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Electroless Ni-P deposition over polyvinylidene fluoride thin films with wet acid treatment

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Polyvinylidene Fluoride (PVDF) is a very versatile polymer with enough potential to provide a great development in materials science and technology, due to its piezoelectricity, low energy surface, low cost, flexibility, mechanical and chemical resistances. For electrical applications, like piezoelectric sensors and actuators, for example, PVDF surface metallization is essential. This paper describes an alternative metallization method, called electroless nickel-phosphorus deposition (Ni-P), in PVDF films deposited on glass substrate with some geometric structures fabricated by Photolithography. After a wet pre-treatment to improve adherence, electroless contact layer is deposited over PVDF masked by photolithography, using the lift-off technique. This process combination is very versatile, simple and gives good results, related to the Ni-P adhesion on PVDF surface and to the pattern resolution of photolithographic structures. Chemical composition of the alloyed film were measured by SEM/EDS (Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy), the PVDF surface treatment was examined using Infrared Spectroscopy and the resolution of Ni-P deposition evaluated by the Scanning Electron Microscope. This work opens a possibility of a new metallization technique for PVDF piezoelectric devices.

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1. Introduction

Fluoropolymers are materials of large technological importance, characterized by high chemical inertness, thermal stability and electrical insulating properties. They also have very low surface energy, which causes negligible adhesion to other materials, especially metals. The characteristics of fluorine-containing polymers are the low surface energy, hydrophobic property, and poor adhesion to other materials, and there is the necessity to modify the hydrophobic surface into hydrophilic one without the degradation of electrical properties [1,2]. The combination of low surface energy of PVDF thin films, Ni-P electroless deposition and photolithography techniques is a innovation of this work. The method has played an important role as an indispensable metallization for miniaturization of planar structures, and represents a possibility to deposit Ni-P layer in a controlled and located way. In the case of PVDF, surface modification of fluoropolymers has been of particular interest, as these materials belong to one of the most important families of engineering polymers [3-9]. Fluoropolymers exhibit good thermal stability, excellent chemical inertness, low friction coefficient, low surface energies and low dielectric constants due to the high dissociation energy for C–F bonds and the high electronegativity of fluorine atoms, [10-13]. However, these properties, which are very important for certain applications, also present considerable disadvantages where adhesion is necessary. Therefore, surface pretreatment is always necessary to improve the bonder of the fluoropolymers. Numerous surface treatments have been developed to improve the adhesion properties of fluoropolymers. These methods have included chemical treatment, ion beam treatment, plasma treatment, ozone treatment and graft copolymerization [14-19]. On the other hand, the electroless deposition of metal onto polymer surfaces is a simple and convenient method to metallize the polymer surfaces. The process has been widely used in the automotive and microelectronics industries. Normally, the polymer surface is activated via the two-step or one-step process [20].

The objective of the present research is to use the two-step process in which the polymer deposited on a glass surface was immersed successively in $SnCl_2$ and in $PdCl_2$ solution [21]. Finally, the polymer is immersed in a Ni-P solution, which is described by the electroless Ni-P deposition on PVDF thin films combined with the lift-off photolithography techniques. In this paper, samples treated with an acid solution are investigated. This process expected to offer several advantages, such as the simplicity of operation and the low cost, compared with the conventional sputtering process [22]. Moreover, the chemical treatment surface has also the advantage to be easier operation and low cost, compared with plasma techniques.

2. Materials and methods

Nickel phosphorus films were deposited over PVDF substrate fixed on a glass plate using wet process. The sequence of process used to fabricate samples includes the glass plate preparation, PVDF deposition, surface treatment and photolithography, nucleation and electroless deposition, as described below.

Glass Plate Preparation: The 2 inches glass plate was submitted to a sandblasting process, in order to increase surface roughness and washed in a neutral detergent 3%v/v at 60^0C during 10 minutes using ultrasound equipment. The glass plate was then washed with deionized water and dried with nitrogen.

PVDF Deposition: The PVDF film deposition was performed by the spin-coating technique, with a solution of PVDF 20% (w/w) in dimethylacetamide. The approximate thickness of the film was 10 microns measured with a micrometer. A post backing of 70 ° C for 5 minutes was performed to evaporate the solvent and solidify the film.

Surface Treatment and Photolithography: The polymer film was treated prior to thin film deposition with an acid solution, containing sulfuric and nitric acid 19:1 (v/v) at 90°C for 4 minutes. The structures were fabricated by the photolithographic process using AZ 1518 photoresist at 5000 rpm for 35s, and a backing of 90°C during 1 minute. Under these conditions a direct UV exposition employing a Karl Suss MBJ3 mask aligner, was done for 20 seconds, followed by revelation using pure MIF 300 developer for 30 seconds and a post-backing of 120°C for 15 minutes.

Nucleation: The seed layer on polymer surface containing photoresist is obtained by sensitizing the polymer with an acid stannous chloride solution (1 g/L), then activating it with palladium chloride solution (0,25 g/L). The samples were immersed three times in these solutions for 30s.

Electroless Deposition: After surface treatment, an autocatalytic acid solution of electroless Ni-P was used. The composition of electroless Ni-P solution used in previous works [21, 23-25] is: $NiCl_2.6H_2O$ (15g/L), $NaH_2PO_2.3H_2O$ (30g/L), $CH_3C_2OONa.3H_2O$ (10g/L), NH_4Cl (50g/L). Each component has a specific function: nickel chloride as a Ni ion source, sodium hypophosphite as a reducing agent, sodium acetate as complexing agent and ammonium chloride as a buffer. In addition, a stabilizer was used to prevent decomposition of the Ni plating solution [26]. The temperature of plating bath was maintained at 60°C. After a few seconds of the Ni-P deposition, lift-off process was done in acetone at room temperature to remove the photoresist. The Ni-P was then thickened to a 1µm.

Analysis: The chemical composition of the Ni-P alloy was measured by SEM/EDS (Scanning Electron Microscopy - Energy Dispersive X-Ray Spectroscopy), the PVDF surface treatment was examined using Infrared Spectroscopy and the resolution of Ni-P deposition evaluated by the Scanning.

3. Results and discussion

3.1 Acid Pre-treatment

Considering that PVDF is chemically inert, no significant chemical difference (analyzed with Infrared Spectroscopy) was observed between the untreated and treated PVDF films. However, this acid treatment is very important, because it favors the anchoring of Sn and Pd atoms, preparing the PVDF surface to be metalized with the Ni-P alloy. This is the key idea of the PVDF surface metallization [27,28].

3.2 Nickel-phosphorus deposition

The nickel reaction with hypophosphite as a reducing agent was represented in previous works [29,30], which indicate that nickel ion is reduced to nickel metal and that the hypophosphite ion is also reduced to elemental phosphorus, respectively. Therefore, the electroless nickel deposition, with hypophosphite as a reducing agent, would be a Ni-P alloy.

The chemical adherence between the Ni-P layer and the PVDF is a result that must be considered with special attention, especially due to the low surface energy of this polymer. This work opens new perspectives of research about metallization of polymers with low surface energy, which is the special case of fluoropolymers in general. The nickel-phosphorus composition was analysed by SEM/EDS. The characteristic emission lines of the spectra are registered in the Fig. 1 and Table 1 [31].

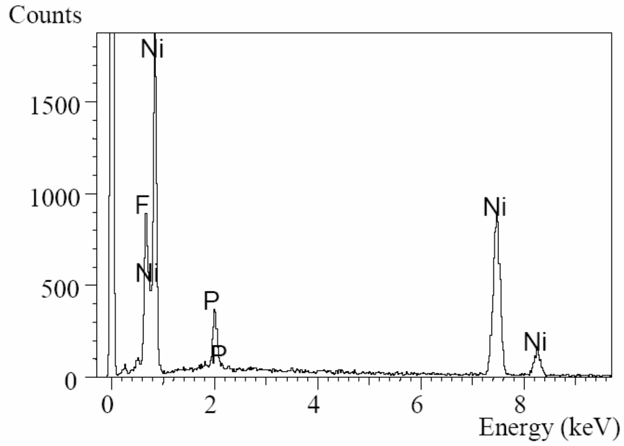

Fig. 1. SEM/EDS spectra for the Nickel-Phosphorus film.

Table 1. Characteristic Emission Lines from the EDS Spectra.

Element	**$K\alpha_1$ / keV**	**$K\alpha_2$ / keV**	**$K\beta_1$ / keV**	**$K\beta_2$ / keV**
F	0,677			
P	2,015	2,014	2,136	
Ni	7,477	7,460	8,264	8,328

With the SEM/EDS technique, the quantitative analysis of the Ni-P film was done: 22.30% of Fluorine, 6.53% of Phosphorus and 71.17% of Nickel. The fluorine concentration is related to the X-Ray penetration at the PVDF layer, below the nickel-phosphorus deposition and the EDS spectrum reveals that film deposit consist mainly of Ni and P, accordingly with the expected.

The sandblasting process improves the glass plate roughness, which is favorable for the PVDF film adhesion on the glass plate. This deposition can be visualized in the square geometries of the Fig. 2, obtained by Scanning Electron Microscopy.

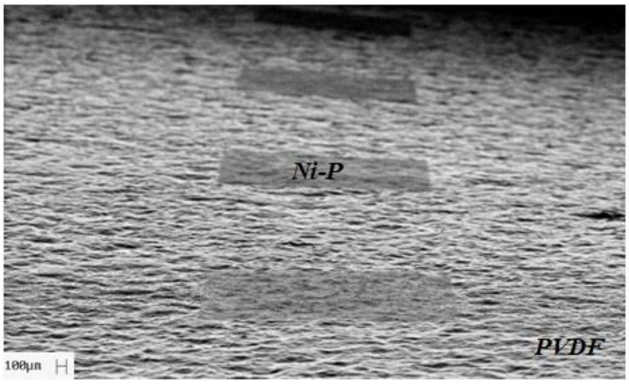

Fig. 2. Scanning electron microscope (SEM) of the Ni-P on the glass plate with the PVDF thin film.

4. Conclusions

Considering that in general metallic films do not present good adherence when deposited directly over polymeric substrate like PVDF, we proposed an acid pre-treatment, as an alternative to high-cost vacuum equipments or plasma surface activation processes.

After the pre-treatment, a nucleation process followed by electroless deposition was realized in order to obtain a Ni-P film with good adhesion on PVDF surface. These steps permitted the development of a full wet Ni-P film deposition process, without the use of high-cost equipments like sputtering, being a good alternative to obtain thin high performance metallic PVDF films.

This deposition technique is very versatile, simple and gives good results, related to the Ni-P adhesion on PVDF surface and to the pattern resolution of photolithographic structures. Combining the low surface energy of PVDF thin films with the techniques of the electroless Ni-P deposition and photolithography, it was possible to deposit a Ni-P layer in a controlled and located way. This process presents a lot of possibilities for technological applications, because the integration of different techniques in the same system, which is a powerful strategy in the Micro and Nanotechnology contexts, especially for the micro or nanofabrication of piezoelectric sensors and actuators.

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