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Electroless nickel plating onto plexiglass through simple covalent grafting of polyvinylpyridine-like seed layer

Viet Anh Ly *[1], Thi Thu Hương Trương [1], Trong Dai Dương , Thi Thu Dung Nguyen [1], Thi Bich Ngoc Nguyen[1]
[1]*Thai Nguyen University of Technology; 3-2 Street, Thai Nguyen City, Vietnam*

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ABSTRACT:Recent developments in the fabrication of micro-electro-mechanical systems (MEMS) are moving away from the deposition/mask/etch paradigm and instead exploiting useful properties of polymers. Many polymeric insulating materials, such as PMMA, HSQ, SU-8 and KMPR, have attracted attention in microfabrication lately, because of their low cost and significantly easy processing procedures [1,2]. Metallization of these polymers is required for their integration in MEMS technology. While conventional microfabrication methods for preparing metallic thin films on insulating substrates are limited to vapor deposition techniques, we have recently demonstrated that electroless deposition can be considered as an alternative and efficient approach [3]. Presently used process of electroless plating onto plastics requires a pretreatment based on chromic acid etching for oxidizing the surface. This pretreatment increases the surface energy and wettability for the subsequent step of surface activation with noble metal catalysts. Thus, the development of simple, cost-effective and environment friendly strategies, such as avoiding chromic acid etching and/or minimizing the gravimetric use of noble metal, to metallize the surface of insulating substrates is of huge interest. Here, we report for the first time, a simple one step covalent grafting of polyvinylpyridine-like layer on the surface of commercial plexiglass (PMMA) employing diazonium-based aqueous chemistry. These pyridine functionalities allow minimizing the quantity of palladium cations used as catalyst for the subsequent electroless nickel deposition, as well as offer excellent adhesion between PMMA and the nickel film. The article presents the logo of Thai Nguyen University of Technology made from plexiglass (PMMA) before (a) and after (b) electroless deposition of nickel through our completely aqueous metallization route. X-ray photoelectron spectroscopy is carried out to elucidate the mechanism of surface functionalization with pyridine groups. We then focus our attention on the comprehensive characterization of the metallic thin film through scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy techniques.

KEYWORDS: Metallization of plastics, diazonium chemistry, covalent grafting, environment plating process, MEMS fabrication.

I. INTRODUCTION

In this paper i.ecamless engine, the valve motion is controlled directly by a electromagnetic actuator there's no camshaft or connecting mechanisms .Precise electromagnetic actuator or solenoid controls the valve operations, opening, closing etc. The project looks at the working of the electromagnetic actuator camless engine, its general features and benefits over conventional engines Since the invention of engine and till now four stroke IC engines are working on camshaft Mechanism. Although the conventional system has proven to be convenient and safe. Its fixed valve timing is necessarily a compromise of combustion stability, fuel economy and maximum torque objectives. Cam is an integral part of an engine as it controls valve actuation which in turn is responsible for supply of air-fuel mixture into the combustion chamber and for the removal of exhaust gases from the combustion chambers.

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Products made from insulating material are increasingly widely used in civil and industrial applications. They do not require high mechanical load-bearing capacity with a variety of types based on the following advantages: (1) Corrosion resistance, resistance to the effects of water and high humidity environments; (2) light, weight about 1/10-1/20 compared to corresponding metal products [4]; (3) high aesthetics. To improve surface mechanical properties, create electrical or thermal conductivity, create optical properties, prevent electromagnetic interference or create functional coatings in microelectromechanical technology (MEMS), etc., as well as aesthetics For products made from non-conductive materials, people often plate, cover metal, alloy or paint on the product surface [5].

There are many methods of plating and coating metal on the surface of non-conductive materials, of which chemical plating is the most popular due to low cost and simple technology. However, to be able to plate or coat metal on plastic surfaces, the substrate needs some pre-treatment and treatment before plating. In the chemical plating method, these steps often require using chromic acid containing Cr^{6+} chromium, which can cause cancer and is toxic to humans [6]. The European Union and North American countries have very limited use of this method to minimize harm to the environment and humans [7]. Furthermore, after surface acidification, the substrate must be activated with expensive rare metals, such as Palladium (Pd), Platinum (Pt), gold (Au), etc. [8]. Therefore, research on plating methods that do not use hexavalent chromium (Cr^{6+}), while minimizing the amount of expensive activators, is a highly scientific and very practical issue.Thus, the development of simple, cost-effective as well as environment friendlystrategies to metalize the surface of insulating substrates, such as avoiding chromic acidetching and/or minimizing the gravimetric use of relatively expensive noble metals,have attracted attention of several research works [9,10].Electroless plating on insulating Plexiglass substrates via surface amination has appeared to be a promisingalternative to the chromic-based strategy, as the amine groups allow a well-controlledamount of the noble metallic catalysts and good adhesion of the deposited film.Amination of polymeric substrates can be achieved through different plasma-assistedmethods or through various multiple-step chemical method [11-14].

Here, we report a one-step chemical process based on the diazonium chemistry to covalently functionalize the polymeric substrates of interest with Vinyl groups.These amine-terminated surfaces are activated by simply immersing the substrates in acidic palladium chloride solution (Figure 1). Details concerning the mechanism of surface functionalization as well as the metallic behavior of the deposited thin film will be discussed based on the XPS, EDX, SEM and AFM results.

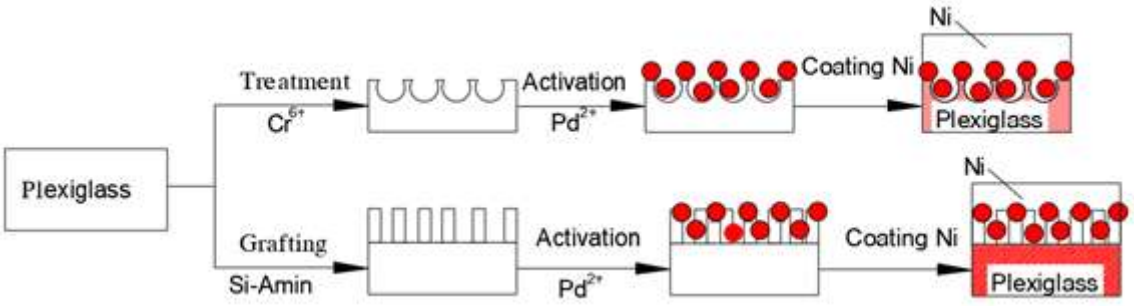

Figure 1: The traditional Copper chemical plating processes on PMMA and our new method

II. EXPERIMENTAL SECTION

2.1. Sample preparation

The logo of Thai Nguyen University of Technology (TNUT) made from plexiglass has a diameter of 50mm, with 5mm thick sheet. Afterwards all samples were repeatedly cleaned with deionized water and isopropanol, and dried with nitrogen gas.

2.2. Surface treatment process with a solution of Hydro-Peroxide Acid

The solution used for pretreatment of plexiglass surface includes 37% HCl solution, 50% H2O2 old oxide, and deionized water with a involume ratio of 1: 1: 5. The temperature needed during the process is about 800C in the period of 8-12 minutes.

2.3. Grafting of vinylpyridine seed layer by diazonium induced anchoring process

4-nitrobenzenediazonium tetrafluoroborate (97%, Sigma Aldrich) was first

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dissolved into 0.5 M HCl (Fisher) and then of 4-vinylpyridine (97%, 0.975 g/mL, Sigma Aldrich) was added to it. The mixture was stirred until a homogeneous solution was obtained. The volume of this solution was finally adjusted to 1000 mL by adding 0.5 M HCl, thus the concentration of vinylpyridine and diazonium cations in the final solution were 0.05 mol/L and 0.005 mol/L, respectively. An amount of 250 mL of the solution was then poured in a flask and 0.2 g Fe powder (b10 µm, Alfa Aesar) was added to it. At this point, Plexiglass substrate was immersed in the solution covering the whole surface of the sample. The experimental setup was protected from UV light during grafting and the grafting was performed in the absence of mechanical agitation to the solution. The samples were removed from the solutions after 90 min. The samples were thoroughly washed with HCl (0.5 M), deionized water and isopropanol under ultrasonic condition repeatedly, and dried with nitrogen gun.

2.4. Electroless nickel plating

Electroless nickel plating takes place while immersing the substrate activated with Pd complexes into nickel solution containing a reducing agent [1]. In this case, we used a conventional nickel-plating bath containing 0.1 M nickel sulfate hexahydrate, 0.2 M citric acid monohydrate and 0.05 M dimethylamine borane (DMAB). Tetramethylammonium hydroxide (TMAH) was used to adjust the pH of the solution at 9. Electroless nickel plating can be achieved at an appropriate temperature (65°C). The whole deposition process can be briefly described as follows: Pd^{2+} cations are first reduced to Pd metal. This noble metal nuclei catalyzes the subsequent reduction of nickel cations to Ni metal atoms. Once metallic nickel is formed around the Pd nuclei, this metallic Ni catalyzes further reduction reaction of nickel cations from its solution. This autocatalytic reaction results in formation of a continuous film on the substrate.

2.5. Using X-ray photoelectron spectroscopy to identify chemical bonds

An X-ray photoelectron spectrometer (K-Alpha, Thermo Scientific), equipped with a micro-focused Al Kα X-ray source (1486.6 eV) was used to record survey and high-resolution scans with energy steps of 1 and 0.1 eV, respectively. The electron takeoff angle was set at 90° during data acquisition. The spectral energies were calibrated by setting the binding energy of the C 1s component corresponding to C=C-C bonds to 284.8 eV.

2.6. Using Scanning electron microscopy (SEM) to identify microscopic structure

Top view and cross-section scanning electron micrographs of Nickel/KMPR/Silicon stack were recorded on a Hitachi SU3500 operating at 10 kV in secondary electron imaging mode. The tool was also equipped with energy dispersive X-ray (EDX) detection system.

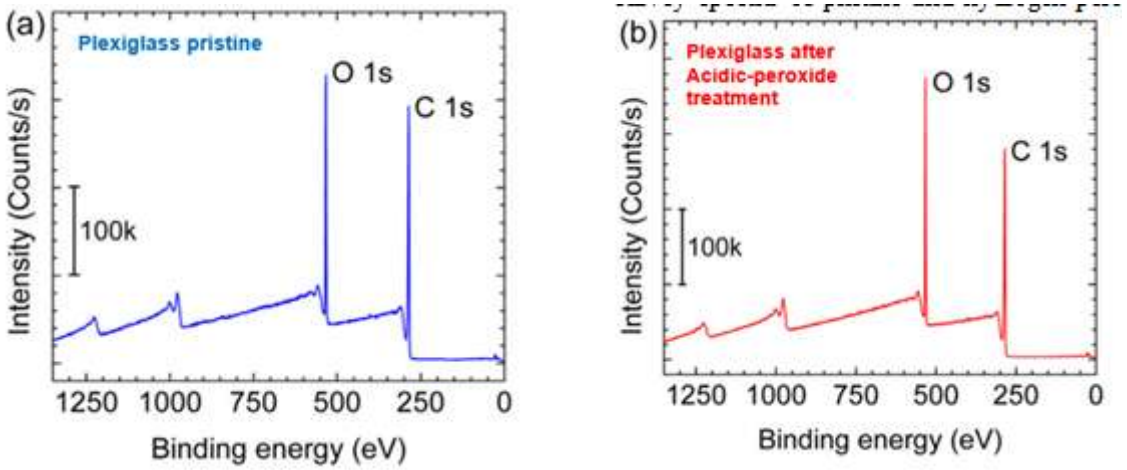

Figure 2: XPS survey spectra ofthe pristine Plexiglass (a) and acidic peroxide treated Plexiglass (b)

2.7. Using ASTM-D standard to identify adhesion

A dry nylon cloth was used to brush off any flakes. A pressure-sensitive tape was applied over the grid, smoothened and rubbed over to ensure good contact. After 90 seconds of application, the tape was removed by seizing the free end and pulling it off rapidly back upon itself at as close to an angle of 180^0 as possible. The adhesion was rated according to the ASTM

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standard. A minimum of three tests were performed for the evaluation of adhesion.

III. RESULTS AND DISCUSSION

3.1. Functionalization of Plexiglas with vinylpyridine seed layer by means of diazonium chemistry

Survey scans range from 0 eV to 1350 eV and scan resolution with energy steps of 1 and 0.1 eV. A charge neutralization gun was used to avoid surface charge accumulation during X-ray scanning. The data acquisition procedure was performed using CasaXPS software (version 2.3.16).

Among various acid, alkaline and organic wet cleaning processes which are well-established in the semiconductor industry, the peroxide-based cleaners not only remove organic and metallic contaminants on silicon surface, but also leave the surface hydrophilic with silanol groups (Si–OH). In particular, mixtures of HCl, H_2O_2 and H_2O (commonly referred as Standard Cleaning 2 or SC_2 solutions) have recently been proved efficient in hydroxylation of many diverse surfaces. XPS survey spectra of pristine and hydrogen peroxide cleaned plexiglass are shown in Figure.2. The O/C atomic ratio of plexiglass increases after cleaning, albeit slightly, from 0.31 at.% to 0.34 at.%, which suggests the introduction of oxygen-containing groups on plexiglass.

Once the surface hydrophilicity is increased after hydrogenperoxide treatment, the presently established industrial electroless plating processes for the semiconductor and polymermicro-systems require immersing the substrate into organosilane solution to functionalize the surface with noble metalliccatalysts prior the chemical metallization.

It is important to characterize the surface of palladium complexes functionalized PLEXIGLASS for an evidence. As expected, in addition to the C 1s (285 eV) and O 1s (530 eV) peaks, which are the main elements of pristine PLEXIGLASS polymer, the survey spectrum recorded on the modified surface clearly shows the presence of Si 2 s (152 eV), Si 2p (102 eV), N 1 s (400 eV) and Pd 3d (338 eV) peaks (Figure.3a). Notably, the Si 2p core level spectrum shows only one component at 102.4 eV with full width at half maximum (FWHM) of 1.6 eV(Figure.3b).

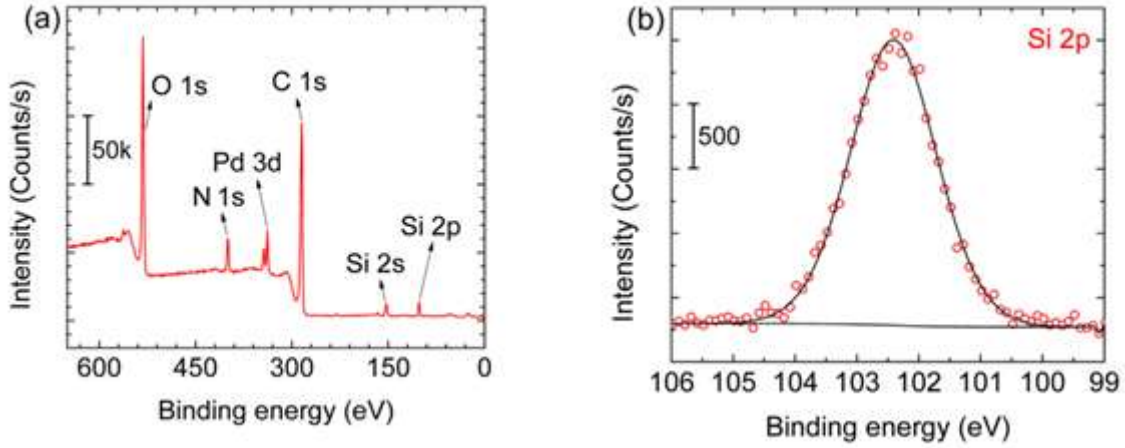

Figure 3: XPS survey (a) and Si 2p core level (b) spectra of the plexiglass surface functionalized with palladium complex

3.2.Electroless nickel plating on the palladium activated vinylpyridine seed layer

It is well-established that electroless nickel plating takes place while immersing an insulating surface functionalized with Pd^{2+} via amine groups into nickel solution containing a reducing agent. The whole process can be summarized as follows: The Pd^{2+} are first reduced to Pd metal, which become catalytic nuclei for the subsequent reduction of nickel cation to Ni metal. This metallic Ni, in turn, catalyze further reduction of nickel cations from the solution. This results in continued deposition of Ni on the substrate via catalytic action of the deposit itself to form a continuous film. The mechanism of electroless nickel plating in presence of dimethylamine borane reducing agent can be found elsewhere, and therefore it is not repeated here. In our case, it is important to note that initiation of electroless nickel plating on the surface can be evidenced through the local hydrogen evolution. Such a selective initiation is obviously attributed to the catalytic palladium nuclei. In fact, it has been reported thatthe electroless plating is characterized by the selective reduction of metal ions only at the surface of catalytic substrate immersed into an aqueous

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solution of the said metal ions. After the immersion into the electroless nickel solution at 65 ◦C for 7 min, a nickel film entirely covers the palladium complexes functionalized plexiglass substrate (Figure 4).

Figure 4: Nickel plating on logo by Plexiglass; (a) before plating; (b, c) after plating

Figure 5 shows the SEM and AFM images recorded on the top of the pristine Plexiglass (a, b) and electrolessly plated surface (c, d), respectively. As expected, the roughness on the plated surface is relatively high as compared to that of the pristine Plexiglass, however the SEM image (c) clearly indicate that the plated film is compact, continuous and without any pinholes within the film. Indeed, the nanoscale AFM images also point out that the plated surface is completely covered by a metallic film and the morphology of that metallic film is relatively homogeneous. The SEM and AFM images were also recorded at various other locations on the substrates and presented very similar surface morphologies.

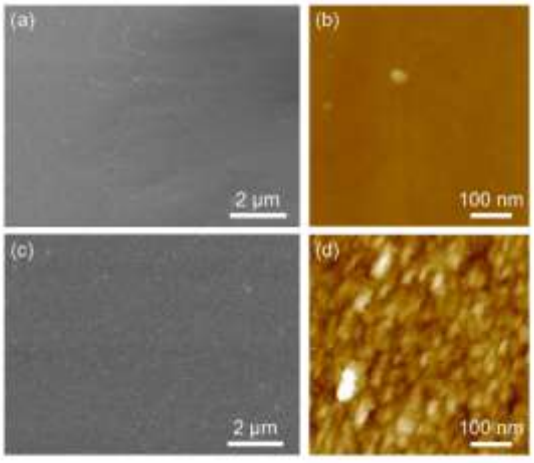

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Figure 5. SEM and AFM images recorded at the surface of Plexiglass before (a, b) and after the (c, d) electroless plating of nickel, respectively.

Figure6 shows various stages of the scribe tape test for the evaluation of film adhesion. The adhesion is considered to be adequate when a level 5B is attained on the ASTM D3359-09 standard, i.e. when 0% area of coating is pulled off by the tape when it is removed. As clearly seen in Figure. 6, the film did not peel off at any area over the grid and the film adhesion attains a level of 5B. It has been observed in the literature.

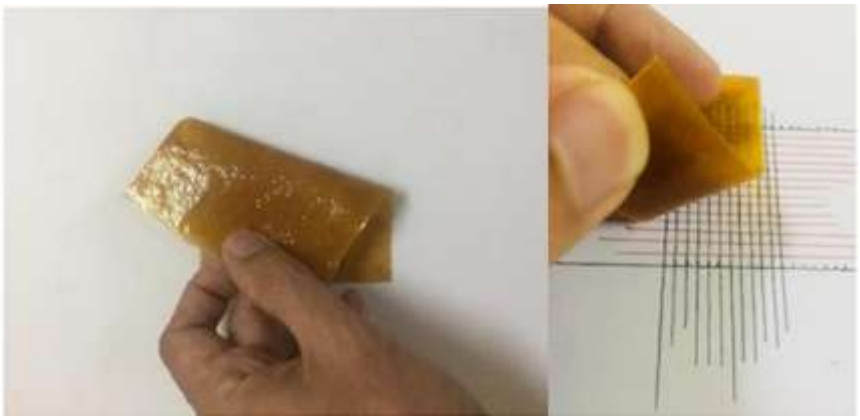

FIGURE 6.ADHESION TEST

CONCLUSION

In this work, we have reported a cost-effective and completely aqueous chemical route for the metallization of Plexiglass, which is among the most widely used polymers. First, we grafted vinylpyridine seed layer onto Plexiglas® through a simple one-step diazonium-based chemical process without requiring any surface pretreatment. This seed layer does not only strongly adhere to the polymer substrate by considering the versatility of diazonium chemistry, but also assists with the chemisorption of palladium activators on the functionalized Plexiglass surface, by taking advantage of the high affinity of the vinylpyridine towards palladium complexes. These surface conditions are ideal for depositing electroless Ni-B film on our structured Plexiglass substrate with an excellent film adhesion. This simple metallization strategy can be extended to other polymers. This robust method appears to be a promising alternative for the fabrication of microelectro-mechanical systems, as recent developments in MEMS processes provide an optimistic outlook for a shift of the deposition/ mask/etch paradigm towards polymeric structural materials, such as PMMA, HSQ, SU-8 and KMPR, by exploiting their useful properties (low-cost and significantly easy processing procedures).

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