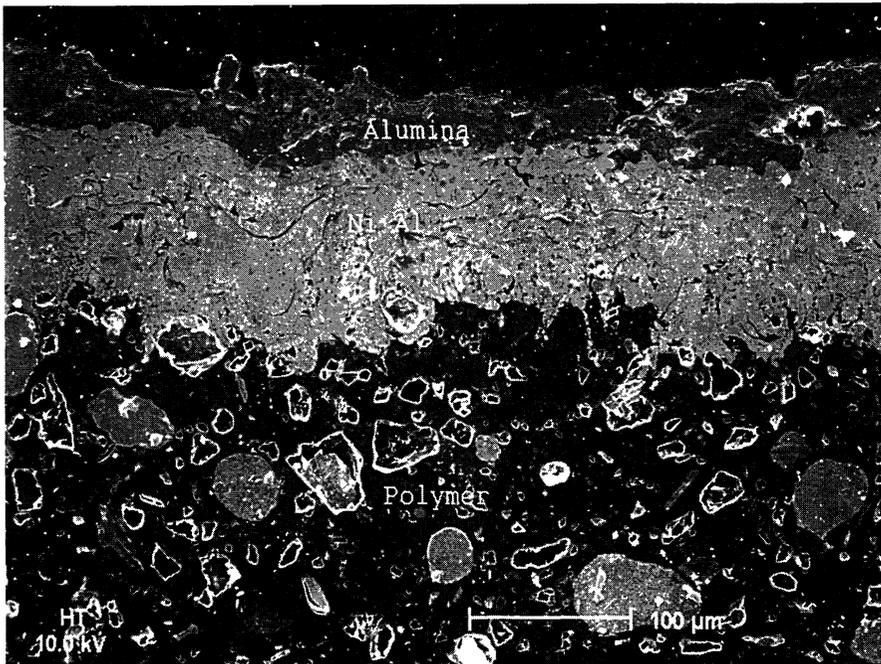


Photo 5. — SEM micrograph of a cross section of a ceramic/metal/polymer sample. (Current probe: 0.08 nA).

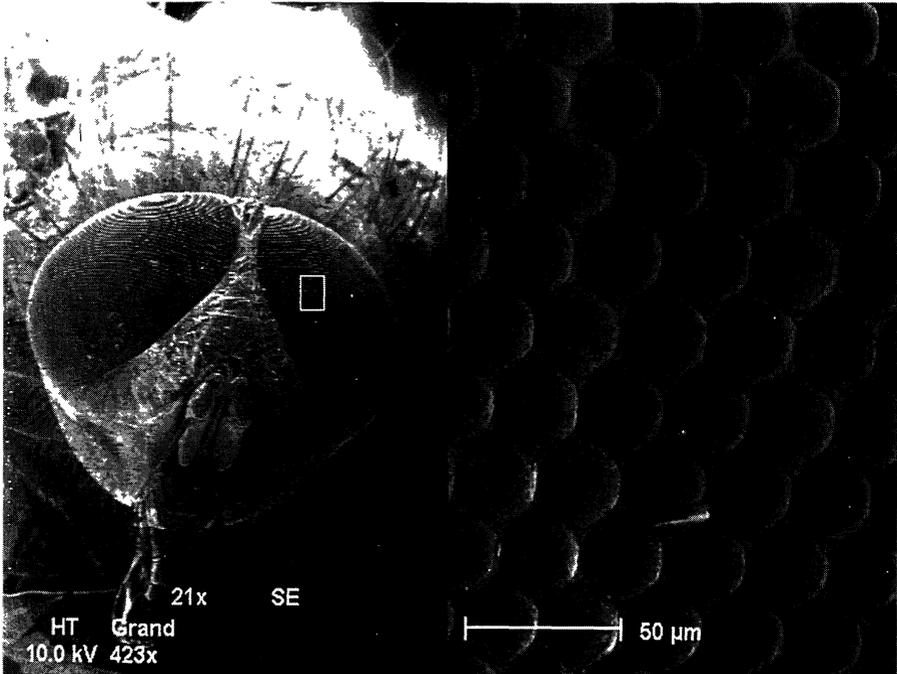


Photo 6. — SEM biological observation: fly head and eyes! (Current probe 0.014 nA).

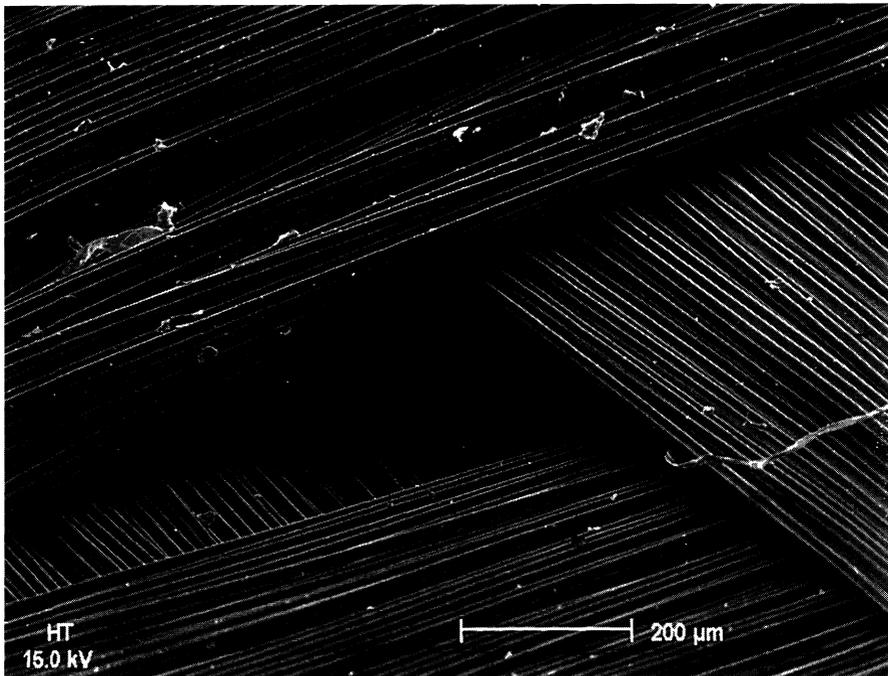


Photo 7. — SEM micrograph of glass fiber tissue. (Current probe: 0.25 nA).

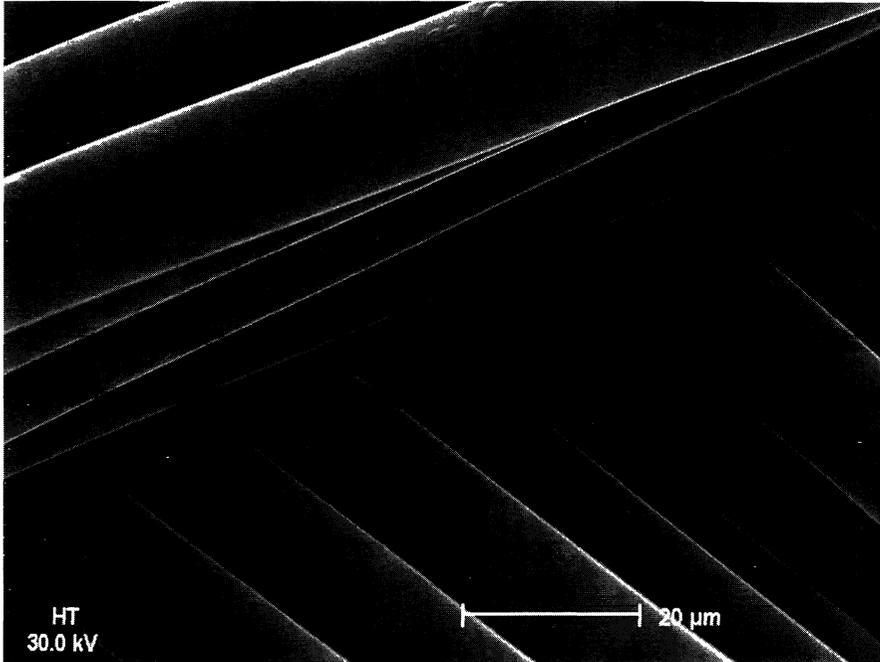


Photo 8. — SEM micrograph of glass fibers with 30 kV beam energy. (Current probe: 0.058 nA).

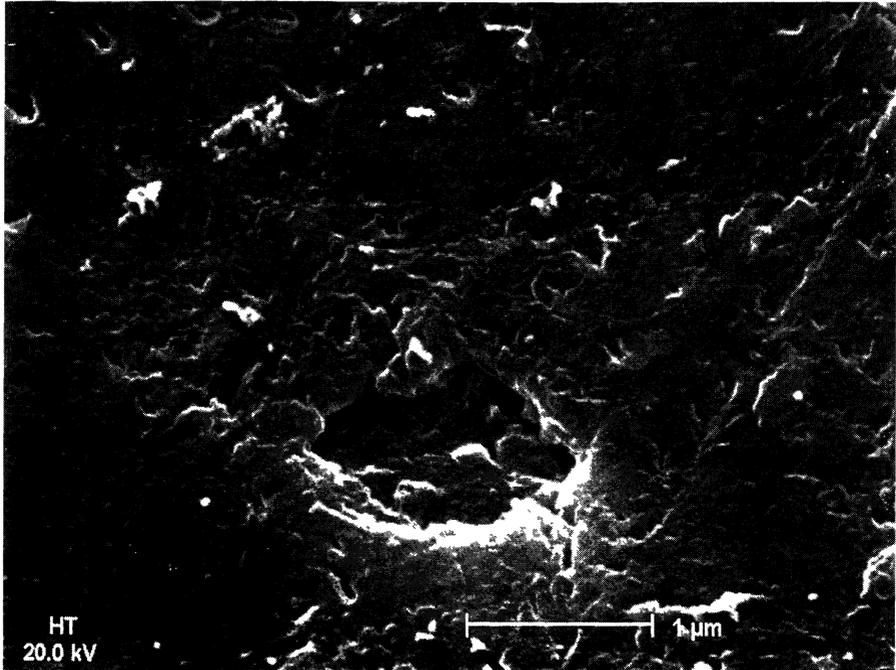
3.3.3.3 High Tension, High Magnification. — In the wide range of substrates tested with the colloidal preparation, we do not observed any charge effect at low and particularly high tension voltage. Photo 8 shows a S.E.M. image of glass fibers with 30 kV beam energy.

To S.E.M. observation, the colloidal coating preparation does not limit the magnification. Photo 9 shows an ABS S.E.M. observation, before and after a chemical treatment. This ABS surface was previously etched with a sulfochromic solution to increase the roughness; then the sample was dipped into the colloidal solution. A high magnification (X: 25000) can be reached and permit to observe the surface evolution without artifacts.

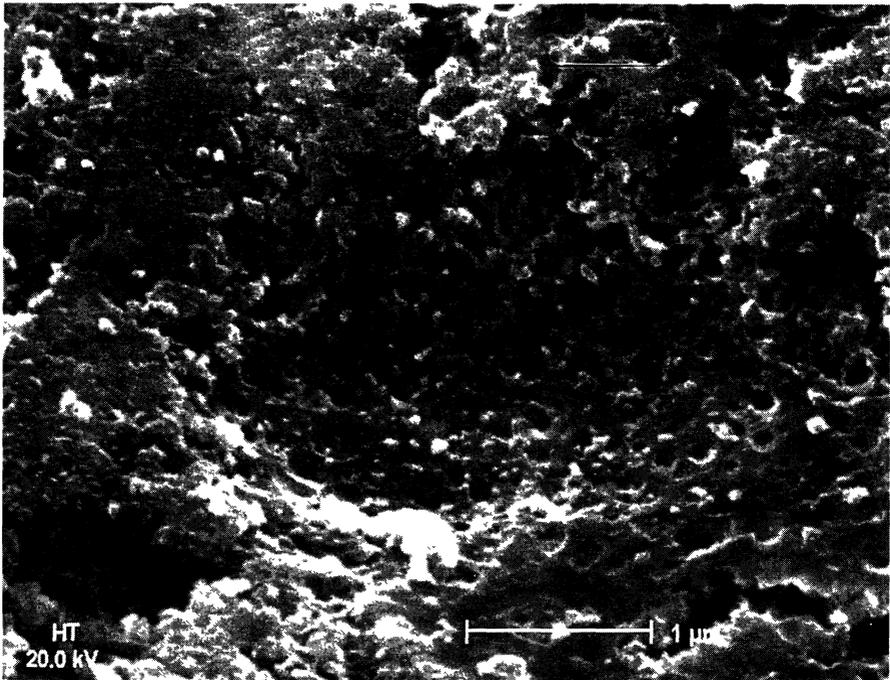
Moreover, the “wet” colloidal preparation for SEM observation does not modify the polymer surfaces and specially the geometric 2D and 3D patterns. The photo 10 shows a SEM image of a photolithographic patterns realized onto a semiconductor surface with a photosensitive resin, the poly-methyl methacrylate (PMMA).

4. Conclusion

“Wet technique” metal deposition for SEM observation of non conductive surfaces is a low cost and attractive method which does not need sputtering or evaporation devices. Among these “wet” preparation, the Sn-Pd colloidal coating is cheaper than the sputtering coating (about ten times cheaper), and very quickly to use (not exceed 15 min). 100 ml of colloidal solution, as it is prepared in our process, permit to prepare 1 m² of sample surface for SEM observation. This technique preparation is particularly well adapted for 3D samples.



a)



b)

Photo 9. — SEM micrograph of ABS. a) without chemical etching, b) with chemical etching.

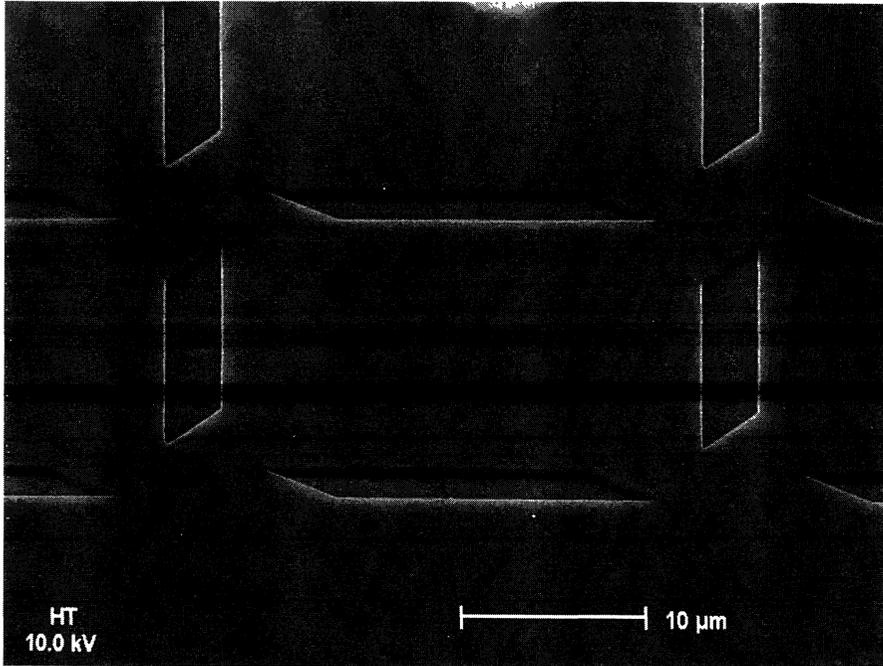


Photo 10. — SEM micrograph of PMMA photolithographic patterns onto Si. (Current probe: 0.014 nA).

Acknowledgements

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