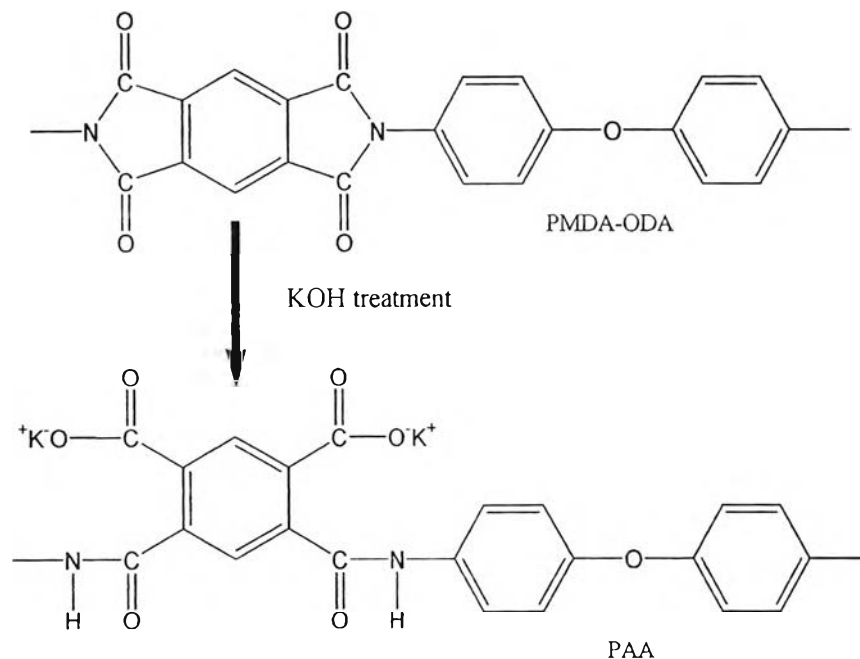




#### 4.1 Surface modification

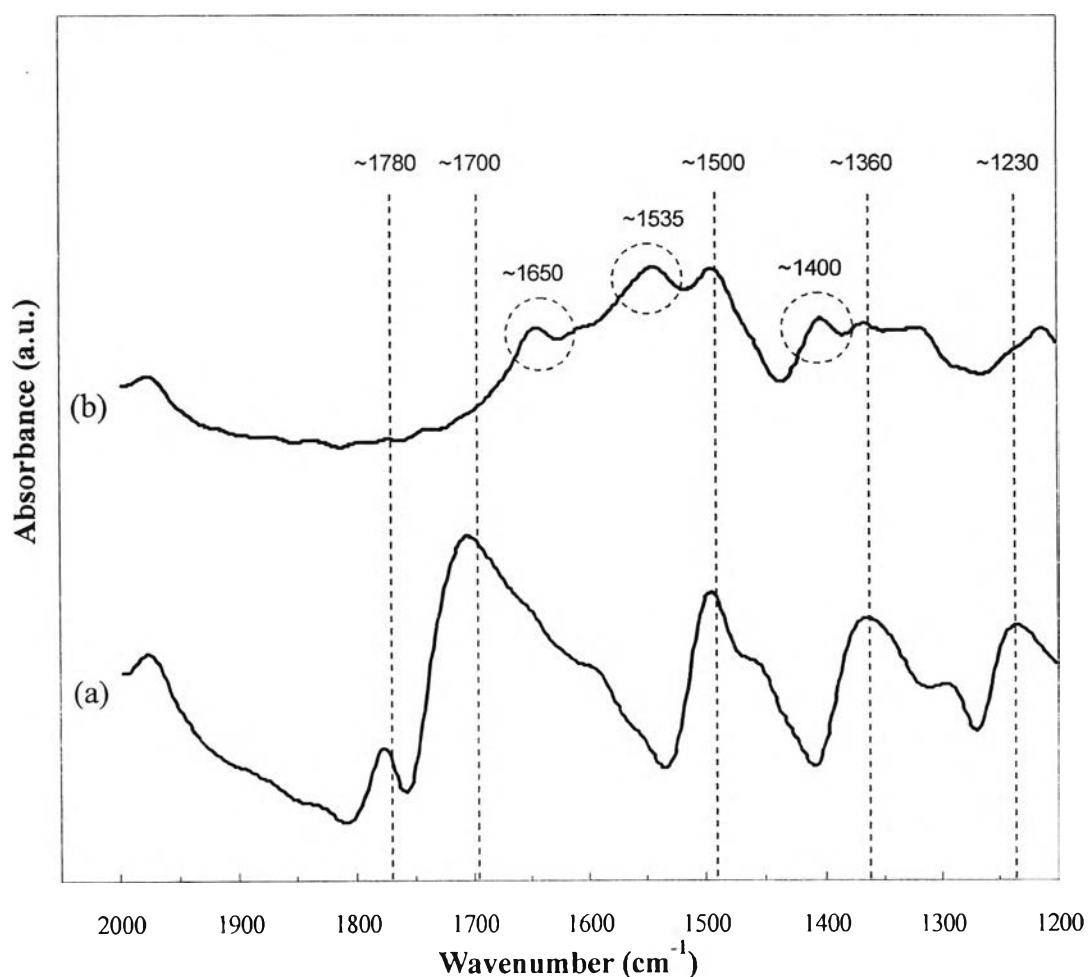
The first step of silver coating onto polyimide film surface is changing surface bonding of polyimide film by KOH aqueous solution (see Figure 4.1). The changes in bonding of polyimide on the surface after modified with KOH were monitored by ATR-FTIR. Figure 4.2 shows ATR-FTIR spectra of polyimide before and after modification with KOH. In Figure 4.2(a), characteristic bands of pristine polyimide surface (PMDA-ODA) are clearly visible at wavenumber of about 1780, 1700, 1500, 1360, 1230  $\text{cm}^{-1}$ , corresponding to symmetric C=O stretching, asymmetric C=O stretching, C=C in benzene ring, C-N-C stretching in imide ring, and aromatic ether (Ar-O-Ar) stretching vibrations, respectively (Hisao et al., 2008).



**Figure 4.1** Mechanism of surface modification with KOH.

After the modification with KOH, the absorption bands at wavenumber of about 1780 and 1700  $\text{cm}^{-1}$  from symmetric and asymmetric C=O stretching in imide structure have completely disappeared, while broaden bands can be seen at

wavenumber  $1400\text{--}1600\text{ cm}^{-1}$  (see Figure 4.2). In detail, these bands are results from the vibration of carboxyl group ( $\sim 1650$  and  $\sim 1400\text{ cm}^{-1}$ ) complexed with  $\text{K}^+$ , superposition of the vibration of amide I ( $\sim 1650\text{ cm}^{-1}$ ) and amide II ( $\sim 1535\text{ cm}^{-1}$ ) (Wu et al., 2005). This result indicates that KOH treatment cleaves the imide ring to form carboxyl and amide groups. The fact that the absorption bands at wavenumber  $\sim 1780$  and  $\sim 1700\text{ cm}^{-1}$  are eliminated after KOH modification means polyimide surface is completely hydrolyzed to form potassium polyamate.

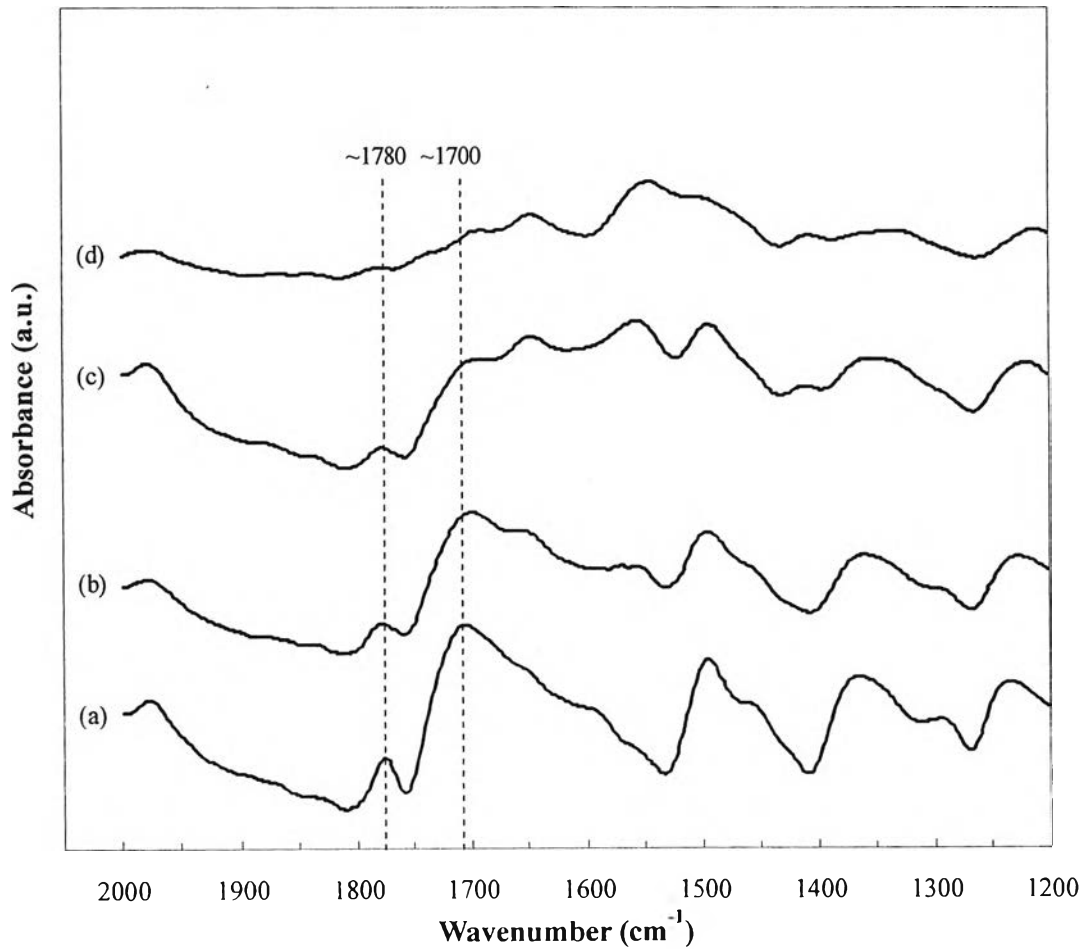


**Figure 4.2** ATR-FTIR spectra of polyimide film surface before (a) and after (b) modification with KOH.

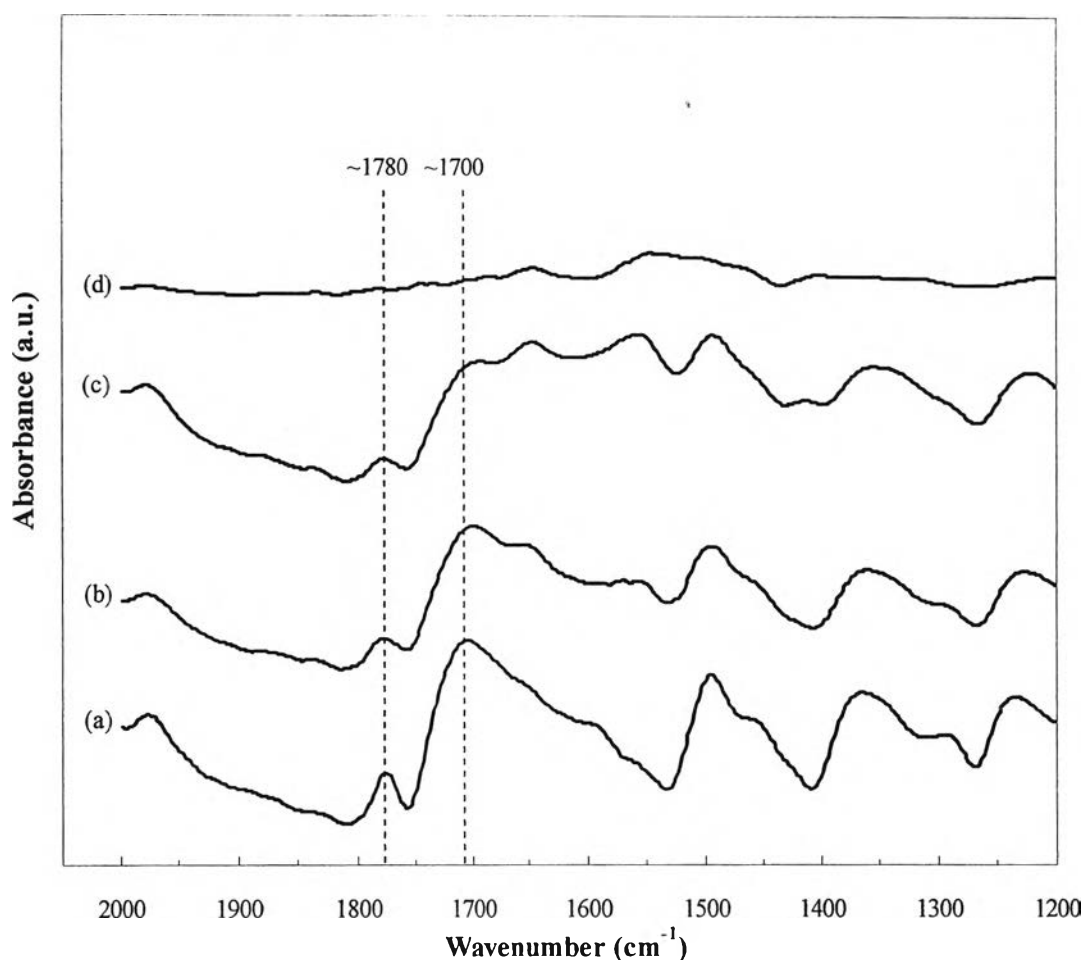
#### 4.1.1 Effect of time and temperature in surface modification

According to Figure 4.3 and Figure 4.4, when polyimide film surface is modified with KOH for prolonged period of time or at increased temperature, the absorption bands at  $\sim 1780$  and  $\sim 1700\text{ cm}^{-1}$  are significantly decreased. It means that these conditions results in the cleavage of imide rings in greater extent. Table 4.1 and

Table 4.2 show relative imide content on the surface, which was calculated from the normalized value of the ratio between height of absorption bands at  $1700\text{ cm}^{-1}$  (asymmetric C=O stretching in imide) and  $1365\text{ cm}^{-1}$  (N-H stretching). When the modification time is increased, the relative imide content decreases from 100% to 10.98% within only 5 minutes. For the effect of temperature, the relative imide content decreases to 0 when the modification temperature is increased to  $70\text{ }^{\circ}\text{C}$ .



**Figure 4.3** ATR-FTIR spectra of pristine polyimide film surface (a) compared with KOH at  $50\text{ }^{\circ}\text{C}$  for 1 minute (b), 3 minutes (c) and 5 minutes (d).



**Figure 4.4** ATR-FTIR spectra of pristine polyimide film surface (a) compared with polyimide film surface modified with KOH at 50 °C (b), 60 °C (c) and 70 °C (d) for 1 minute.

According to the 2<sup>k</sup>-factorial design of experiments, it was found that the modification temperature has greater effect than the modification time when 2 M of KOH aqueous solution is used (with the statistical parameters of 34.14 versus 16.26). This result also indicates that the diffusion of KOH into PI played an important role during the modification step.

**Table 4.1** Relative imide content on the surface of polyimide film modified with KOH at 50 °C for various periods of time.

Conditions	Peak height	Peak height	$H_{1700}/H_{1365}$	Relative imide content (%)
	at 1700 $\text{cm}^{-1}$ ( $H_{1700}$ )	at 1365 $\text{cm}^{-1}$ ( $H_{1365}$ )		
(a) Pristine PI	0.8662	0.3904	2.2188	100
(b) Modified for 1 min	0.3542	0.2684	0.9073	40.8912
(c) Modified for 3 min	0.1605	0.2164	0.4111	18.5292
(d) Modified for 5 min	0.0951	0.0171	0.2436	10.9790

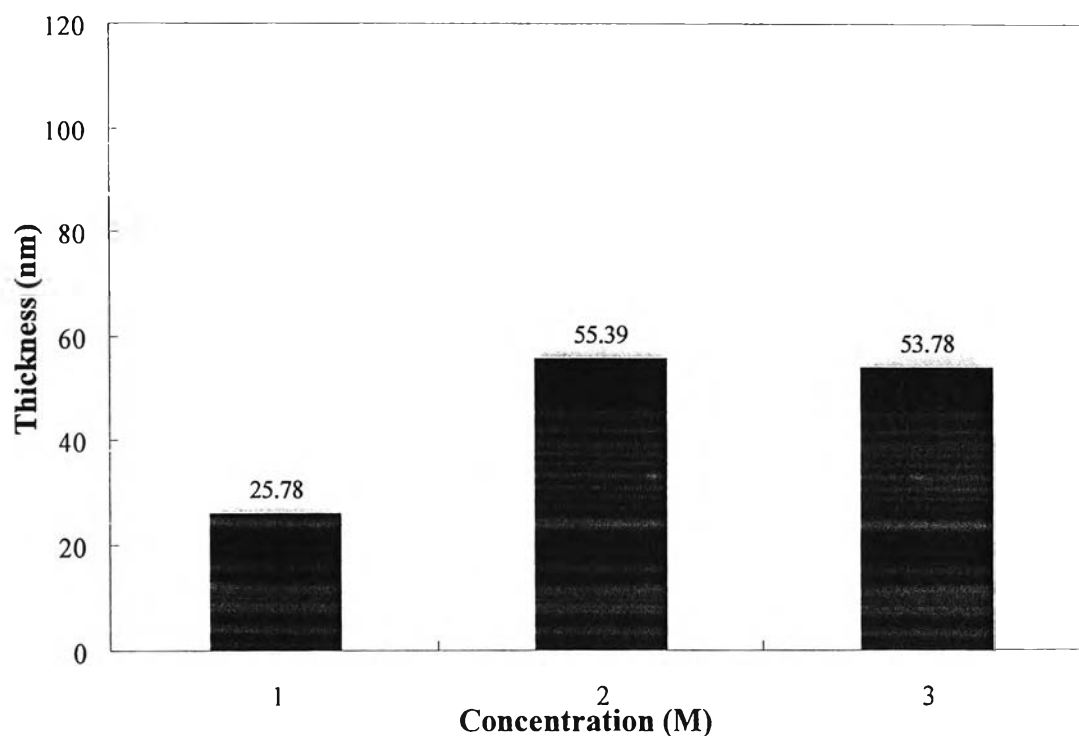
**Table 4.2** Relative imide content on the surface of polyimide film modified with KOH at various temperatures for 1 minute.

Conditions	Peak Height	Peak Height	$H_{1700}/H_{1365}$	Relative imide content (%)
	at 1700 $\text{cm}^{-1}$ ( $H_{1700}$ )	at 1365 $\text{cm}^{-1}$ ( $H_{1365}$ )		
(a) Pristine PI	0.8662	0.3904	2.2188	100
(b) Modified at 50 °C	0.3542	0.2684	0.9073	40.8912
(c) Modified at 60 °C	0.1896	0.2478	0.4857	21.8887
(d) Modified at 70 °C	0	0.0193	0	0

#### 4.1.2 Effect of concentration in surface modification

Figure 4.5 shows thickness of silver layer after ultraviolet irradiation with different concentration of KOH solution. It was found that 1 M of KOH solution has a little effect to thickness of silver layer. The thickness of the silver layers is significantly increased after the modification with 2 M of KOH (25.78 to 55.39)

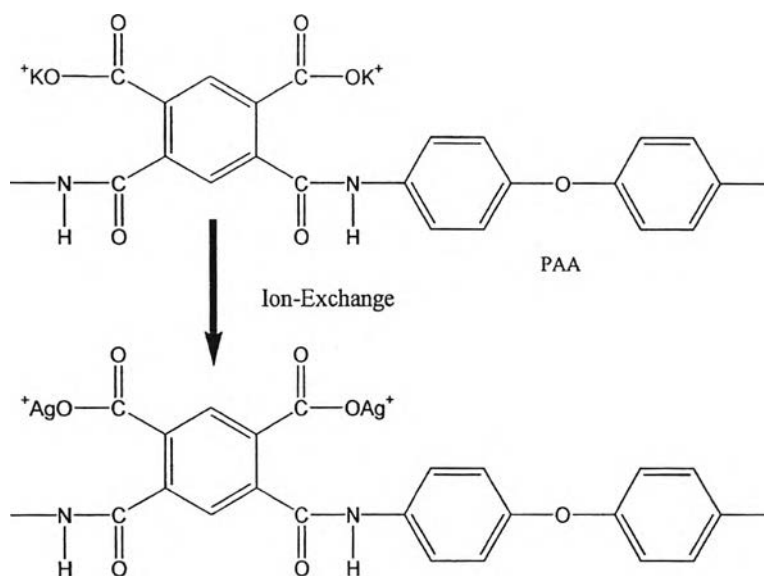
solution. Effects from 2 and 3 M KOH solution are not different. However, this effect at high concentration can not be confirmed because film becomes thinner after KOH modification.



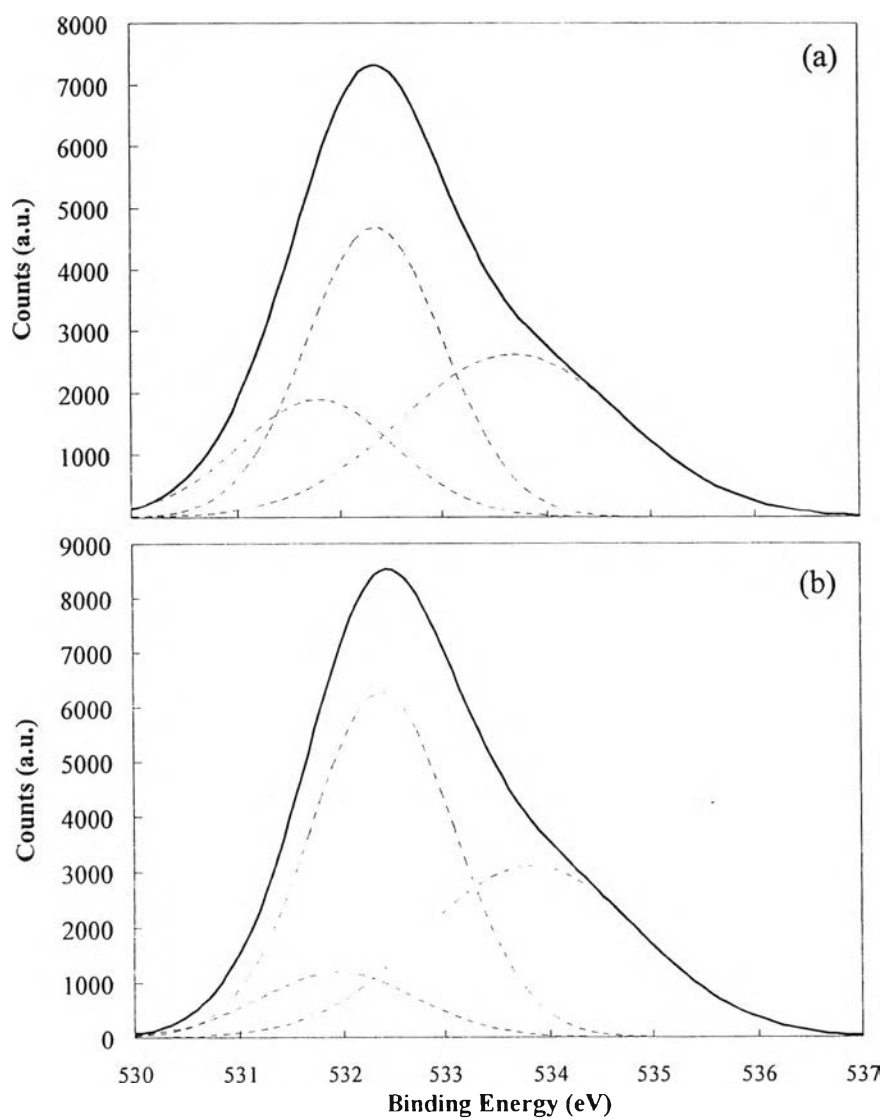
**Figure 4.5** Thickness of silver layer after conventional UV irradiation on PI modified with KOH at different concentration.

#### 4.1.3 Silver impregnation

After modification with KOH, the imide ring of polyimide film surface is cleaved to form carboxyl group for exchange ion with silver ion (see Figure 4.6). According to XPS analysis shown in Figure 4.7(a), XPS spectrum of O1s core-level of pristine polyimide film can be deconvoluted into 3 peaks, i.e. at 533.6 eV corresponding to COOH, at 532.4 eV corresponding to CO and at 531.7 eV corresponding to carbonyl groups (C=O, COOH and CONH) (Qi et al., 2009). After impregnation with silver, intensity of the peak at 531.7 eV (carbonyl groups) decreases substantially as shown in Figure 4.7(b). This is an evidence that carbonyl group is modified by forming C-O-Ag bonding.



**Figure 4.6** Mechanism of silver impregnation to polyimide film.

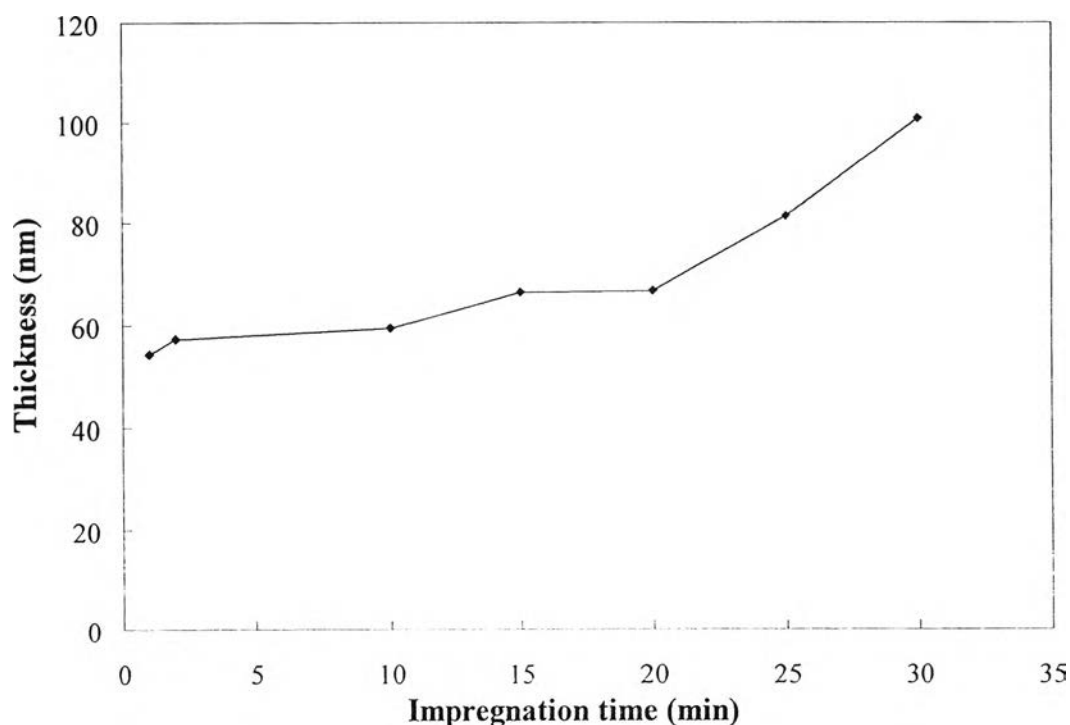


**Figure 4.7** XPS spectra of O1s core-level of: a) pristine PI and b) ion exchange with silver.

Amount of silver in polyimide was determined based on the thickness of silver layer obtained after reduction by ultraviolet irradiation (the calibration curve for the determination of the thickness of silver layer is shown in Appendix A). Figure 4.8 shows that the increase in time for silver impregnation results in increased thickness of silver layer. The result is due to the fact that large number of silver ion can be exchanged when the silver impregnation time is prolonged, as witnessed from the increase in Ag 3d signal observed by XPS analysis show in Table 4.3.

**Table 4.3** Relative atomic concentration (at. %) of PI impregnated with silver for various periods of time, monitored by XPS.

Silver impregnation time (min)	Relative atomic concentration (at. %)		
	C1s	O1s	Ag3d
10	24.7178	22.1585	53.1237
20	23.7002	22.759	53.5405
30	25.8545	20.5686	53.5768
40	25.7119	19.1539	55.1341
50	25.2669	18.9903	55.7427



**Figure 4.8** Thickness of silver layer obtained by ultraviolet irradiation, as function of time for silver impregnation.

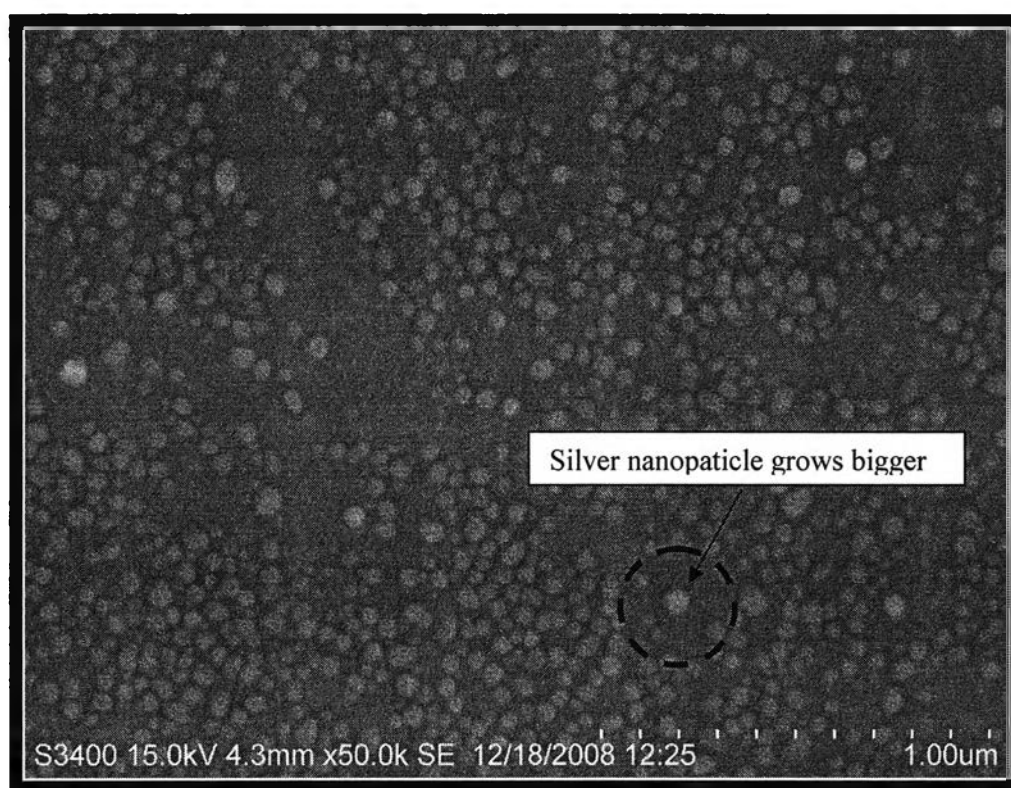


## 4.2 Ultraviolet irradiation

After Silver-impregnated polyimide film was reduced by irradiation with ultraviolet light, small clusters of silver nanoparticles were formed on polyimide film surface according to this possible reaction mechanisms (Akamustsu et al., 2003).

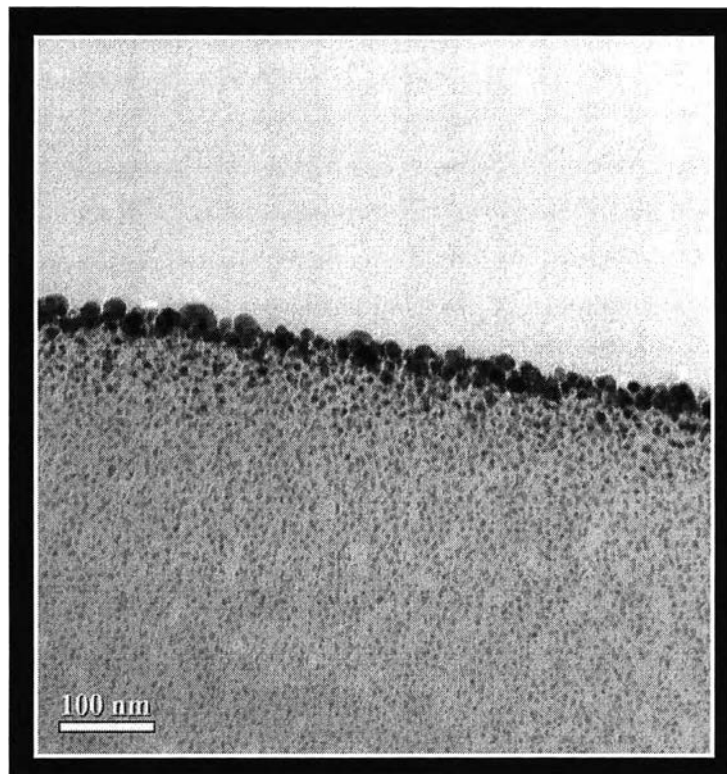


Ultraviolet-light-induced reaction of silver ions can be initiated by electron transfer from carboxyl group to silver ions, which forms carboxyl radicals and silver atoms. The agglomeration of silver atoms produced silver nanoparticles as shown in Equation (2). SEM image of polyimide film surface after ultraviolet irradiation (Figure 4.9) clearly shows cluster of silver nanoparticles. It should be pointed out that the growth of silver nanoparticles is the result from migration of the surrounding silver atoms/ions into the silver seed. Therefore, the area surrounding a nanoparticle is found to be empty (Tang et al., 2009).

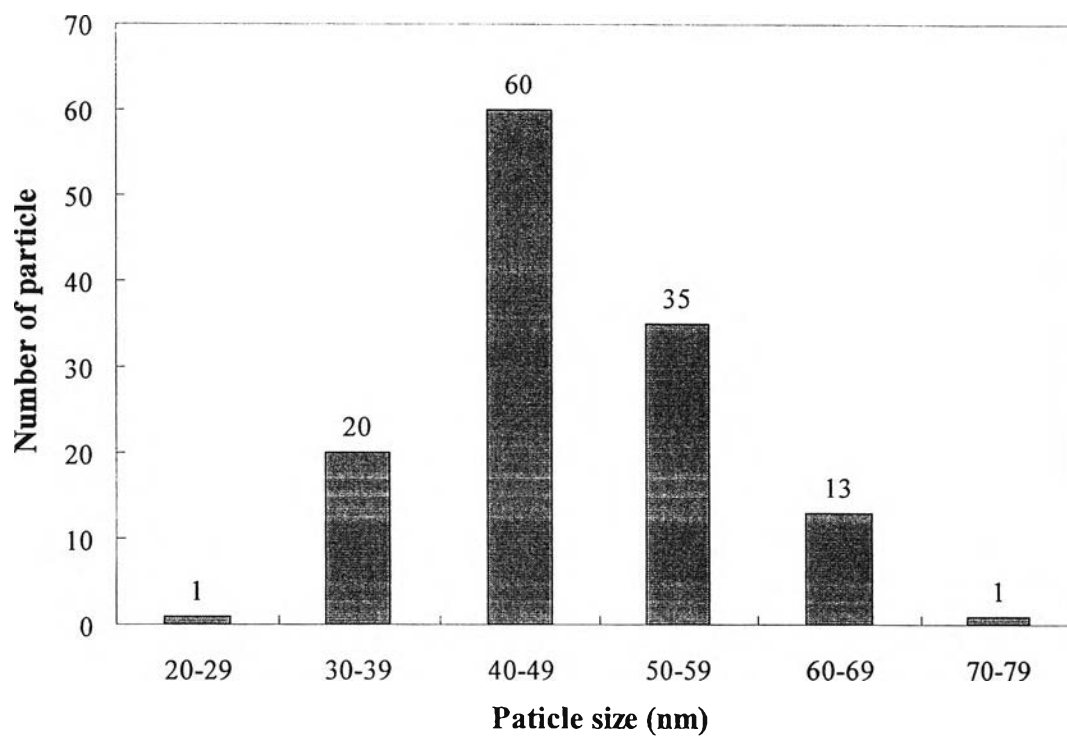


**Figure 4.9** SEM image of silver nanoparticles on polyimide surface reduced by ultraviolet irradiation.

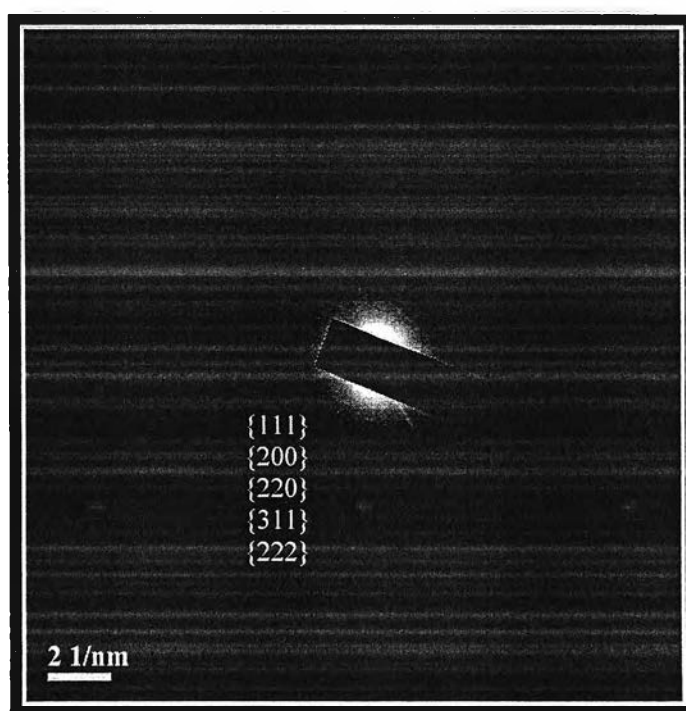
According to Figure 4.10, which is a TEM cross-section image, distribution of silver nanoparticles on polyimide surface are wide-spread because the growth of silver nanoparticles needs accumulation of silver atoms ( $\text{Ag}^0$ ) from nearby area to form larger particles. Size of the silver nanoparticles varies from 20-79 nm, but most particle size is in range from 40-49 nm and the average size is 43.23 nm. The size distribution is shown in Figure 4.11. The selected area electron diffraction (SAED) pattern of the silver layer is illustrated in Figure 4.12, in which the diffraction rings are indexed to pure silver in FCC structure (Wang et al., 2008).



**Figure 4.10** TEM cross-section image of polyimide coated with silver nanoparticles, reduced by ultraviolet irradiation.



**Figure 4.11** Size distribution of silver nanoparticles on polyimide film surface reduced by ultraviolet irradiation.



**Figure 4.12** SAED pattern of silver layer formed on polyimide film surface by ultraviolet irradiation for 3 hours. The diffraction rings are assigned to  $\{111\}$ ,  $\{200\}$ ,  $\{220\}$ ,  $\{311\}$  and  $\{222\}$  reflections of silver metal respectively.

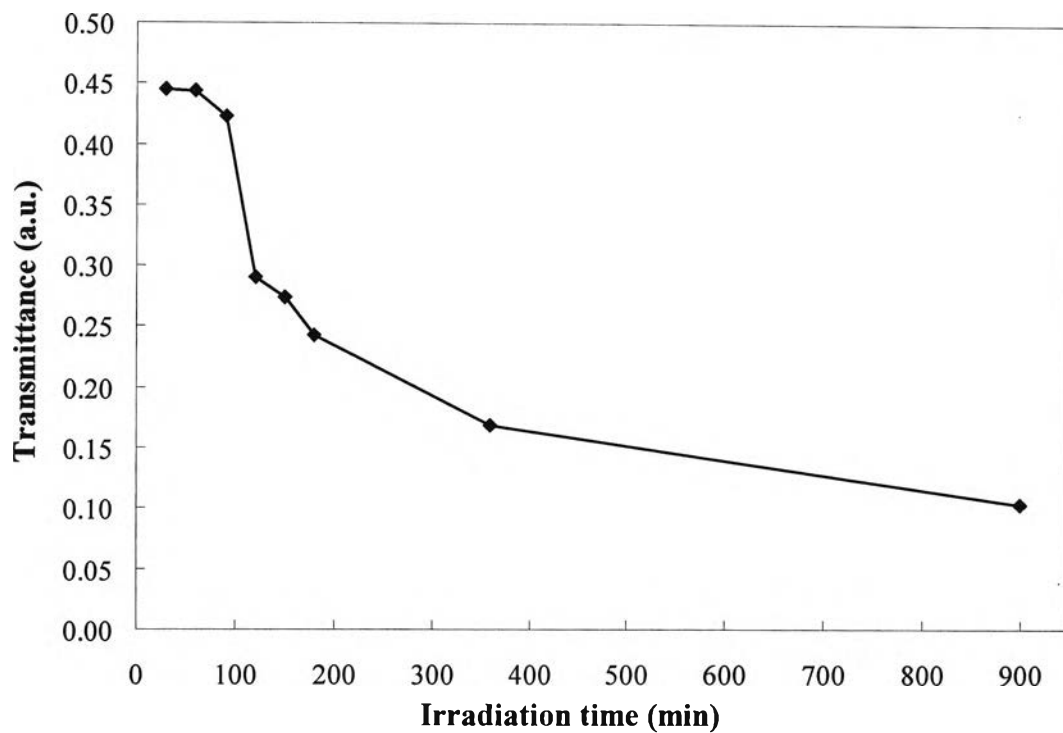
Figure 4.10 also shows that size of silver nanoparticles decreases along the depth from polyimide film surface. This is the result from the fact that, when silver on the surface is reduced by ultraviolet light and grows into particles, carboxyl group underneath can not effectively absorb ultraviolet light. Consequently, silver nanoparticles are formed in smaller size at deeper level from the surface.

#### *4.2.1 Effect of irradiation time*

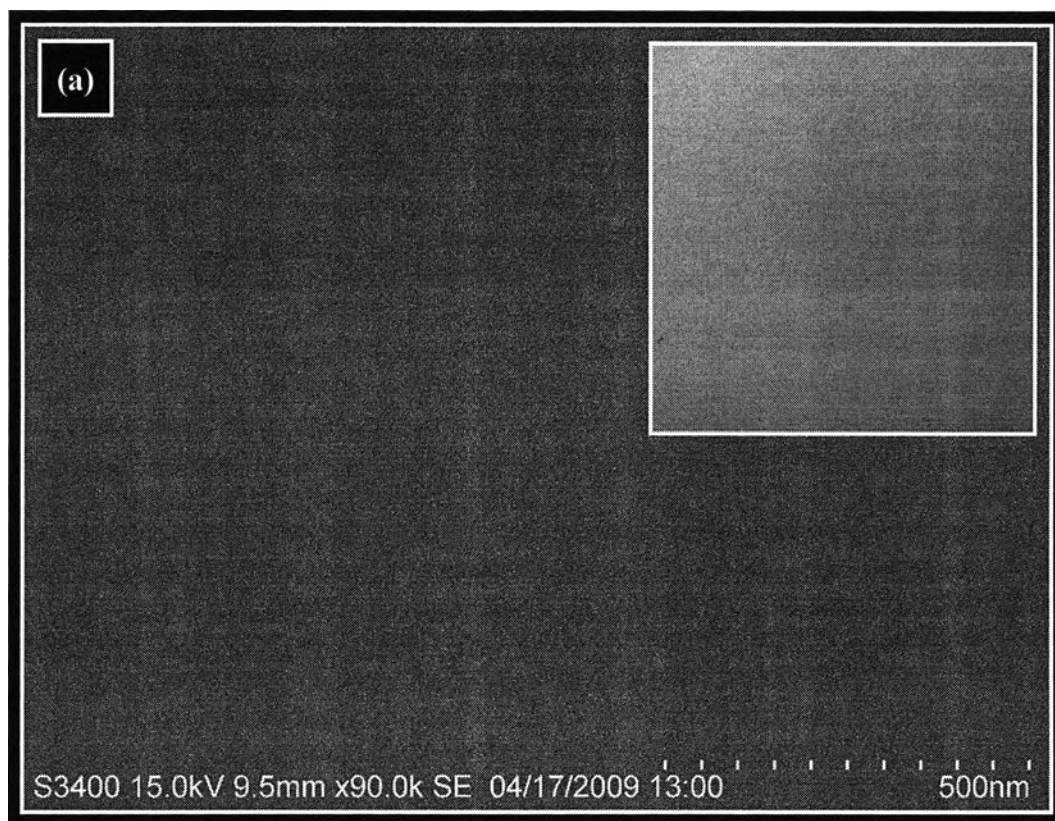
Figure 4.13 shows transmittance of light at wavelength 550 nm through polyimide film that was already irradiated by ultraviolet light for the period of 0 to 900 minutes. It can be seen that the transmittance significantly decrease after the polyimide film is exposed to ultraviolet light for a short period of time, which indicates abrupt growth of silver layer during the initial period of ultraviolet irradiation. After 360 minutes, the transmittance is not decreased as much as the first 360 minutes because silver nanoparticles near the surface have already grown thicker and blocked ultraviolet light not to pass through to the inner layer of the polyimide film.

The inset in Figure 4.14 are photographs of polyimide surface after ultraviolet irradiation for various periods of time. It is shown that as the time of irradiation is increased, the polyimide film becomes darker. This means the number of silver nanoparticles formed is increased because the silver-attached carboxylate group has received enough energy to reduce silver ion as well as the energy to growth for the growth of silver nanoparticles.

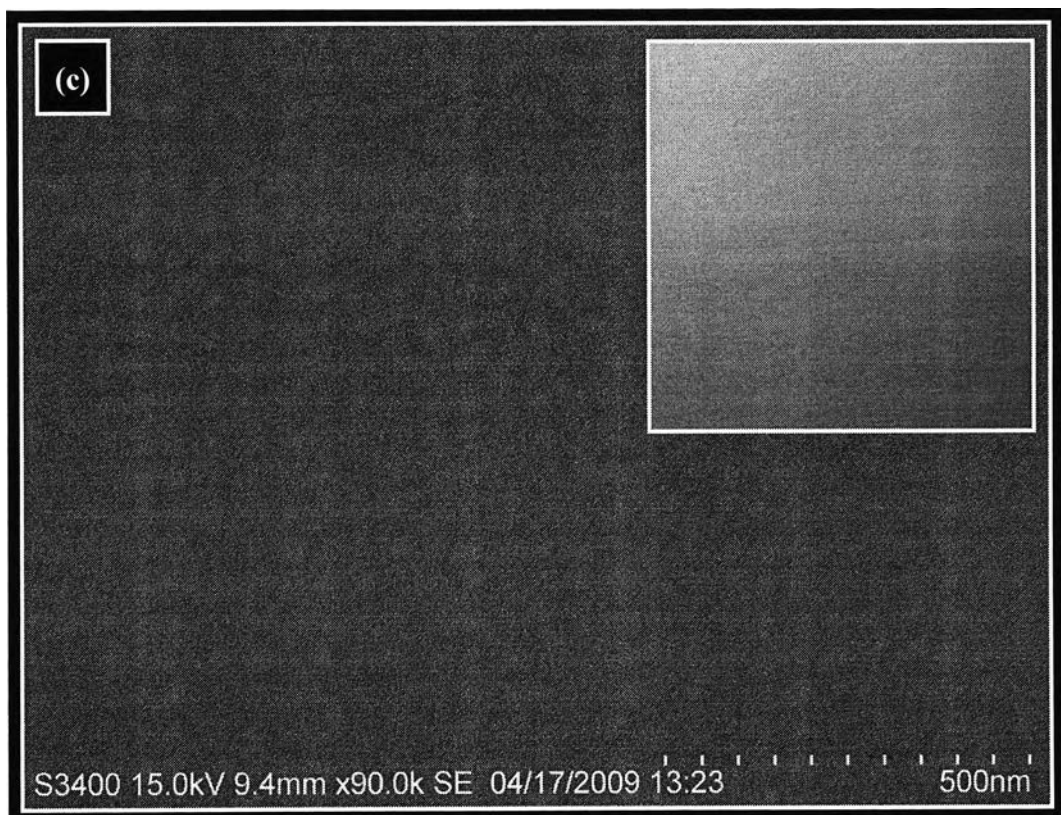
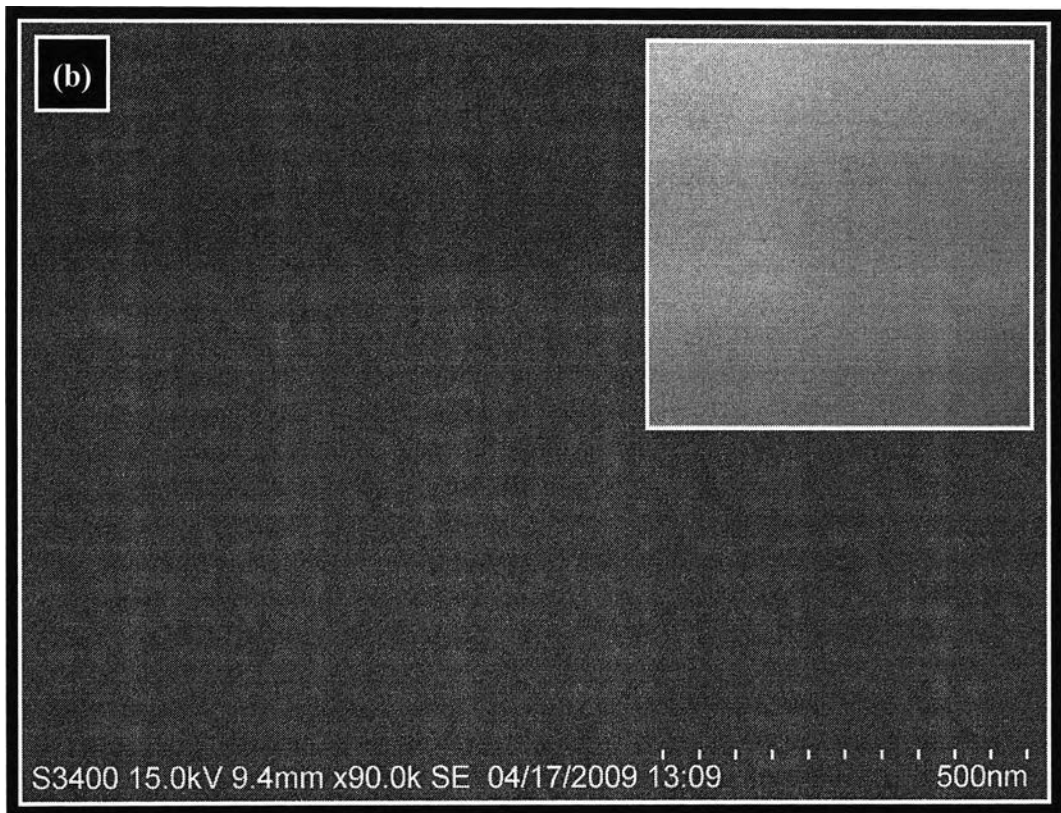
Figure 4.14 is SEM images of polyimide surface after ultraviolet irradiation for various periods of time. It is shown that the number of silver nanoparticles near the surface increases with the prolonged irradiation time. According to Figure 4.14(a) to Figure 4.14(d), no significant change in the number of silver nanoparticles formed on the surface is observed. However, after the irradiation time exceeds 150 minutes, amount of silver nanoparticles near the surface increases significantly, as shown in Figure 4.14(e) to Figure 4.14(h). This result agrees with blocking effect of silver nanoparticles formed on the surface described earlier.



**Figure 4.13** Transmittance of light at wave length of 550 nm through polyimide film after irradiated for various periods of time.



**Figure 4.14** SEM images of PI film after ultraviolet irradiation for various periods time: (a) 30 min, (b) 60 min, (c) 90 min, (d) 120 min, (e) 150 min, (f) 180 min, (g) 360 min and (h) 900 min.



**Figure 4.14** (Continued)

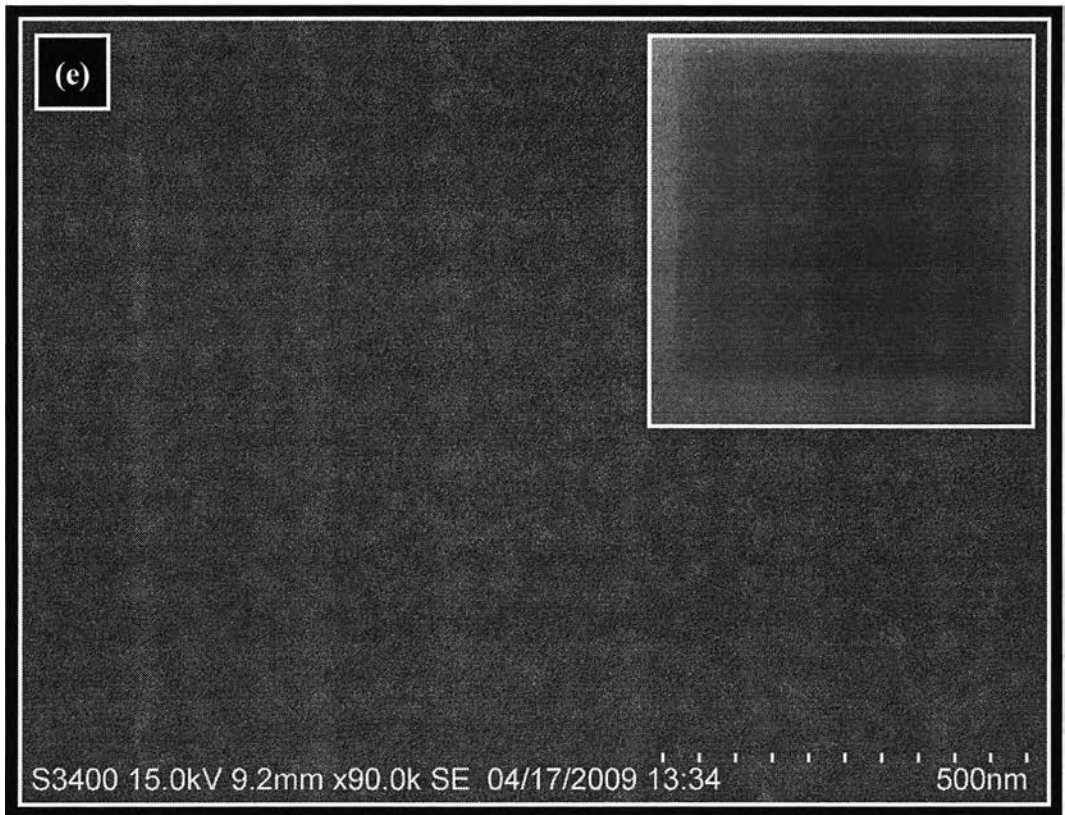
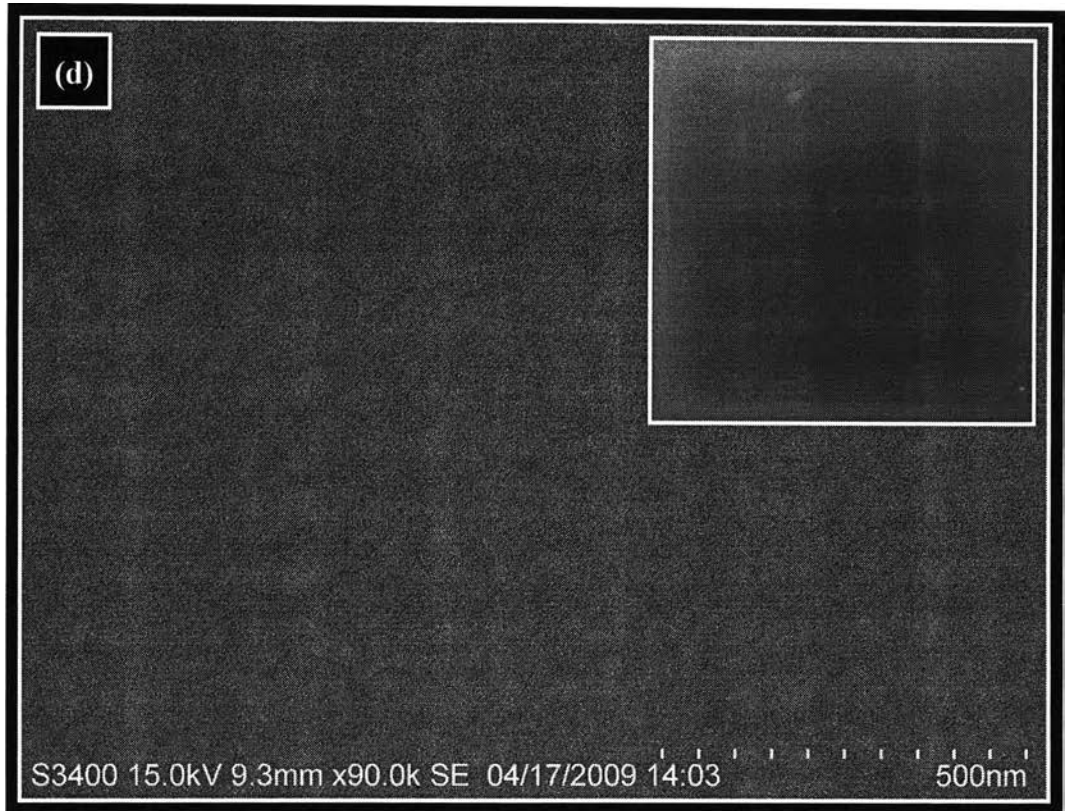
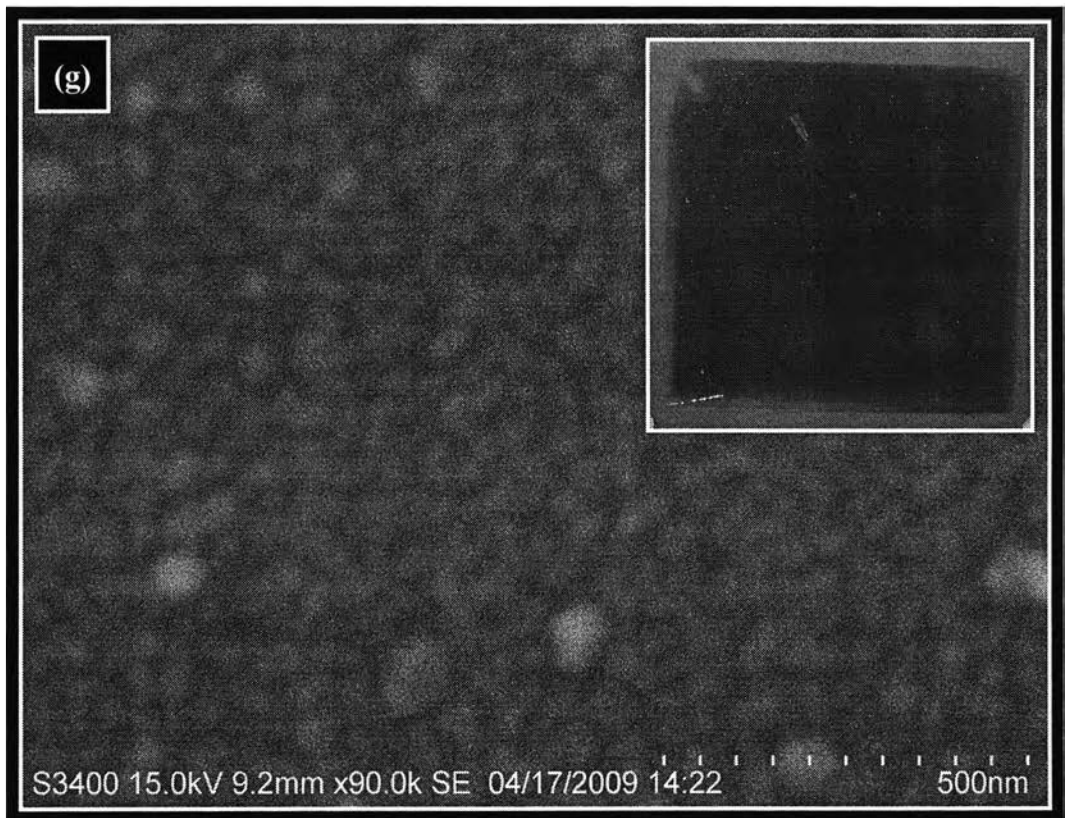
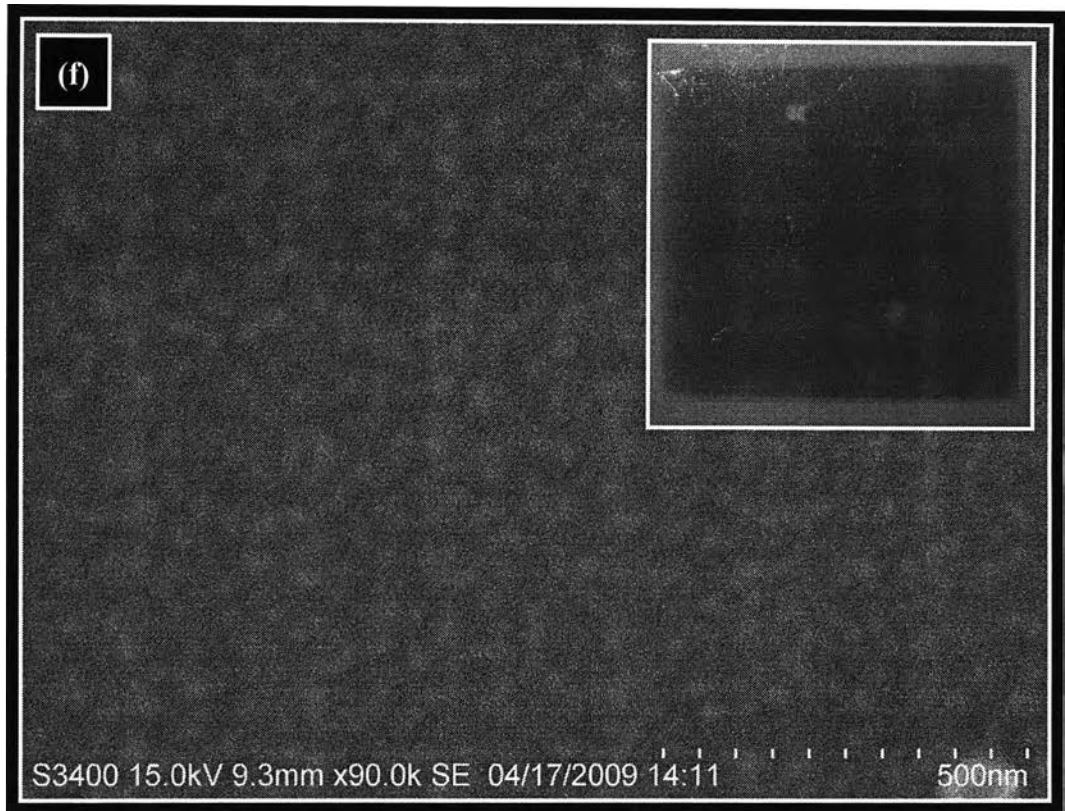
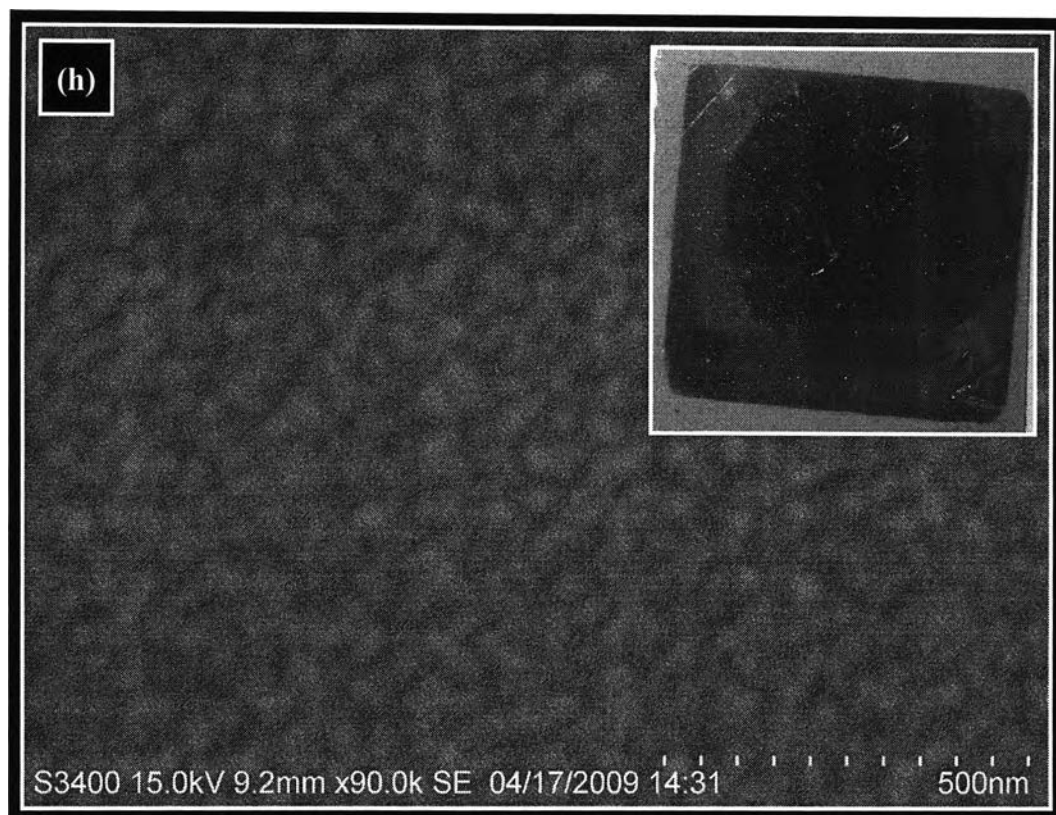


Figure 4.14 (Continued)



**Figure 4.14** (Continued)

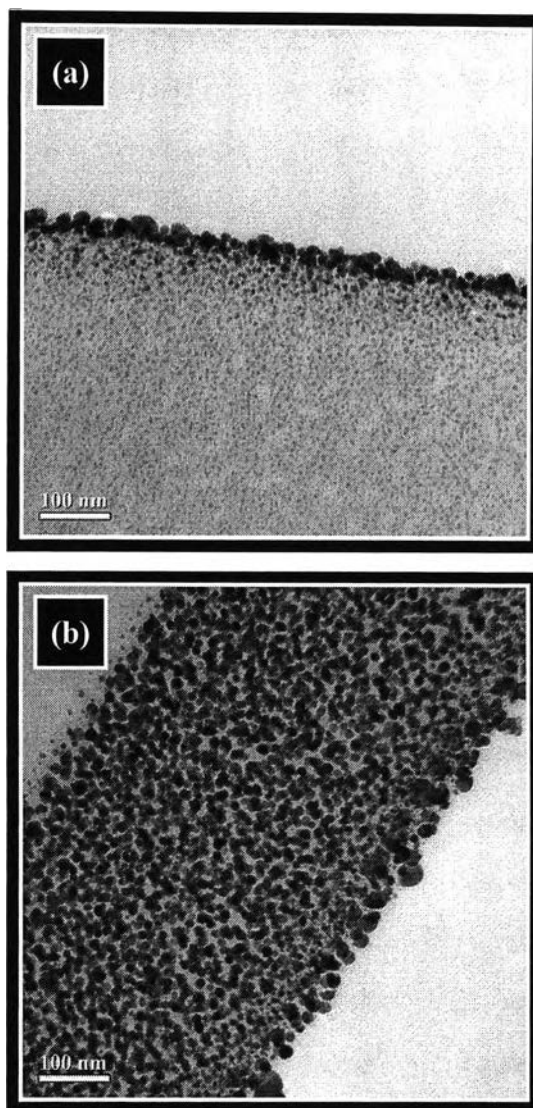




**Figure 4.14** (Continued)

#### 4.2.2 *Effect of heat treatment*

Growth of silver nanoparticles is increased when direct heat is supplied to polyimide film, after ultraviolet irradiation, by hot plate at 200 °C. Figure 4.15 shows that, after heat treatment, size of silver nanoparticles increases dramatically, especially in the deeper level underneath the surface, because direct heat gives more energy than ultraviolet lamps can provide and there is no blocking effect. So that thermal growth of silver nanoparticles is greater than that from ultraviolet irradiation. However, thermal growth needs silver nanoparticle seeds. If nanoparticle seeds are not present, heat treatment will not result in silver layer as thick as expected.



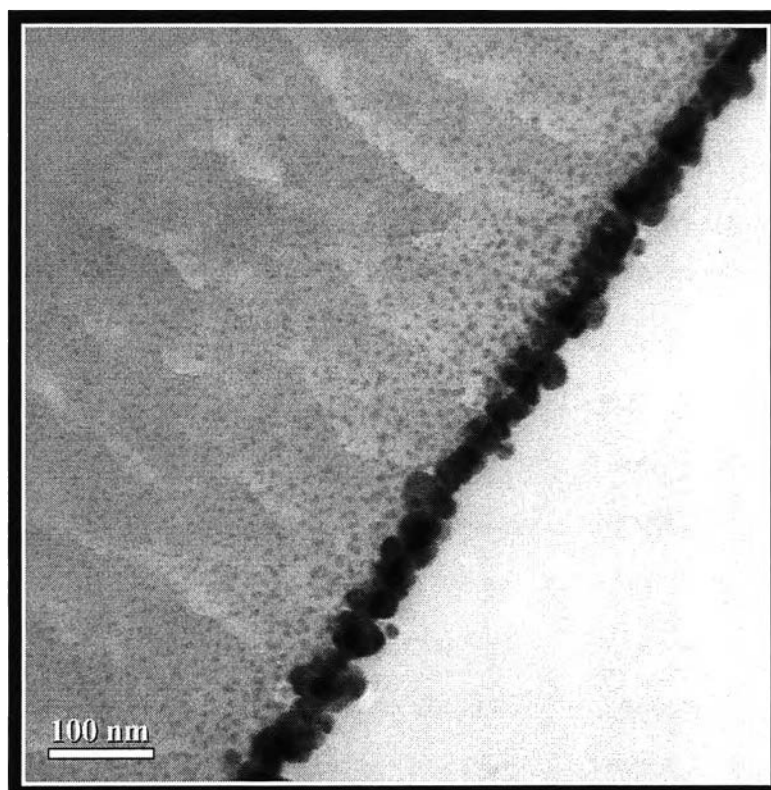
**Figure 4.15** TEM cross-section image of polyimide coated with silver nanoparticles, reduced by ultraviolet irradiation for 3 hours: (a) before heat treatment, (b) after heat treatment.

### 4.3 Water-assisted irradiation

In the photochemical process presented, the existence of water on polyimide surface plays an essential role in the growth of the silver thin films. Without water, small number of silver islands are formed on the surface after ultraviolet irradiation. On the contrary, when water was added onto the surface of the polyimide film during ultraviolet irradiation, much thicker layer of silver was formed on the film. This implies that the ultraviolet irradiation of silver ions is a water-accelerated process. Possible reaction mechanisms for the formation of Ag nanoparticles are:



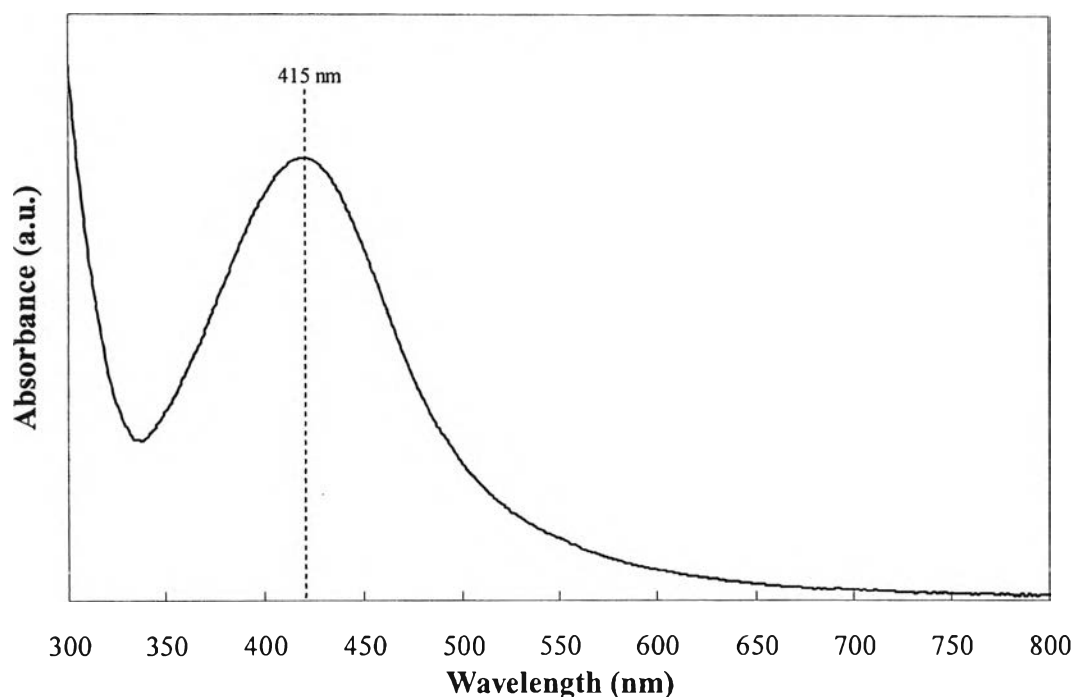
Figure 4.16 shows TEM cross section image of silver layer formed by ultraviolet irradiation assisted by distilled water. It shows that, under the existence of water, silver nanoparticles are formed near the surface, because carboxyl group were formed on polyimide surface after was dropped on the surface, according to Eq. 3. High concentration of carboxyl group near the surface leads to diffusion of silver ion bound with the carboxyl group from the deeper layer of modified film to the film surface via ion exchange mechanism. This mechanism can occur because the concentration of proton near the surface is grater than the deeper level of the modified film (Akamatsu et al., 2003). As the result, metallic silver thin film is formed near the surface. To confirm the assumption, liquid on the surface of polyimide was further analyzed.



**Figure 4.16** TEM cross section image of silver layer formed on polyimide surface by reduction via ultraviolet irradiation assisted by water.

The distilled water that was dropped onto polyimide changed to bright yellow solution after irradiation for 30 minutes. Figure 4.17 shows UV/visible spectra of the

bright yellow solution. A broad absorption peak at wavelength of 415 nm matches the excitation according to surface plasmon resonance (SPR) of the spherical silver nanoparticles (Yang et al., 2007; Wang et al., 2008). This result is consistent with the assumption that silver ions diffuse from the underneath to the surface and some of the silver ions diffuse further into water film coated on the surface. Subsequently, they are reduced by ultraviolet irradiation to form metallic silver ( $\text{Ag}^0$ ) nanoparticles.

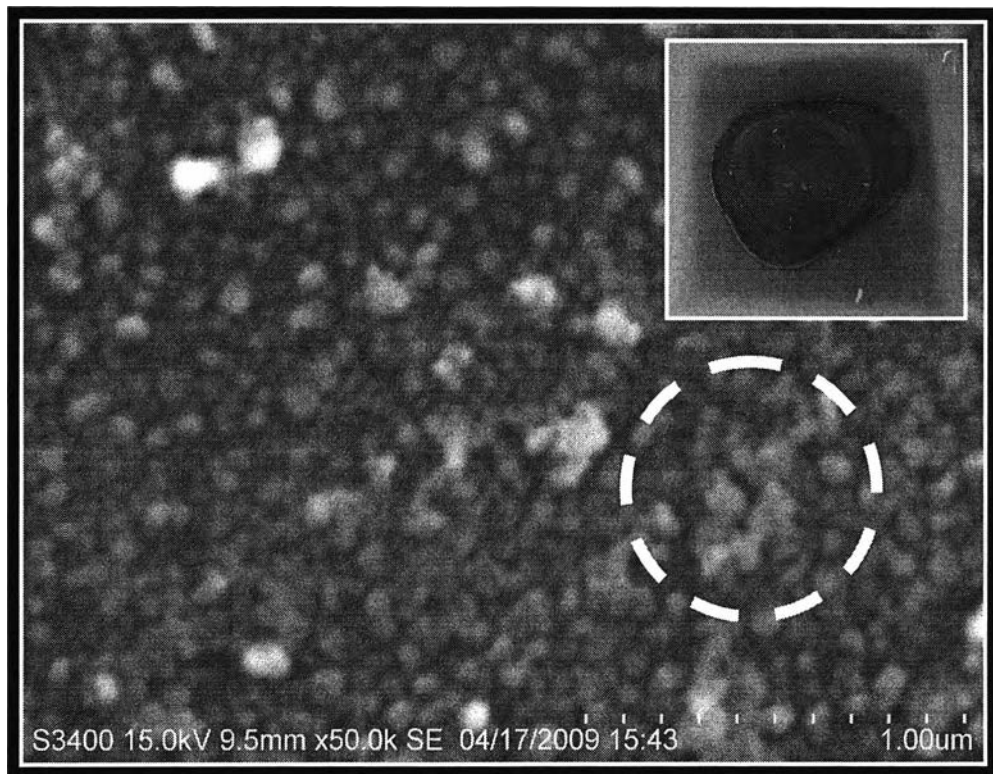


**Figure 4.17** UV/Visible spectrum of the solution on polyimide film surface after irradiation for 30 minutes.

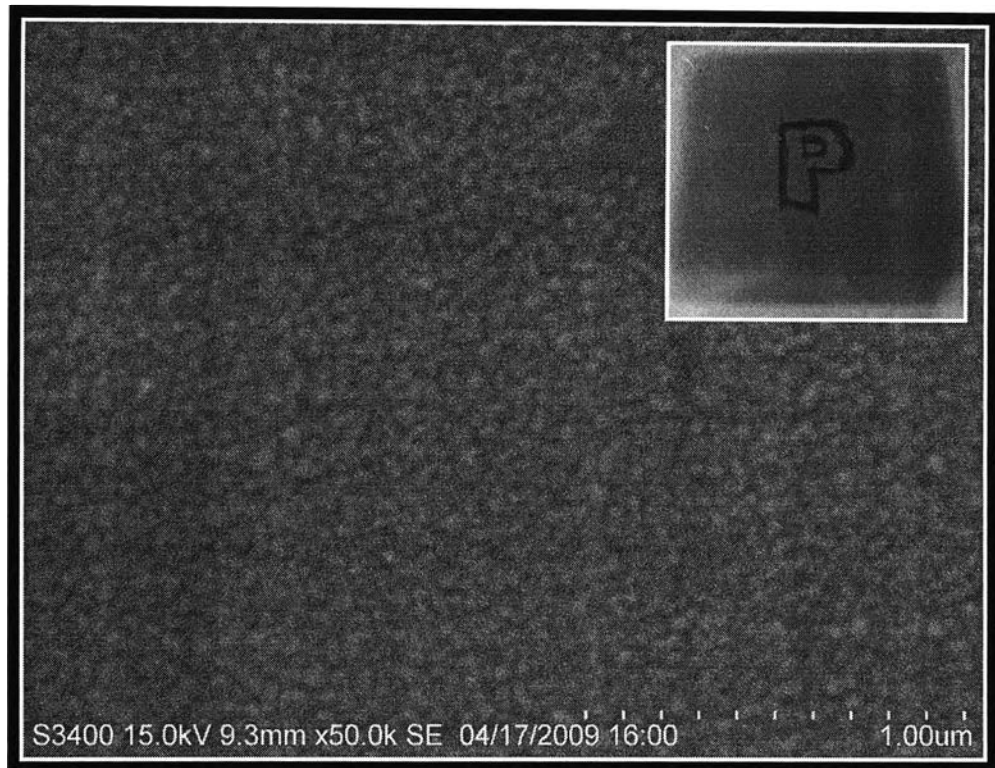
Figure 4.18 show a SEM image of polyimide surface after ultraviolet irradiation assisted by water for 3 hours. It is found that although silver nanoparticles are scattering on the film surface, some of them agglomerate into small group (as seen in white circle). These silver nanoparticles should be reduced in the solution phase above the surface (the bright yellow solution) and later agglomerated with silver nanoparticles formed on the polyimide surface when all of the solution are evaporated, leaving stains of metallic silver on the surface as shown in Figure 4.18.

#### 4.3.1 Effect of amount of water in assisted irradiation

Figure 4.19 shows SEM image of the silver layer formed by ultraviolet irradiation assisted for 3 hours, by water in form of thin film. By comparing with the micrograph in Figure 4.18, it can be shown that the silver coated polyimide film formed by the assistance of water in form of drop (Figure 4.18) is darker than that assisted by water film (Figure 4.19). The comparison of the thickness of the silver layer (Figure 4.22) confirms the result. It is suggested that the time that water exists on the polyimide surface plays the major effect. When the time for the diffusion of silver ions is limited, nanoparticles can not be formed in water. Consequently, there is no agglomeration of silver nanoparticles on the surface.



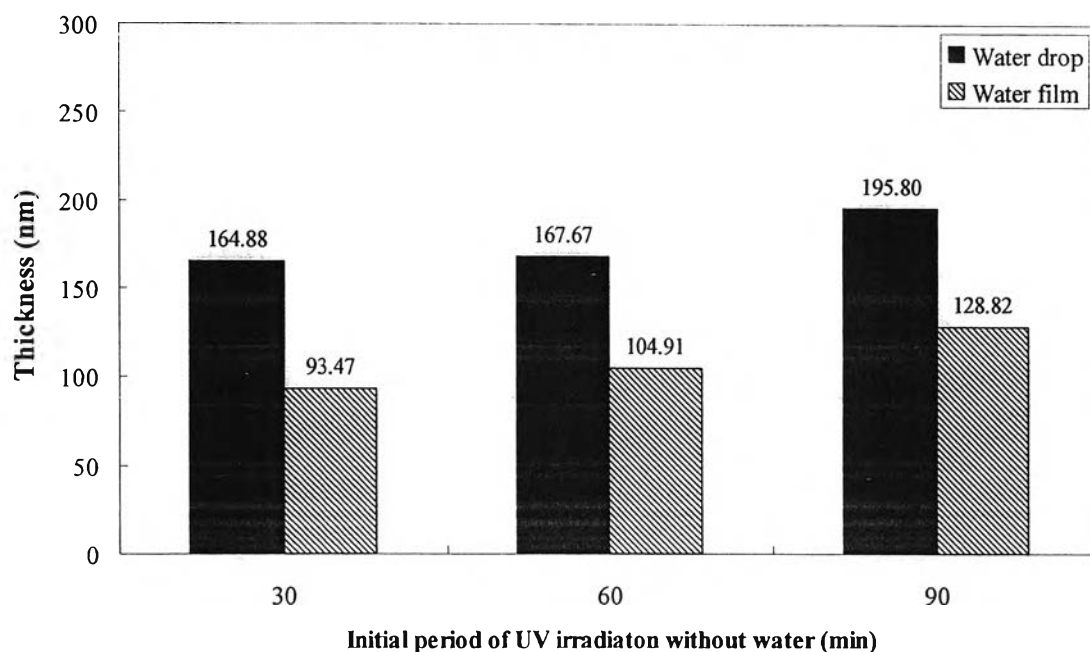
**Figure 4.18** SEM image of silver nanoparticles formed on polyimide surface by ultraviolet irradiation for 3 hours, assisted by water droplet.



**Figure 4.19** SEM image of silver nanoparticles formed on polyimide surface by ultraviolet irradiation for 3 hours, assisted by water film.

#### *4.3.2 Effect of irradiation time before assisted with water*

In this section, silver-impregnated polyimide film was reduced by ultraviolet irradiation for certain period of time. Next, water was added (in the form of either droplet or thin film) onto the surface as the assistance to the ultraviolet irradiation. All samples were then irradiated until the total irradiation time reached 3 hours. According to Figure 4.20, the thickness of silver layer is increased with the duration of the first period (i.e. irradiation without water). The ultraviolet irradiation in the first step causes the formation of silver nanoparticles near the surface.



**Figure 4.20** Thickness of silver layer on polyimide film reduced by ultraviolet irradiation for total of 3 hours. Water was added after certain period of ultraviolet irradiation without water.

#### 4.4 Cycle irradiation

As the ultraviolet irradiation proceeds, silver nanoparticles grow larger, especially near the surface of the film. However, growth of silver nanoparticles near the surface has a lot of blocking effect for ultraviolet light to pass through to the inner layer of the polyimide film as described earlier. So, in this section, the surface of the film was re-activated by immersing the irradiated polyimide film into KOH solution, reimpregnating with  $\text{AgNO}_3$ , before exposing to ultraviolet light again. This process was repeated in cycle. By this procedure, silver nanoparticles near the surface will be partially removed by KOH aqueous solution.

##### 4.4.1 Effect of KOH aqueous solution after ultraviolet irradiation

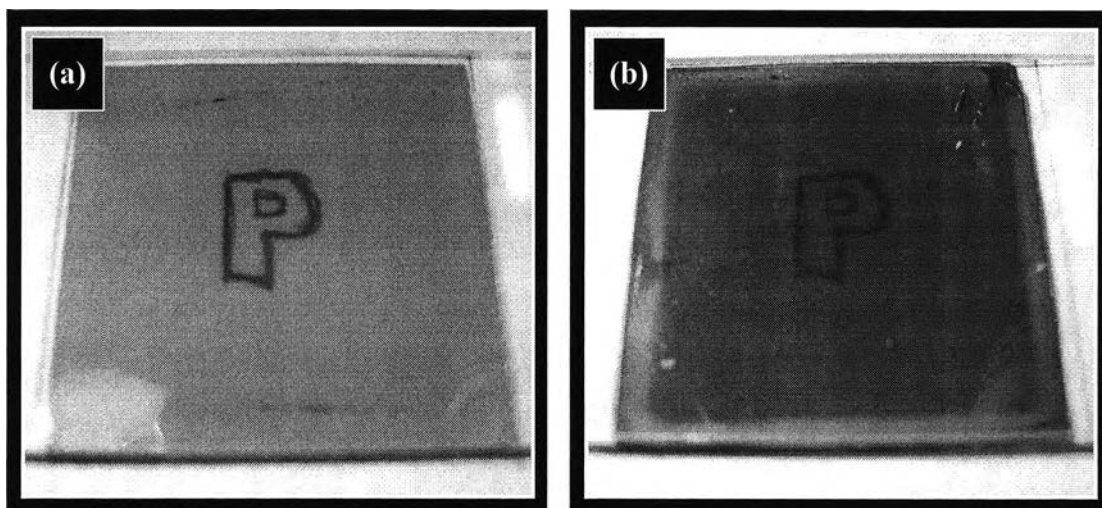
Figure 4.21 shows image of silver-coated polyimide film before and after immersed in KOH and subsequently irradiated with ultraviolet light. It is shown that, after the second cycle, polyimide film becomes darker. During the exposure to KOH solution, silver nanoparticles near the surface is partially removed (as witnessed from bright yellow solution obtained after rinsing the polyimide film with DI water). That

makes room for ultraviolet light to pass through to reduce silver ion underneath the polyimide film.

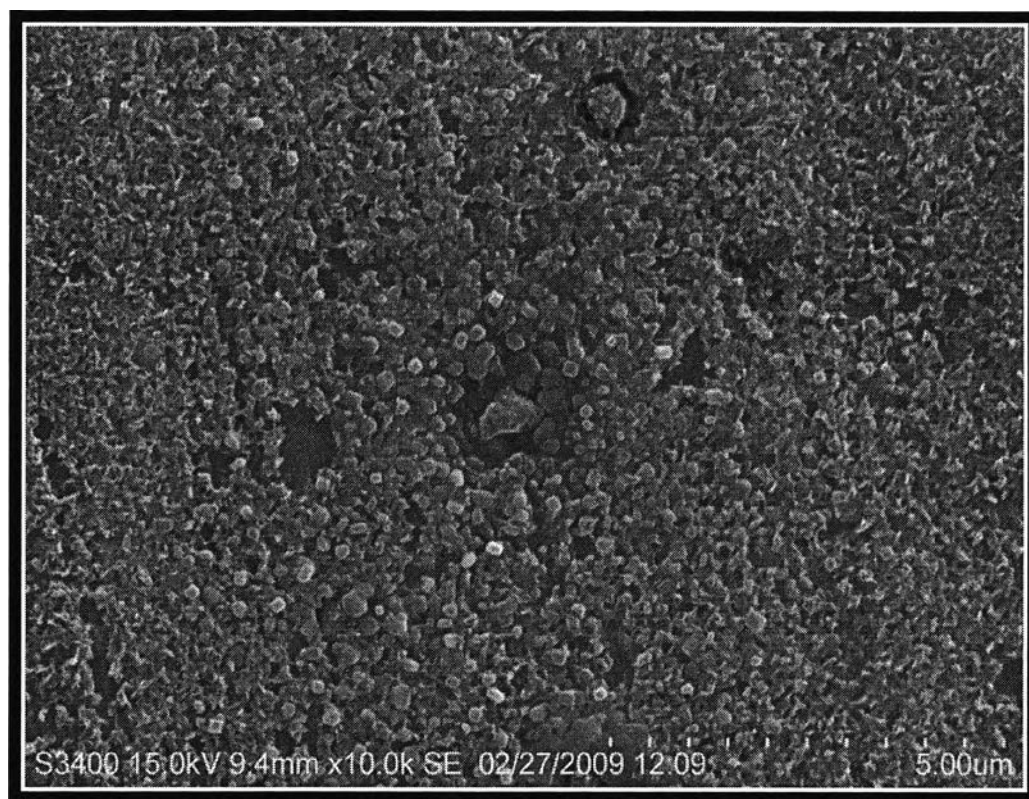
Figure 4.22 shows SEM image of the rinsing water (bright yellow solution) after dispersed on aluminum foil and put in an oven for 2 hours. It shows a collection spherical shape particles of what is supposed to be silver, since it has been known that colloidal silver is bright yellow solution in color. To confirm the assumption, the bright yellow solution was characterized by UV/Visible spectroscopy.

Figure 4.23 shown UV/Visible spectra of bright yellow solution obtained from KOH re-modification step in many deposition cycles. A single broad absorption peak centered at 425 nm is observed from the wash of polyimide film at the beginning of the second cycle. It should be noted that the position of peak in the absorption spectrum depends on sized and the shape of the particle. For the result obtained in this work, it is suggested that silver nanoparticles in spherical shape are formed (since spherical silver nanoparticles have been reported to show a single peak centered at about 400 nm). After the KOH treatment in the third cycle, the center of the broad absorption peak shifts from 425 nm to 418 nm and the peak becomes narrow. This indicates that the silver nanoparticles are still spherical, but the particle size and amount of the particles are increased (Sileikaite et al., 2006; Wang et al., 2008). Nevertheless, the absorption peaks for the second, third and fourth cycle wash are not significantly different in term of intensity and width because the amount of the silver nanoparticles formed near the surface are still not significant. For the fifth cycle, however the intensity of the absorption peak is increased clearly, but the width of the absorption peak remains unchanged, which means that the amount of silver nanoparticles on the surface is increased but the size of silver nanoparticles is roughly the same.

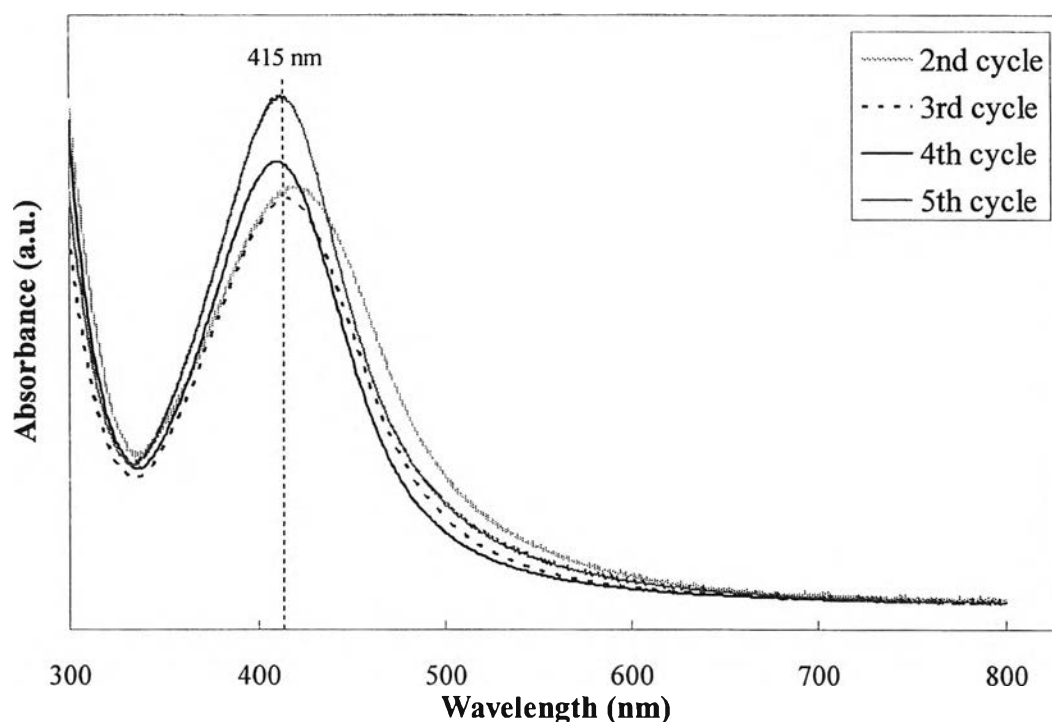




**Figure 4.21** Image of silver-coated polyimide film before (a) and after (b) second cycle of UV irradiation.



**Figure 4.22** SEM image of residue from the rinsing water after KOH treatment in the second cycle.



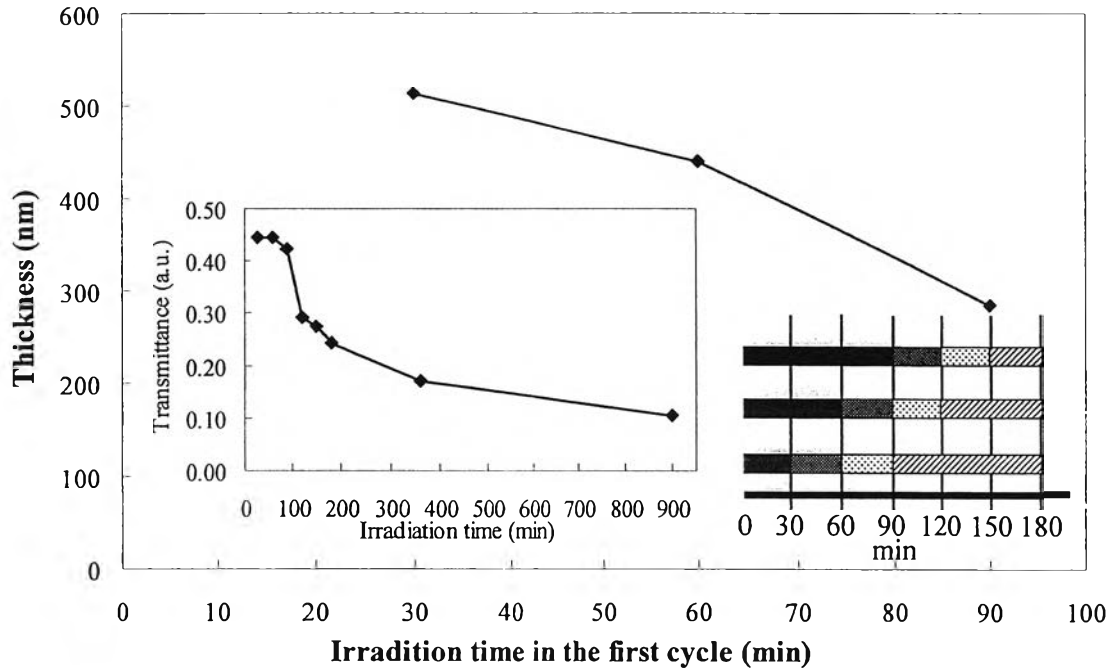
**Figure 4.23** UV/Visible spectra of the rising water after KOH treatment in various cycles of silver reduction.

The preliminary results previously presented suggest that KOH solution can partially remove silver nanoparticles from the surface, hence overcome the ultraviolet blocking effect that limits the thickness of the obtained silver layer on polyimide film. In the following section, the effect of KOH exposure is further investigated.

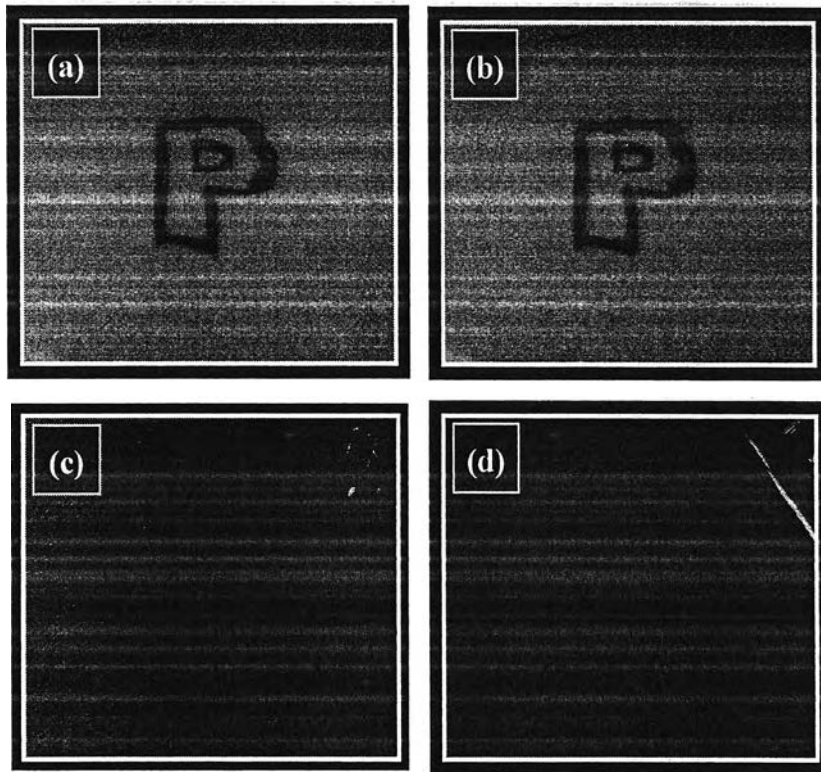
According to Figure 4.24, the thickness of silver layer decreases with irradiation time in the first cycle. The irradiation time in the first cycle plays an important role because a small number of silver nanoparticles are formed within the first 90 min of irradiation. This also means that just a small number of silver nanoparticles will be cleaned from the polyimide surface. Due to this reason, if the length of time in the first cycle is over 60 minutes, the total irradiation time for the first through the third cycle will exceed 90 minutes, which gives thick layer of silver near the surface that still poses the blocking effect.

Silver nanoparticle grow a lot after surface cleaning as indicated by color of polyimide film that becomes darker as shown in Figure 4.25. The color of the polyimide film obtained after the first cycle is not difference from the pristine polyimide. However, after the second and the third cycle, polyimide film becomes

darken because a lot of silver nanoparticles are formed in polyimide film. From this result, it means that growth rate of silver nanoparticles inside the polyimide film is greater than that near the surface during the later cycle.



**Figure 4.24** Thickness of silver layer on polyimide film reduced by ultraviolet irradiation for the total of 3 hours, in 4 cycles.

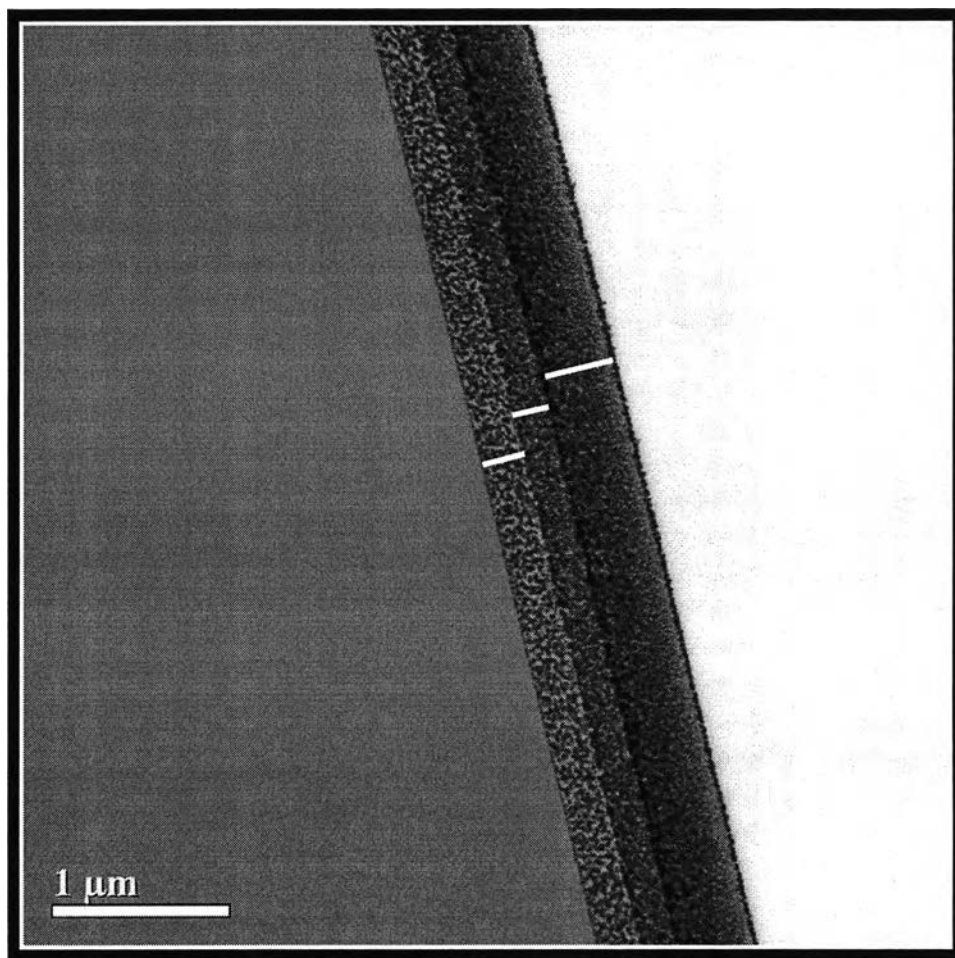


**Figure 4.25** Images of polyimide film: a) pristine PI, b) after the second cycle, c) after the third cycle and d) after the fourth cycle.

Figure 4.26 shows TEM image of polyimide film after cycle irradiation and subsequent heat treatment. It shows that 3 layers of silver are formed. The first layer is the normal layer that occurred in conventional irradiation, but silver nanoparticles formed by this procedure are close to each other because after the immersion in KOH in the second cycle, silver ion is added into polyimide and part of silver nanoparticles are cleaned out, which makes silver nanoparticles in top of first layer are dot around. The second layer occurs after the third cycle, in which by some of KOH solution diffuses to deeper layer of polyimide and undergoes protonation with  $\text{COO}^-$  to form  $\text{COOK}$ . Third layer mechanism is the same as that for the second layer.

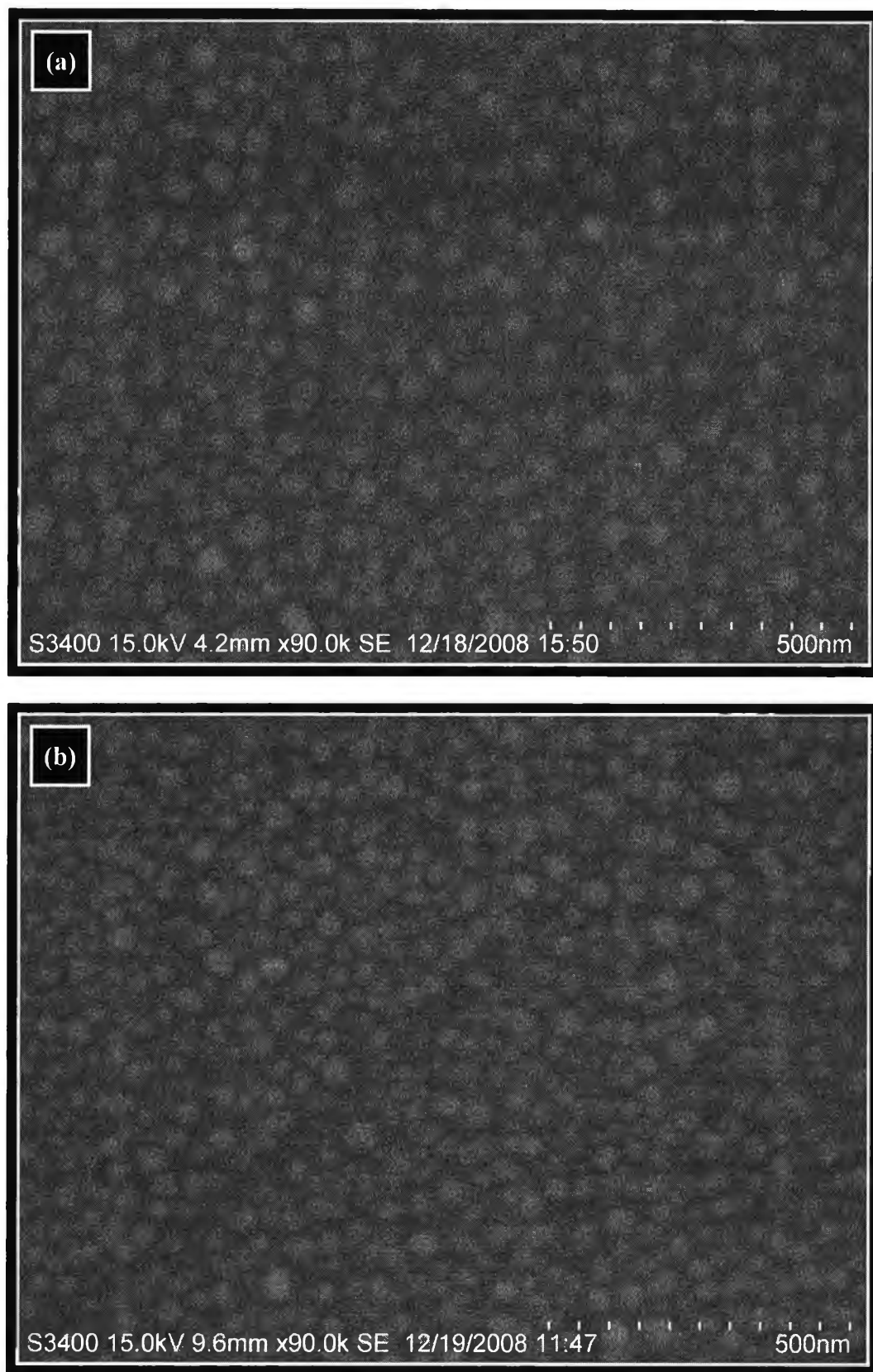
Amount of silver nanoparticles formed is related to amount of silver ion and silver seed. As shown in Figure 4.26 the first layer has the highest density of silver nanoparticles because, every time that polyimide is immersed in KOH, silver nanoparticles on top of the first layer will be cleaned and let ultraviolet light passing through to reduce silver to form silver nanoparticles. Silver nanoparticles in the second and the third layers occur by ultraviolet that passes through the first layer. Blocking effect of the first layer makes density of silver nanoparticles in the second and the third layers quite low when compare to that of the first layer. Figure 4.27 shows SEM images of polyimide film surface after the irradiation in each cycle.

KOH solution makes silver nanoparticles near surface peel out as describe above. After silver nanoparticles near surface (large particles) peel out, new particles that growth after will become smaller than before because time in irradiation is too short. As illustrate in Figure 4.27 SEM image of polyimide film surface after immersed in 2 M of KOH.



**Figure 4.26** TEM cross section image of polyimide film reduced by ultraviolet irradiation for total of 3 hours, in 3 cycles.

Figure 4.28 shows size distribution of silver nanoparticles after each cycle. After the first cycle, the particles have size varying from 20-59 nm, but most of particles size is in the range from 40-49 nm with the average size of 40.78 nm. Silver nanoparticles size distribution after the second cycle varies from 20-49 nm, but most of particles size is in the range from 30-39 nm with the average size of 33.22 nm. Silver nanoparticles size distribution after the third cycle varies from 20-49 nm, but most of particles size is in the range from 20-29 nm with the average size of 27.95 nm. It should be noted that this number was counted from SEM images in Figure 4.27. Comparing among the last 3 cycles it is found that when the number of cycle increased the size of silver nanoparticles will decrease (ultraviolet light can passed through easier) because of the effect of KOH that peels silver nanoparticles near surface as described earlier. These results agree with the result of UV/Visible analysis of the bright yellow solution obtained from the wash after immersed with KOH.



**Figure 4.27** SEM image of silver nanoparticles on polyimide film surface after immersed in KOH solution before at a) second cycle, b) third cycle and c) forth cycle.

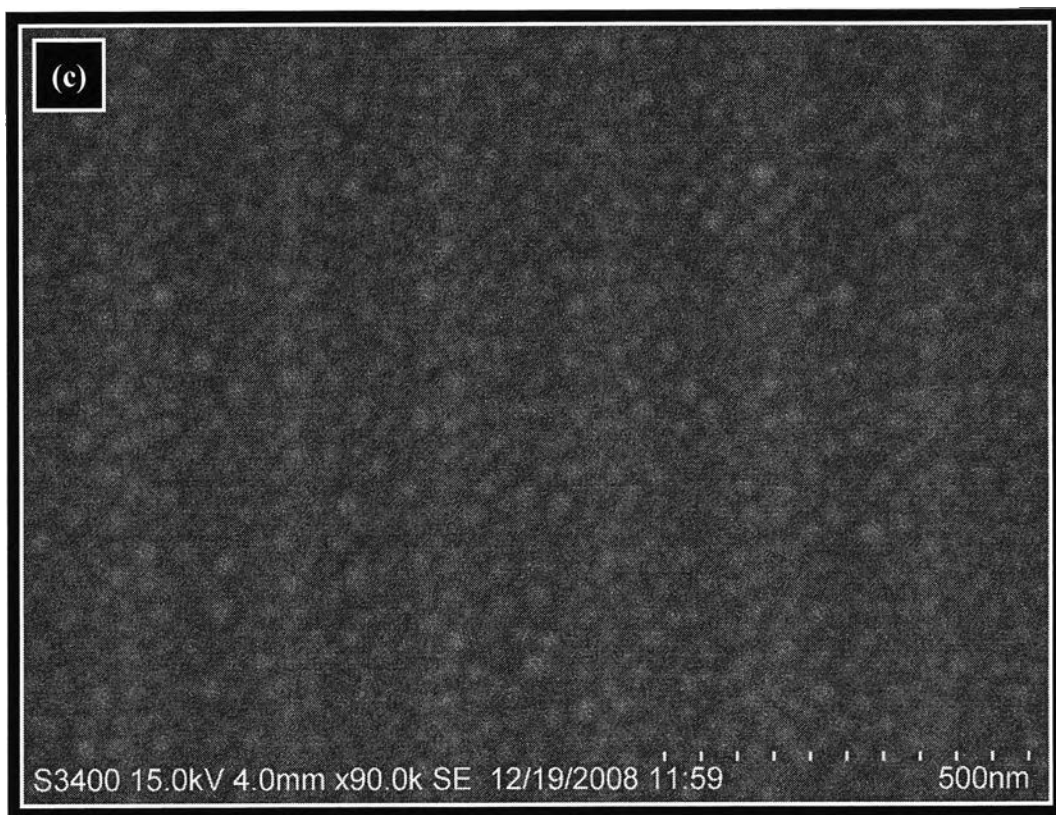


Figure 4.27 (Continued)

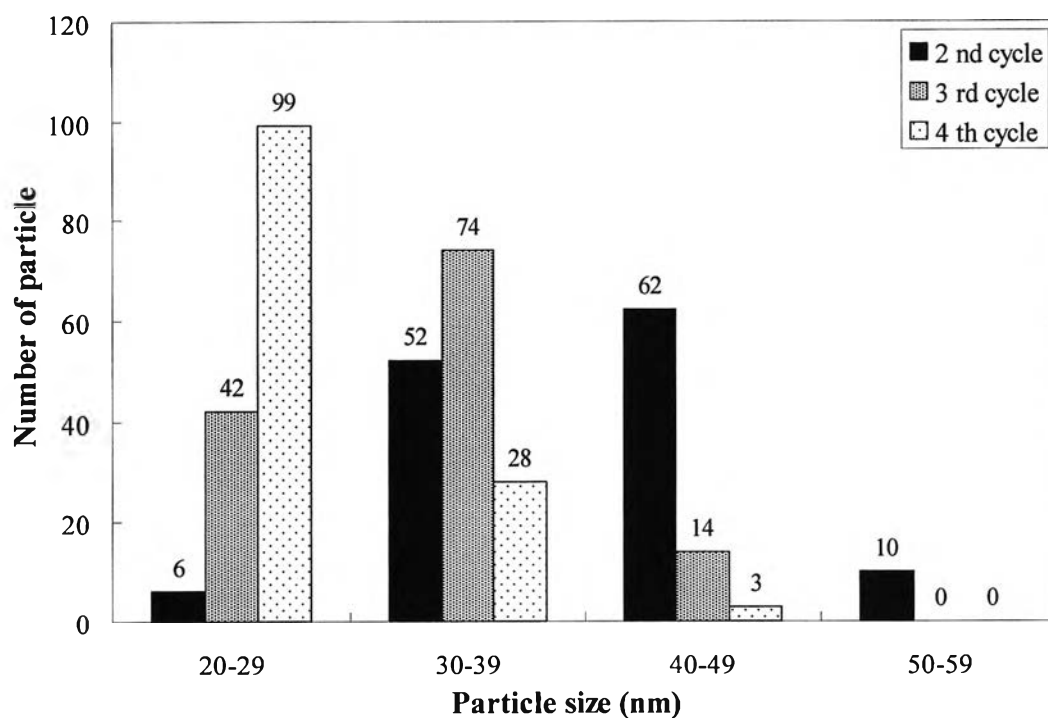


Figure 4.28 Size distributions of silver nanoparticles on polyimide surface reduce by ultraviolet irradiation for 3 hours, in 4 cycles.

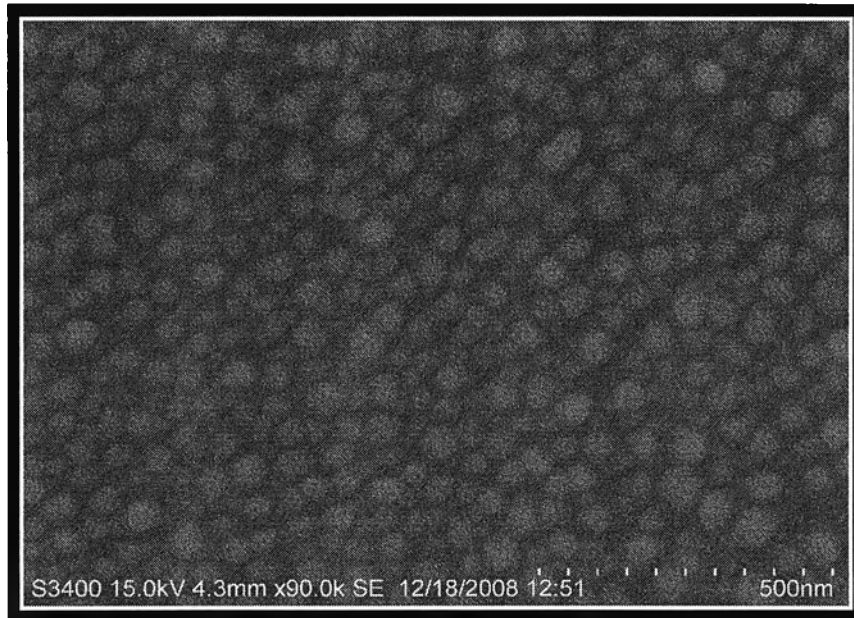
#### 4.4.2 Effect of immersion in silver nitrate solution after irradiation

Figure 4.29 shows SEM image of polyimide surface after irradiation and immersed in 0.001 M of silver nitrate solution in 3 cycles, without using KOH. It is found that silver nanoparticles growth larger when compared with the conventional irradiation.



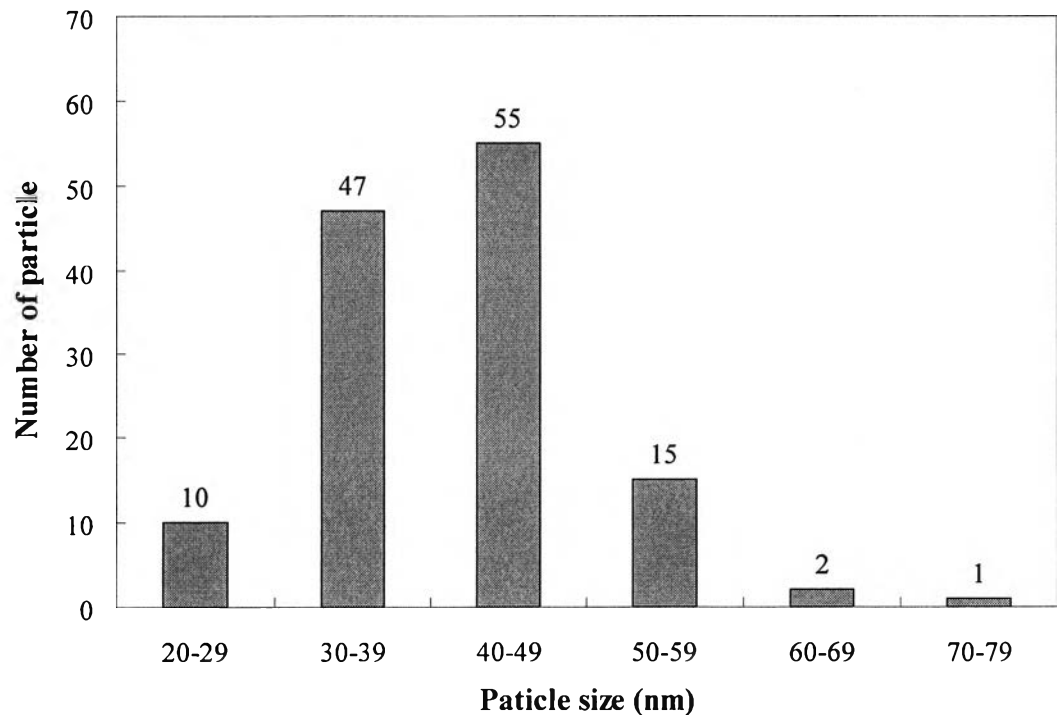
Silver nanoparticle seeds ( $\text{Ag}_2\text{S}$ ) play a role as adsorbents (carriers) to adsorb  $\text{Ag}^+$  from the solution. When Ag particles deposit on the surface of  $\text{Ag}_2\text{S}$ , it will form  $\text{Ag}_2\text{S}/\text{Ag}$  binary seeds, which will act as the autocatalyst in silver reduction. These Ag particles could supply more active sites to adsorb  $\text{Ag}^+$ , promoting the reduction of  $\text{Ag}^+$  through partial compensation of unpaired electrons between particles and ions. After irradiation is complete silver nanoparticles will become larger as show in Equation 6 [ $2(\text{Ag}^0)_{n+1} / (\text{Ag}^0)_2\text{S}$ ] (Chen et al., 2007).





**Figure 4.29** SEM image of silver nanoparticle on polyimide surface after immersed in silver nitrate and reduced by ultraviolet irradiation for 3 hours, in 3 cycles.

Figure 4.30 Size distributions of silver nanoparticles after immersed in silver nitrate and reduce by step irradiation show that distribution of silver nanoparticles varies from 30-89 nm but most of particles size was in range from 50-59 nm and the average size was 46.54 nm.

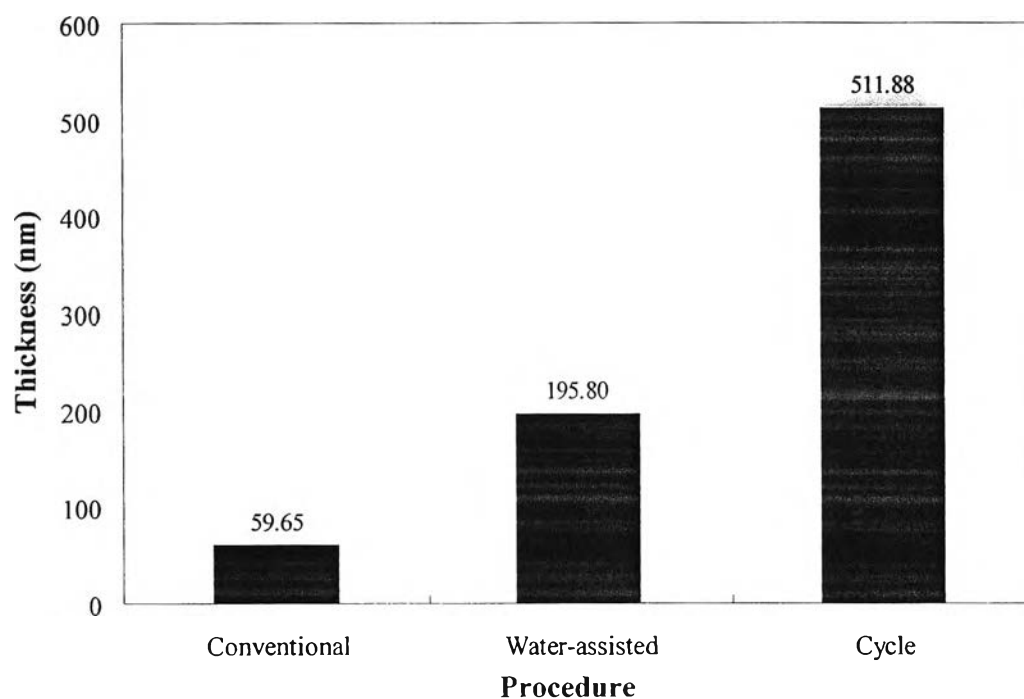


**Figure 4.30** Size distribution of silver nanoparticles after immersed in silver nitrate and reduced with UV irradiation in cycle.

## 4.5 Comparison between 3 deposition procedures

### 4.5.1 Thickness of silver layer

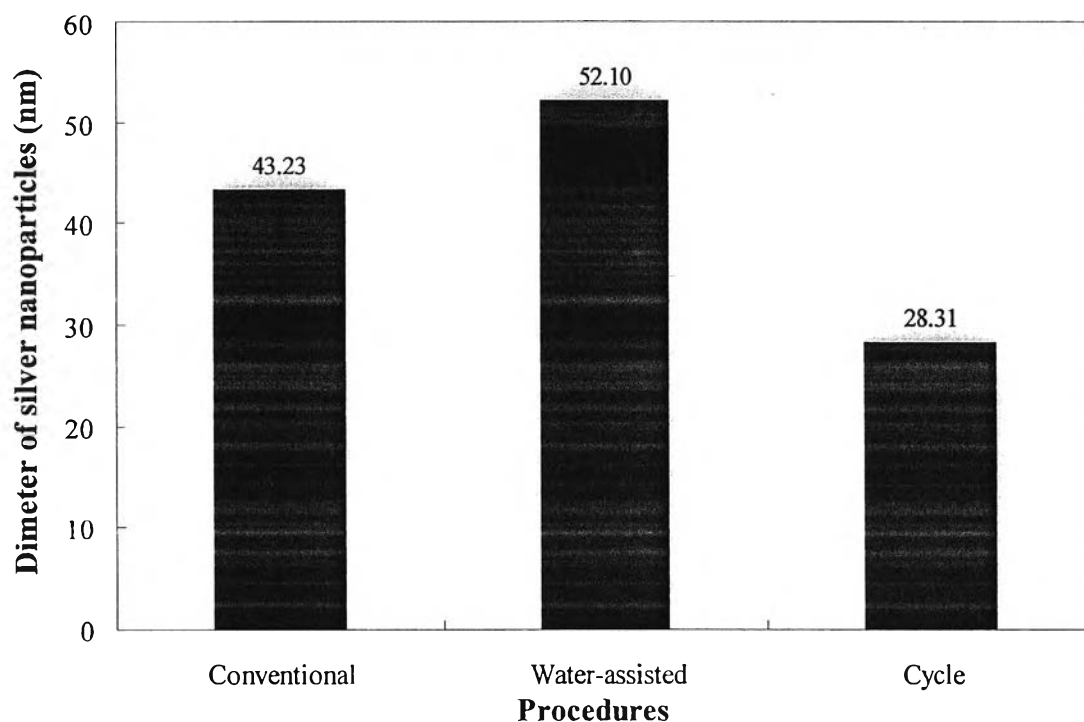
Thickness of the silver layer was determined based on the transmittance of visible light through the film (via the calibration curve in Appendix A). The thickness of the silver layer achieved by 3 different procedures (Figure 4.31) indicates that irradiation in cycle fashion results in the thickest layer because it overcomes the blocking effect of silver nanoparticles near the surface. The second place is the reduction via ultraviolet irradiation assisted by water drop because of the effect that makes silver in the deeper level diffuses to the surface while irradiated. According to Figure 4.31, the achievable thickness of the silver layer from these 3 procedures is significantly different. The thickest one is almost ten times of that achieved by the conventional ultraviolet reduction.



**Figure 4.31** Comparison of the thickness of silver layer achieved from 3-hour ultraviolet irradiation by 3 different procedures.

#### 4.5.2 Size of silver nanoparticles

Figure 4.32 shows that the reduction by ultraviolet irradiation in cycle fashion gives a small size of silver nanoparticles on the surface. That is because large particles have already been removed by KOH treatment taking place in each cycle. The largest size of silver nanoparticles is achieved from water-assisted irradiation because of the agglomeration of silver nanoparticles formed within the water droplet.



**Figure 4.32** Comparison of size of silver nanoparticles on the surface of polyimide achieved by 3-hour ultraviolet irradiation by 3 different procedures.

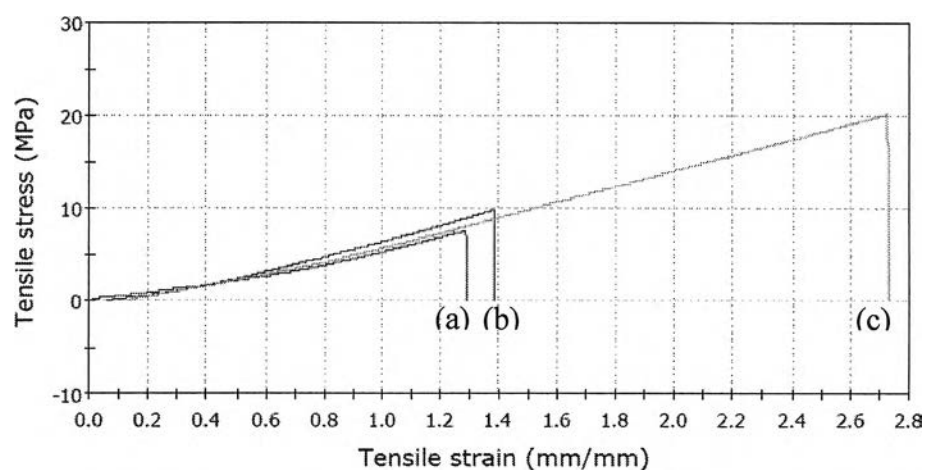
#### 4.5.3 Dielectric property of the coated polyimide surface

All of silver-coated polyimide films surface after irradiation still have high surface dielectric property because grain boundaries of silver nanoparticles are not continuous.

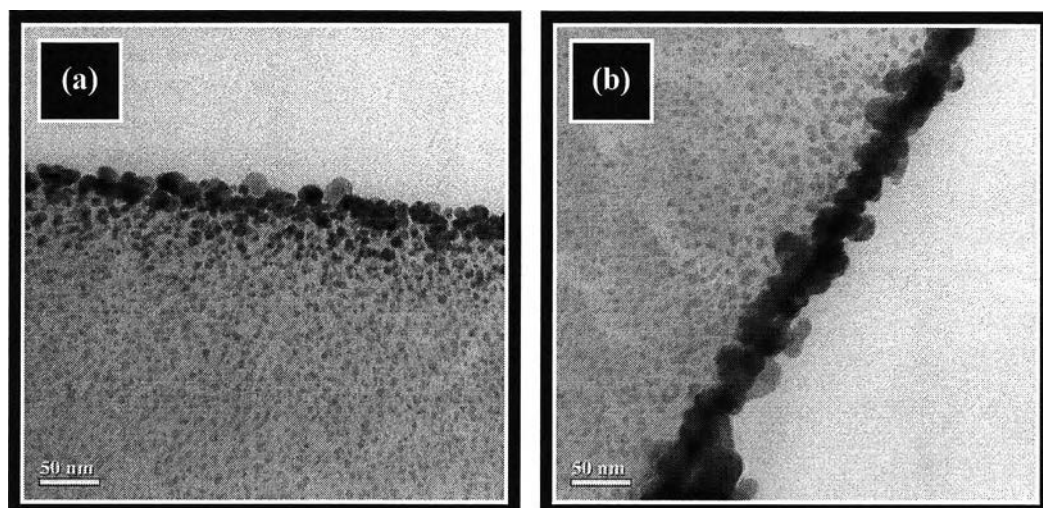
#### 4.5.4 Adhesion of silver to polyimide surface

Peeling test of 3 silver-coated polyimide films fabricated by 3 different irradiation procedures was conducted (results shown in Figure 4.33). It was measured

by attaching two circle stubs ( $D=2$  cm) on both sides of polyimide specimen, using superglue. Then it was pulled apart by using an universal testing machine with rate of 1mm/rmin. The result reveals that the irradiation in cycle results in the highest adhesion between silver layer and the polyimide substrate because silver nanoparticles are formed deep down into the bulk of polyimide. Adhesion property of silver layer formed by water-assisted method is slightly greater than that of the conventional irradiation because of the growth mechanism that makes silver nanoparticles cluster into larger group than that achieved by conventional irradiation as shown in Figure 4.34.



**Figure 4.33** Result from peeling test of 3 silver-coated polyimide films fabricated by 3 different procedures for 3 hours: a) conventional irradiation, b) water-assisted irradiation and c) irradiation in cycle.



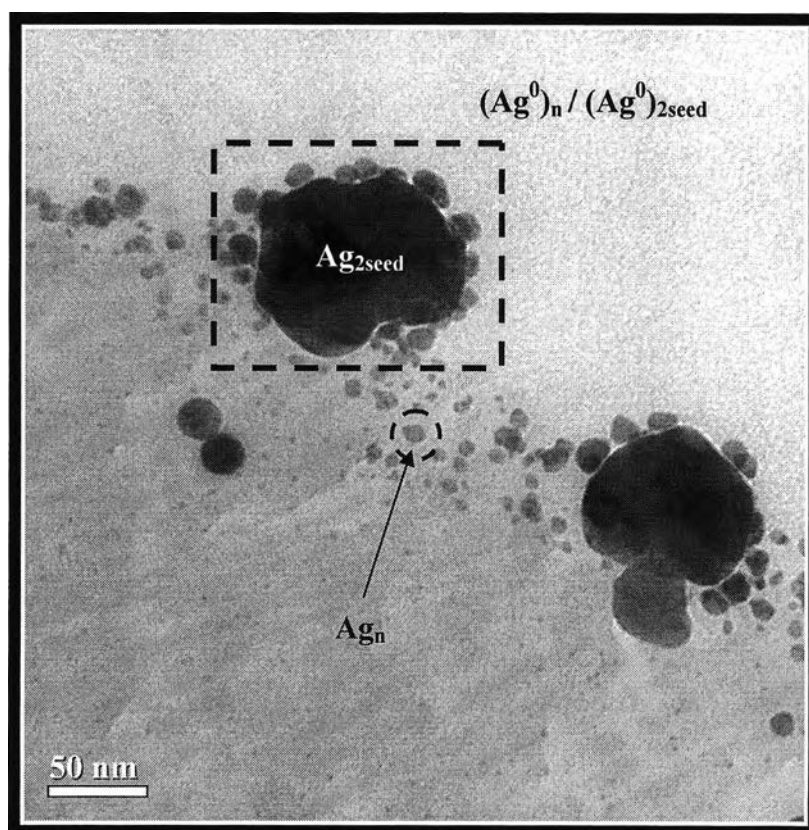
**Figure 4.34** TEM cross section image of silver nanoparticles formed on the surface of polyimide by: a) conventional irradiation and b) water-assisted irradiation.

#### 4.6 Growth mechanism of silver nanoparticles

In this section, growth mechanism for silver nanoparticles is suggested. The possible reactions are:



After silver ions are reduced to metallic silver by electron donation of carboxylate group, metallic silver atoms bond together to form silver nanoparticles. After that, group of silver nanoparticles sinter to form silver seed  $[(\text{Ag}^0)_{\text{seed}}]$  as shown in Equation 3 and grow larger. TEM image of polyimide surface after irradiation in Figure 4.35 shows that large silver particles are formed by sintering of small silver particles.

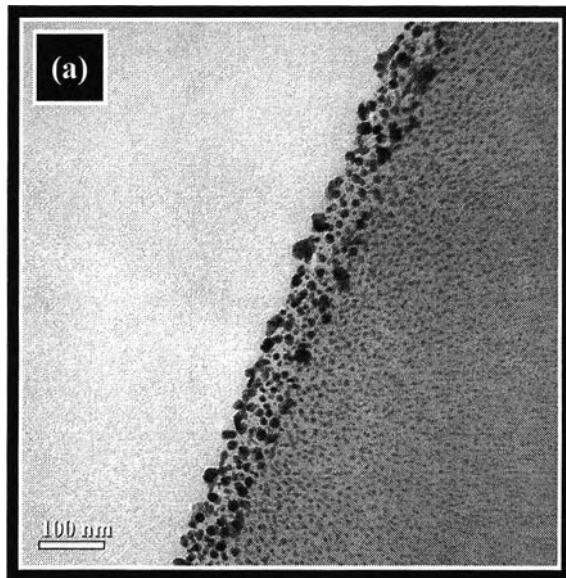


**Figure 4.35** TEM cross section image of silver nanoparticles formed on the surface of polyimide by ultraviolet irradiation.

## 4.7 Reduction with sodium borohydride ( $\text{NaBH}_4$ )

### 4.7.1 Effect of sodium borohydride concentrations

Figure 4.36 shows TEM images of silver film formed by reduction with  $\text{NaBH}_4$  at different concentrations. In Figure 4.36(a), (c) and (d), silver nanoparticles are spherical, but silver nanoparticles in Figure 4.36(b) sinter and grow into plate shape. This result means that the form of silver particles reduced by chemical reduction can not be controlled. An increase in concentration of  $\text{NaBH}_4$  makes silver layer on polyimide surface thicker and the silver layer becomes more continuous. Figure 4.37, which shows SEM images of polyimide surfaces, shows that the increased concentration of  $\text{NaBH}_4$  results in cracks in silver layer on polyimide surface because growth rate of silver layer is too fast.



**Figure 4.36** TEM cross section image of silver nanoparticles formed on the surface of polyimide by reaction with sodium borohydride with different concentration for 20 seconds at room temperature: a) 0.0001 M, b) 0.001 M, c) 0.01 M and d) 0.04 M.

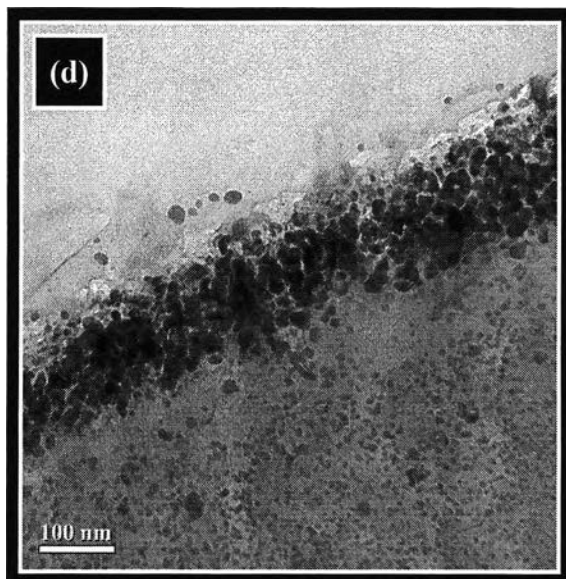
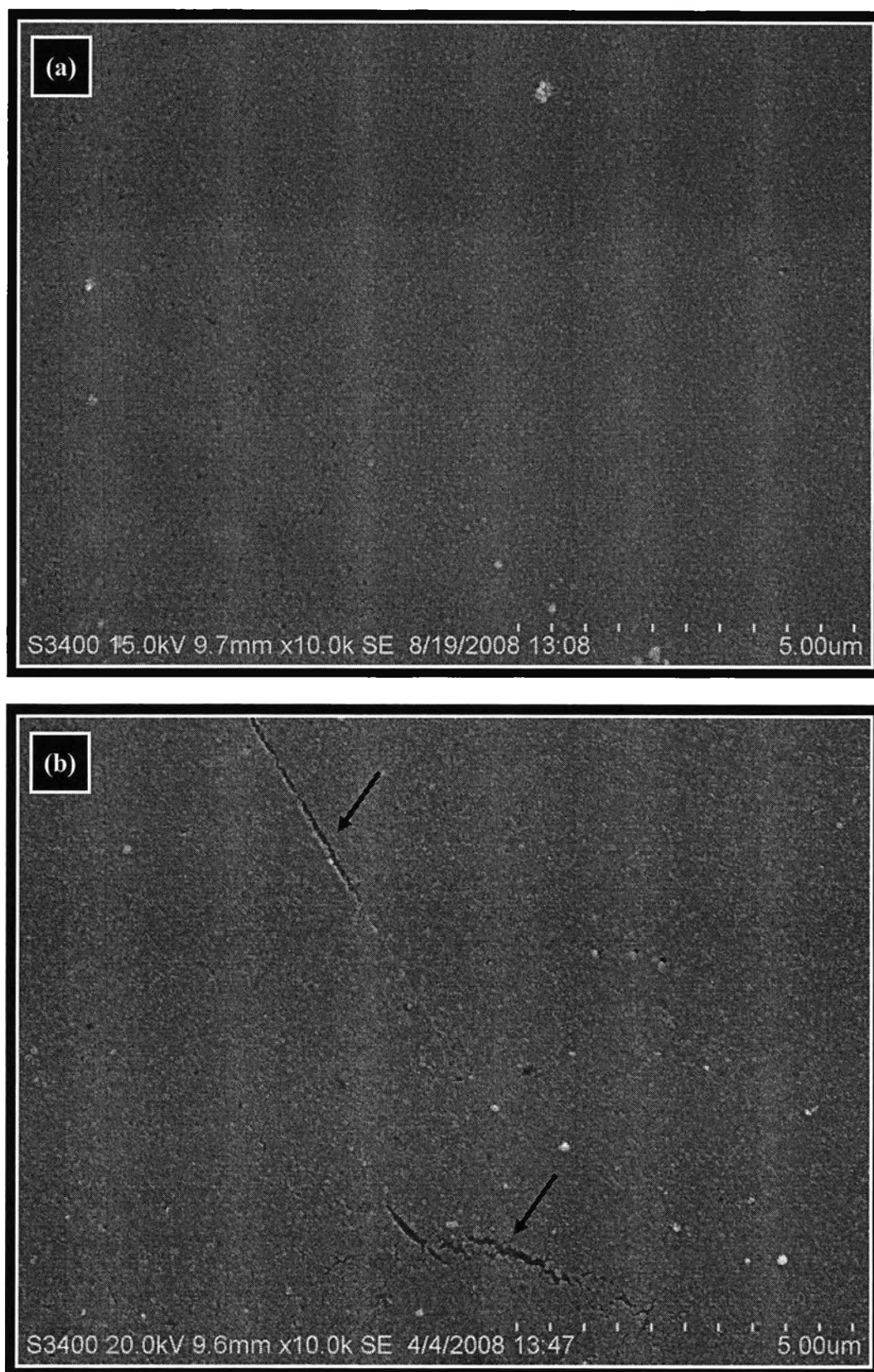


Figure 4.36 (Continued)

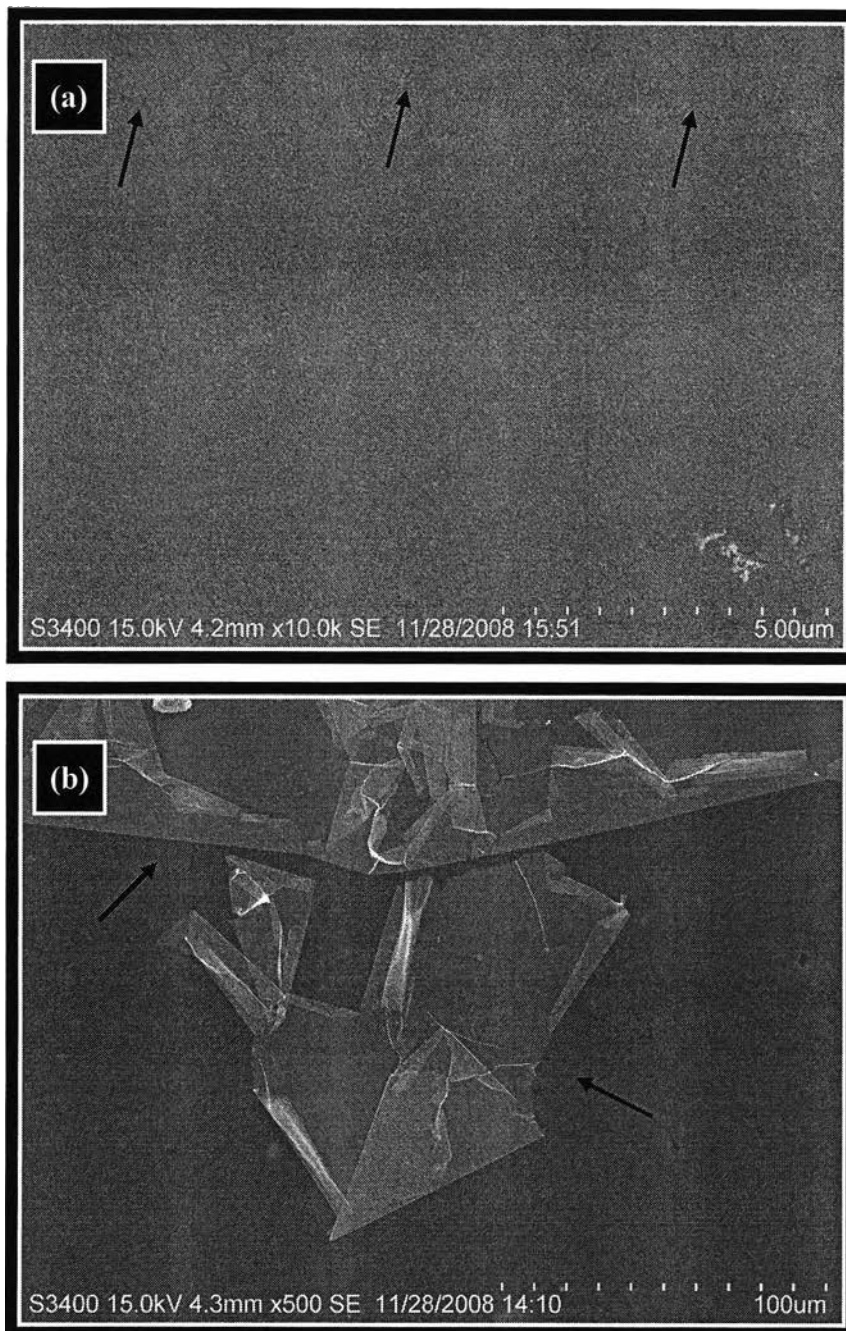


**Figure 4.37** SEM image of polyimide surface reduced by sodium borohydride for 20 seconds at room temperature: a) 0.01 M and b) 0.04 M.



#### 4.7.2 Effect of sodium borohydride exposure after reduction

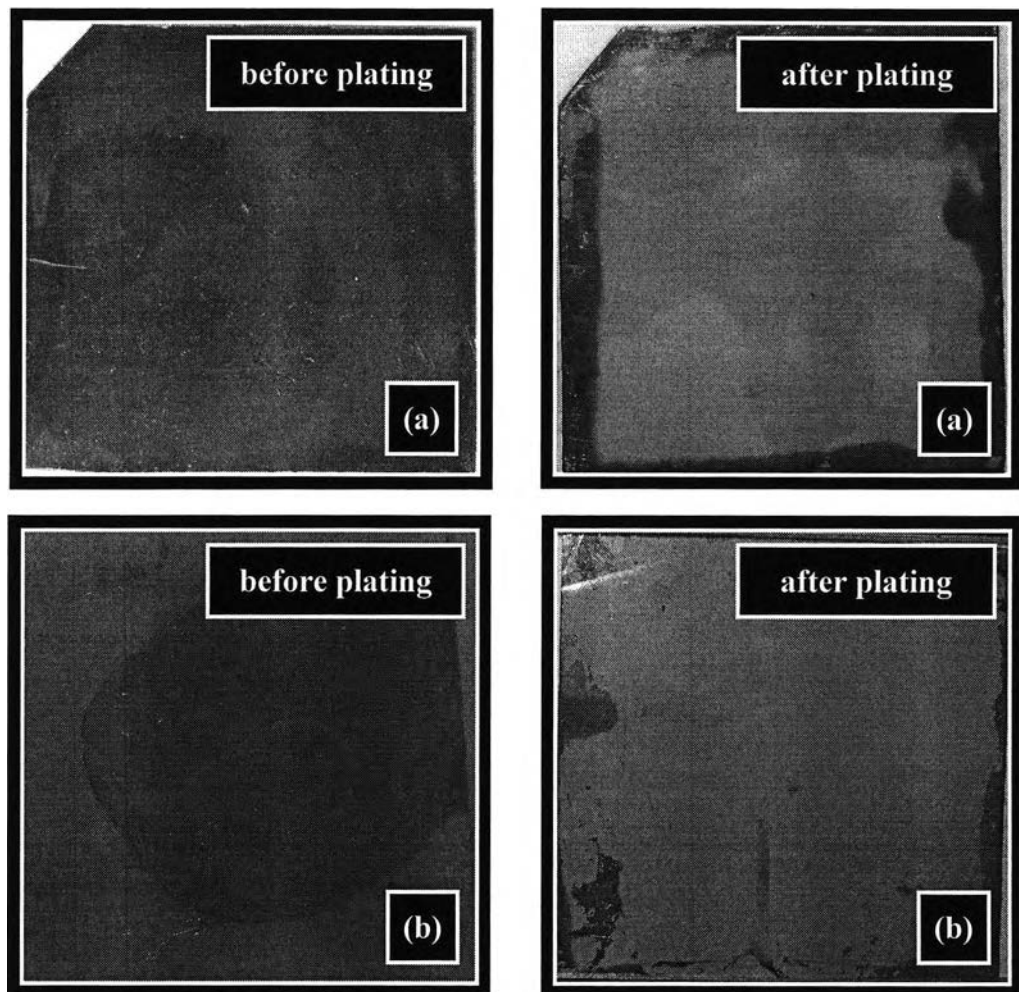
Figure 4.38 shows SEM image of polyimide surface after immersed in  $\text{NaBH}_4$  for 20 second after it has already been reduced by  $\text{NaBH}_4$  once. It is found that silver layer on the surface is peeled off from the polyimide surface, especially when the film was heated before the second immersion in  $\text{NaBH}_4$ .



**Figure 4.38** SEM image of polyimide surface after second reduce with 0.01M of  $\text{NaBH}_4$  for 20 second at room temperature: a) not heated and b) heated.

#### 4.8 Electroless copper plating

Figure 4.39 shows images of polyimide film after electroless plating with copper using the solution with pH  $\sim$ 13. It is found that only the silver-coated film fabricated by cycle irradiation can be subsequently plated with copper. As described earlier, KOH can remove silver nanoparticles from the polyimide surface. The chemical agent used as electroless plating solution also contains KOH, so silver on polyimide surface is removed during the plating process. Only silver grown by cycle irradiation can withstand this condition because most of the silver resides in the inner layer of the polyimide surface. After the successful plating, the electrical resistance of the polyimide surface is reduced from extremely high value (open circuit) to 20 ohm.



**Figure 4.39** Images of silver-coated polyimide films before and after electroless plating with copper. The films were prepared by different procedure: a) chemical reduction, b) water-assisted irradiation, c) water film-assisted irradiation, d) conventional irradiation and e) cycle irradiation.

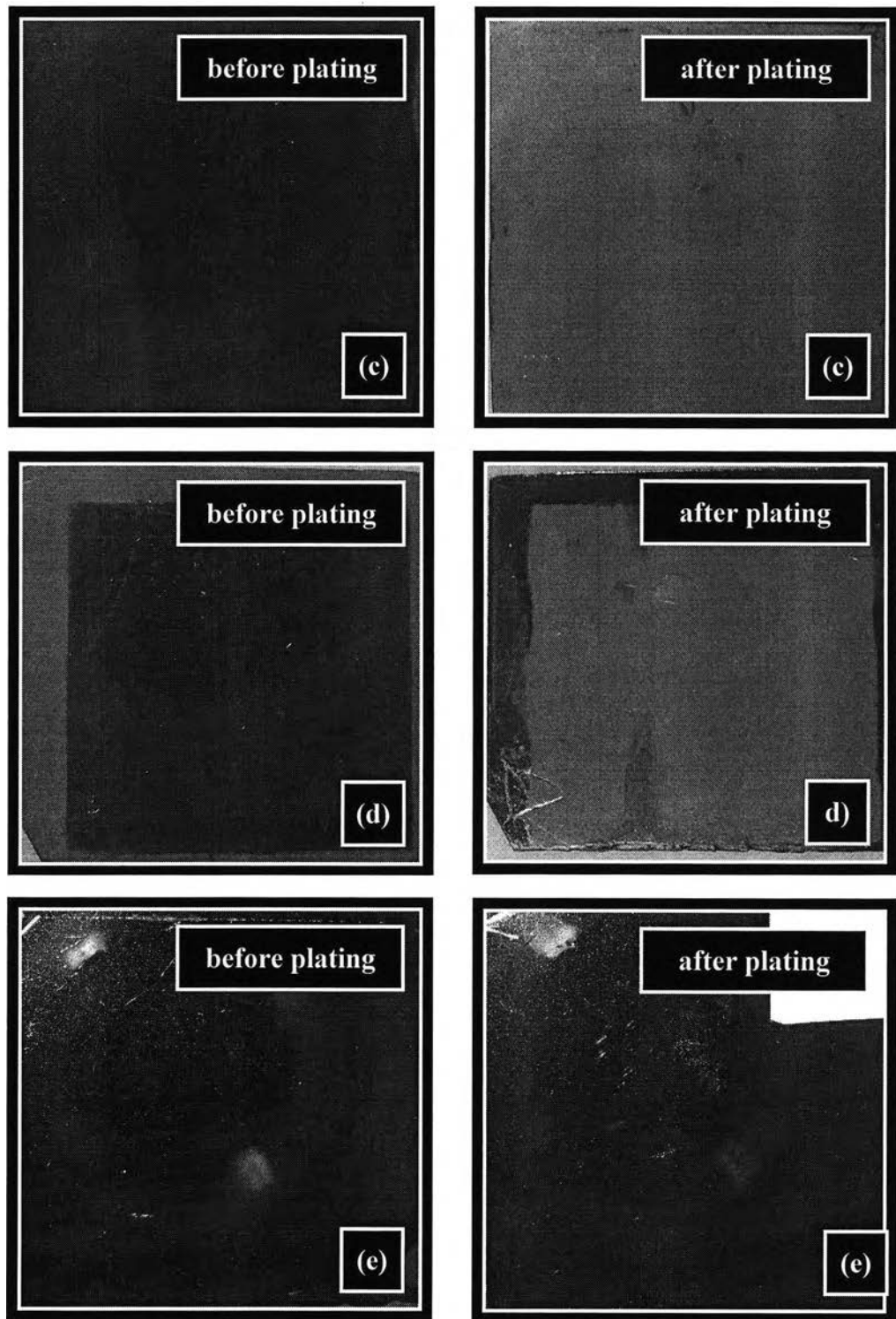


Figure 4.39 (Continued)