

An AFM Study on Polymers Electrodeposited on Active Metals with Different Counter Electrodes

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Abstract— Electrodeposition of polypyrrole was carried out on aluminum coated silicon substrates using various counter electrodes in the galvanostatic mode. It was found that the counter electrode plays a vital role along with the working electrode in the electrodeposition of polypyrrole. The electrodeposited films were studied under Atomic Force Microscope in contact mode. There were significant differences in the morphology of the PPy/TBACF₃SO₃ films electrodeposited using different counter electrode material. The counter electrodes used were Ti, stainless steel, Ni, Pt and Au. This study reveals that Pt counter electrode gives very uniform and well grown PPy films while stainless steel is the best cost effective choice when a low grown but uniform film is needed.

Index Terms—AFM study, conducting polymer, active metals, counter electrode, film morphology, surface morphology

I. INTRODUCTION

SINCE the conducting polymers were first reported in the late seventies[1], there is a lot of interest in these materials for various applications such as senso, actuators[2], batteries, and biomedical applications[3]. The most studied conducting polymers include polyacetylene, polyaniline, polythiophene, and polypyrrole(PPy). Due to easy synthesis, environmental stability and wide range of pH stability, polypyrrole has become one of the most widely studied among all the above mentioned conducting polymers. Therefore, this has been the material of choice for various sensors and actuators. Polypyrrole can be synthesized chemically as well as electrochemically. Electrochemical synthesis of polypyrrole has been done on various substrate materials like titanium, iron, steel, aluminum[4], and gold[5]. Though there are studies on synthesis of polypyrrole on different working electrodes[6], there are hardly any studies on the effect of various counter electrodes on the electrodeposition process.

It was observed some major morphological differences in films when deposited with different counter electrodes for a long time(4 hours) while keeping all the other parameters including the working electrode material unchanged. This observation ignited the need of carrying out a study on the

effect of counter electrode material on film morphology and this study revealed that the choice of counter electrode with respect to the working electrode is very important for the electrodeposition process. For this study, a metal in the upper side of the electrochemical activity series (an active metal) has been chosen as the working electrode and different metals below it in the same series were chosen as counter electrodes to analyze the morphological changes of films. Therefore, in this study electrodeposition of polypyrrole(PPy) was carried out on aluminum coated silicon wafer using Tetra-n-Butylammonium Trifluoromethanesulfonic acid (TBACF₃SO₃) as dopant and methyl benzoate as solvent with Ti, stainless steel(SS), Ni, Pt and Au as counter electrodes in galvanostatic mode. The morphologies of the synthesized PPy/TBACF₃SO₃ films were studied using atomic force microscopic(AFM) technique in contact mode.

II. ELECTRODEPOSITION OF POLYMERS

Polymer formation on metals can be performed in different methods such as electrodeposition, spin-coating and casting. Though, spin-coating is good for making thin uniform films and casting is very good for making thick films, they both are suitable only for small size and simple shape samples. When the sample size become larger and complicated in shape, it is common in industrial environments to use electrodeposition as an alternative method. There are many reports in the literature on electrodeposition of polymers as a protective coating on active metals[7,10]. In many of them the contribution of polymer, doping substance or electrolyte has been analyzed. Moreover, in many cases it is conventional to use noble metals as counter electrode. Despite the fact that this setup provides good results in small samples, it is obvious that the use of large noble metal counter electrodes is uneconomical in large scale industrial production systems. Thus a suitable metal as counter electrode has to be chosen from non-noble metals. Keeping this objective in mind, it was decided to carry out a study on the effect of counter electrode on the quality of polymer film deposited on active metals.

As mentioned in the introduction, it has noticed the open side surface morphology of synthesized free standing films vary with the counter electrode material for long time depositions. Therefore, the film formation from the early stage

of deposition should be investigated to make a decision on the influence of counter electrode on the film quality. To fulfill this target, it was decided to carry out an Atomic Force Microscope (AFM) study on the very early stage of film formation. The solvent used for electrodepositon has to be carefully chosen because the literature reveals that a thin layer of working electrode may dissolve and covers the electrode before the polymerization takes place.

PPy films synthesized in organic solvents studied by Bazzauri et al.[11] report that homogenous films can be produced by pre chemical treatment of working electrode with aqueous sodium solution. Different techniques such as composite metal working electrodes and catalysts have also been tested by various researches in the past to improve the film quality[12]. Aqueous solutions of polymers are also used to synthesize polymer coatings on metal substrates. However in the case of active metals, the initial oxide layer formation with aqueous solutions is a problem for the adhesion between the electrode and the film. There are mixed results on the aqueous solutions based film quality. However, the adhesion between the polymer and the substrate has been greatly improved by using chemically oxidized titanium substrates[13].

PPy coating on active metals have been investigated into a great depth by Schirmeisen and Beck and according to them the solvent and salt for polymerization has to be carefully chosen. Especially in this experiment the PPy film is going to be investigated under AFM, only a few nanometers thick layer is going to be formed. If the solvent dissolved the active metal working electrode, the PPy film layer will be washed away during preparation process.

Aqueous solutions of pyrrole monomer have been used in many previous studies[14,15] and it is popular due to easiness and low cost of preparation. However, Schirmeisen and Beck stated that PPy polymerization from aqueous solvents through electrodeposition process is in trouble if the substrate dissolves simultaneously at the beginning of polymerization process. To avoid this it is a common practice to pre-treat the working electrode by electro-polishing or forming a very thin porous oxide layer on the working electrode. Unfortunately it is not possible to use these techniques in this study as the very initial stage of film formation is going to be investigated and the surface modifications of working electrode will affect the film morphology. Therefore non-aqueous solvents became more appealing for this study. Acetonitrile, methanol, Benzene solution diethyl ether and are the commonly used organic solvents for PPy electrodeposition[11]. However, Prejza et. al. reports that PPy electrodeposition in acetonitrile on a thin aluminum layer (2000-3000Å) coated on a silicon substrate was not possible as the aluminum layer was dissolved before the polymerization takes place. Since it was planned to go for a further thin (300 Å) aluminum layer in this experiment to avoid the substrate roughness come into play, acetonitrile was not a suitable organic solvent. With previous experience in PPy electrodeposition[14,15], it was decided to go for methyl benzoate as the organic solvent for this study.

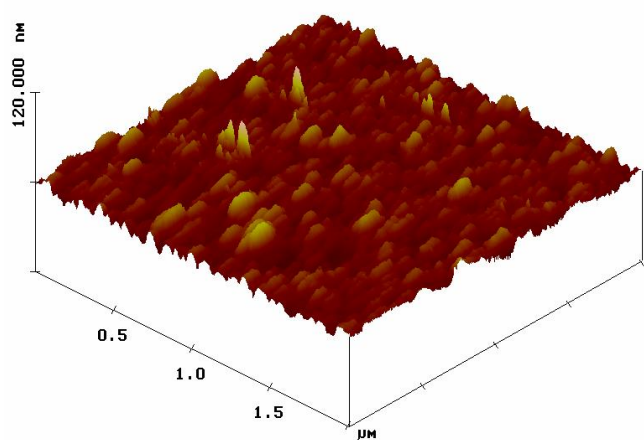
In this study, it was expected that the use of methyl benzoate as solvent will minimize the initial oxidation on working electrode since the film needed for AFM analysis is extremely thin. Otherwise any oxide film formed at the initial stage would affect the initial polymer layer to a great extent and would affect the examined film morphology.

There are many studies on polymer synthesis on active metals[16-20] and it reveals that Aluminum is a good substrate for growing polymers. Therefore, in this study aluminum was used as the active metal working electrode. These aluminum substrates were prepared by thermally depositing aluminum on silicon substrates under high vacuum to obtain a smooth deposition surface.

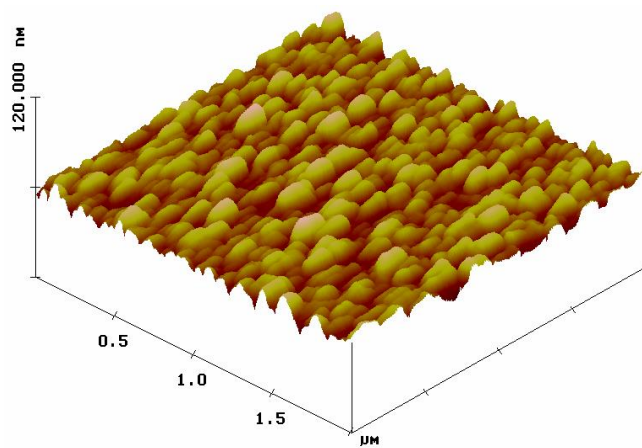
III. EXPERIMENTAL

The working electrode used was aluminum coated silicon wafer and this aluminum was coated using thermal evaporation technique under high vacuum. These silicon substrates were sonic cleaned with ethanol and acetone respectively. The deposited aluminum film thickness measured with ULVAC CRTM-1000 quartz crystal microbalance system was 300Å. This aluminum vapor deposition was carried out at 4.9×10^{-6} Torr at a deposition rate of 1Å/second. This low deposition rate ensures a very smooth layer of aluminum on the silicon substrate. The area of the working electrode used was 0.5cm². Pyrrole monomer was obtained from Wako chemical company (Japan) and TBACF₃SO₃ was purchased from Tokyo Chemical Industries (TCI). All the chemicals used in this experiment were of analytical grade. Freshly distilled pyrrole monomer was dissolved in methyl benzoate to make a 0.2M pyrrole monomer solution. Required weight of TBACF₃SO₃ was then dissolved in the same solvent to have 0.2M TBACF₃SO₃ solution in methyl benzoate. The solution was mixed well using a magnetic stirrer at 25 °C for a long time in a dark environment while the vessel carrying the solution was closed air tight to avoid degradation due to light and oxidation. The aluminum coated silicon substrates were used as working electrode in all experiments. Electrochemical deposition of polypyrrole was done by Hokuto Denko electrochemical synthesis/measurement system (model HA 151) in galvanostatic mode using a current density of 0.2mA/cm² for 1 minute. Deposition was carried out on Al working electrodes with titanium, stainless steel (SS), nickel, platinum, and gold as counter electrodes separately. The deposited PPy films were taken out from the solution immediately after the deposition and held vertical while the bottom edge was touching on a blotting paper to remove excessive liquid from the sample. Then the sample was dried in open air at 25°C before AFM imaging. Atomic force microscope model Nanoscope IIIa (from Digital Instruments Inc. USA) was used to study PPy/TBACF₃SO₃ films. The AFM was used in contact mode for all the imaging trials.

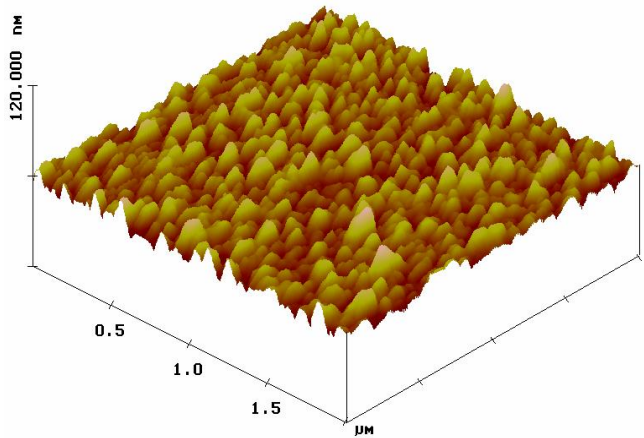
IV. RESULTS AND DISCUSSION



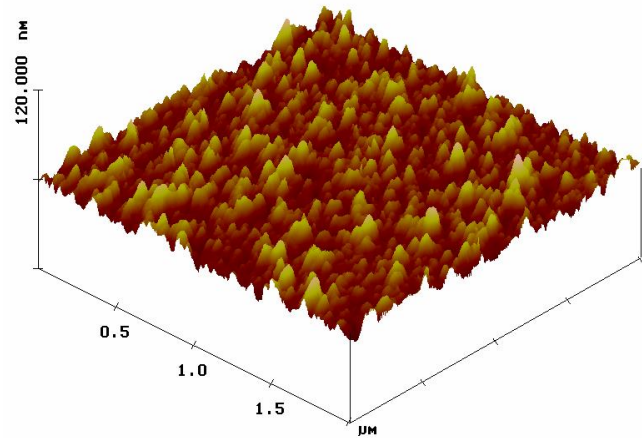
(a)



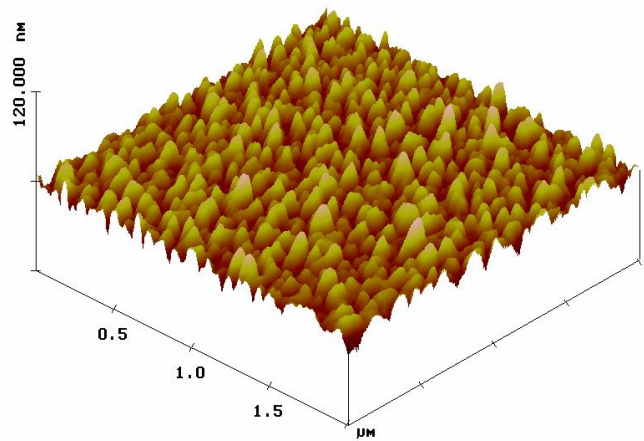
(b)



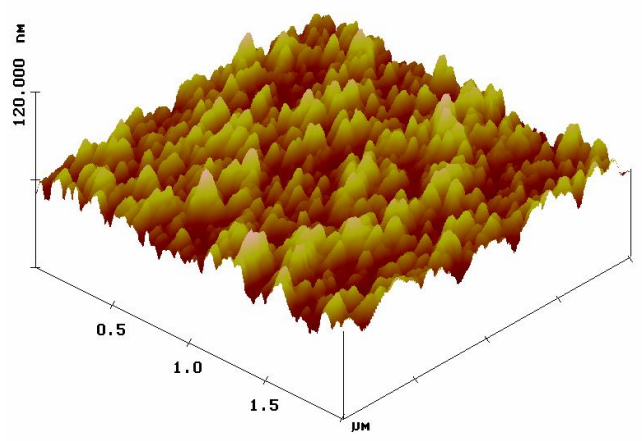
(c)



(d)



(e)



(f)

Fig.1 AFM images of films deposited on Al working electrode with different counter electrodes. (a) Blank Al Electrode. Films deposited with (b) Ti Counter Electrode, (c) Stainless Steel Counter Electrode, (d) Ni Counter Electrode, (e) Pt Counter Electrode, (f) Au Counter Electrode

The electrodeposited PPy/TBACF₃SO₃ films on aluminum coated silicon wafer with different counter electrodes were studied using AFM in contact mode. AFM images in Fig.1(a) through Fig.1(f) show the morphological changes observed in each case. Fig.1(a) depicts the AFM image of the bare aluminum coated silicon substrate and will serve as the reference. Remaining figures show the morphology of PPy/TBACF₃SO₃ synthesized using different counter electrodes. Bare aluminum surface in Fig.1(a) shows a morphology of closely packed lumps of aluminum deposited on the silicon surface. The 300Å layer of aluminum deposited looks fairly enough to cover the silicon substrate surface as there are no visible pores or uncovered areas in this image. Further, the surface morphology visible from the bare aluminum surface has almost planar surface. As it can be seen from the Fig.1(b), there is only a little growth of the PPy film observed in case of Ti counter electrode. However the formed film has large areas (approximately 0.1 ~ 0.5µm) of polymer growths with the lowest roughness among all imaged films and that contributes to the smoothness of the film. In contrast, stainless steel produced a little better growth of PPy but the surface morphology reveals that it has a high number of very small polymer mountains, significantly contributing to the roughness as observed in Fig.1(c). However the distribution of these PPy islands is fairly uniform and the standard deviation of heights is lower compared to most of the other films. The uniformity of the film with stainless steel counter electrode is comparable to the film produced by titanium counter electrode as the calculated film roughness are 3.543nm and 3.564nm for Titanium and stainless steel respectively.

The growth of the PPy films starts to occur better with nickel counter electrode as it can be seen in Fig.1(d) in comparison to the Fig.1 (b) and (c). In this case the uniformity is little lesser compared to film grown with stainless steel counter electrode. This is evidenced by the film roughness value of 3.962nm calculated from the AFM image Fig.1 (d). Platinum and gold counter electrodes led to the formation of much better grown PPy films than titanium, stainless steel and nickel counter electrodes. This was clearly seen in the PPy AFM images in Fig.1(e) and Fig.1(f) for platinum and gold respectively. Though gold resulted in a PPy film with a very high growth, it was not uniform compared to the film grown with platinum as observed in the AFM images. In comparison, platinum resulted in a highly uniform PPy film with little lesser growth than to the film grown with gold counter electrode.

By comparing AFM images for all films deposited with different counter electrodes, it was observed that there is a relationship between the choice of the counter electrode and the working electrode used for the electrodeposition. In this study, I used aluminum coated silicon wafer as the working electrode and titanium, stainless steel, nickel, platinum and gold as counter electrodes which are below aluminum in the electrochemical activity series. On the other hand, ease of oxidation decreases from titanium to gold with reference to aluminum. Hence, the choice of counter electrode depends on the standard reduction potential of the metal used for the

counter electrode with reference to the working electrode. Generally, noble metals such as platinum and gold are preferred materials to act as counter electrodes since they are well below all the other metals in the electrochemical series. This was indeed the case for the electrodeposited PPy films when platinum or gold were used as counter electrodes against aluminum working electrode.

Fig 1(b) shows that the film thickness as well as the surface roughness of a polymer electrodeposited with titanium counter electrode is lower compared to the film electrodeposited with a gold electrode shown in Fig.1(f). This counter electrode is good for applications need low film thickness and high evenness in the films. Fig 1 (c), (d), (e) and (f) show the film thickness as well as the roughness grows from stainless steel to nickel, platinum and gold in that order. This is matching with the electrochemical potential differences between individual counter electrode material and the working electrode material, in this experiment, aluminum.

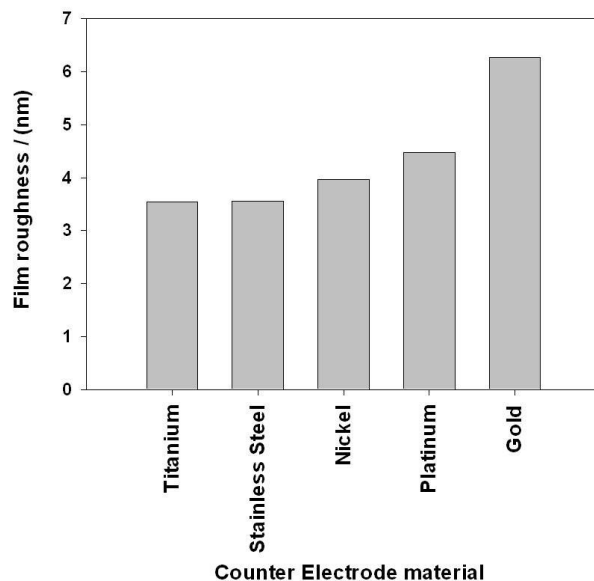


Fig.2. The RMS roughness values calculated from AFM images.

This result was also supported by the calculated RMS roughness values for the AFM images of the PPy films for different counter electrodes. The calculated RMS roughness values increases from titanium to gold as reported in Fig. 2. The trend observed was similar to that in the electrochemical series. The RMS roughness of bare aluminum electrode was 3.008 nm.

The polypyrrole film deposited under a constant current happens in a series of steps. The initial layer starts to grow on the aluminum surface in an arbitrary pattern, but the electrode potentials at both the electrodes play a greater role there. The rate of growth of arbitrary polypyrrole seed modules greatly depends on the relative potential difference in the electrochemical series between the chosen two metals for working and counter electrodes. Further, this potential

difference governs the number of seed modules start at the beginning. Therefore the outward growth of polypyrrole seeds and the spacial distribution both depends on the selected letal as counter electrode. However, the experiments carried out in this study reveals that the growth rate and the spatial distribution are not propotional to each other.

V.CONCLUSIONS

In the above study, I have experimentally investigated the effect of various counter electrodes on the electrodeposition of PPy films using titanium, stainless steel, nickel, platinum and gold against aluminum coated silicon wafer as working electrode. The study revealed that the choice of counter electrode has a significant effect on the electrodeposition process. Generally, gold and platinum electrodes are believed to be the best counter electrodes when a fast growing film is concerned, but this study revealed that a metal somewhat bellow the working electrode in the electrochemical series would result a fair growth and evenness when platinum or gold is not an economical option. Therefore, when the deposition surface is large, stainless steel can serve as a good counter electrode if the film thickness can be sacrificed for the uniformity. Therefore I recommend stainless steel counter electrodes for large scale polypyrrole electro-deposition applications. I finally conclude that the film surface morphology is highly governed by the relative places of working and counter electrodes in the electrochemical series.

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