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Thickness Characteristics and Improved Surface Adhesion of a Polypyrrole Actuator by Analysis of Polymerization Process

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Characterizing electrochemical polymerization of polypyrrole film on a substrate depends on many parameters. Among them, potential difference and cumulative charges play important role. The level of potential difference affects the quality of the polypyrrole. On the contrary, cumulative charge affects the thickness of the polypyrrole. The substrate surface is adjusted physically and chemically by treating with sandblasting and the addition of thiol for surface adhesion improvement. Experimental results show that the sandblasted and thiol treated substrate provides better adhesion than non-sandblasted and non-thiol treated substrate.

Key Words: Polypyrrole, Actuator, Thiol, Electroactive Polymer, Surface Adhesion

1. Introduction

Recently low voltage actuated electro-active polymer actuator becomes attractive to many scientists and researchers for various applications due to its softness, lightness, flexibility and biocompatibility compared to other actuators such as piezoelectric, electro active ceramic (EAC) and shape memory alloy (SMA). An actuator like SMA can produce large force and long elongation (Seunghak et al., 2003). However, SMA consumes relatively large electric power. On the contrary, the electro-active polymer actuator requires and consumes relatively low voltage and electric power, and produces fairly large bending motion compared to EAC and SMA actuators. In addition, the electro-active polymer actuator can be actuated in a wet condition or even in water. Among the electro-active polymer actuators, ionic polymer metal composite (IPMC) and polypyrrole based actuators show reliable actuation and consume reasonable energy for actuation. Previously, various applications using the IPMC actuator such as a micro catheter (Shuxiang et al., 1996) and a micropump (Shuxiang et al., 1999) were realized. Compared to an IPMC based actuator, a polypyrrole based actuator is even more attractive than IPMC based actuator due to easy integration with micro fabrication and process on a silicon wafer. Among the conductive polymers, polypyrrole is one with ease of polymerization by electrochemical method

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and biocompatible material. Polypyrrole based devices were investigated by many researchers. Edwin et al.(2000) proposed and fabricated an attractive application using polypyrrole based actuators integrated with MEMS such as micro-fingers. The 2-degree-of-freedom walking robot (Edwin et al., 2000) movable in aqueous solution and automatic-foldable box (Edwin et al., 2001) are also proposed and fabricated with polypyrrole. In addition, microvial and microvalve using polypyrrole actuator were also fabricated (Edwin et al., 1999a ; 1999b ; 2002). However, unlike other polymer based actuators such as IPMC and electrostrictive polymer (EP), the characteristic of a polypyrrole actuator depends on various growth parameters such as polymerization temperature, applied potential difference, and solvent (Diaz and Bargon, 1986), which later affect the conductivity, surface morphology, mechanical strength, and uniformity of film (Wallace et al., 2002).

The surface quality of polypyrrole relies on potential difference during polymerization. In fact, the film growth is faster at high voltage than at low voltage. However, the thickness profile becomes non-uniform (Elisabeth, 1999). In electrochemical polymerization, its edge area was deposited more than the center area (Elisabeth and Nikolaj, 1999). As well as its thickness variance, the adhesion between a substrate and polypyrrole film plays an important role in fabricating the polymer-based actuator integrated with MEMS based process. In this paper, we investigate the characteristics and surface morphology of polypyrrole focusing on its thickness related with operation and reliability of polypyrrole based actuators. In addition, we propose the simple process and method to improve the adhesion between polypyrrole and a substrate.

2. Experimental

2.1 Electrochemical polymerization of polypyrrole

In electrolytic solution, the polypyrrole interacts with ions in the solution in accordance with applied voltage. As a result of that, the volume of polypyrrole changes with entrance and exit of ions. Polypyrrole is easily applied with micro fabrication technique because of convenience of electrochemical polymerization in a small area on Au and Pt. The chemical structure of polypyrrole is shown in Fig. 1. Polypyrrole has positive charge as doping of dopant A- and this makes whole structure neutral. The positively charged polypyrrole is called "polaron" which acts as P-type semiconductor. Polypyrrole could have higher electric conductivity as the polymerization temperature increases. Since electrons move on the polymer chain, the direction of the polymer chain plays important roles on mobility of electrons (Youn, 1996).

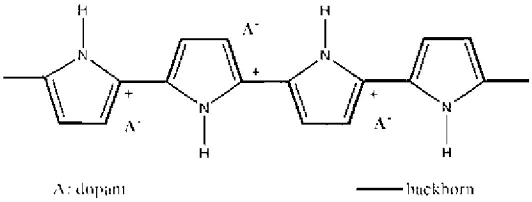


Fig. 1 Structure of polypyrrole molecule

Cr and Au deposited wafers by an e-beam evaporator with 300 Å and 2000 Å respectively is used as a working electrode, and as a reference electrode, Ag/AgCl with porous ceramic (Aldrich) is used. The 20 by 20 cm of stainless steel plate is used for counter electrode. 0.1 M of pyrrole monomer and 0.1 M of NaDBS is used for the

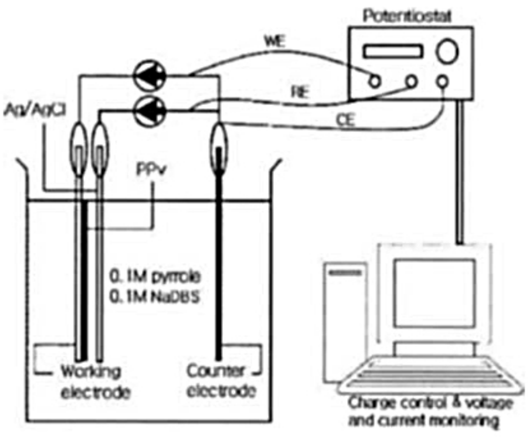


Fig. 2 Schematic of polypyrrole electrochemical polymerization system

electrolyte solution. In the experiment, three electrodes system is used and the potentiostatic (Advanced Micromachining Tools) is used for electrochemical composition of polypyrrole. The whole electrochemical composition system is mainly composed of a potentiostatic and a computerized data acquisition system. The working and counter electrodes are connected directly to the computer and the corresponding voltage and accumulation charges are measured and recorded. LabView (National Instrument) is used to acquire data from potentiostatic. Mainly the voltage and cumulative charges between working and counter electrodes are observed and recorded by LabView. During the polypyrrole growing process, constant voltages are applied to the substrates rather than constant currents. Fig. 2 shows schematic view of the experiment and measurement system for amount of charges.

2.2 Thickness characteristics of polypyrrole actuator

A Cr and Au deposited silicon wafer were used as a seed layer in the experiment. The seed layers were patterned with four different sizes of rectangles. The solution with 0.1 M of DBS with distilled polypyrrole (DI water : 500 ml, DBS : 19.4 g, pyrrole : 5 ml) was prepared. To find out the relationship among charge (Q), voltage (V), and thickness, the following experiments were performed. First, to understand the relationship between the thickness and amount of charge, various amounts of charges were applied to the seed layer at different voltages. Secondly, applied voltages were varied according to the different amount of charges to understand the relationship between the thickness and potential difference. In all cases, the potential difference means the potential difference between reference and counter electrodes. Under the constant voltage, the cumulative charges of 8, 16, 24, and 32 mC were applied to seed layers and corresponding thicknesses were measured with thickness profiler meter. Under the constant cumulative charges, the effect of the voltage variation was observed as well. Finally, to verify repeatability of the thickness of the polypyrrole film on a seed layer, the cumulative charge was applied to the designated areas with different sizes of 4, 8, 12, 16, 20 and 24 mm^2 and the corresponding cumulative charges of 4, 8, 12, 16, 20 and 24 mC were applied to make the charge per area of all samples become 1 $\mathrm{mC/mm}^2$.

2.3 Measurements of adhesion

The adhesion force between polypyrrole and a seed layer depends on many parameters during the electrochemical composition of polypyrrole such as processing voltage, charge, and time, surface quality of the substrate, and concentration of NaDBS solution. Among these parameters, we are interested in voltage and amount of charges with respect to the surface quality of polypyrrole layers on seed layers. To increase its surface adhesion during electrochemical composition of polypyrrole film on a seed layer, two additional procedures were added chemically or physically. Chemically, a well known additive chemical, thiol that is diluted with DI water 100 times is added to the seed layer right before the electrochemical polymerization of polypyrrole. To change the surface condition of seed layers physically, surface roughening by sandblasting process is used on the surface of the wafer to provide coarse surface condition. Totally, we prepare total of 4 different samples. They are non-sandblasted wafer without thiol treatment, non-sandblasted with thiol treatment, sandblasted wafer without thiol treatment, and sandblasted wafer with thiol treatment. The applying voltage of 0.6, 0.8, and 1.0 V are applied in accordance with the charge variation of 8, 16, 24, and 32 mC in each voltage step. The actual stripping-off force was measured with force sensor and various adhesive plastic

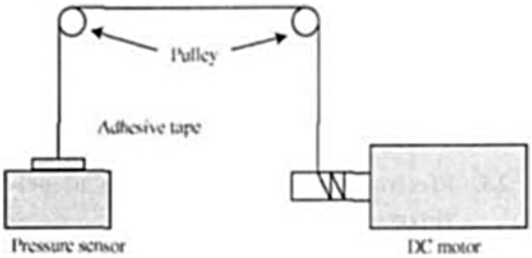


Fig. 3 Measurement of stripping-off force with pressure sensor

tapes. The schematic of stripping-off force measurement system is provided below in Fig. 3. To perform measurement of actual stripping-off force of the adhesive tapes, a DC motor was used to pull the adhesive tapes off from the force sensor. This generates pressure in the force sensor. The angular speed of the motor was set to 16 RPM. Three different models of tapes were used to generate different forces. The actual range of the adhesive force varies from 100 gf to 400 gf.

3. Results and Discussion

3.1 Thickness and accumulated charge relaionship

As shown in Fig. 4, as the cumulative charge increases from 8 mC to 32 mC with the increment of 8 mC, the thickness of the polypyrrole on the seed layers of 8 mm^2 increases proportionally regardless of the applied potential differences of 0.6 V, 0.8 V, and 1.0 V. As the amount of charges increases from 8 mC to 32 mC, the thickness increases from 0.5 μm to 2.3 μm. The potential difference contributes to processing time of electrochemical composition rather than the growth rate of polypyrrole film. Namely, the higher potential difference makes the faster electrochemical process of polypyrrole composition. Fig. 5 shows the relationship between the applied voltage and its thickness variation. The applied voltages of 0.6 V, 0.7 V, 0.8 V, 0.9 V, and 1.0 V are applied to the seed layers with the accumulation of charges of 8 mC and 16 mC. As shown in Fig. 5, the thickness of polypyrrole on seed layers does not vary with applied voltage. However, the thickness of polypyrrole changes with the accumulation of charges. It proves that the actual thickness does not depend on the applied voltage, which is shown in Fig. 4 previously. To test the repeatability in thickness of electrochemical composition of polypyrrole, experiments are performed with 6 different sizes of samples 4, 8, 12, 16, 20 and 24 mm^2 with 6 different accumulations of charge 4, 8, 12, 16, 20 and 24 mC. Each level of accumulation of charge is applied to the equal corresponding area respectively. Therefore, the accumulation of charge for given unit area sets to 1 mC/mm^2. Fig. 6 shows that the thickness of polypyrrole is highly influenced by amount of charge density during electrochemical polymerization regardless of potential difference. Under the constant charge density of 1 mC/mm^2, the measured thickness of polypyrrole layer is ranged from 0.6 to 0.8 μm. As the voltage increases from 0.6 V to 0.9 V, which is the voltage between references and counter electrodes, the actual voltage, between reference and working electrodes, increases with proportion as shown in Fig. 7.

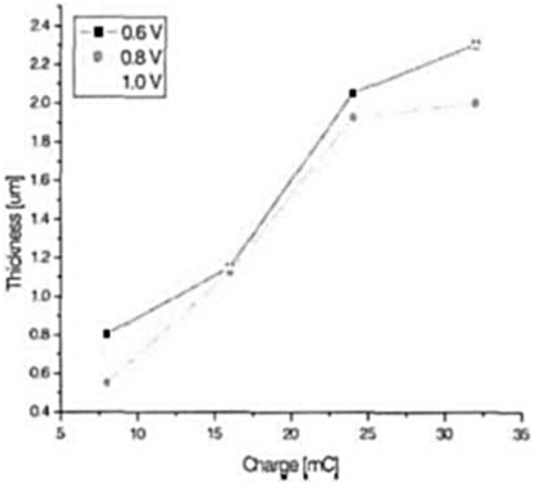


Fig. 4 Accumulated charge vs. thickness (Applied area : 8 mm^2)

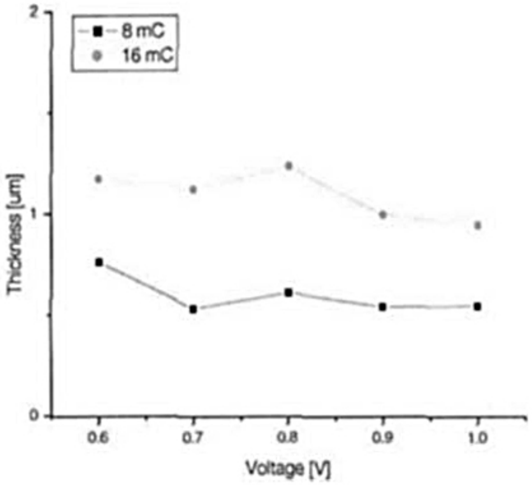


Fig. 5 Variation of voltage vs. thickness (Applied area : 8 mm^2)

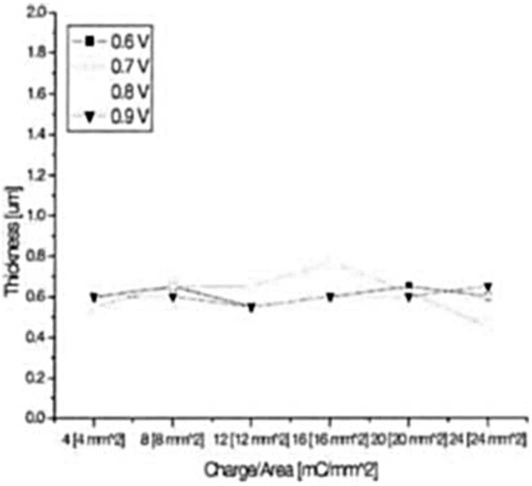


Fig. 6 Charge per unit area vs. thickness in different voltages

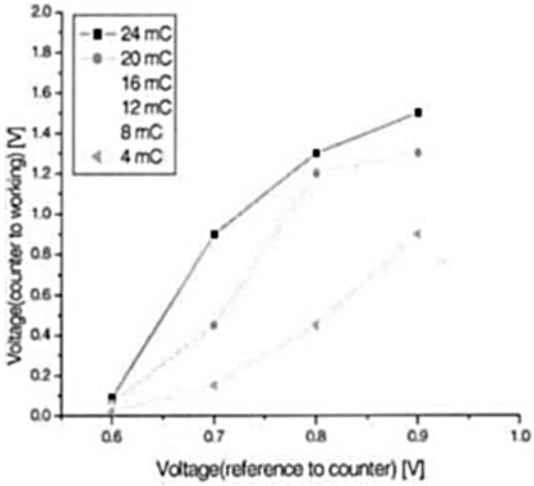


Fig. 7 Reference voltage vs. actual voltage

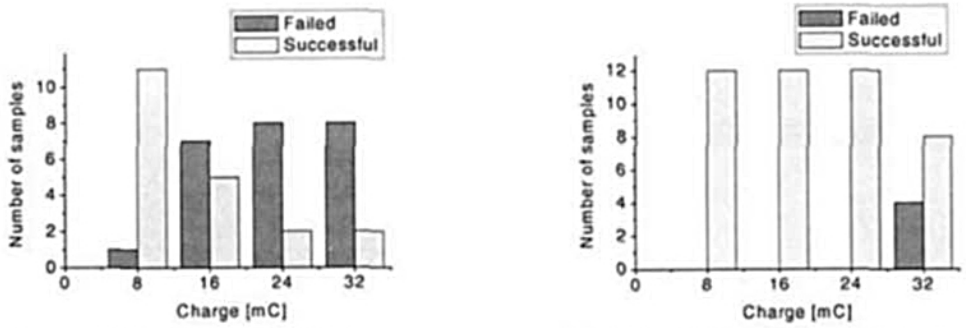
On the other hand, as the cumulative charge decreases, the actual voltage also decreases. This is because that when the reference voltage is applied to the substrate, the actual voltage takes little time to reach its steady state.

Table 1 The force and pressure measured using DC motor and pressure sensor

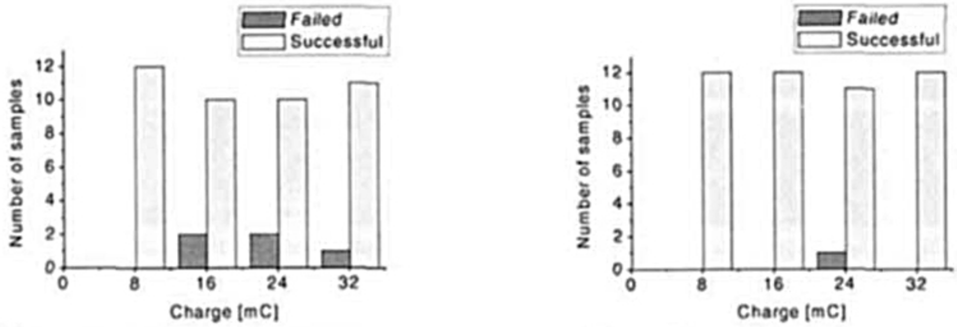
	Force 1	Force 2	Force 3	Force 4
Max force [gf]	100	150	250	400
Area [mm^2]	19.6	19.6	19.6	19.6
Pressure [gf/mm^2]	5.1	7.6	12.7	20.4

3.2 Surface adhesion of the polypyrrole film on different seed layers

The results of stripping-off tests on various substrates are provided below. The tests are processed based on how many polypyrrole films successfully endure from stripping-off test. The Fig. 8 shows the relationship between amount of charges and stripping-off tests. The Fig. 9 is relationship between applied voltage and stripping-off tests. There were totally 48 samples for each case and all samples were tested with respect to the corresponding pressure previously categorized in Table 1. As seen in Fig. 8(a), as the amount of charge increased, the polypyrrole films were more frequently peeled off from seed layers. Only 24 samples out of 48 samples succeeded in the stripping-off test under the condition without sandblasting and thiol treatment. However, as the surface of the substrate was treated with thiol, then the success ratio against failure dramatically increased. Totally, the successes of 44 samples out of 48 samples were achieved, increasing success ratio from 50% to 92% approximately. As well, the success ratio of sandblasting of substrates increases from 50% to 90%. In addition, the results show that the combination of sandblasting and thiol treatment makes success ratio increase to 98%. By using physical and chemical methods, the available surface area for polypyrrole to be coated on seed layers increases. The surface is roughened and expands attachable area for polypyrrole comparing to non-sandblasting seed layers by sandblasting. Similarly, applying thiol to seed layers creates s-bond and becomes self-assembled on Au layers, the process which could create strong bond between polypyrrole and seed layers by enhancing the surface adhesion. In Fig. 9(a) which was performed under without sandblasting and thiol treatment, among 48 samples, 24 samples with 0.8 V and 1.0 V were failed, but under other conditions, different results were achieved. Even though there were some failed conditions for (b), (c), and (d), these number were relatively small compared to the condition (a) and were considered as experimental errors. The images of surface morphology of polypyrrole

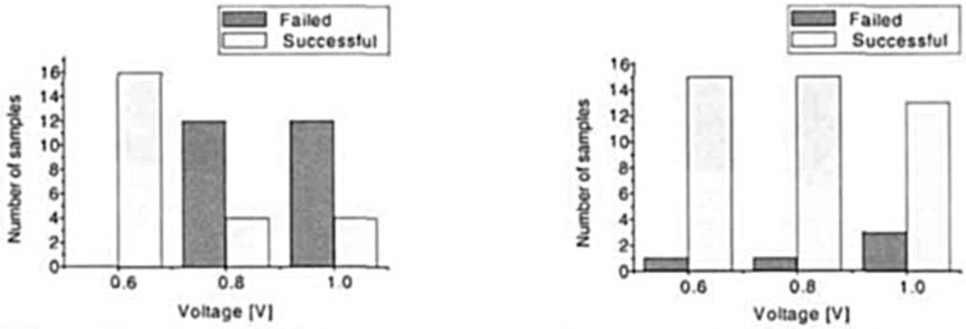


(a) Non-sandblasted without thiol treatment (b) Non-sandblasted with thiol treatment

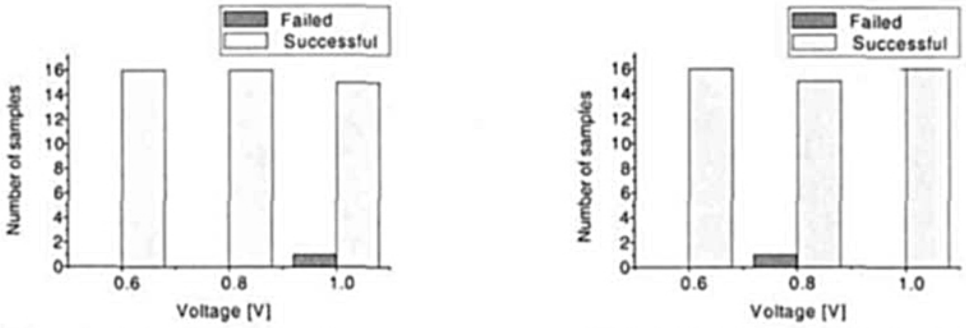


(c) Sandblasted without thiol treatment (d) Sandblasted with thiol treatment

Fig. 8 Results of adhesion tests for each case with respect of applied charges (8, 16, 24, and 32 mC)

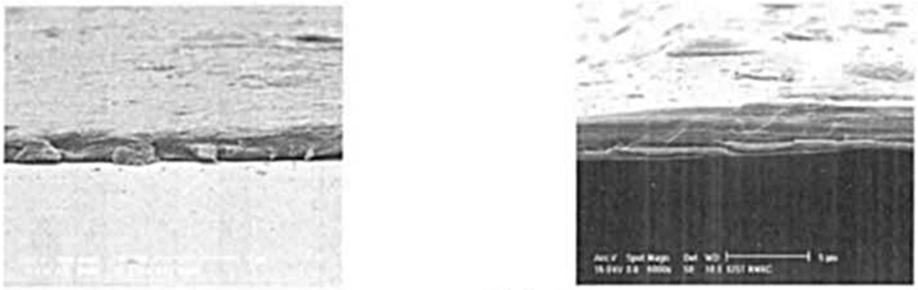


(a) Non-sandblasted without thiol treatment (b) Non-sandblasted with thiol treatment

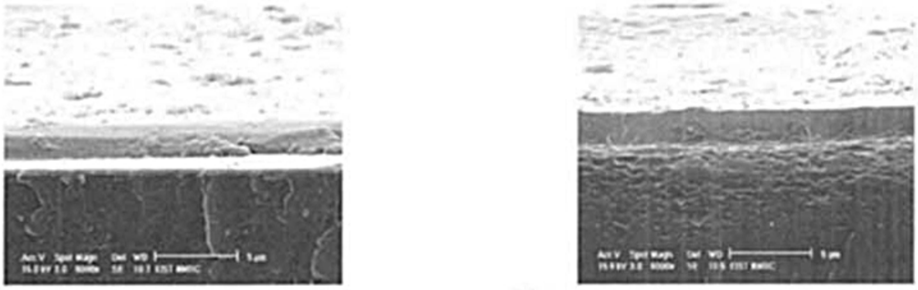


(c) Sandblasted without thiol treatment (d) Sandblasted with thiol treatment

Fig. 9 Results of adhesion tests for each case with respect of applied voltages (0.6, 0.8, and 1.0 V)

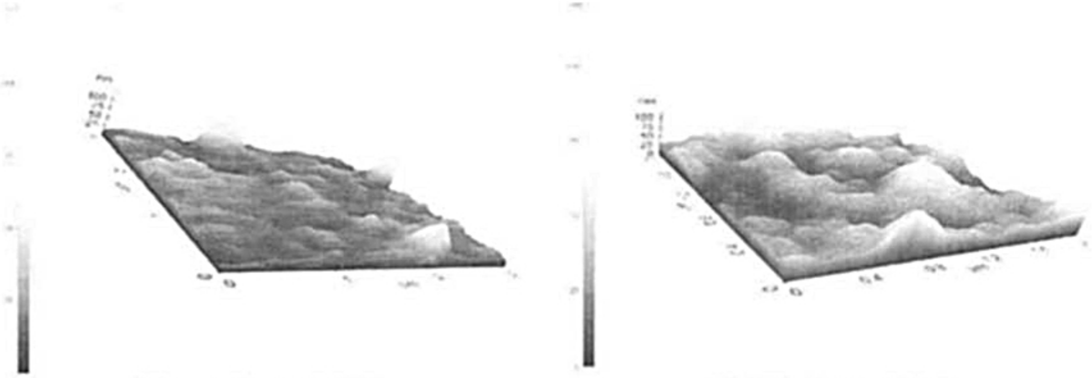


(a) Non-sandblasted seed layer without thiol treatment (b) Non-sandblasted seed layer with thiol treatment

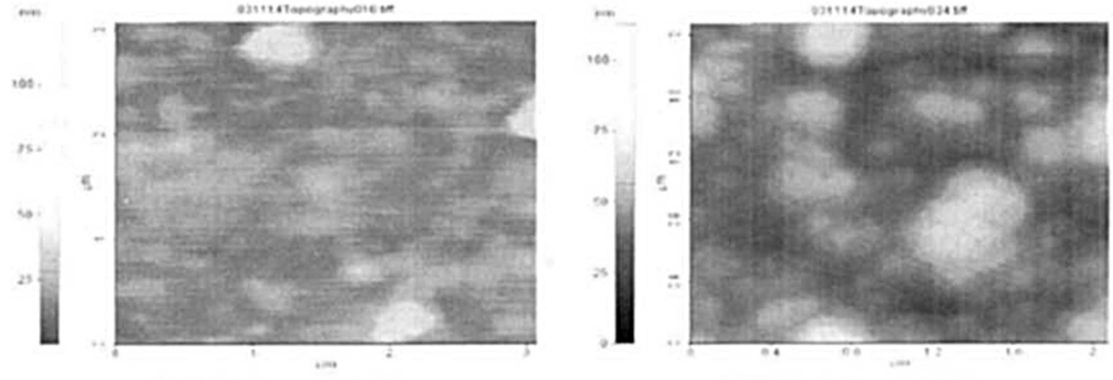


(c) Sandblasted seed layer without thiol treatment (d) Sandblasted seed layer with thiol treatment

Fig. 10 Scanning electron microscope pictures of the surface of polypyrrole



(a) 3-D picture of 0.6 V (b) 3-D picture of 1.0 V



(c) 2-D picture of 0.6 V (d) 2-D picture of 1.0 V

Fig. 11 Surface pictures taken by atomic force microscope with two different voltages film on four different substrates which are magnified to 6000x are pictured with scanning electro microscope. The samples prepared with the potential difference of 0.8 V and the charge density of 2 mC/mm^2. As seen in Fig. 10, it is observed that a sample without Thiol and sandblasting treatment shows separation between the substrate and polypyrrole film. However, other samples do not show any separation between the substrate and polypyrrole film and provide well-established contact with use of Thiol and sandblasting treatment. These results show that why thiol and sandblasting treated substrates demonstrate the better adhesion performance in stripping-off tests. Fig. 11 taken by an atomic force microscope shows the size of polypyrrole nodules. According to Fig. 11, the roughness of 0.6 V is approximately 122 nm (root mean square) and that of 1.0 V is approximately 176 nm (root mean square). Since the higher potential difference creates the larger nodule size of polypyrrole on substrates, high potential difference makes the volume of polymer chain swollen rapidly in vertical direction. Therefore, each polypyrrole nodule cannot be formed evenly which results in poor surface adhesion on substrates.

3.3 Performance tests of polypyrrole actuator

The polypyrrole based cantilever type actuator has been fabricated and tested for real performance. The charge density of 1 mC/mm^2 with the voltage of 0.6 V was applied. The combination of amount of charge per area produces the thickness less than 1 μm of polypyrrole film on seed layers according to our experiments. The samples were prepared on non-sandblasted and sandblasted wafer for performance comparison. In addition, one sample is treated with thiol and the other sample is not. The size of the actuator is 2 by 2 mm and fabricated with differential adhesion method that was proposed by E. Smela (Elisabeth, 1999), which is using poor surface adhesion between a silicon wafer and Au layer. The actuator was tested under the frequency of 0.1 Hz and the voltage of 2.0 V. We successfully operated the polypyrrole actuator on a non-sandblasted seed layer. However, we failed to move polypyrrole actuator out of the surface on a sandblasted seed layer because of its high adhesion between the surface of the seed layer and thin film of Cr. Since the whole surface of the wafer is sandblasted, not only the surface adhesion between Au and polypyrrole, but also the surface adhesion between the wafer and the thin film of Cr and Au layer increases. It seems that the polypyrrole actuator should produce more power to be able to be erected from the sandblasted surface. Therefore, with the same of thickness of polypyrrole, we are not able to successfully actuate the polypyrrole out of the surface plane. The sequential motion of a polypyrrole actuator on a seed layer is shown in Fig. 12. The non-thiol treated actuator is operated for more than 16 hours consecutively without peeling-off of polypyrrole film from the surface of the seed layer. On the contrary, the thiol treated actuator expands the consecutive operation time up to 55 hours. Thiol treatment makes the surface adhesion increase as well as it increases operating time.

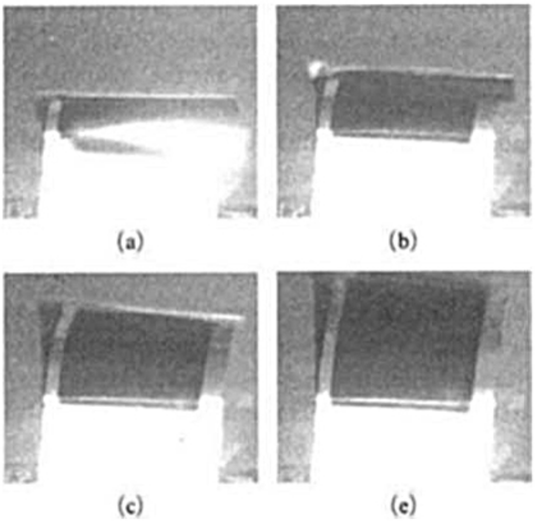


Fig. 12 Captured images of sequential motion of polypyrrole based actuator on a substrate

4. Conclusions

We are able to control the thickness of polypyrrole film in electrochemical polymerization process by adjusting the amount of charges. The thickness mostly depends on the amount of charges rather than the potential differences. By applying lower potential difference during electrochemical polymerization, the quality of the surface adhesion and operation reliability is improved. Experiments show that the surface adhesion test between polypyrrole and substrates demonstrates the significant improvement of surface adhesion in treating with thiol and sandblasting process. Thiol treatment on the surface of substrates makes improvement of adhesion as well as reliability of operation. We fabricate polypyrrole based cantilever type actuators on a silicon wafer and successfully operate them for approximately 16 hours. However, the addition of thiol expands its operating time to 55 hours with the frequency of 0.1 Hz. For the next step, we find the optimal thickness of polypyrrole producing maximum force so as to be used in an optimal polypyrrole actuator design.

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