Development and Morphological Characterization of Novel Polyimide/Metal nano Hybrid Materials

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Abstract: Two different polyimide structures were synthesized by two-step polycondensation reaction in solution, in the first step using equimolar amounts of one of two aromatic diamine (DDM or MMDA) and one dianhydride (6HDA) in N,N-dimethylacetamide (DMAc) to obtain the poly(amic acids), followed in the second step by thermal imidization. In order to obtain novel polyimide/metal nano hybrid materials, conductive Ni/Cu nanoparticles were embedded on polyimide substrates, using laser ablation technique. The morphology of the resulted thin metal layers was investigated using atomic force microscopy (AFM), scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). The results highlighted different surface characteristics of the auto-organized metallic/polymer nanoparticles, depending on the chemical structure of the polyimide substrate, the parameters of the laser ablation setup, the deposition time, the type of the metallic target. The obtained features of these polyimide/metal nano hybrid materials can be employed as an indicator of the possibility of using them for potential applications as conductive circuits or substrates for adhesion control.

Keywords: polyimide, metal/polymer aggregates, laser ablation, nano hybrid materials, morphology

1. Introduction

The versatile metal nanoparticle/polymer hybrid materials are very important because combine the characteristics of the polymer structure with metal nanoparticles. Embedding metal nanoparticles inside the polymer films can facilitate immobilization and auto-organization of metal nanoparticles. These nanostructures can be used in nonlinear optics, in Raman scattering, microwave absorption etc. [1]. Some composites (organic-inorganic) utilizing metal (Cu, Ni, Au, Ag etc.) nanoparticles embedded in organic layers have shown potential applications in memory devices [2–4]. In general, among other polymers, polyimides are useful in microelectronic applications because of their unique properties: thermal and chemical stability, high electrical resistivity, low dielectric constant, and good processibility [5]. Sava and his collaborators induced surface relief gratings on azo-polyimide and azo-copolyimide surfaces via laser irradiation through phase masks with different pitch [6-8], which were subsequently used as substrate for gold deposition by sputtering [8]. In this case, the application was metallic reflective gratings, gold being preferred due to its high optical performance [8]. O'Sullivan et al. highlighted the fact that electrolessly deposited materials (cobalt, nickel) on polyimide films can be investigated as possible diffusion barrier layers for multilayer microelectronic structures [9]. The bonding (adhesion)

between the polyimide film and electrolessly deposited layers can vary depending on the applied technique [9]. Other studies have shown that metals, such as copper and nickel, are conductors and by introducing them into a polyimide matrix, the interfacial information and stability can be investigated, helping to control the oxidation of the nanometal and create new metal/polymer materials with high dielectric constant and high processibility [5].

Thus, the objective of this paper was to analyse a class of polymers for the realization of polymer/metal multilayer systems. In this context, it has been shown that some of the substrates based on organic polymers have presented a number of advantages over inorganic ones: they are more flexible, they offer a domain variable rigidity and may adopt different forms as a result of external stimuli. More, the properties of the polymeric material can be adjusted according to the specific requirements by chemical modification or variation of the polymerization and/or crosslinking conditions. Micro- and nanostructures obtained on a polymeric support can be extremely useful for a wide variety of applications as well as for obtaining conductive circuits or substrates for adhesion control. In this context, metal nanoparticles (Cu, purity 99.4% and Ni, purity 99.6%) were deposited on polyimide substrates by laser ablation. Studies on surface structuring capability of polymer thin films have shown that the irradiation conditions present a significant influence. International research on nanostructure phenomena followed until now the synthesis of materials capable of generating a controllable surface structure without making a direct link between the chemical structure of the polymer used and the nanostructure mechanism. To date, there are several theoretical models and mechanisms in the literature that try to explain the processes of reordering the surface of polymeric materials, based on two types of phenomena: the first group of theories involves a reorganization of the polymeric material and their compression under the UV radiation action, and the second group proceeds from the hypothesis of moving the polymeric material (photoinduction) [6-8]. In this context, the degree of novelty in this paper refers to the fact that the chemical structure of the polymer will essentially influence the type of mechanism through which the nanostructuring process is carried out.

## 2. Materials and methods
2.1. Materials
4,4'-Isopropylidenediphenoxy-bis(phthalic anhydride) (6HDA), and 4,4'- diaminodiphenylmethane (DDM) were purchased from Aldrich, and has been used as received. Melting point (m.p.) of 6HDA was 184–187°C; m. p. of DDM was 90-92°C. 3,3'-Dimethyl-4,4'-diaminodiphenylmethane (MMDA) was obtained in our laboratory by a previously reported method [10,11]. m.p of MMDA was 155–157°C.

2.2. Polymer synthesis
The investigated polymers have been obtained by two-step polycondensation reaction [12]. The first step was performed at room temperature with equimolar amounts of one aromatic diamine (DDM or MMDA) and dianhydride (6HDA) in N,N-dimethylacetamide (DMAc), at a total concentration of 14–15%, under inert atmosphere during 6 - 7 h. In the second step, thermal imidization of the resulting poly(amic acid) in solution was performed in the same reaction flask by heating the solution at reflux temperature (170-180 °C) for 5-6 h, under a slow stream of nitrogen to remove the water of imidization. The final product was precipitated in water, washed with water and ethanol, and dried in vacuum oven at 105°C. The structures of the resulted polyimides are shown in Figure 1.
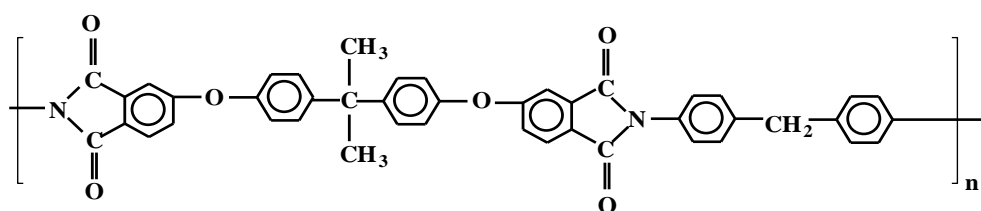
PI-I
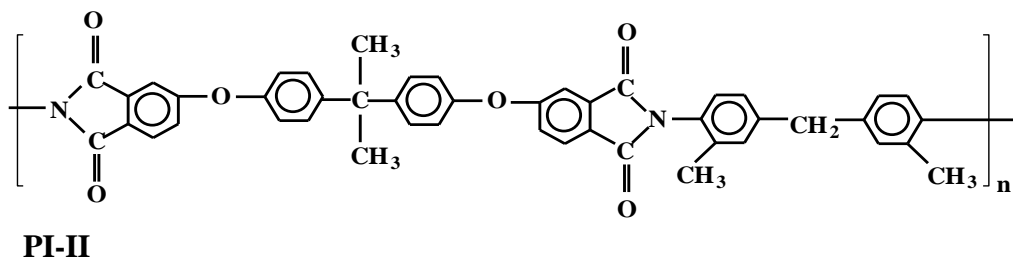
PI-II

Figure 1. Chemical structure of polyimide based on 4,4'-(4,4'-isopropylidene diphenoxy) bis (phthalic anhydride) and 4,4'-diaminodiphenylmethane (DDM-6HDA) (PI-I) and 4,4'-(4,4' isopropylidenediphenoxy) bis (phthalic anhydride) with 3,3'-dimethyl 4,4'-diaminodiphenylmethane (MMDA-6HDA) (PI-II)

2.3. Preparation of films

The polyimide films were obtained by casting the polyimide solutions of 15% concentration in DMAc onto a glass plate and by drying it at 60 °C for 4 h. Then the films were further dried at 100°C, 150, 200, and 250°C for 1 h at each temperature. Finally the films were kept at 260°C for 2 h and they were used afterwards for various measurements. The thickness of such films was in the range of 30 – 40 µm. In polyimide films, we have to consider interactions with electronic charge transfer between polymer chains. Polymer chains resulting from load transfer interactions form nano-aggregates in which pairs of atomic structures appear as electronic charge donors and pairs as electronic load acceptors (Figure 2).
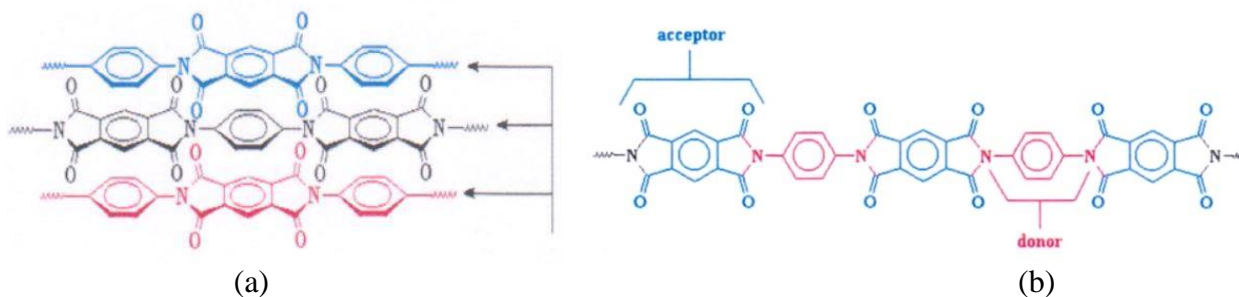

(a)   (b)

Figure 2. (a) Nanostructured aggregates in polyimide films. Polyimides may stack like this allowing the carbonyl of the acceptors on one chain to interact with the nitrogen of the donor on adjacent chain; (b) carbonyl groups from the acceptor unit and nitrogen groups as donors

2.4. Ni and Cu nanoparticle deposition

The metal nanoparticles were embedded using the deposition set-up presented in Figure 3. The Cu and Ni targets were mounted on a multi-axis manipulator placed inside the vacuum chamber. The experiments were conducted at a pressure of ~10^{-2} Torr. The polyimide films were placed on the substrate holder at a 2 cm distance from the target surface. The energy of the laser pulse (30 mJ) and the irradiated surface (1.5 mm^2) were kept constant during all experiments, leading to a fluence of 2 J/cm^2. The varied experimental parameter was the deposition time. Half of the experiments were done by irradiating the target for 40 seconds and half for 600 s. Table 1 summarizes the investigated samples and the conditions in which were obtained.
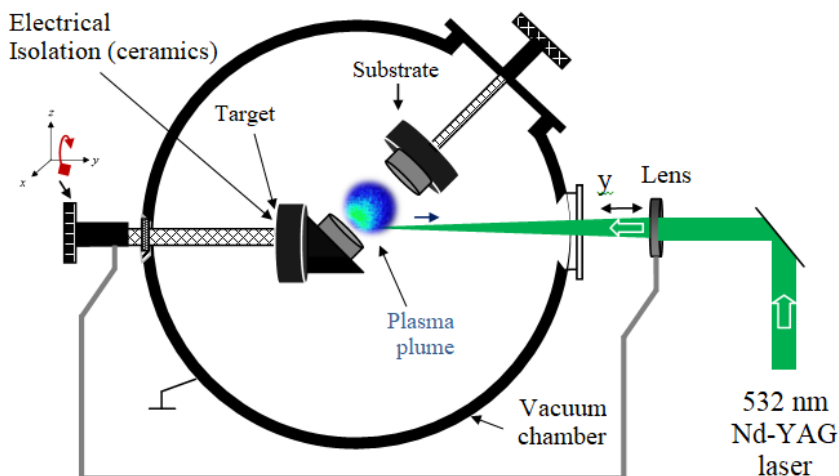
Figure 3. Schematic representation of the experimental set-up
used for thin film deposition

Table 1. Experimental parameters used for the
sample synthesis

Sample	Polyimide (substrate)	Metal (target)	Deposition time (seconds)
PI-I/Cu/40s	DDM-6HDA(PI-I)	Cu	40
PI-I/Cu/600s	DDM-6HDA (PI-I)	Cu	600
PI-I/Ni/40s	DDM-6HDA(PI-I)	Ni	40
PI-I/Ni/600s	DDM-6HDA(PI-I)	Ni	600
PI-II/Cu/40s	MMDA-6HDA(PI-II)	Cu	40
PI-II/Cu/600s	MMDA-6HDA(PI-II)	Cu	600
PI-II/Ni/40s	MMDA-6HDA(PI-II)	Ni	40
PI-II/Ni/600s	MMDA-6HDA(PI-II)	Ni	600

2.5. Atomic force microscopy (AFM)

The metal-polymer nano-aggregates were studied by performing the atomic force microscopy(AFM) measurements on a Scanning Probe Microscope (Solver PRO-M, NTMDT, Russia), at room temperature (23°C), in semi-contact mode, using a commercially available NSG10 (Solver PRO-M, NTMDT, Russia) silicon cantilever with a tetrahedral shape tip with curvature radius of 10 nm. The resonant frequency of the cantilever was 373 kHz. The cantilever's planar dimensions were: length = 95±5 μm, width = 30±5 μm, thickness = 2±0.5 μm. For image acquisition on 5×5 μm^2, Nova v.1.26.0.1443 software was used. In order to calculate the 3D morphological parameters and to make the grain analysis, Image Analysis 3.5.0.18542 software was used.

2.6. Scanning electron miscroscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

Images have been acquired through scanning electron microscopy using a Crossbeam System Neon 40ESB FIB/SEM microscope from Carl Zeiss, with thermal Schottky field emission, equipped with EDS, In-lens, SE and EsB detectors. Electron beam resolution: 1.1÷2.5 nm for U = 20÷1 kV. Electrons accelerating voltage used for the SEM images- 20kV. Working distance was around 5 mm. For the EDX analysis an X-Max 50 from Oxford Instruments detector was used; electrons accelerating voltage 20 kV, working distance 5.1 mm.

3. Results and discussions

The surface morphological changes induced on the polyimide films **PI-I** and **PI-II** after embedding of the metal nanoparticles, were investigated by means of atomic force microscopy. Using bi- and three-dimensional AFM images presented in Figures 4 and 5, two 3D roughness parameters have been estimated, namely the root mean square roughness (Sq), which is the root mean square of the surface departures from the mean plane within the sampling area and the developed interfacial area ratio (Sdr) which is a hybrid parameter described in the literature as the increment of the actual scanned area (the area of the surface area taking into account the z height) relative to the projected area (the area of the flat (x,y) plane) [13]. Their values were introduced in Table 2.
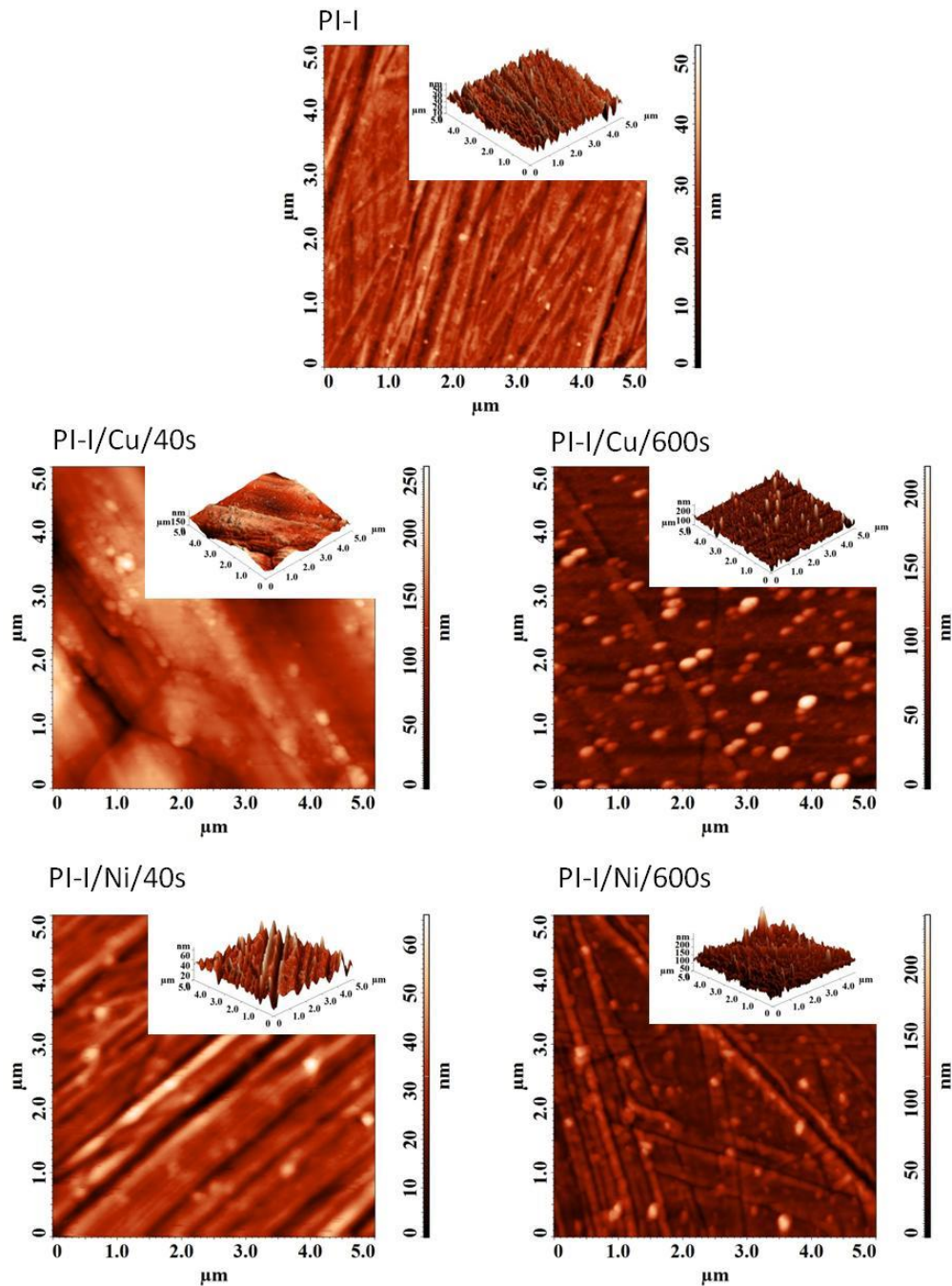

Figure 4. Bi- and three-dimensional AFM images of polyimide PI-I, before and after Cu and Ni nanoparticles were embedded. The deposition time was 40 and 600 s, respectively
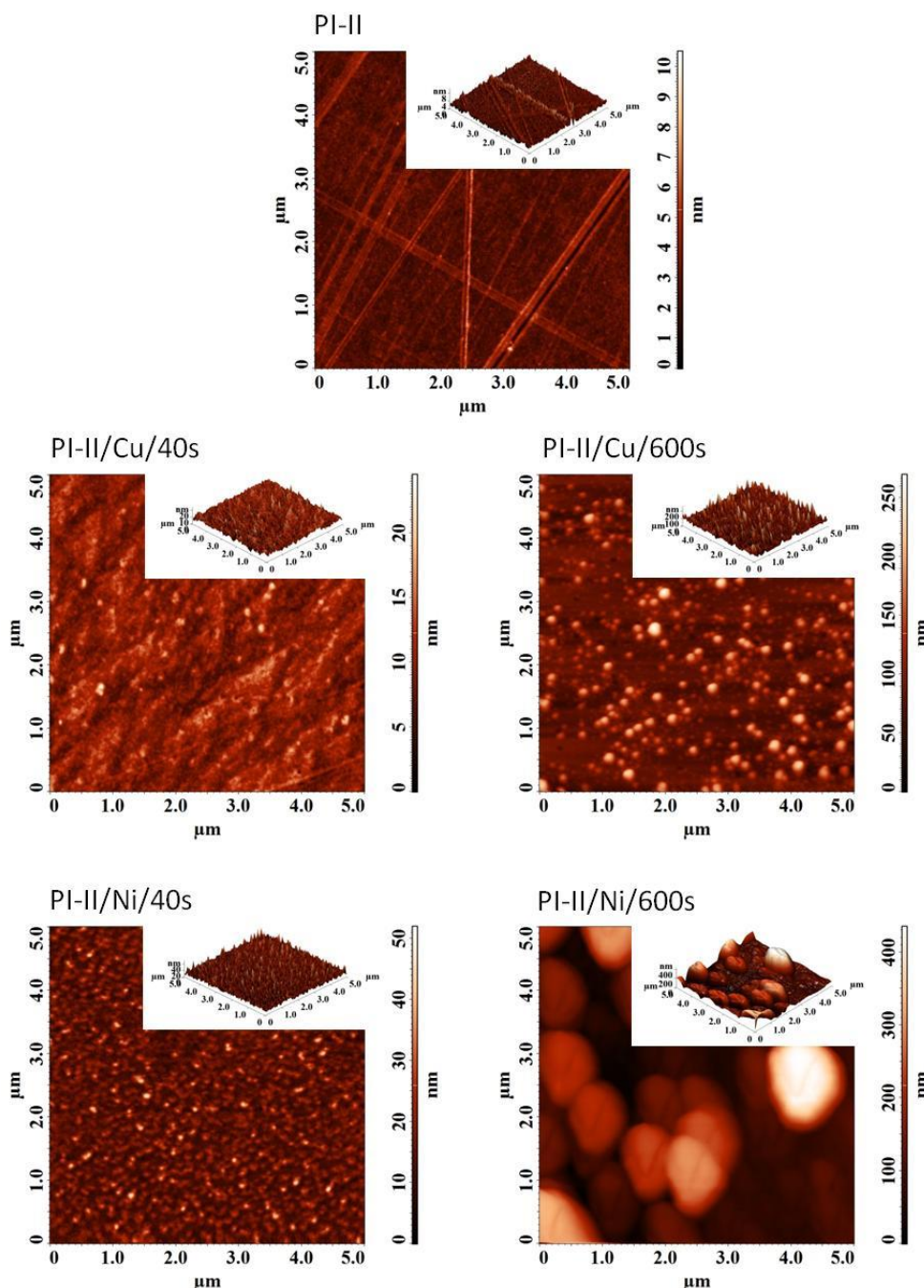
Figure 5. Bi- and three-dimensional AFM images of polyimide **PI-II**, before
and after Cu and Ni nanoparticles were embedded. The deposition time
was 40 and 600 s, respectively

According to Figures 4 and 5 and Table 2 the pristine samples **PI-I** and **PI-II** shows morphologies generally characteristic to polyimide films, slightly influenced by the glass substrate on which they were deposited, with relatively low root mean square roughness and developed interfacial area ratio. Depending on the structure of the polyimide film used as substrate, more precisely depending on the aromatic diamine that was used in the synthesis of the polyimide (DDM or MMDA), the type of the embedded nanoparticles (Cu or Ni) and the deposition time (60 or 400 s), the metal-polymer nano-aggregates formed on the surface and clearly visible in Figures 4 and 5 differ in size and appearance.

Table 2. Roughness parameters and characteristics of the Cu/Ni-containing nano-aggregates

Sample	Roughness parameters		Metal-polymer nano-aggregates characteristics					
	Sq(nm)	Sdr (%)	d_{min} (nm)	d_{max} (nm)	P (nm)	A (nm^2)	f_{elong}	f_{shape}
PI-I	4.9	1.08	-	-	-	-	-	-
PI-I/ Cu/40s	31.4	2.67	143±2	299±41	921±28	43200±6780	0.48±0.06	0.60±0.05
PI-I/ Cu/600s	23.3	13.54	128±15	291±24	823±55	37600±7640	0.45±0.02	0.68±0.04
PI-I/ Ni/40s	8.5	0.85	146±13	272±41	872±180	40300±9760	0.52±0.03	0.56±0.11
PI-I/ Ni/600s	22.8	12.42	99±3	169±11	489±27	16850±1060	0.62±0.04	0.86±0.04
PI-II	0.8	0.09	-	-	-	-	-	-
PI-II/ Cu/40s	2.2	0.37	67±2	151±8	382±14	10150±220	0.42±0.03	0.79±0.04
PIII/ Cu/600s	29.5	26.48	83±2	148±4	421±14	12100±280	0.57±0.01	0.83±0.03
PI-II/ Ni/40s	5.0	2.77	54±1	112±7	274±1	6150±540	0.47±0.02	1.03±0.09
PI-II/ Ni/600s	87.2	9.95	612±61	1065±71	3715±319	654000±10889	0.59±0.02	0.55±0.01

Sq	- root mean square roughness
Sdr	- developed interfacial area ratio
d_{min}	- minimum Feret diameter
d_{max}	- maximum Feret diameter
A	- particle area
P	- particle perimeter
f_{elong}	- elongation factor
f_{shape}	- shape factor

The calculations of the shape parameters, namely the elongation factor, f_{elong}, and the shape factor, f_{shape}, (displayed in Table 2) were performed on nano-aggregates considered representative for the entire investigated surface. Thus, the average value and standard deviation were presented for each characteristic. The elongation factor was calculated using the equation (1):

$$f_{elong} = \frac{d_{min}}{d_{max}} \qquad (1)$$

where d_{min} is the minimum Feret diameter of the nano-aggregate and d_{max} is the maximum Feret diameter of the nano-aggregate. Also the shape factor was obtained using the equation (2):

$$f_{shape} = \frac{4\pi A}{1.064 \, P^2} \qquad (2)$$

where A is the nano-aggregate area and P is the nano-aggregate perimeter. The perimeter was corrected for the effects produced by the image digitization, by using the factor 1.064 [14,15].

Thus, when PI-I containing 4,4'- diaminodiphenylmethane was used as substrate for Cu deposition by irradiating the target for 40 seconds, on the surface of the polyimide the resulted Cu layer was uneven, fact reflected by the very large value of Sq, namely 31.4 nm (Table 2). Still the complexity of the surface described by the Sdr value of 2.67 % was moderate. The Cu-polymer nano-aggregates were hardly observable individually. As the deposition time was increased at 600 seconds, the deposited layer was uniformized, Sq significantly decreasing till 23 nm. The increasing complexity of the surface, reflected by a large value of the Sdr (13.54 %) was determined by the metal-polymer nano-aggregates with small diameters, as seen in Table 2, but more well-defined, as observed in Figure 5. The trend was quite different in case of Ni deposition. For the irradiating time of 40 seconds of course the roughness was higher than that obtained for the pristine sample, PI-I, but significantly lower than that calculated for the

600 seconds deposition time. The deposited metallic layers seem to follow the initial relief of the polymeric substrate. As in the case of Cu deposition, the higher was the deposition time, the smaller were the aggregate sizes (Table 2) and higher the surface complexity (*Sdr*).

PI-II containing 3,3'-dimethyl-4,4'-diaminodiphenylmethane behave differently when it was used as substrate for Cu and Ni deposition. Initially, at low deposition time, the metallic-polyimide nano-aggregates were smaller, causing a lower roughness (2.2 nm and 5.0 nm, respectively) and small developed interfacial area ratio (0.37 % and 2.77 %, respectively). When the deposition time was 600 seconds the roughness increases significantly. The bigger formed Cu-polyimide nano-aggregates were well-defined and uniformly distributed over the surface, thus increasing the complexity of the morphology (*Sdr*=26.48%) (Table 2). For PI-II/Ni/600s, a spectacular phenomenon happens, the aggregates reaching even up to 1 µm in diameter, although the topography is relatively simple (*Sdr*=9.95%).

The elongation factor, which depicts the elongation level of the metal-polymer nano-aggregates, independently of the contour, was lower than 1 for all the samples (Table 2), describing an elliptical form of the features. Also, the vast majority of samples have a shape factor lower than 1 (Table 2), indicating that the formations have irregular contour. The exception seems to be PI-II/Ni/40s sample, who has f_{shape}=1.03±0.09, and implicitly a smooth circumference of the aggregates. It should be remembered that in this case, their dimensions were the smallest.

Analyzing all the AFM data, one can conclude that, from the nano-aggregates distribution point of view, the best results for the targeted applications were obtained when Cu layer was deposed for 600 seconds on both DDM-based and MMDA-based polyimide substrate.

Taking into account the previous discussions, forwards the images acquired through scanning electron microscopy and EDX analysis were performed only on the samples with Cu or Ni layer deposed for 600 s on both polyimide substrates (Figure 6), in order to identify the actual presence of Cu or Ni nanoparticles.

The SEM images highlighted the overall view of the resulted metal surface, indicating uniform distributions of the Cu or Ni, which follows the initial relief of the polyimide. The chemical structure of the polyimide essentially influenced the mechanism through which the metallic nanoparticles bind to the support. The thickness of the metal layer resulting from the laser ablation process was of about 90 nm (estimated using FIB- Focused Ion Beam technique).

The EDX analysis, taken in three different regions for each sample, confirms that all the samples consist of only Cu or Ni (depending on the deposed metal), C and O (all results were in atomic %). Therefore, the purity of all nano-aggregates is high without any trace of other impurities. From these data we can also establish that, in the same experimental conditions, PI-I sample present a higher affinity for Ni, and PI-II for Cu.

The obtained features of these polyimide/metal nano hybrid materials can be employed as an indicator of the possibility of using them for potential applications as conductive circuits or substrates for adhesion control.
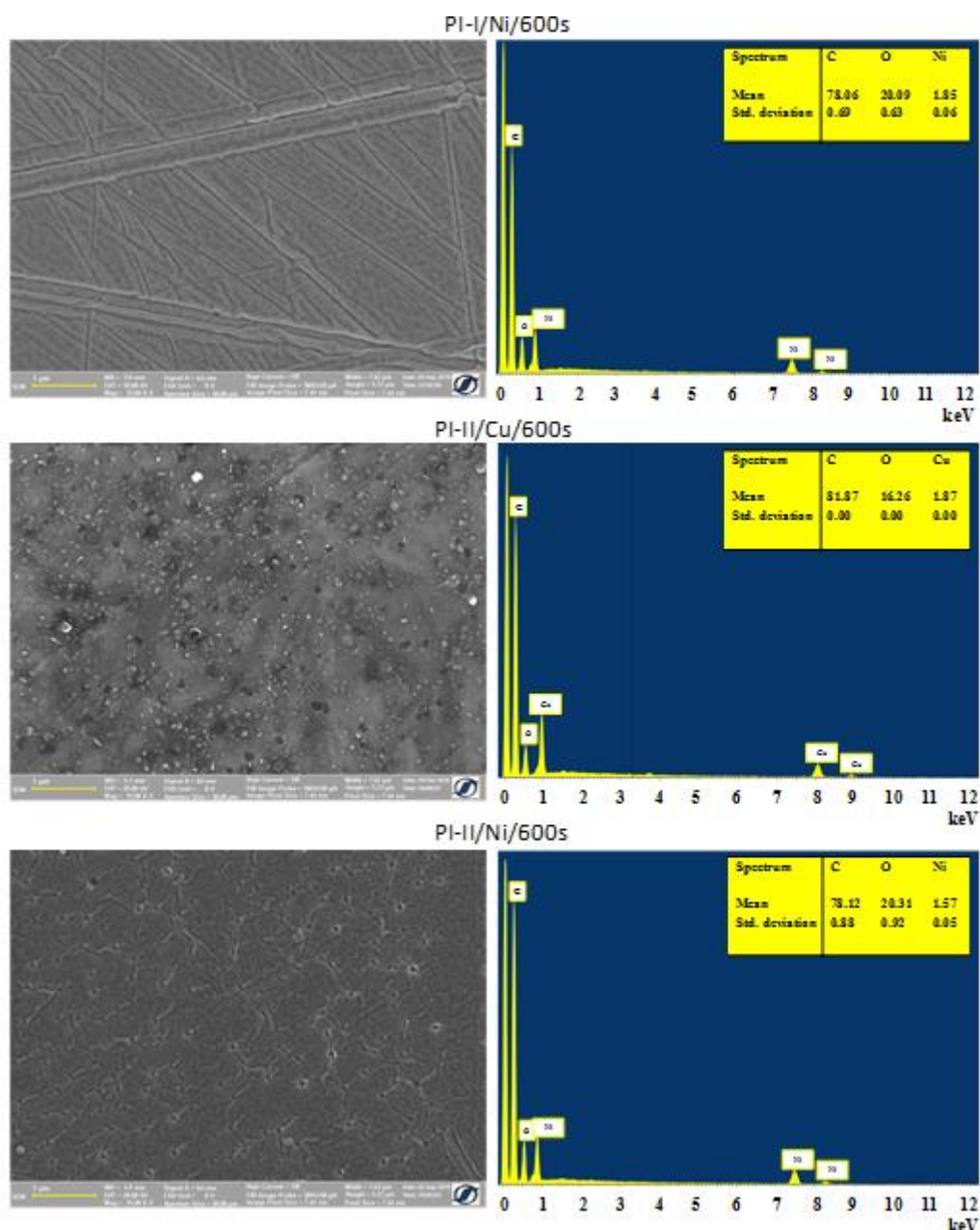

PI-I/Cu/600s

Spectrum	C	O	Cu
Mean	82.14	16.30	1.55
Std. deviation	0.56	0.45	0.04
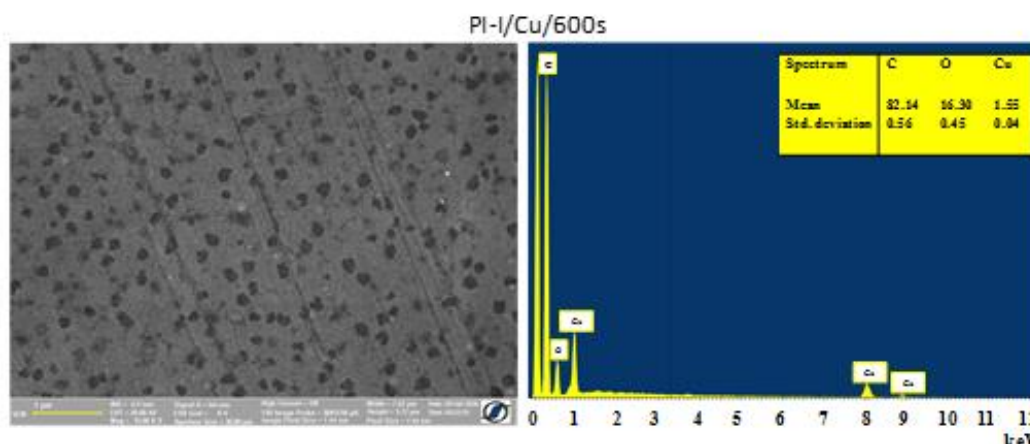
Figure 6. SEM images and EDX spectra of polyimides **PI-I** and **PI-II**,
after Cu and Ni nanoparticles were embedded. The deposition time was 600 s

4. Conclusions

Two different polyimides were used as substrates for embedding conductive Ni/Cu nanoparticles through a laser ablation process, for the purpose of obtaining polyimide/metal nano hybrid materials. The pristine polyimide samples showed morphologies generally characteristic to the polyimide films, with relatively low root mean square roughness and developed interfacial area ratio. The auto-organized metal/polyimide nano-aggregates formed on the surface differ in size and appearance, depending on the aromatic diamine (DDM or MMDA) that was used in the synthesis of the polyimide employed as substrate, the type of the embedded nanoparticles (Cu or Ni) and the deposition time (60 or 400 s). The results show that the deposited metallic layers seem to follow the initial topography of the polymeric substrate, indicating uniform distributions of the Cu or Ni nanoparticles. The EDX analysis confirmed that all the samples consist of only Cu or Ni (depending on the deposed metal), C and O. The purity of all nanoparticles was high without any trace of other impurities. In addition, the chemical structure of

the polyimide essentially influences the mechanism through which the metallic nanoparticles bind to the support. Using the same experimental parameters, the complexity of the nano-aggregates was higher in the case of PI-II containing

3,3'-dimethyl-4,4'-diaminodiphenylmethane, comparative with PI-I containing 4,4'- diamino-diphenylmethane. Analyzing all data, for the targeted potential applications of these polyimide/ metal nano hybrid materials as conductive circuits or substrates for adhesion control, the best results from the nano-aggregates distribution point of view were obtained when Cu layer was deposed for 600 s on both DDM-based and MMDA-based polyimide substrate.

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