



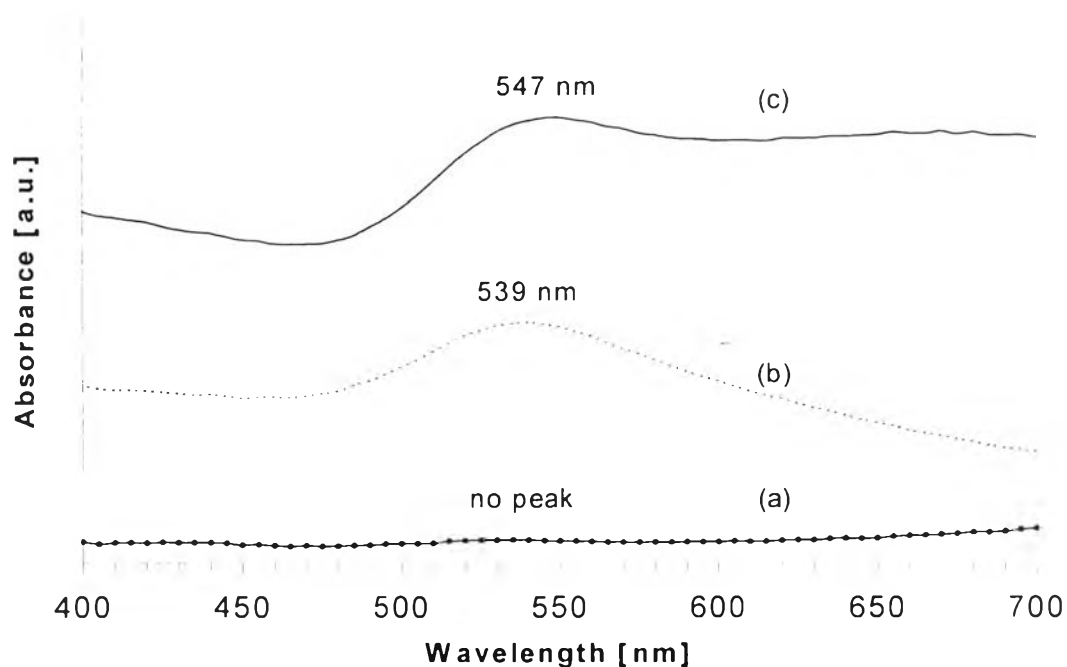
## CHAPTER IV

### RESULTS AND DISCUSSION

This chapter describes the results and discussion of experiments used in this study. This chapter is divided into two sections. Section 4.1 discusses the results for the fabrication of AuNPs thin film. This part concerns about morphology of AuNPs thin film on glass slide and polyimide surfaces, modified by various functional compounds (i.e. MPTMS, APTMS and PEI) and quality and quantity of AuNPs deposited on modified glass slide. Section 4.2 describes about the effects of various deposition conditions on the AuNPs film. The effect of the modifying agent concentration, surface modification time, AuNPs deposition time and annealing temperature are presented in section 4.2.1, 4.2.2, 4.2.3 and 4.2.4, respectively.

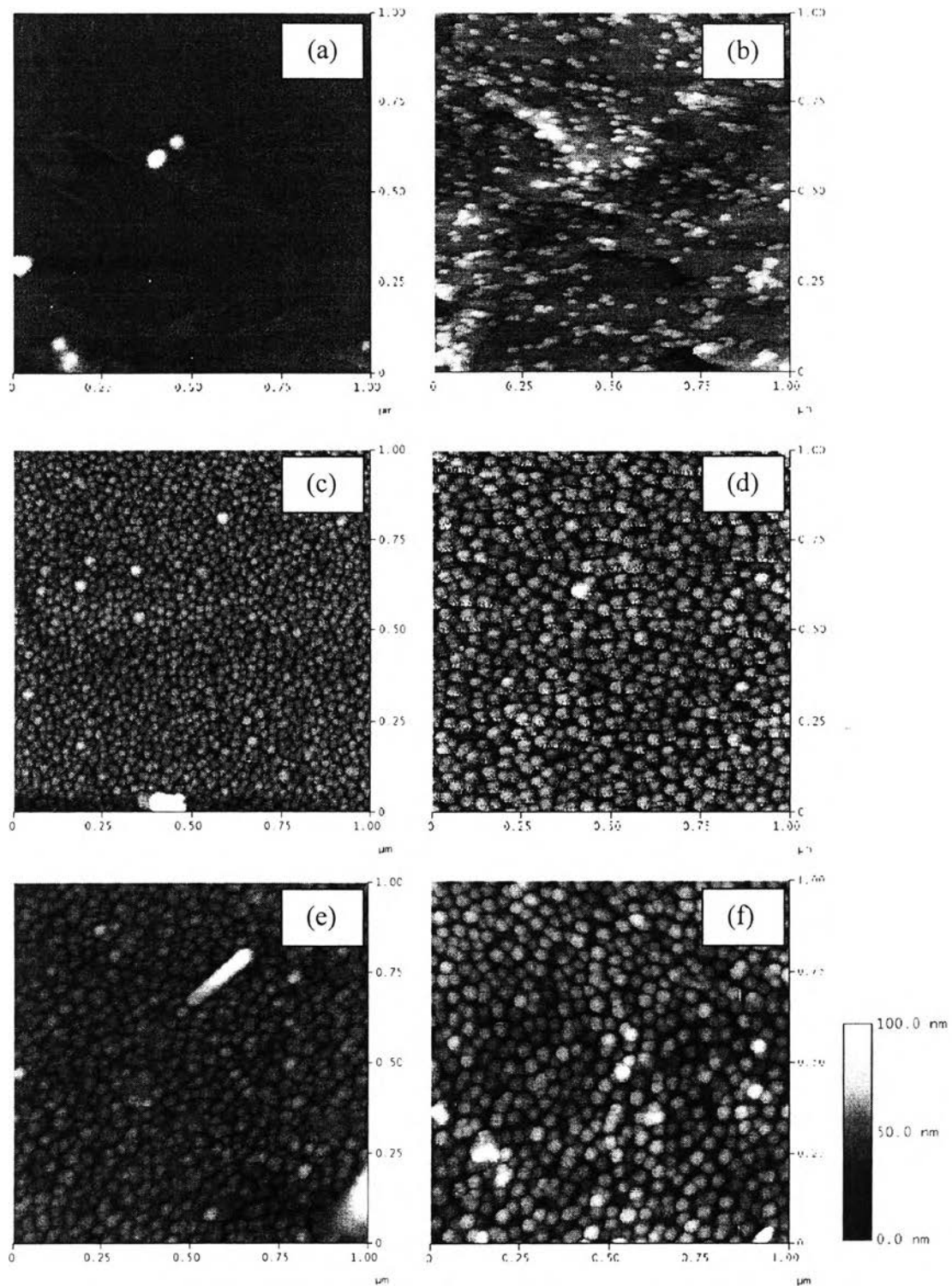
#### 4.1 Fabrication of AuNPs Thin Film

The optical absorption spectra of AuNPs thin film coated on glass silde, which have been modified by various agents, are shown in Figure 4.1. Figure 4.1(a) shows the optical absorption spectra of AuNPs thin film on MPTMS-modified surface, which does not exhibit any absorption peak corresponding to plasmon resonance. Figure 4.1(b) shows the optical absorption spectra of AuNPs thin film on APTMS-modified surface, in which the absorption due to the plasmon resonance is centered at 539 nm. Finally for AuNPs thin film on PEI-modified surface, the spectra in Figure 4.1(c) shows the absorption due to plasmon resonance at 547 nm. These peaks confirm that gold nanoparticles are deposited on the surfaces modified with APTMS and PEI. The different in peak position (i.e. 539 versus 547 nm) is probably due to difference in size of gold nanoparticles. On the other hand, the absence of the plasmon resonance peak MPTMS-modified surface indicates that gold nanoparticles are scarcely deposited on MPTMS-modified surface.



**Figure 4.1** UV-Visible spectra of AuNPs thin film on various modified glass slide: (a) MPTMS-modified surface, (b) APTMS-modified surface (c) PEI-modified surface.

The surface topography images of AuNPs coated on glass and polyimide, using various surface modifying agents, are investigated by AFM and shown in Figure 4.2 It should be noted that the concentration of the surface modifying agent was fixed at 1.25% wt. Both surface modifying period and AuNPs deposition period were 12 hours.



**Figure 4.2** Morphology of AuNPs film on : glass modified with (a) MPTMS, (c) APTMS and (e) PEI. ; polyimide modified with (b) MPTMS, (d) APTMS and (f) PEI.

According to Figure 4.2, the AuNPs deposition appears to form monolayer film. It is clearly observed that AuNPs deposited on the glass slide are quite uniform in size and distribution. However, the uniformity of the depositions depends upon the surface modifying agent used. AuNPs scarcely deposit on MPTMS-modified substrates, while the uniform monolayer coating of AuNPs can be observed on APTMS-modified surfaces. For PEI-modified surface, AuNPs surface coverage is much higher than that of APTMS-modified surface. The average particle sizes of AuNPs formed on MPTMS-, APTMS- and PEI-modified glass slide are 33.5, 18.84 and 25.46 nm, respectively. It should be noted that there might be some errors in AFM measurement from the tip convolution effect. The image of the particles may appear distorted in x- and y- direction. However, the height data is always accurate [95].

The deposition of AuNPs on polyimide is similar to that on the surface of glass slide. MPTMS-modified substrate is rarely deposited by AuNPs. The extent of the deposition is dramatically increased on APTMS- and PEI-modified substrates, respectively. The average particle sizes of AuNPs formed on MPTMS-, APTMS- and PEI-modified polyimide are 15.3, 28.56 and 33.98 nm, respectively. The AuNPs deposition tend to increase when surface is polyimide, as shown in Figure 4.2.

The XPS analysis (Table 4.1) also reveals higher content of gold on the surface of PEI-modified substrate than that on APTMS-modified substrate. It can be seen that the AuNPs film is not quite thick since the X-ray can still penetrate the film and underlying silica is still detected.

**Table 4.1** XPS analysis results of AuNPs deposited glass slides, using various surface modifying agents.

Modifying Agent	Atomic Concentration* (%)				
	Si	O	Au	N	S
MPTMS	26.01	73.92	0.03	-	0.04
APTMS	24.75	70.73	1.93	2.59	-
PEI	23.21	67.18	4.28	5.33	-

\*Carbon was excluded from the results because it could not be differentiated between carbon in sample and carbon from sample holder.

It should be noted that nitrogen detected from APTMS- and PEI-modified samples is part of amine group in molecular structure of both APTMS and PEI, while sulfur is part of MPTMS. The chemical structures of all modifying agents are shown in Figure 4.3.

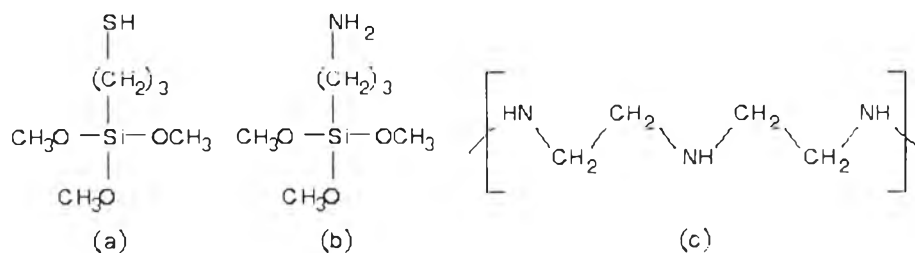
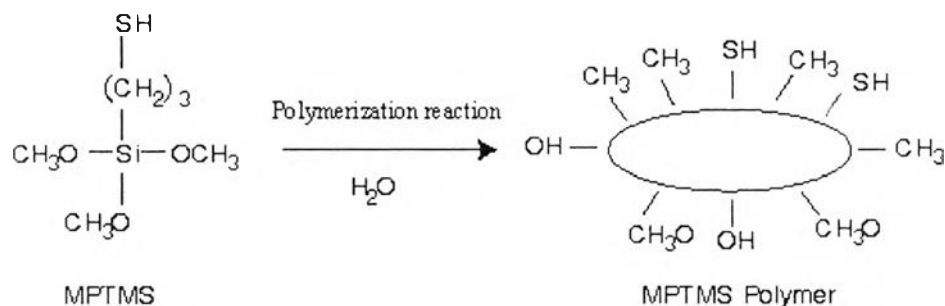


Figure 4.3 Molecular structures of modifying agents :

(a) MPTMS, (b) APTMS and (c) PEI.

Since both APTMS and MPTMS are silaneous compound, they react with hydroxyl groups, resulted from the pretreatment of glass slide with the mixture of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  solution [96], and form Si-O covalent bonding with the surface of the glass substrate. For polyimide, oxygen bonding in the polymer chain may be broken by the mixture of  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{SO}_4$  solution and oxygen atoms can appear on polyimide surface. The AuNPs are then attracted to amine group of APTMS or sulfhydryl groups of MPTMS by electrostatic interaction [24, 73].

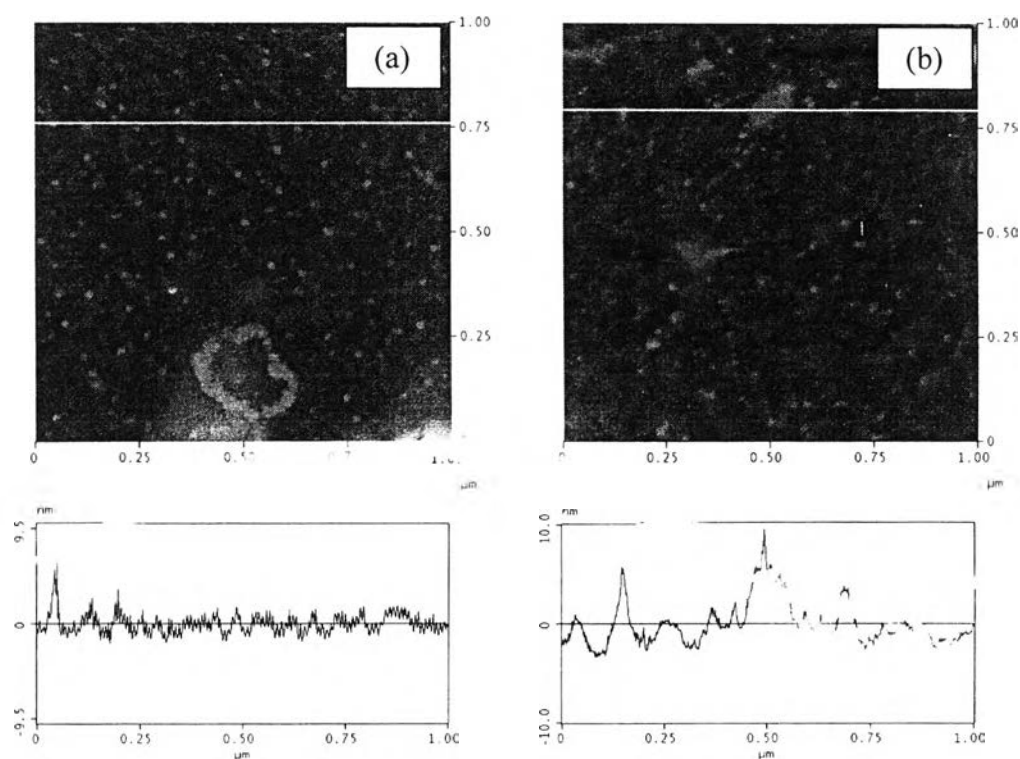
Deposition of AuNPs on MPTMS-modified surfaces was very limited, as seen from very low value of gold content in Table 4.1. Because the structure of MPTMS layers on the surface depend on the quantity of water in the solvent [65], i.e. methanol, self-polymerization reaction of MPTMS molecules to form sub-micrometered particles condensing onto the surfaces, was occurred. The mechanism is in Figure 4.4. When the quantity of sulfhydryl group is decreased, AuNPs deposition is decreased too.



**Figure 4.4** Self-polymerization of MPTMS in the solvent.

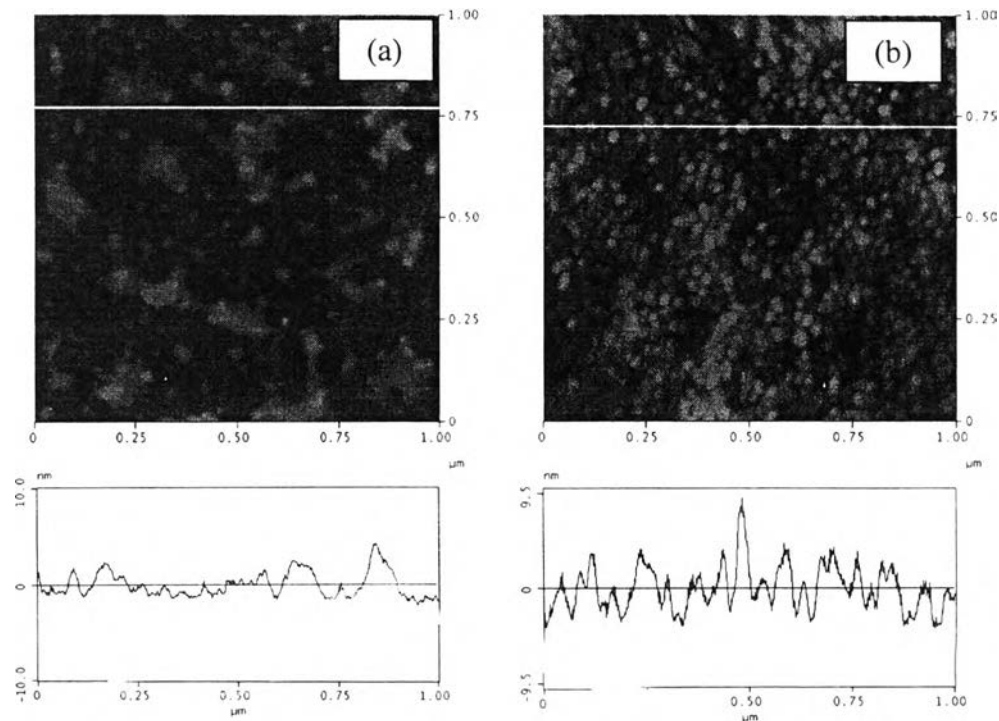
The roughness of MPTMS and APTMS layer can be clearly seen from the contour of the cross-section along the horizontal line in the AFM image, as shown in the bottom panels in Figure 4.5. It should be noted that the AFM images shown in this figure were taken from the modified surface, without the AuNPs deposition. For glass treated with 1.25%wt. APTMS (Figure 4.5(a)), there are many domains that have height shorter than 1 nm while the glass treated with 1.25%wt. MPTMS (Figure 4.5(b)) has domains that are typically 2-3 nm high. Since the thickness of one monolayer of either APTMS or MPTMS is about 0.7 nm [97], these large domains in Figure 5(b) are self-polymerized MPTMS.

The self-polymerization of MPTMS was also confirmed by low content of sulfur detected from the surface (See Table 4.1). It is indicated that sulfhydryl group in MPTMS, which is crucial for binding with AuNPs, was eliminated during the surface modifying process because of the self-polymerization previously discussed [98]. Consequently, gold was hardly detected on the surface. Self-polymerization of APTMS was also detected from the usually high domain observed from the cross section contour [Figure 4.5(a)]. However, the function of the polymerized APTMS was very small. This self-polymerization is the reason that AuNPs did not completely cover the surface of substrate, as shown in figure 4.2(c).



**Figure 4.5** Morphology of modified layer on glass modified with :  
 (a) APTMS and (b) MPTMS

On the contrary, in PEI, which is non-silaneous compound, the amine group can bind to both substrate and AuNPs purely by electrostatic interaction [5]. Figure 4.6 shows AFM images of the surfaces of glass and polyimide, after modified by PEI. Although PEI can react with water in solvent to form polymer in similar manner as MPTMS, PEI molecule contains lots of amine group. Consequently, this effect barely affects the AuNPs deposition on PEI-modified surfaces. Therefore, AuNPs can cover the surface almost perfectly and can be effectively bound to the surface in greater number, as shown in Figure 4.2(e-f). By comparing with surfaces functionalized with APTMS, the PEI-modified surface is more effective in forming monolayer of AuNPs because PEI has much more function group than APTMS.

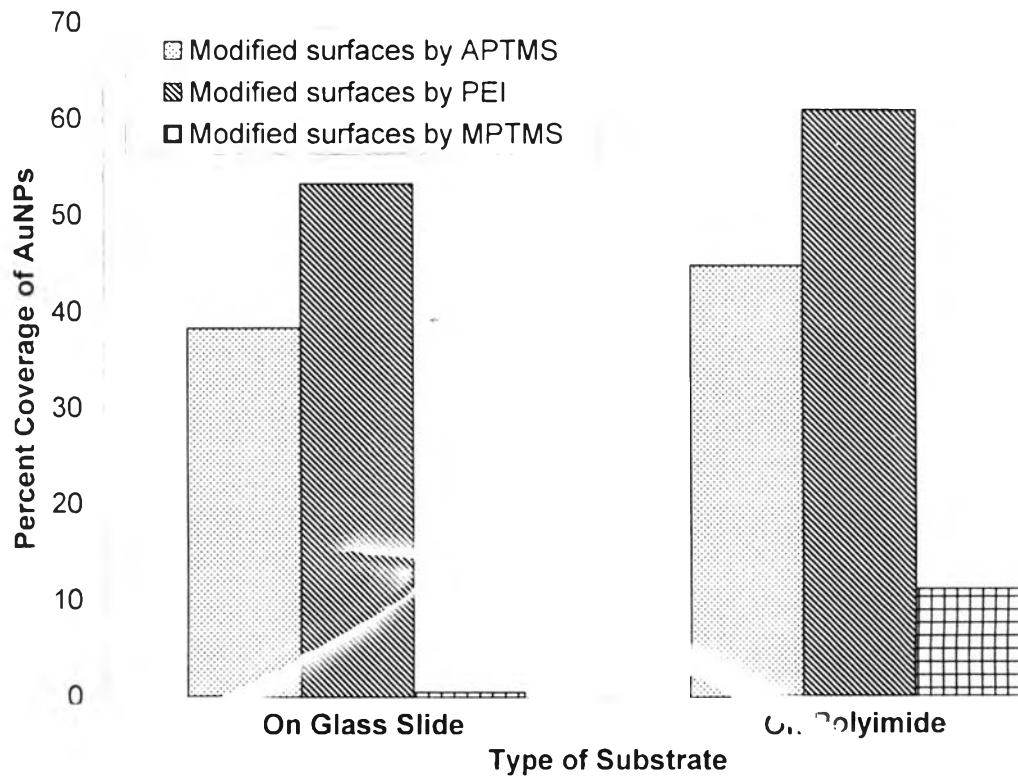


**Figure 4.6** Morphology of PEI-modified surfaces on (a) glass slide and (b) polyimide.

The fraction of AuNPs coverage on the modified surface was investigated by a method, described in Appendix A. Since the size distribution of AuNPs was narrow, the area covered by AuNPs was calculated by multiplying the average of AuNPs to the number of all gold nanoparticles counted on  $1 \times 1 \mu\text{m}^2$  area. The percent coverage was defined by dividing in the area covered by AuNPs on  $1 \times 1 \mu\text{m}^2$  area with  $1 \times 1 \mu\text{m}^2$  area and multiply by 100.

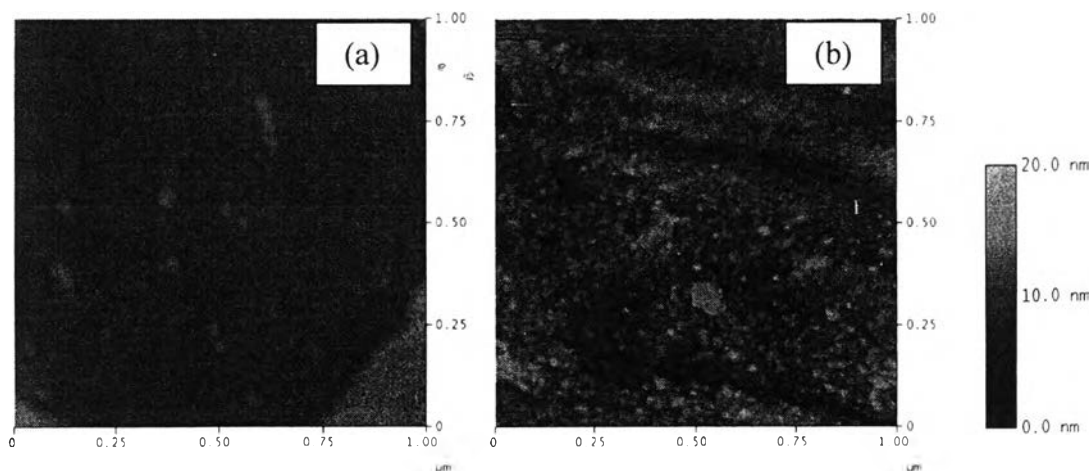
Figure 4.7 shows the percent coverage of AuNPs on various modified surfaces. On the surfaces modified by MPTMS, the surface coverage of AuNPs on glass slide and polyimide are 0.53 and 11.10 %, respectively. For APTMS-modified surfaces, the percent coverage of AuNPs on glass slide and polyimide surfaces are 38.26 and 44.69 % respectively. Finally, AuNPs cover on glass slide and polyimide surface modified by PEI by 53.12 and 60.91 %.





**Figure 4.7** Percent coverage of AuNPs on surfaces modified by MPTMS, APTMS, PEI.

As observed from Figure 4.7, AuNPs are deposited on polyimide in greater number than on glass slide. It may be due to the fact that the surface of polyimide is more rough than glass slide, as clearly seen in Figure 4.8. Besides the electrostatic interactions between AuNPs and the modifying agent anchoring on the surface, the surface roughness also affects the AuNPs depositing on the surface. Therefore, percent coverage of AuNPs tends to increase when AuNPs are deposited on polyimide surface.

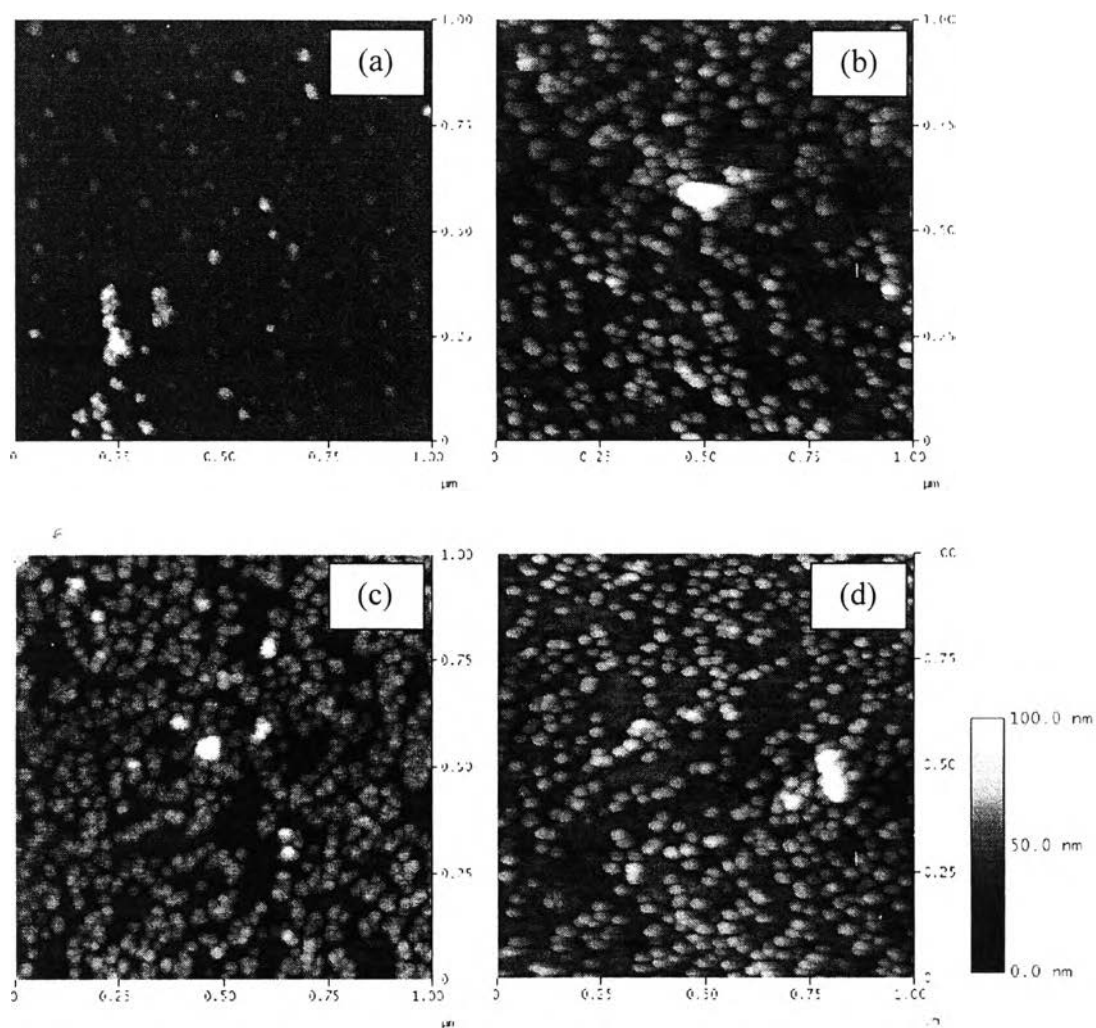


**Figure 4.8** AFM images of : (a) bare glass slide and (b) bare polyimide.

Adhesion test for gold nanoparticles thin film on the modified surface was investigated by “The Standard Test Method for Measuring Adhesion by Tape Test”, as described in Appendix B. Because the AuNPs film was thinner than 5 mils, test method B was used in this research.

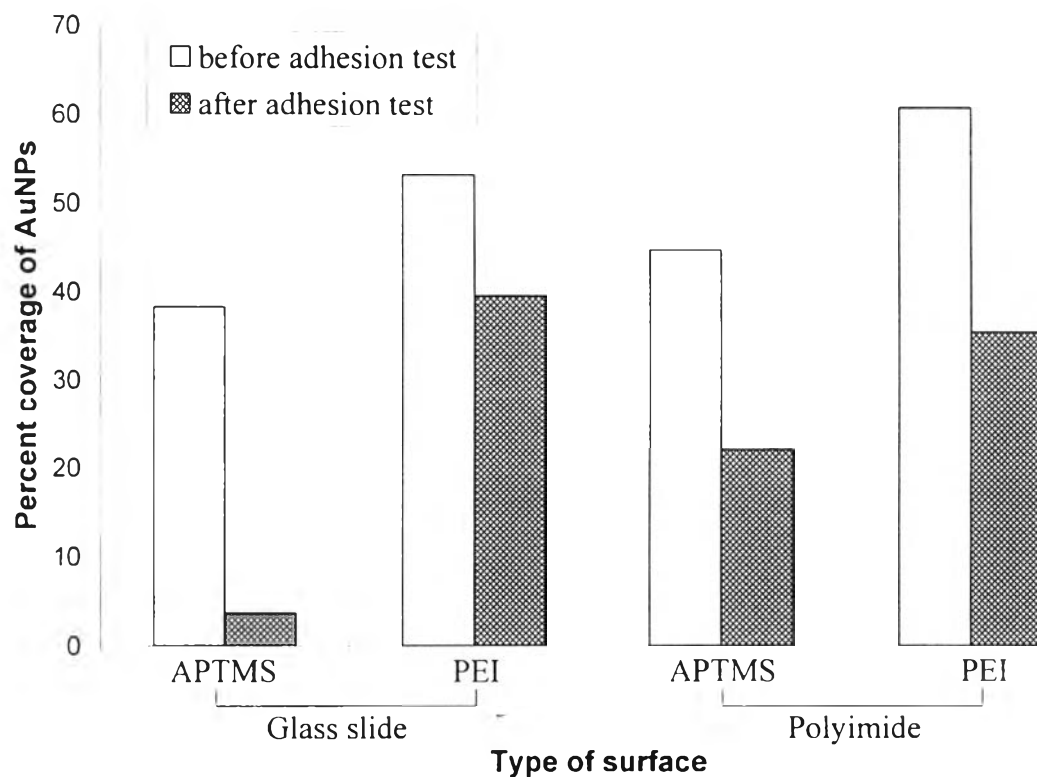
Figure 4.9 shows the surface topography images of AuNPs coated surfaces, after the adhesion test. The surface images of AuNPs on APTMS modified glass slide and polyimide surfaces after measuring adhesion by tape test are shown in Figure 4.9 (a) and (b), respectively. For PEI-modified surfaces, they are shown in Figure 9(c-d).

Percent coverage of gold nanoparticles on the modified surfaces, before and after the adhesion test are shown in Figure 4.10. From figure 4.10, the fraction of AuNPs removed by tape test can be calculated. It should be noted that the percent of AuNPs removed from the APTMS- or PEI- modified surfaces are presented in Table 4.2.



**Figure 4.9** Morphology of AuNPs film after adhesion test :

- (a) APTMS-modified glass, (b) APTMS-modified polyimide,
- (c) PEI-modified glass, and (d) PEI-modified polyimide.



**Figure 4.10** Percent coverage of AuNPs on modified surfaces, before and after the adhesion test.

**Table 4.2** Percent area removal of AuNPs on various modified surface.

Modifying agent / substrate	Percent coverage before tape test	Percent coverage after tape test	Percent area of AuNPs removed
APTMS/Glass slide	38.25 %	3.58 %	90.64 %
APTMS/Polyimide	44.69 %	21.99 %	50.79 %
PEI/Glass slide	53.12 %	39.52 %	25.62 %
PEI/Polyimide	60.91 %	35.51 %	41.70 %

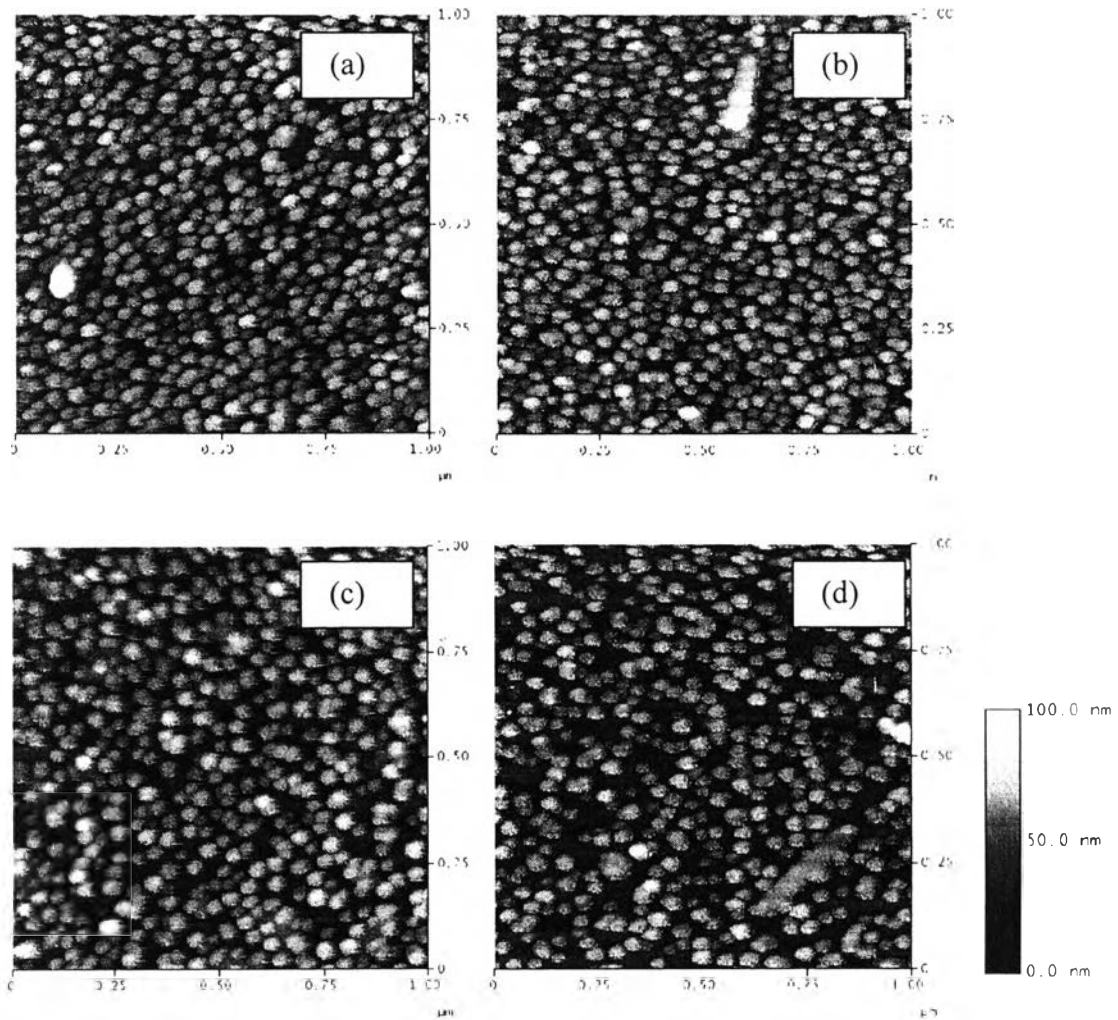
## 4.2 Effects of Deposition Conditions on AuNPs Film

In this section, effects of various conditions such as the concentration of modifying agent, surface modification time and AuNPs deposition time, on the AuNPs film are investigated. Nevertheless, since AuNPs rarely deposit on surfaces modified with MPTMS, MPTMS was not employed as modified agent in this section.

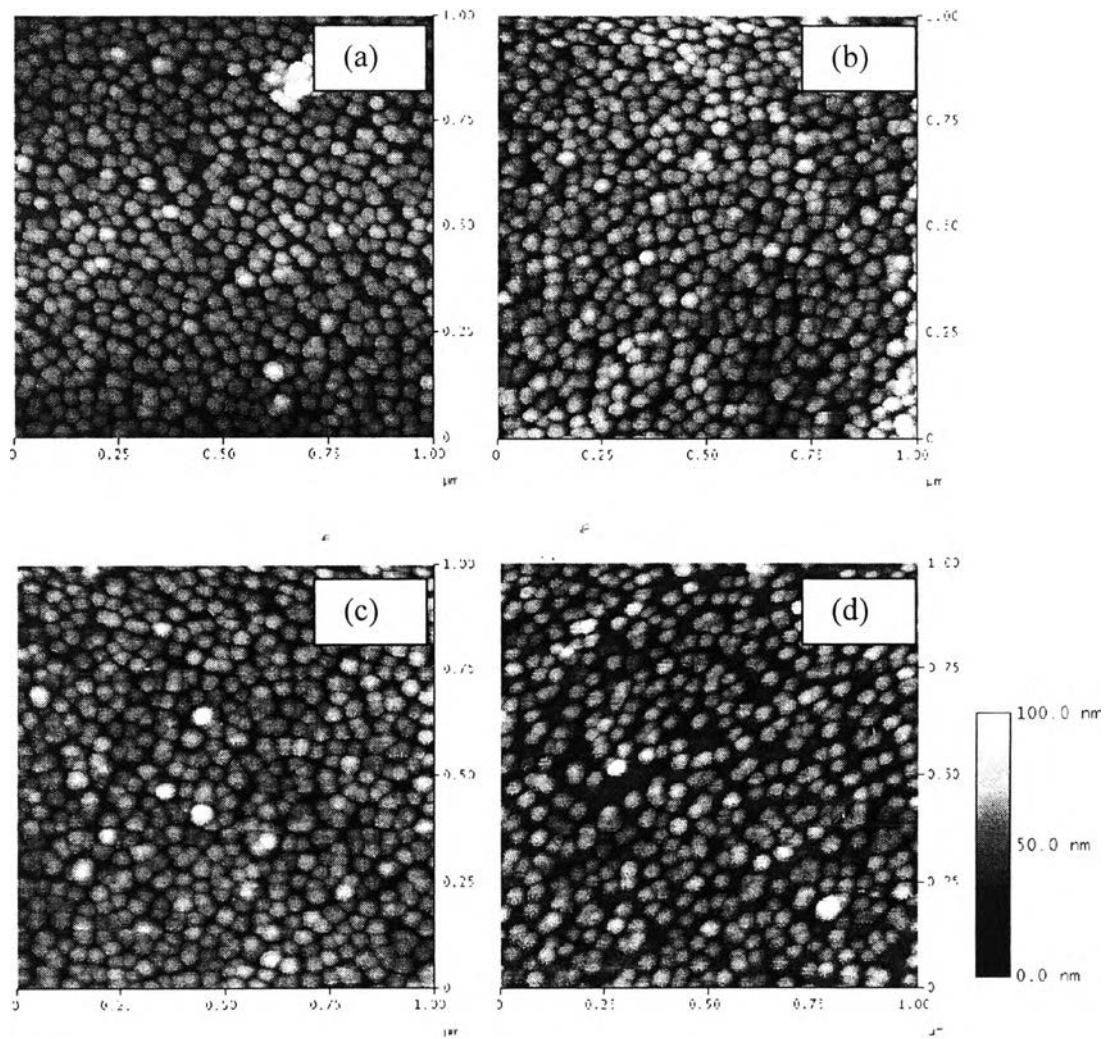
### 4.2.1 Concentration of modifying agents

Effect of modifying agent concentration, i.e. APTMS and PEI, are investigated in this section. The range of concentration studied was 0.3125, 0.625, 2.5, 5 %wt. of the modifying agent. Both surface modification time and AuNPs deposition times were kept constant at 12 hours. After the AuNPs deposition, the films were dried at room temperature. The investigations were conducted on both glass slide and polyimide. The surface morphology of the assembled AuNPs monolayer coated on substrates was investigated with AFM.

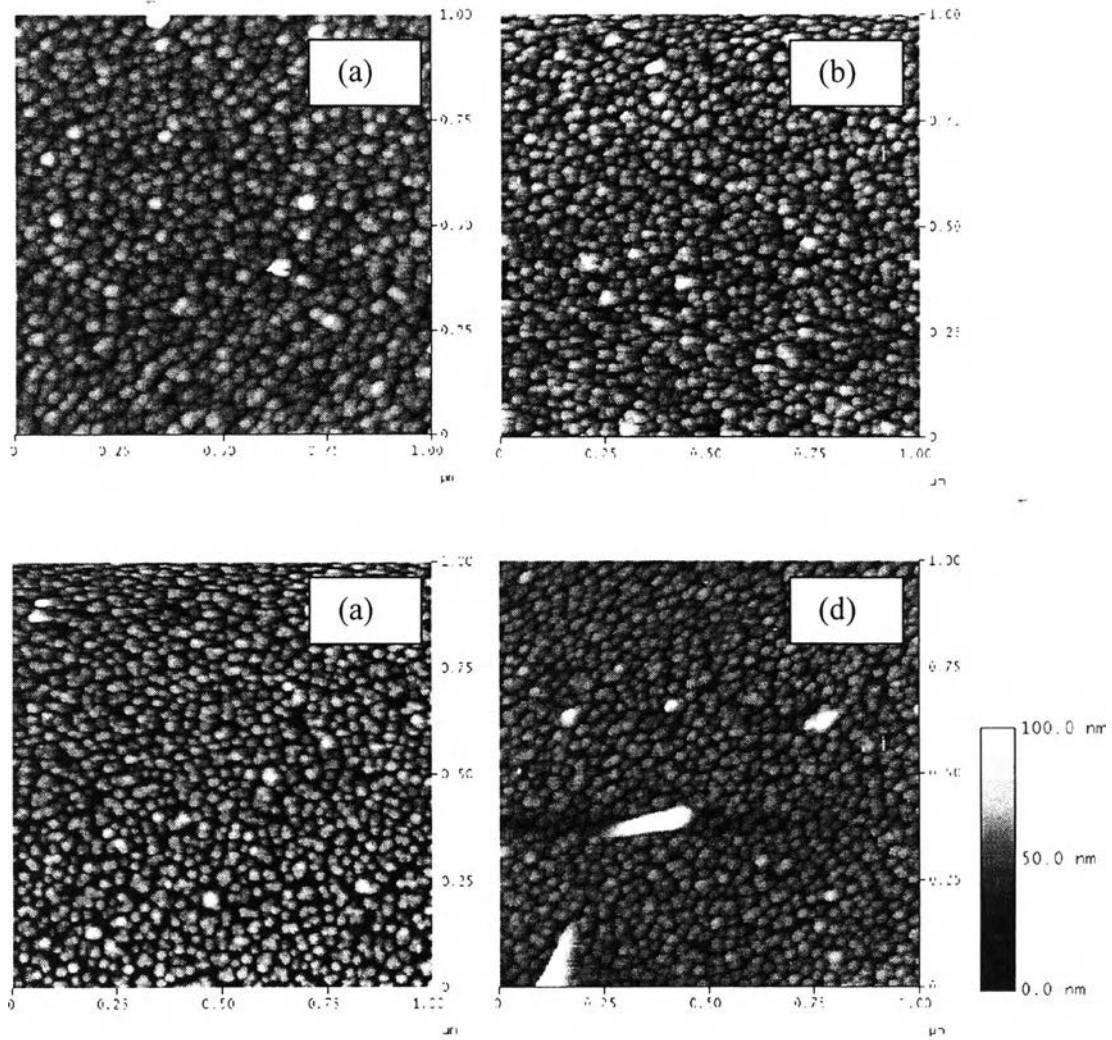
Figure 4.11 shows AFM images of AuNPs deposited on surfaces of glass slide treated with APTMS solution at various concentrations, i.e. 0.3125, 0.625, 2.5 and 5 %wt., respectively. The AFM images for polyimide modified by APTMS under the same condition are shown in Figure 4.12. For the AuNPs deposition on glass slide and polyimide modified by PEI at the same concentration are shown in Figure 4.13 and 14, respectively.



**Figure 4.11** AFM images of AuNPs deposited on glass slide treated with APTMS solution at various concentration : (a) 0.3125 %wt, (b) 0.625 %wt, (c) 2.5 %wt and (d) 5 %wt.

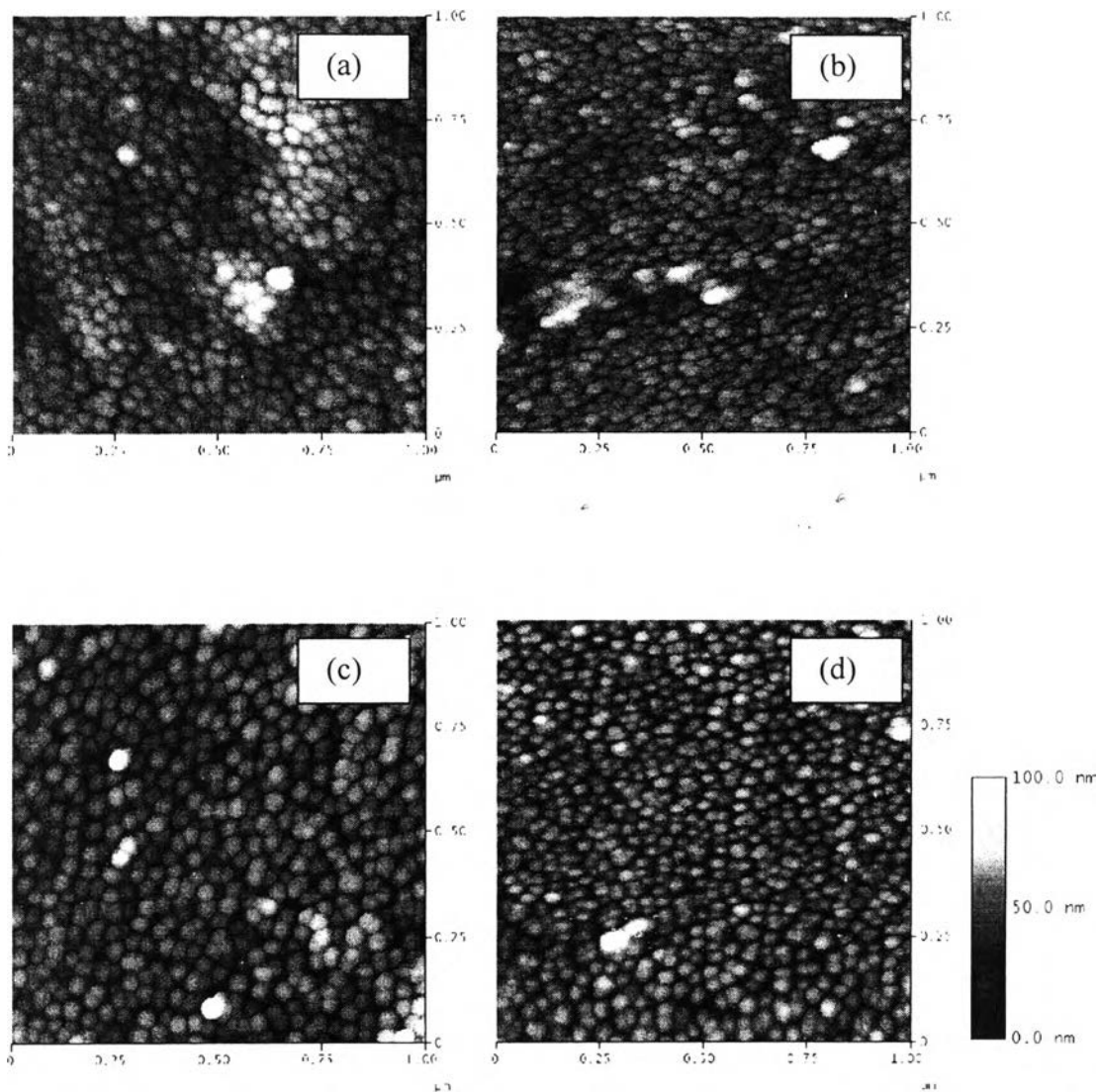


**Figure 4.12** AFM images of AuNPs deposited on polyimide treated with APTMS solution at various concentration : (a) 0.3125 %wt, (b) 0.625 %wt, (c) 2.5 %wt and (d) 5 %wt.



**Figure 4.13** AFM images of AuNPs deposited on glass slide treated with PEI solution at various concentration : (a) 0.3125 %wt, (b) 0.625 %wt, (c) 2.5 %wt and (d) 5 %wt.



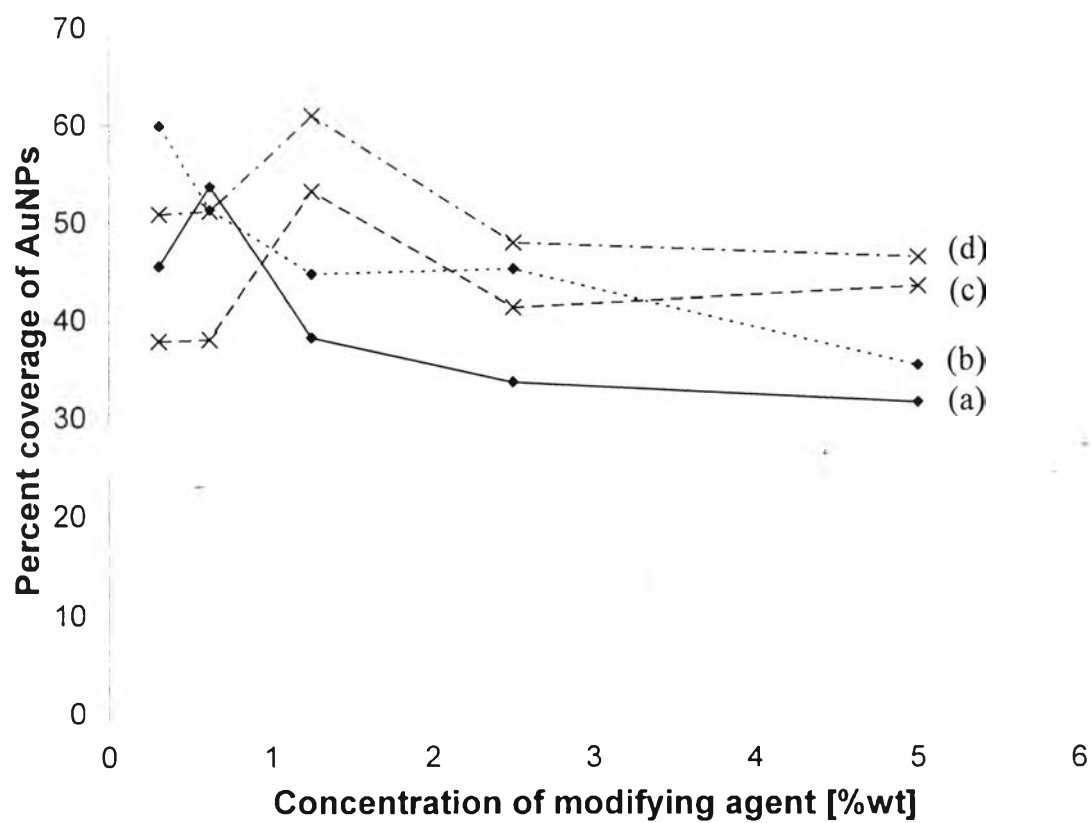


**Figure 4.14** AFM images of AuNPs deposited on polyimide treated with PEI solution at various concentration : (a) 0.3125 %wt, (b) 0.625 %wt, (c) 2.5 %wt and (d) 5 %wt.

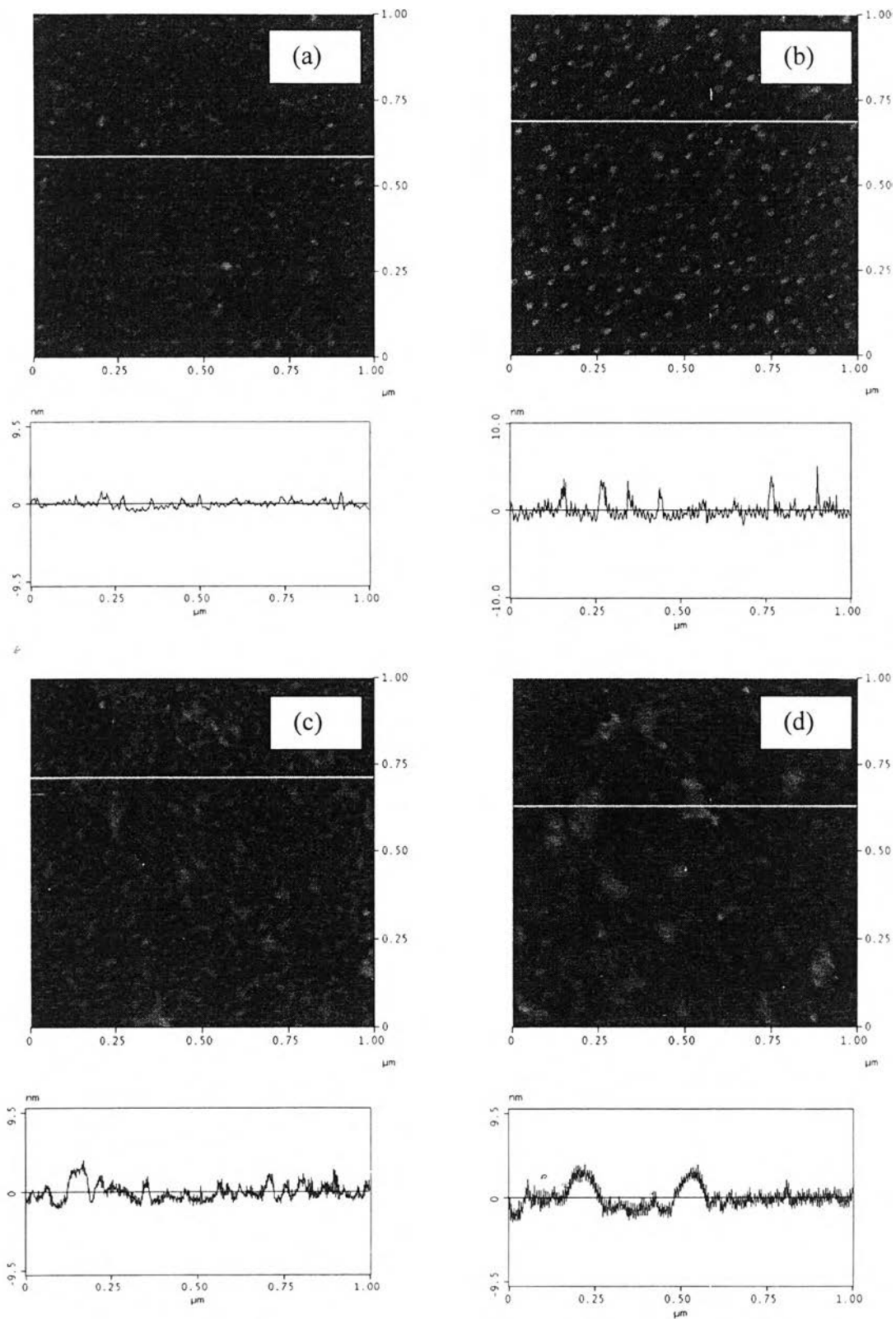
From AFM images in Figure 11-14, the percent coverage of AuNPs of the substrates can be calculated and summarized as shown in Figure 15. Comparison of the percent AuNPs coverage reveals that the AuNPs density on glass decreases with increasing APTMS concentration, as shown in Figure 4.15 (a). Similar result is also observed for AuNPs covering on APTMS-modified polyimide (Figure 4.15(b)). AuNPs density decreases when the concentration of APTMS is increased because APTMS can undergo self-polymerization to, resulting in the reduction in the number of amine group in APTMS layer anchoring on the substrate, in the similar behavior as MPTMS previously discussed. The evidence of the self-polymerization of APTMS is shown in the AFM images of the APTMS-treated surfaces in Figure 16.

Increasing APTMS polymer content are noticeable from increased roughness of APTMS modified surface. AFM is the instrument that is suitable for determining three-dimensional surface morphologies. The top panels in Figure 4.16 show AFM images of SiO<sub>2</sub> surface after the treatment with APTMS. The bottom panels show the cross-sectional contours along the white horizontal line in the corresponding top panel. For glass treated with 0.3125%wt. APTMS (Figure 4.16(a)), most of the domains is smaller than 1 nm in height, while glass treated with 2.5%wt. APTMS (Figure 4.16(c)) had domains that are typically 2-3 nm high. Height and size of the domain tend to increase when the concentration of APTMS is increased to 5 %wt (Figure 4.16 (d)).

The surface morphology of assembled PEI layers formed on SiO<sub>2</sub> substrate was investigated with AFM, as shown in Figure 4.17. The effect of PEI concentration on AuNPs coverage is the same trend, being AuNPs coverage generally decrease with increasing PEI concentration. Although surfaces modified by PEI have greater roughness than APTMS-modified surface at the same concentration, AuNPs coverage content less decrease than modified APTMS surface, as shown in figure 4.15 (c,d). It may be explained that PEI has higher amine content than APTMS. Therefore, self-polymerization process has less effect on PEI.



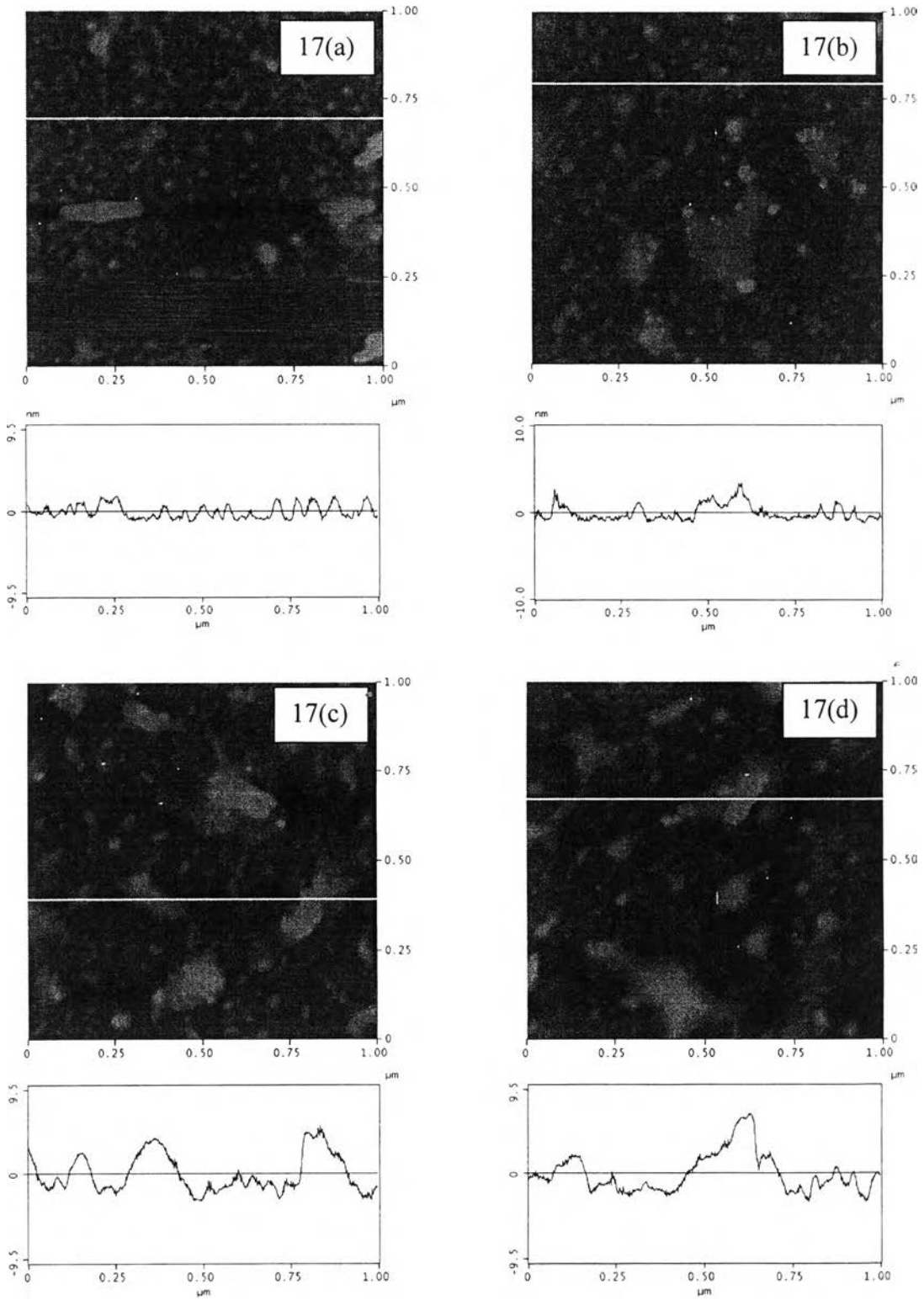
**Figure 4.15** Percent coverage of AuNPs on surfaces, modified by modifying agents at various concentrations: (a) APTMS-modified glass, (b) APTMS-modified polyimide, (c) PEI-modified glass and (d) PEI-modified polyimide.



**Figure 4.16** AFM images of glass slide after surface modification with APTMS :

(a) 0.3125 %wt., (b) 0.625 %wt.,

(c) 2.5 %wt., and (d) at 5 %wt.



**Figure 4.17** AFM images of glass slide after surface modification with PEI :

(a) 0.3125 %wt., (b) 0.625 %wt.,

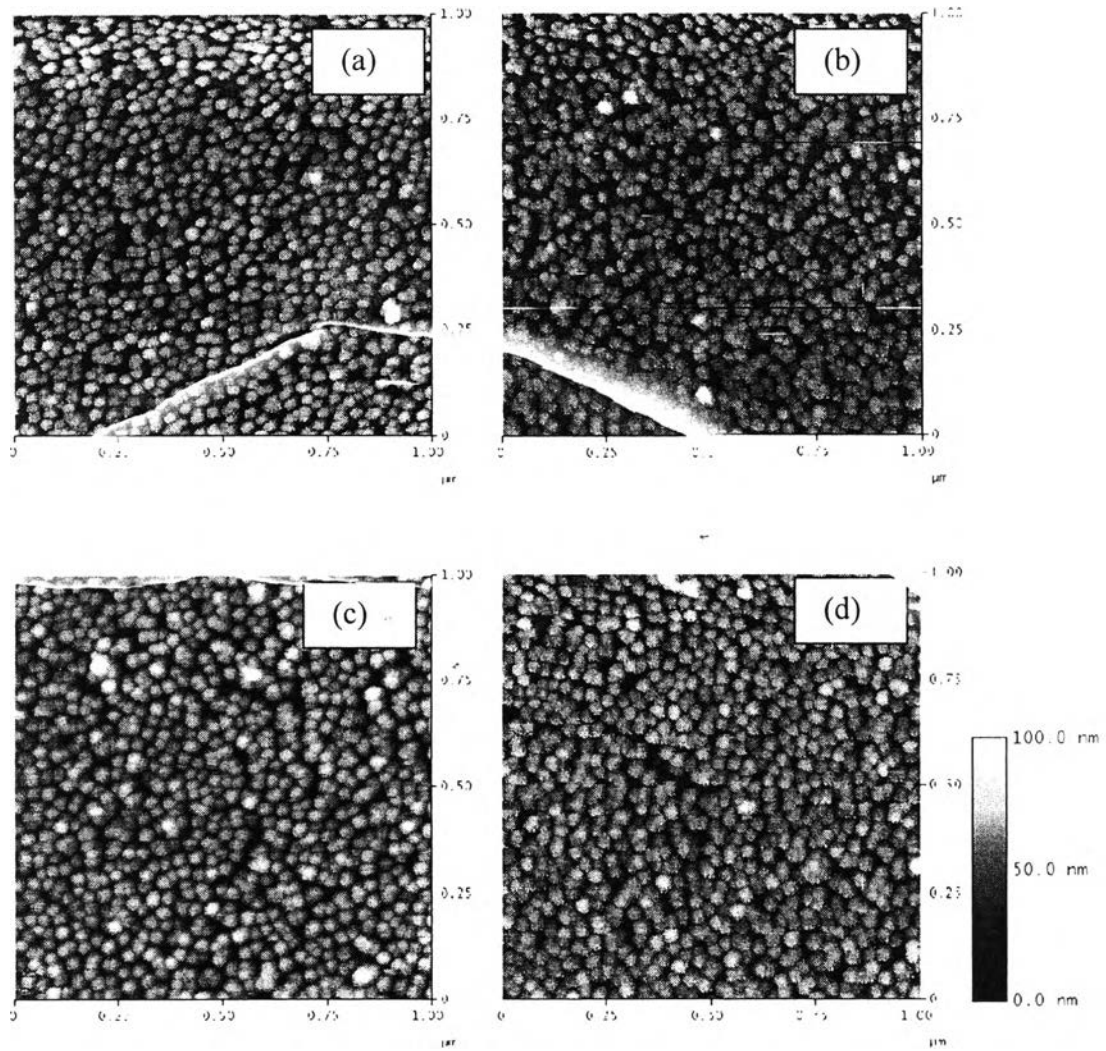
(c) 2.5 %wt., and (d) at 5 %wt.

#### 4.2.2 Surface modification time

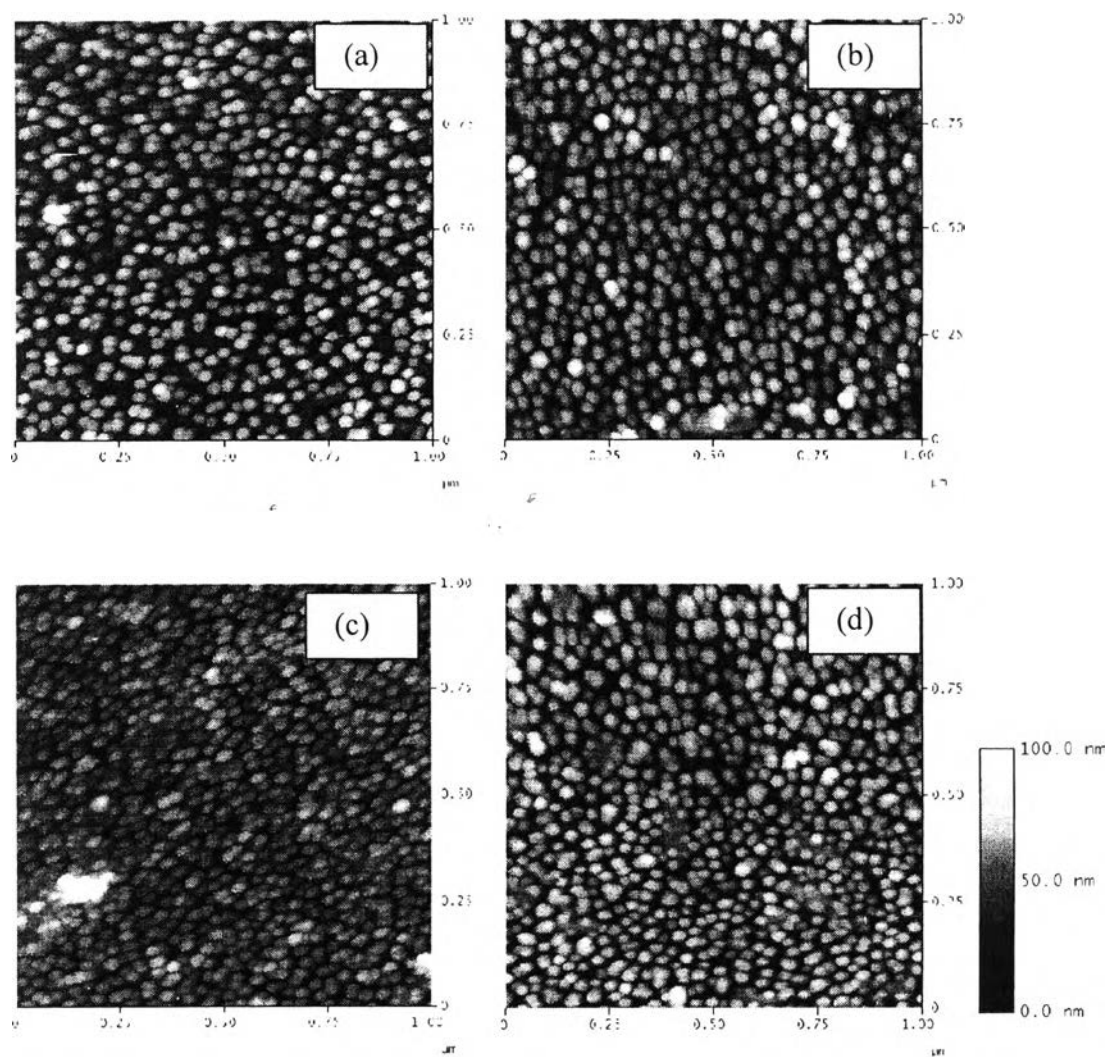
In this section, the concentration of the modifying agent and the AuNPs deposition time were fixed at 1.25 %wt. and 12 hours, respectively. The surface modification time was varied from 4, 8, 16 and 20 hours, respectively. After the AuNPs deposition, the sample was dried at room temperature. These conditions were applied to both glass slide and polyimide surfaces. The surface morphology of assembled AuNPs monolayer on modified substrates was investigated with AFM. Quantity of AuNPs deposited on surfaces modified by APTMS and PEI, for various time was compared.

Figure 4.18 shows the AFM images of AuNPs deposited on glass slide treated with APTMS solution under different durations. The AFM images of AuNPs deposited on glass slide modified with APTMS for 4, 8, 16 and 20 hours are shown in Figure 4.18 (a-d), respectively. In addition, the images of AuNPs deposited on polyimide surface, modified by APTMS solution under same conditions are shown in Figure 4.19. For PEI-modified glass and polyimide, the AFM image showing the effect of surface modification time, are shown in Figure 4.20 and 4.21, respectively.

The quantity of AuNPs deposited on the modified surfaces is shown in Figure 4.22. It is noticed that surface modification time has effected on the percent coverage of AuNPs. The AuNPs quantity is generally increased with the prolonged surface modification time. This behavior can be explained by the fact that the amount of the modifyinf agent anchoring on the substrate is increased with the modification time. This can be clearly seen from Figure 4.23, which shows images of the substrates after modified by APTMS (Figure 4.23(a-b)) or PEI (Figure 4.23(c-d)) for 4 and 16 hours.

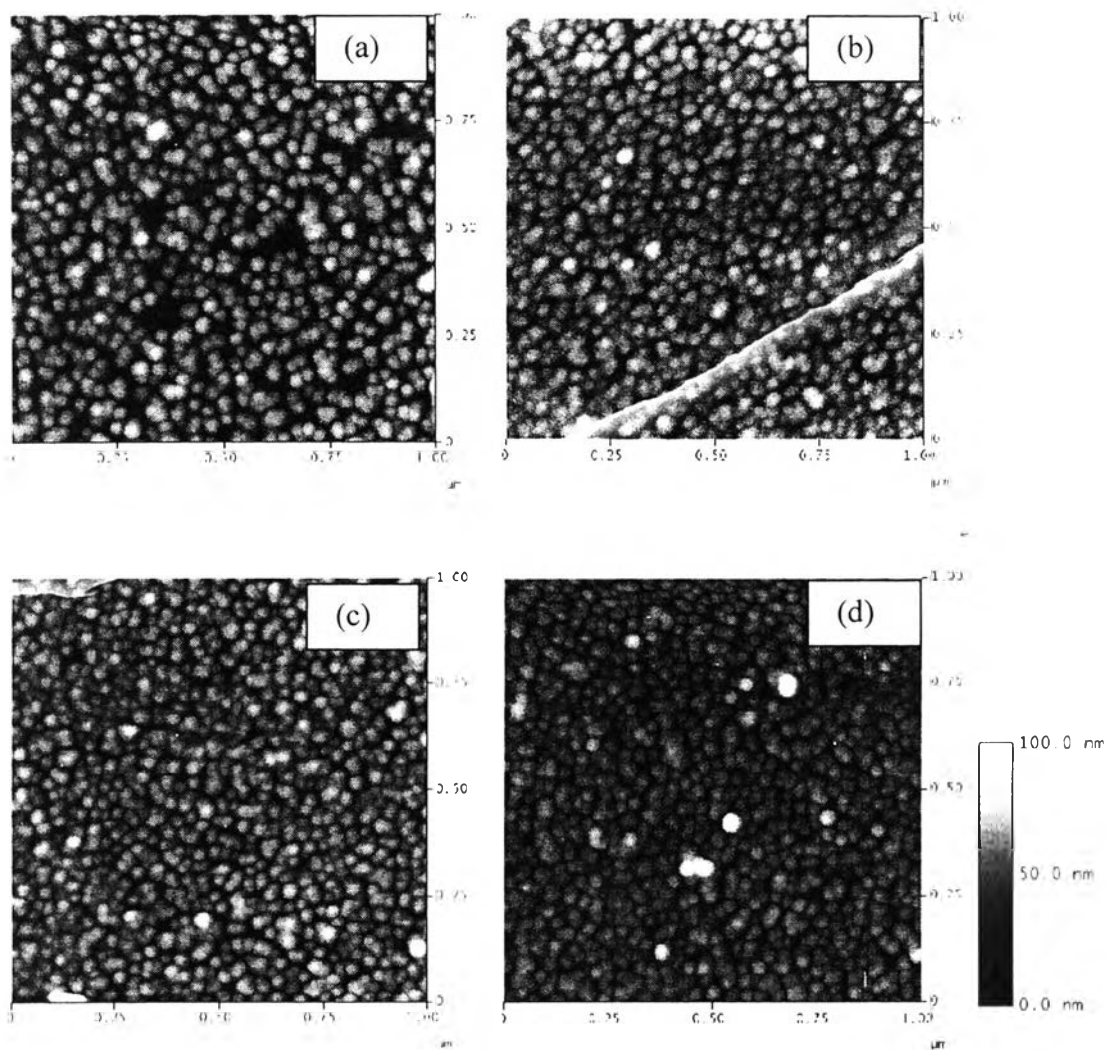


**Figure 4.18** AFM images of AuNPs deposited on glass slide treated with APTMS for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.

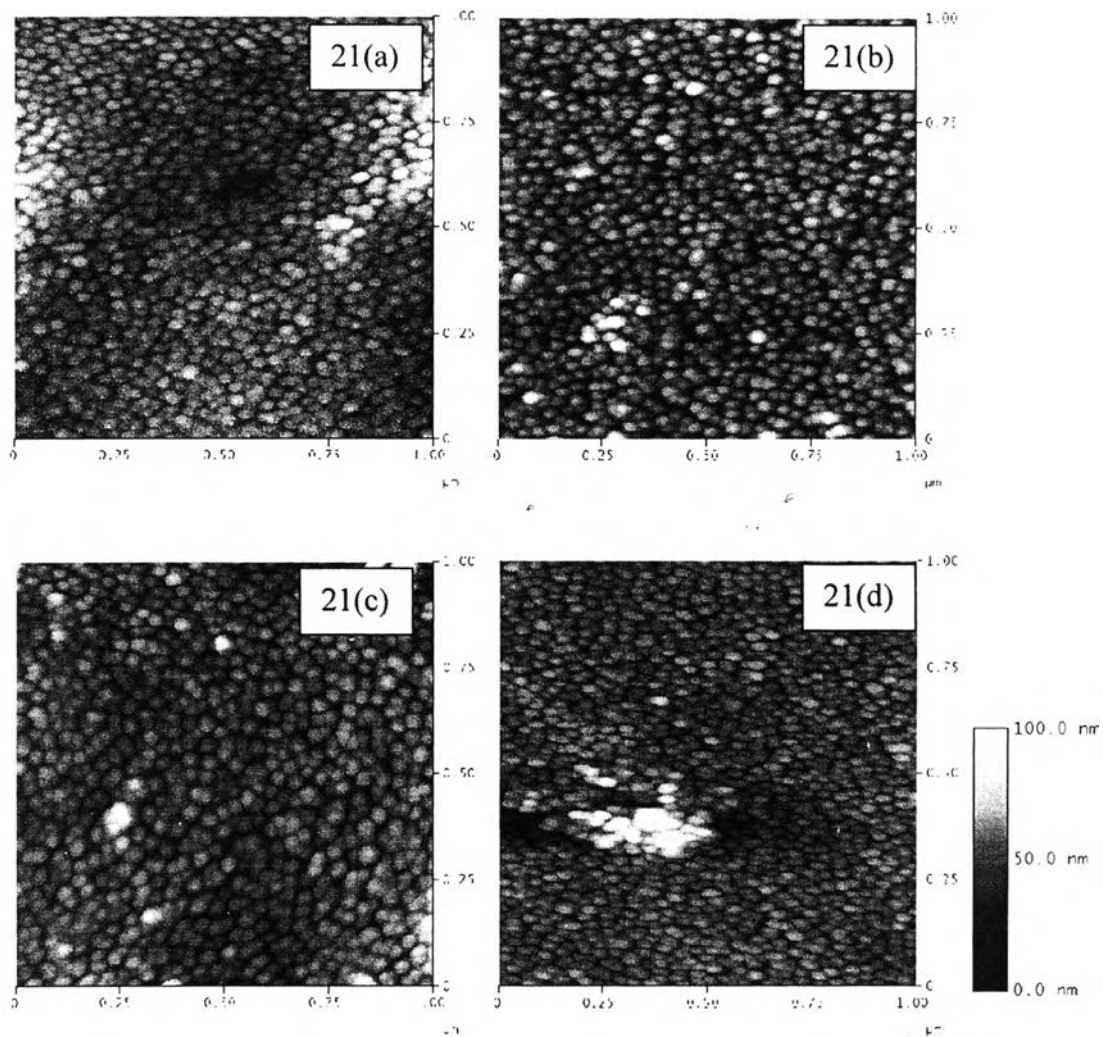


**Figure 4.19** AFM images of AuNPs deposited on polyimide treated with APTMS for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.

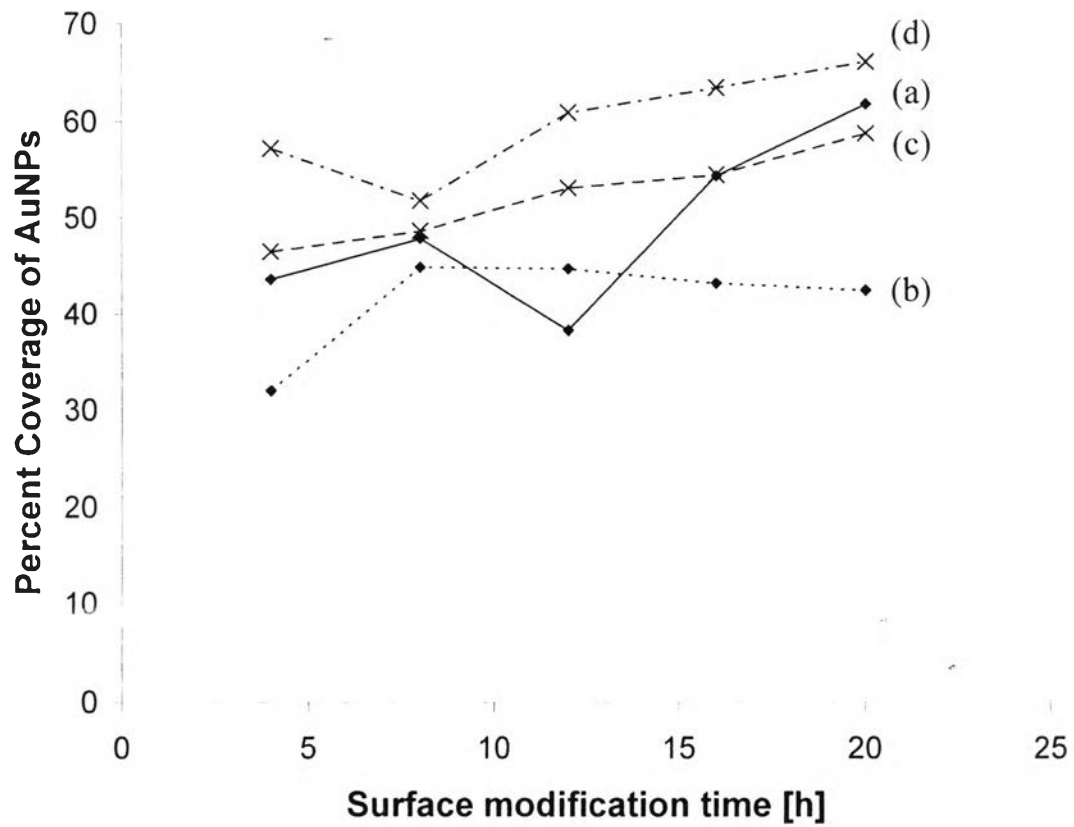




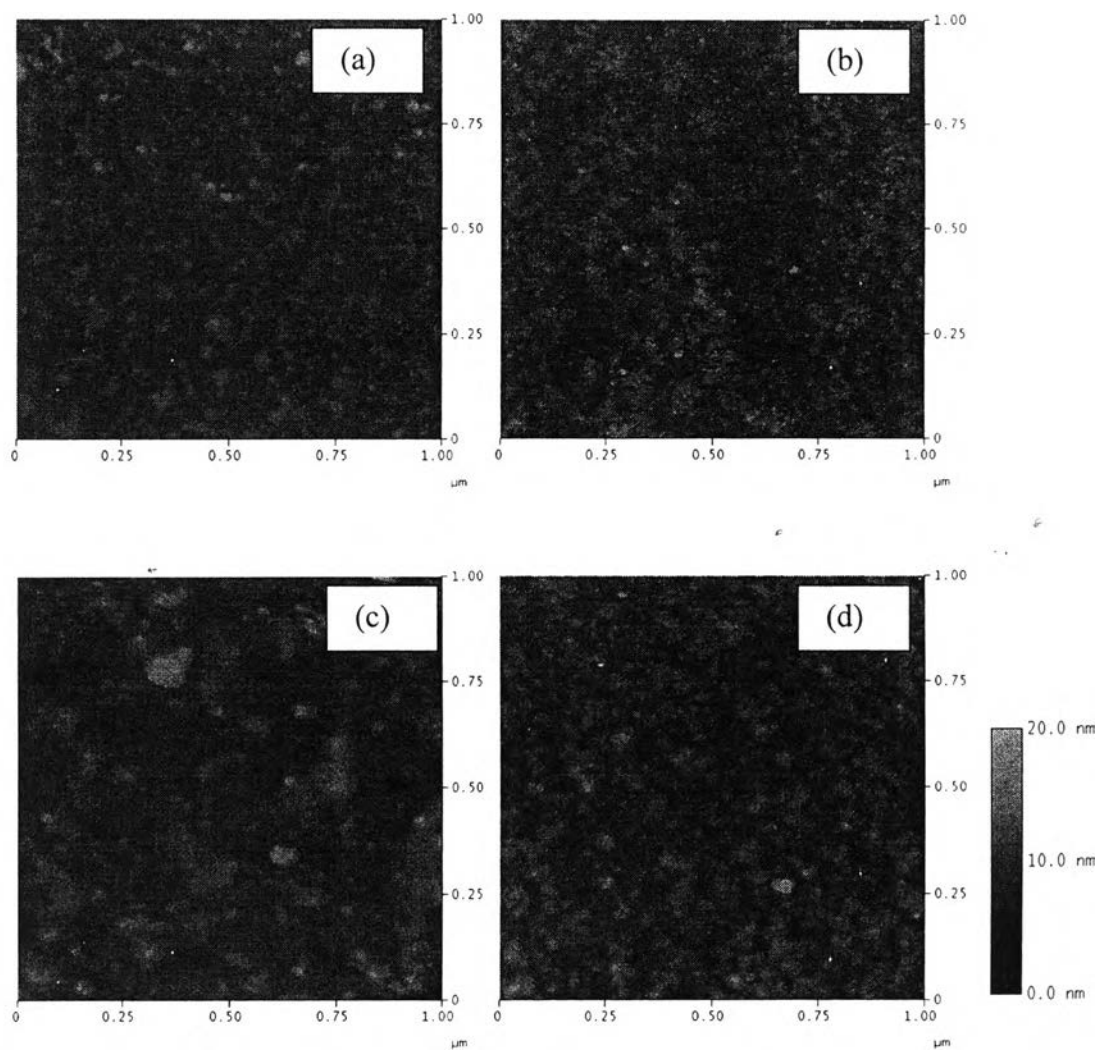
**Figure 4.20** AFM images of AuNPs deposited on glass slide treated with PEI for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.



**Figure 4.21** show AFM images of AuNPs deposited on polyimide treated with PEI for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.



**Figure 4.22** Percent coverage of AuNPs on surfaces, modified by modifying agent for various durations: (a) APTMS-modified glass, (b) APTMS-modified polyimide, (c) PEI-modified glass and (d) PEI-modified polyimide.



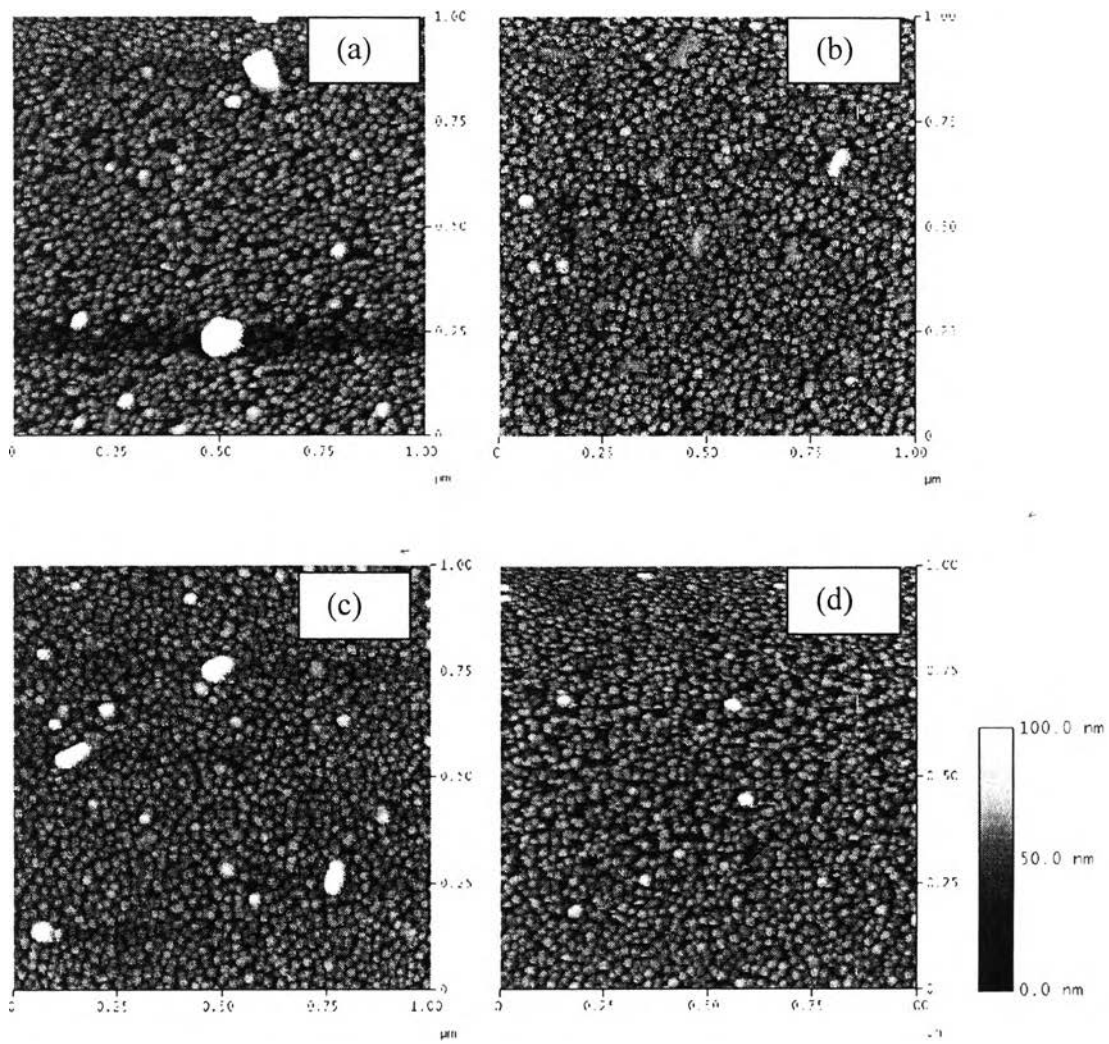
**Figure 4.23** AFM images of glass modified by APTMS for (a) 4 h, (b) 16 h and modified by PEI for (c) 4 h, (d) 16 h.

### 4.2.3 AuNPs deposition time

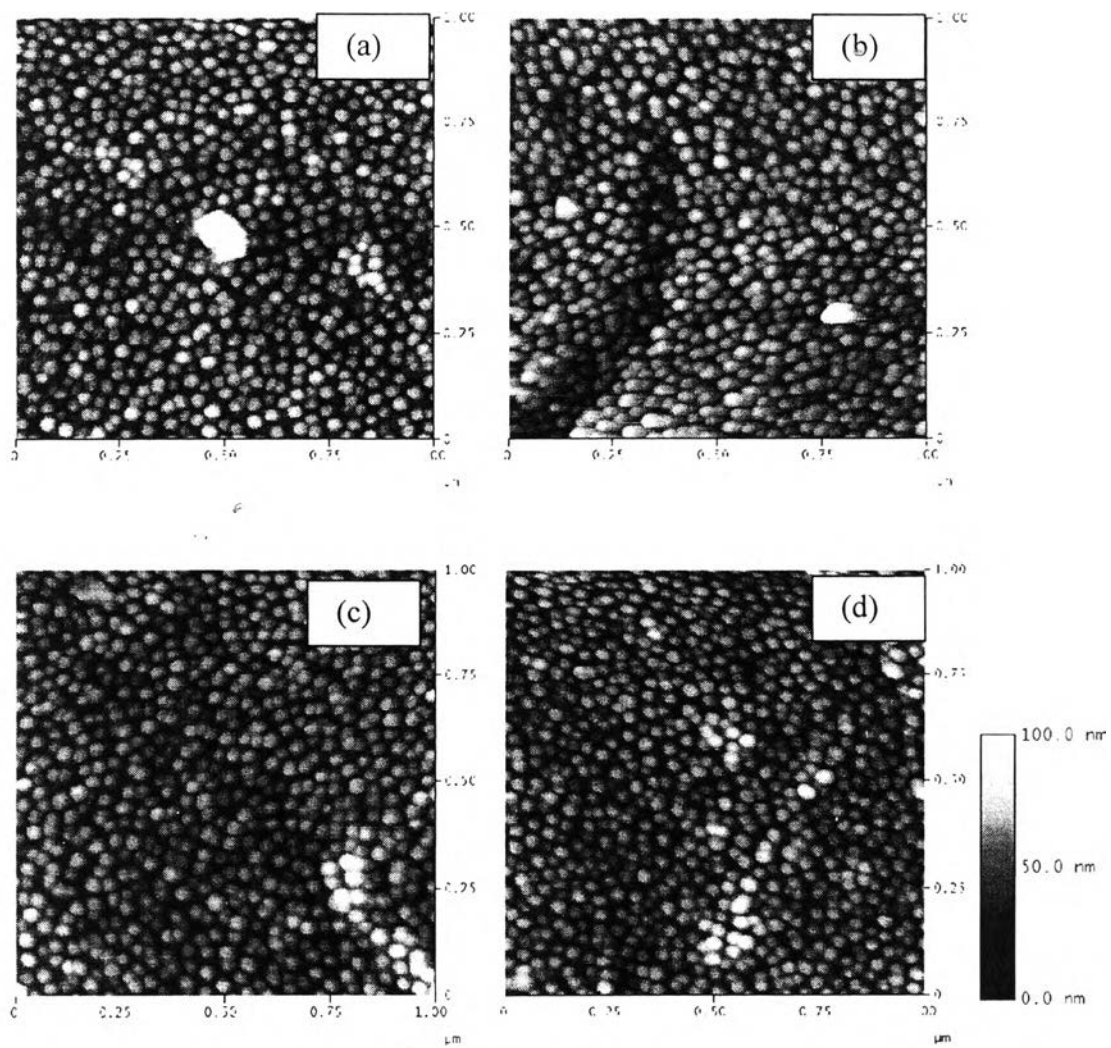
In this section, effect of AuNPs deposition time in the range of 4-20 hours is investigated. The concentration of the modifying agent and the surface modification time were fixed at 1.25 %wt. and 12 hours, respectively. These conditions were used for glass slide and polyimide surfaces. The surface morphology of assembled AuNPs monolayer on modified substrates after drying at room temperature was investigated with AFM. Comparison of the quantity of AuNPs deposited on surfaces modified by APTMS and PEI was AuNPs deposition time of 4,8,16 and 20 hours.

Figure 4.24 shows the AFM images of AuNPs deposited on glass slide surfaces treated with APTMS solution at various AuNPs deposition times. The AFM images of the surface after AuNPs deposition for 4, 8, 16 and 20 hours on APTMS-modified glass slide are shown in Figure 4.24(a-d), respectively. The results for the deposition on polyimide surface under the same conditions are shown in Figure 4.25. The same studies on PEI-modified glass and polyimide are shown in Figure 26 and 27, respectively.

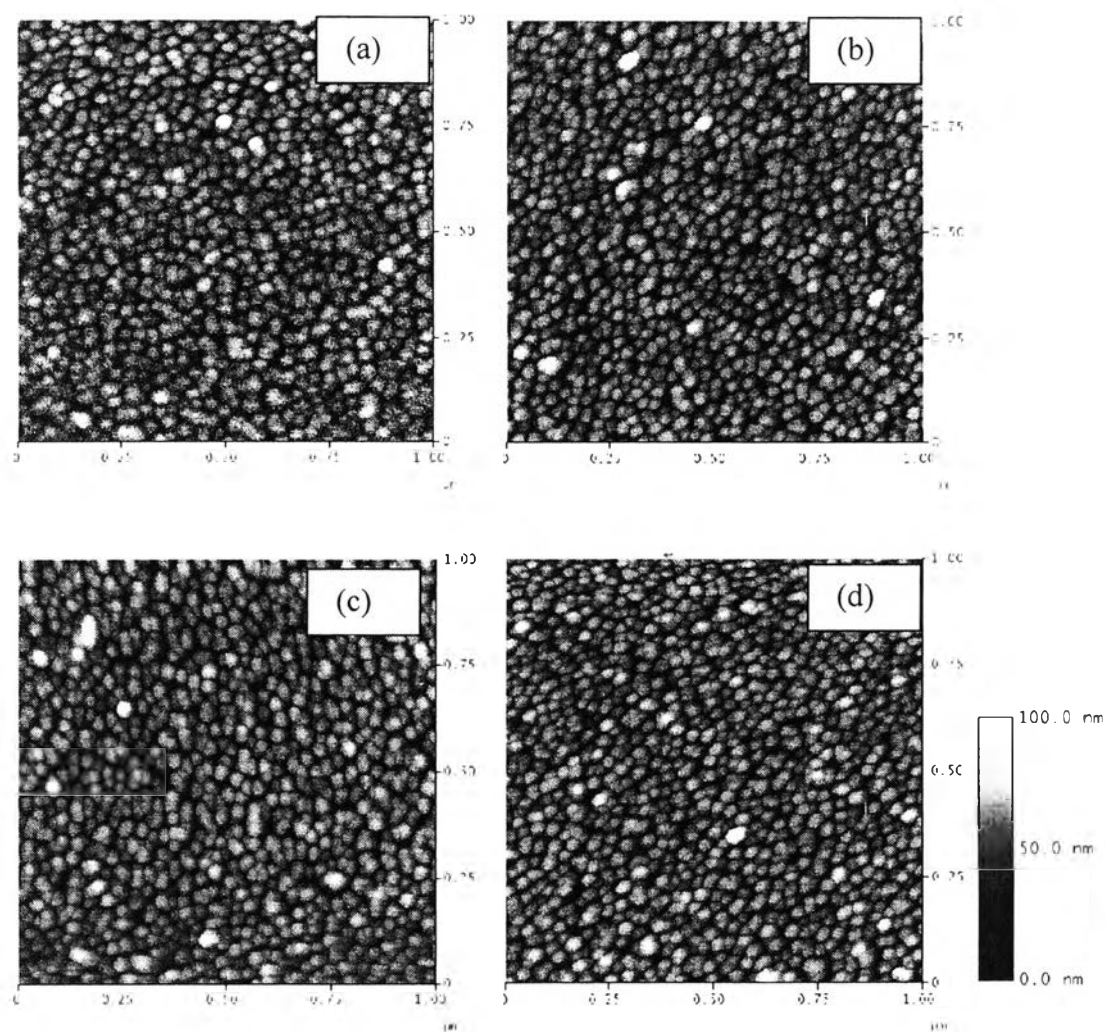
The AuNPs coverage percentage on various modified surfaces is summarized in Figure 4.28. It is found that AuNPs deposition on APTMS modified surfaces is nearly constant for both polyimide and glass surfaces, regardless of the AuNPs deposition time. The same behavior was also observed for the glass and polyimide modified by PEI, as shown in Figure 4.28 (c,d). The AuNPs deposition time has small effect on depositing AuNPs monolayer when the deposition time is more than 4 hours. It is suggested that AuNPs deposited on the modified surfaces have reached the maximum deposition on APTMS or PEI available on the surfaces. Although the deposition time is increased, the percent coverage is almost unchanged.



**Figure 4.24** AFM images of glass slide treated with APTMS solution and deposited with AuNPs for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.

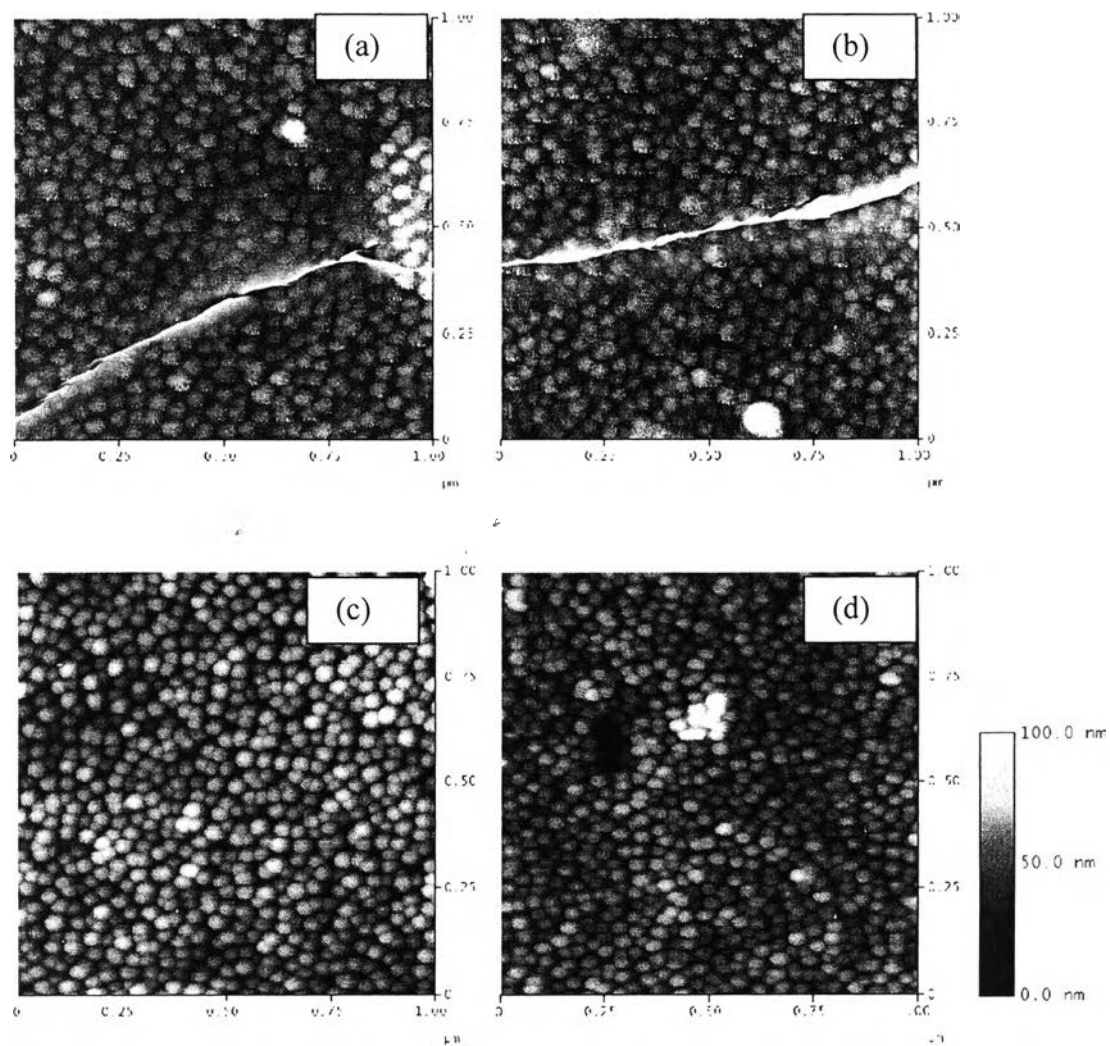


**Figure 4.25** AFM images of polyimide treated with APTMS solution and deposited with AuNPs for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.

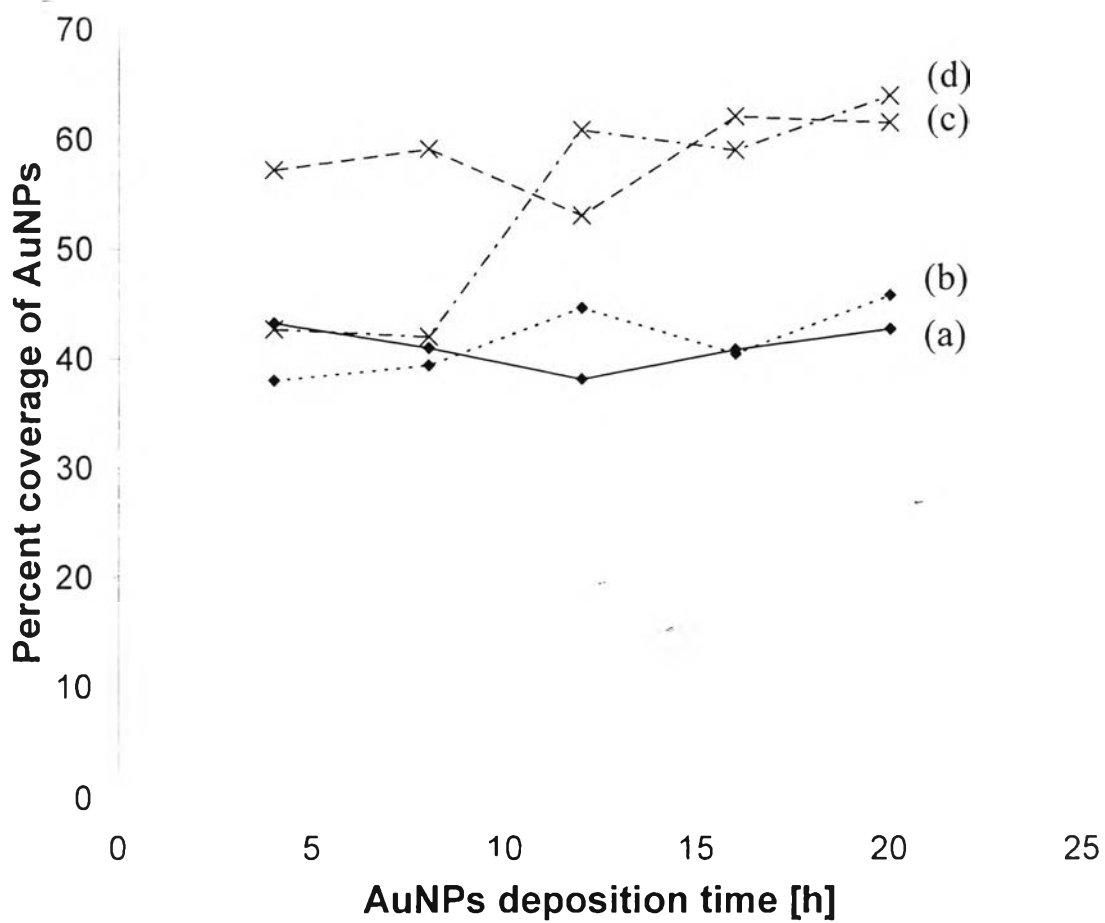


**Figure 4.26** AFM images of glass slide treated with PEI solution and deposited with AuNPs for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.





**Figure 4.27** AFM images of polyimide treated with PEI solution and deposited with AuNPs for: (a) 4, (b) 8, (c) 16 and (d) 20 hours.



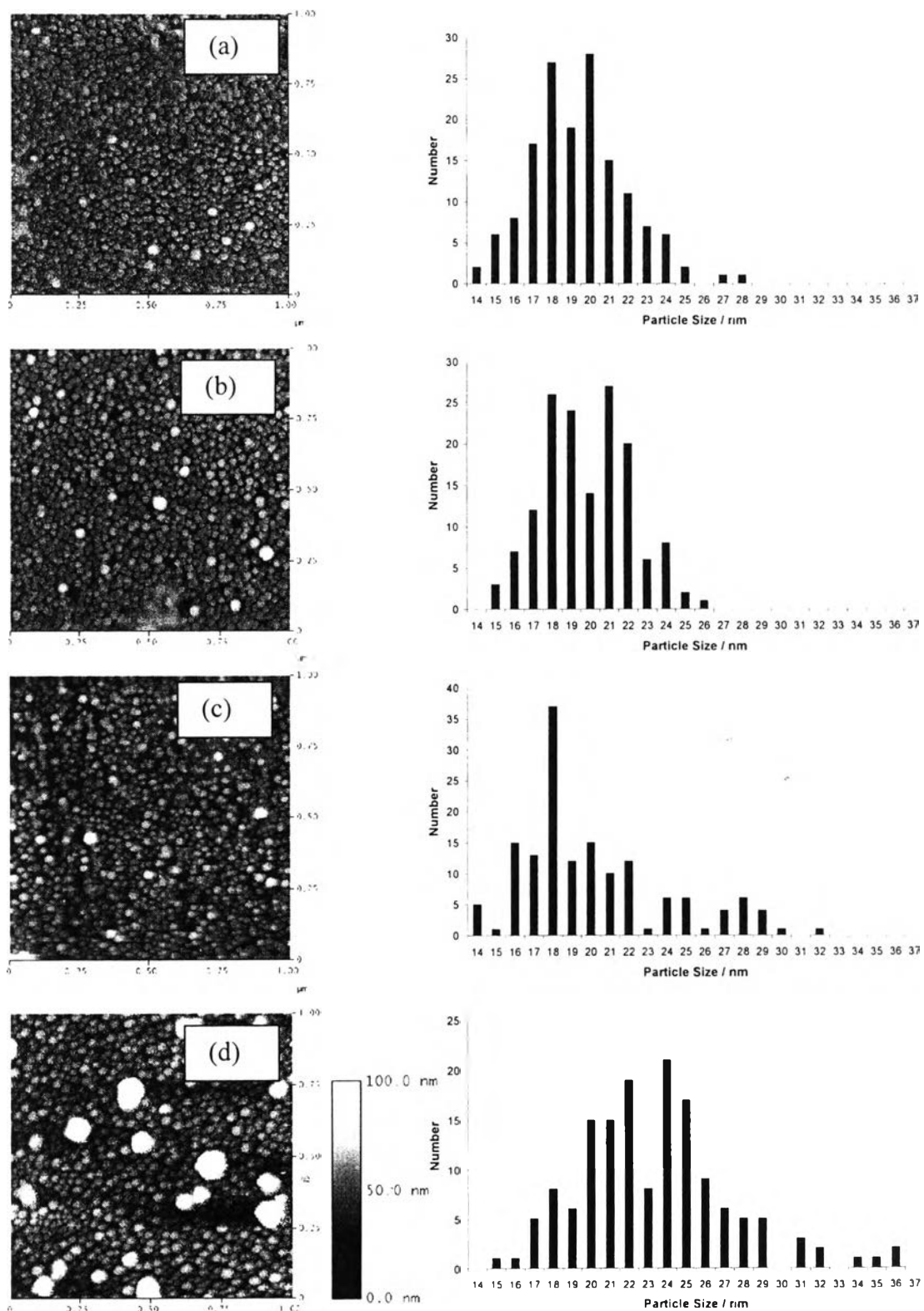
**Figure 4.28** Percent coverage of AuNPs on surfaces modified by modifying agent and deposited by AuNPs for various durations: (a) APTMS-modified glass, (b) APTMS-modified polyimide, (c) PEI-modified glass and (d) PEI-modified polyimide

#### 4.2.4 Annealing temperature

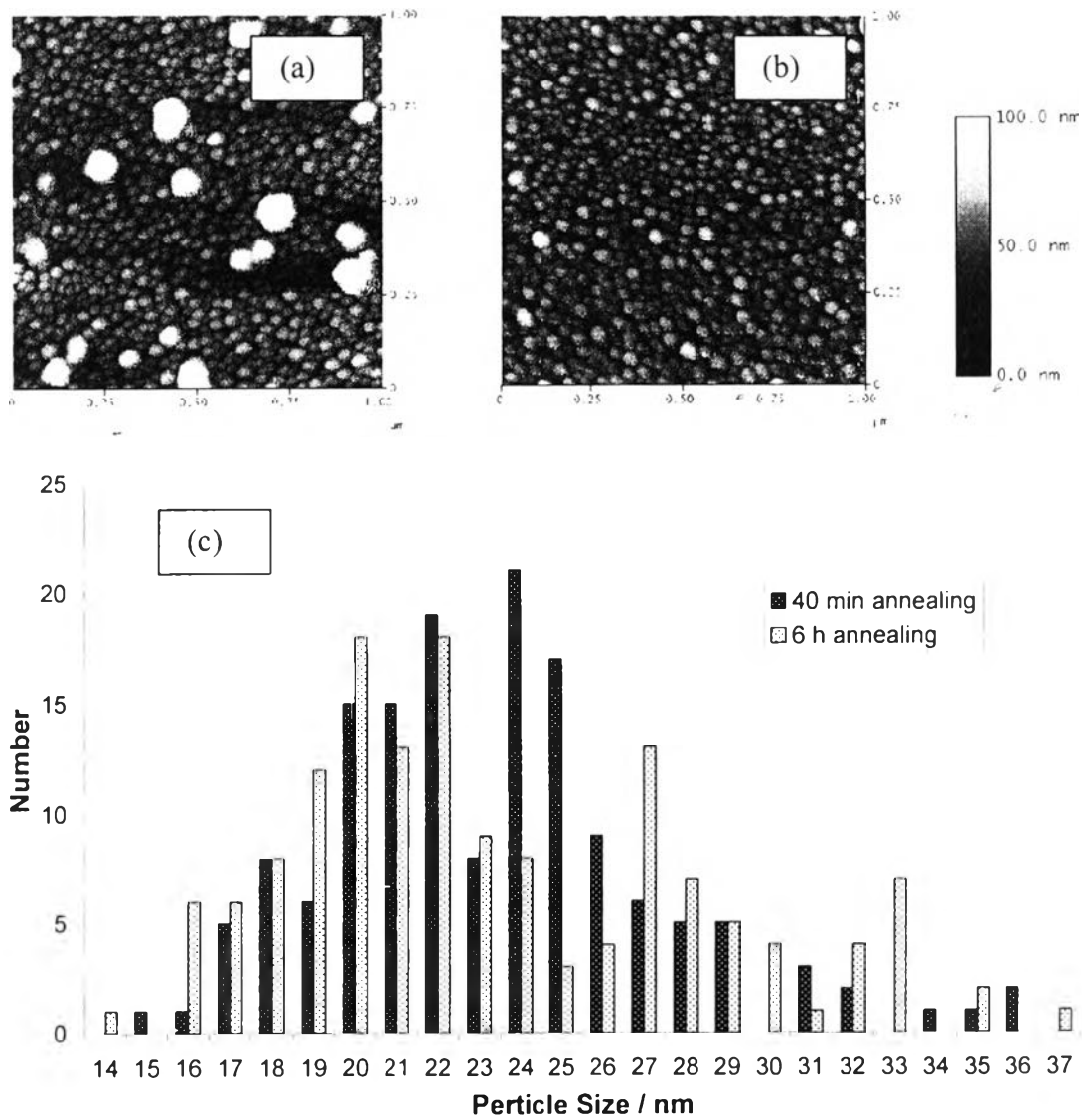
Effect of heat treatment on the AuNPs thin film is investigated in this section. In the study, AuNPs were deposited on glass slide, which is modified by 1.25 %wt. solution of APTMS or PEI for 12 hour. The AuNPs deposition was done for 12 hours. Then, the sample was annealed at 200, 300, 400 and 500°C, for 40 min. Polyimide was not employed in this experiment because it can not withstand temperature higher than 300°C. The surface morphology of assembled AuNPs monolayer on the modified substrate was investigated by AFM.

Figure 4.29 shows the AFM images of AuNPs deposited on glass slide treated with APTMS solution and subsequently annealed at various temperatures. Size distribution of AuNPs deposited is also reported next to the AFM picture. The result for AuNPs on APTMS-modified glass slide annealed at 200, 300, 400 and 500°C are shown in Figure 4.29(a-d), respectively.

According to size distribution of AuNPs in each condition, it shows that particle size is generally increased when annealing temperature is increased. It may be due to the sintering of AuNPs to form bigger gold cluster at higher temperature. Figure 4.30 shows images of AuNPs deposited on APTMS-modified glass, which are subsequently annealed at 500°C for different time. Figure 4.30(a) shows AuNPs image after 40 minutes of annealing time, which the sample annealed for 6 hours is shown in Figure 4.30(b). The comparison of AuNPs size distribution from these two annealing condition can be seen in Figure 30(c). It can be seen that the particle size of AuNPs also increases after extended annealing period. This is caused in the same manner as previously described.

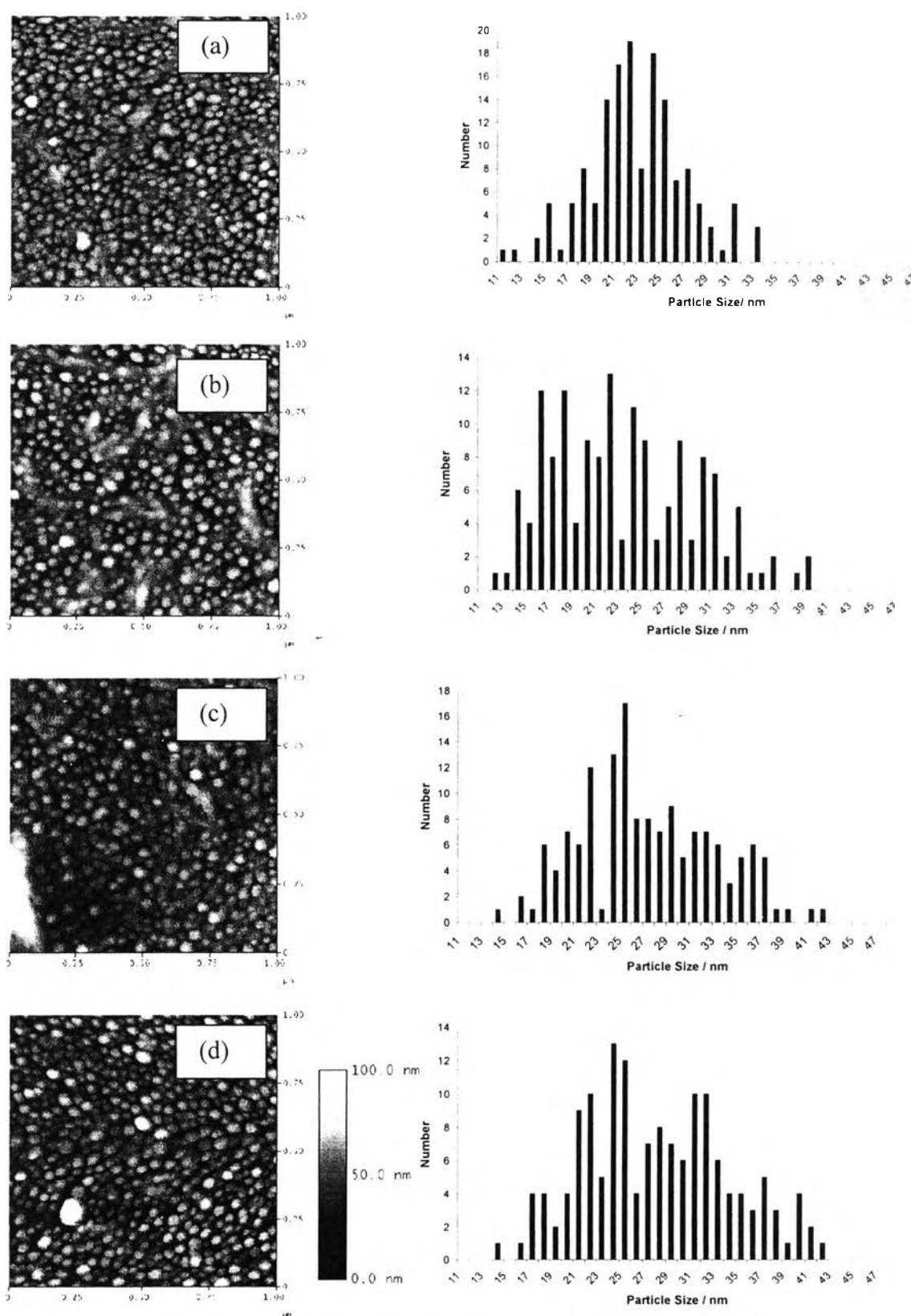


**Figure 4.29** AFM images and particle size distribution of AuNPs film on APTMS-modified glass after annealed at: (a) 200, (b) 300, (c) 400 and (d) 500°C.

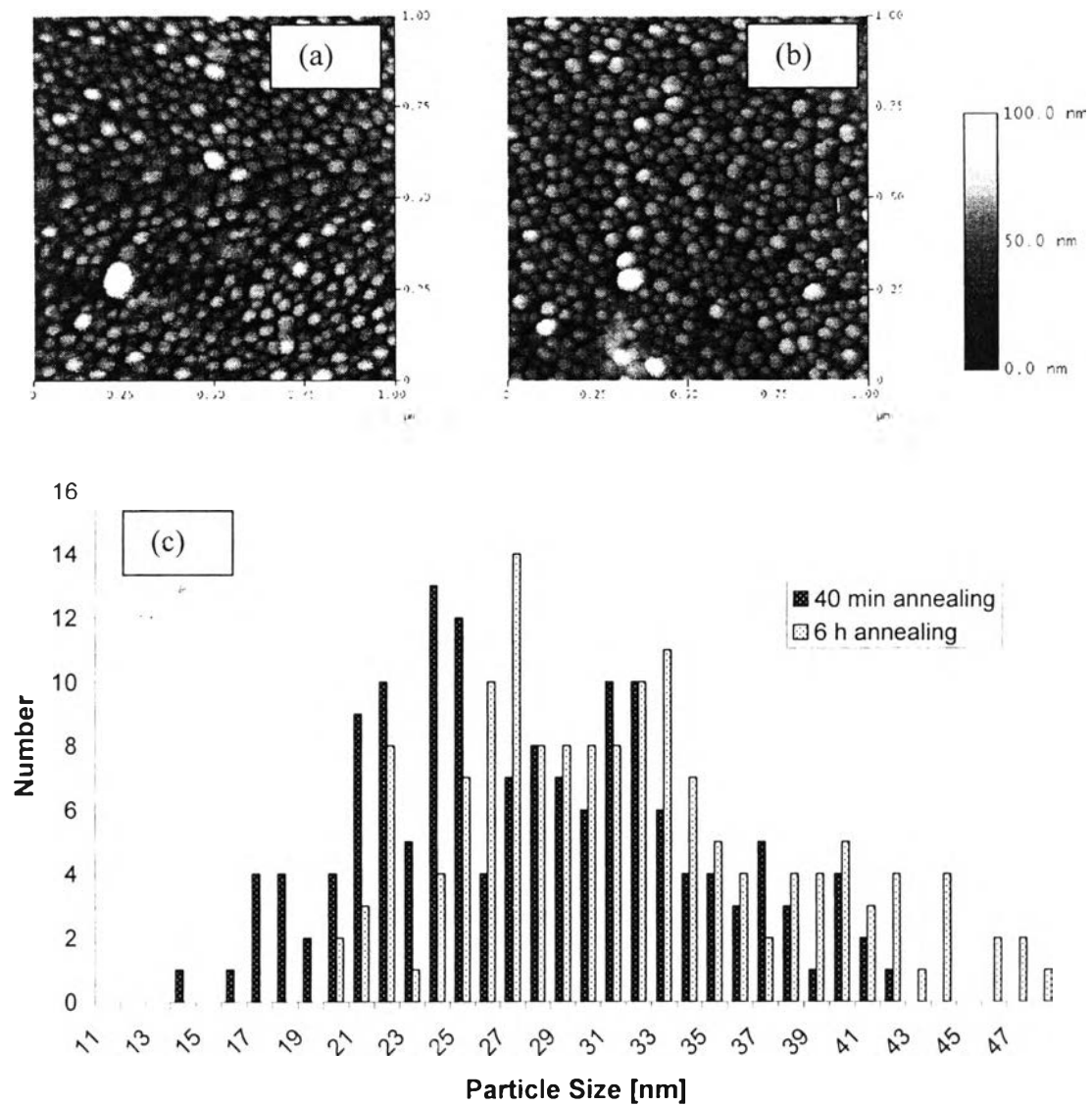


**Figure 4.30** Results of AuNPs deposited on APTMS-modified glass slide and annealed at 500°C: (a) AFM image of sample annealed for 40 min, (b) AFM image of sample annealed for 6 h and (c) size distribution of AuNPs deposited on the substrates.

Figure 4.31 shows the AFM images as well as the size distribution of AuNPs deposited on glass slide treated with PEI solution and subsequently various temperatures. From size distribution data of AuNPs in each condition, it shows that particle size tends to increase when the annealing temperature is increased. It may be due to the fact that AuNPs are sintered together at higher temperature, in the same fashion as previously observed from APTMS-modified glass. The effect of the annealing time on the size of AuNPs deposited on PEI-modified glass is shown in Figure 4.32. It is also found that the size distribution of the deposited AuNPs shifts toward the bigger size due to the sintering.



**Figure 4.31** AFM images and particle size distribution of AuNPs film on PEI-modified glass after annealed at: (a) 200, (b) 300, (c) 400 and (d) 500°C.



**Figure 4.32** Results of AuNPs deposited on PEI-modified glass slide and annealed at 500°C: (a) AFM image of sample annealed for 40 min, (b) AFM image of sample annealed for 6 h and (c) size distribution of AuNPs deposited on the substrates.