Chapter 3
Cu CVD on TaN and TaSiN Substrates

3.1 Introduction

Copper has been used to replace Al and Al-alloys as the interconnection metal because of its higher electrical conductivity and superior electromigration resistance [3-5]. However, Cu diffuses very fast in Si and forms deep level traps in the forbidden energy gap. Moreover, Cu drifts in dielectrics (e.g. SiO_2) under accelerated electric field, and has a poor adhesion to the dielectric layer. Therefore, the use of a diffusion-barrier/adhesion-layer between Cu and its surrounding layer is necessary for the successful application of Cu in silicon-based integrated circuits.

Among the various deposition technique of thin film, the CVD method inherently possesses the advantages of superior conformal film deposition and gap-filling capability [26-27]. Many refractory metals, alloys, and metal nitride, such as W, TiW, TiN, Ta and TaN have been used as substrates for the CVD of Cu films [20, 29-31]. Among them, TiN, Ta and TaN exhibit superior barrier properties against Cu Diffusion. Due to the scaling of ULSI devices to dimensions below 0.90um, the barrier layer must be reduced in thickness, preferably thinner than 10nm, but still be able to act as effective barrier. Ta-based films are considered to be the suitable candidates to meet this requirement [32-33]. It has been reported that TaSi-based alloys could serve as diffusion barrier with a thickness of 10nm and below [34]. In this chapter, we investigate the basic properties of CVD Cu films deposited on TaN and TaSiN substrates.

3.2 Experimental Procedures

In this study, CVD Cu films were deposited on TaN and TaSiN substrates, both of which were sputter-deposited on the oxide-covered Si wafers. The Si

wafers used in this study were p-type, (100) oriented, 4-inch diameter single crystal silicon with 4-7Ω-cm nominal resistivity. After initial standard cleaning, a 500nm-thick SiO_2 was thermally grown at 1050℃ in wet oxygen atmosphere. Then, TaN or TaSiN layer was sputter-deposited on the oxide layer in a dc magnetron sputtering system with a base pressure of 1×10^{-6} torr. The TaN film was sputter-deposited using a Ta target (99.99% purity) in an Ar/N_2 gas mixture; the Ar and N_2 flow rates of 55 and 2.5 sccm, respectively, were used to make the Ar/N_2 gas mixture. On the other hand, the TaSiN film was sputter-deposited using a $TaSi_2$ target (99.99% purity) in the same gas mixture of Ar/N_2. The gas pressure during the sputtering of both films was kept at 7 mtorr, and both films were deposited to a thickness of 25nm. The resistivities of the as-deposited TaN and TaSiN films were determined to be 287 and 305μΩ-cm, respectively, and the film composition, as determined by RBS, was found to be $TaN_{0.8}$ and $TaSi_{0.25}N_{1.05}$

The TaN or TaSiN substrate wafer was loaded into the reaction chamber of the CVD system for Cu films deposition. The substrate wafer was first loaded into the loading chamber of the CVD system. When the pressure of the loading chamber reached 10^{-6} torr, the substrate wafer was transferred to the reaction chamber via the transfer chamber by a robot arm. Prior to starting the process of Cu CVD, the substrate wafer was heated to the desired deposition temperature with the He carrier gas flowing at a rate of 25sccm and the chamber pressure maintained at 150mtorr. Usually, it took about one hour for the substrate sample to reach the preset temperature. At the end of the Cu film deposition, the sample was cooled in the ambient of He gas at the pressure of 150mtorr.

In this study, Cu CVD was performed over a temperature range of 140 to 240℃ at a pressure of 150mtorr with a precursor flow rate of 0.4ml/min and a He carrier gas flow rate of 25sccm. The Cu precursor used in this study is Cu(hfac)TMVS + 2.4 wt TMVS. The distance between the precursor injector

and the substrate surface was 2cm, and the substrate was rotated at an angular speed of 7 rpm in order to obtain a better film uniformity. Major parameters and processing conditions of the Cu CVD used in the study of this chapter are summarized in Table 3-1.

The thickness of the Cu films was measured using a DekTek profiler on the patterned Cu films and was double checked by cross-sectional scanning electron microscopy (SEM). SEM was also used to observe the surface morphology of the deposited Cu films. A four-point probe was employed to measure the sheet resistance. The surface roughness of the Cu film was evaluated by atomic force microscopy (AFM). Crystal structure was identified by X-ray diffraction (XRD) analysis.

3.3 Basic Characteristics of CVD-Cu Films

3.3.1 Growth Rate of Cu film

The effective deposition rate of Cu films as a function of substrate temperature (Arrhenius plot) for Cu CVD on TaN and TaSiN substrates is illustrated in Fig.3-1. The effective deposition rate was calculated using the thickness of the Cu film deposited in a period of 10min. For the deposition temperature below 220℃, the behavior of the Cu CVD belongs to the surface -reaction-controlled regime [16]. The activation energy Ea of the Cu CVD was determined to be 5.91kcal/mole on TaN substrate and 5.48kcal/mole on TaSiN substrate, as showing in Fig.3-1. From the linear segment of the Arrhenius plot by the Arrhenius equation [35]

$$R = R_o \exp(-E_a / kT) \quad (1)$$

where R is the deposition rate, R_o is the pre-exponential factor, k is the Boltzmann constant, and T is the absolute temperature. The Cu CVD on the TaN substrate has a slightly higher effective deposition rate than that on the TaSiN substrate, presumably due to a shorter incubation time.

3.3.2 Effects of Deposition Temperature

Figure 3-2 and Fig.3-3 show the surface morphology of Cu films deposited at various temperatures for a deposition time of 10min on TaN and TaSiN substrates, respectively. It can be seen clearly that the grains of Cu films become larger with increasing deposition temperature [36]. Although the Cu grains for the films deposited at higher temperatures are larger in size, it appears that the grains are not closely stacked and the film contains a lot of voids. The Cu grains are smaller for the films deposited at lower temperatures, but they seem to be better connected and containing less voids. There is no obvious difference in surface morphology between the Cu films deposited on TaN and TaSiN substrates at a given temperature.

Figure 3-4 shows the resistivity of Cu films as a function of deposition temperature for the Cu films deposited in a duration of 10min on TaN and TaSiN substrates. It has been reported that the Cu film resistivity consists of the bulk resistivity and the residual resistivity, which is composed of the contribution from the films surface (ρ_s), impurities (ρ_t), grain boundaries (ρ_g), and intragranular defects (ρ_d) [37, 38]. In other word, the Cu film resistivity(ρ) can be expressed as the following

$$\begin{aligned}\rho &= \rho_b(\text{bulk}) + \rho_r(\text{residual}) \\ &= \rho_b(\text{bulk}) + [\rho_s(\text{surface}) + \rho_t(\text{impurities}) + \rho_g(\text{grain boundaries}) \\ &\qquad + \rho_d(\text{intragranular defects})] \qquad (2)\end{aligned}$$

The term ρ_s is dependent on the smoothness of the film surface. The term ρ_t is related to the content of impurities contamination in the film, such as the reaction by-products carbon (C) and oxygen (O). The term ρ_g is directly proportional to the density of grain boundary in the copper film [39]. The term ρ_d is due to the intragranular defects, including dislocation, stacking faults, twins, and vacancy. For the CVD Cu films at high temperatures, Cu films contain higher levels of impurities due to the higher deposition rate of Cu films

than the removal rate of Cu reaction by-products [31]. In addition, the film surface becomes rougher, and the film tends to contain a lot of voids because the grains may not be closely stacked. As a result, the film resistivity tends to increase with increasing deposition temperature (for temperatures above 160℃). For the CVD Cu films at low temperatures, since all reaction by-products have a lower volatility at low temperatures, the residual impurities from the reaction by-products can be easily incorporated into the deposited Cu films. Moreover, the film deposited at lower temperatures contains a higher grain boundary density because of the smaller grain size. Thus, the film resistivity increases with decreasing deposition temperature (for temperatures below 160℃). In summary, the reisitivity of Cu film is mainly determined by the content of impurities, the density of grain boundary, and the structure of voids between the Cu grains [40].

3.3.3 Surface Roughness of Cu films

Figure 3-5 and Fig.3-6 show the AFM 3D images of the Cu films deposited at various temperatures on TaN and TaSiN substrates for a duration of 10min. It can be seen that the surface roughness increases with increasing temperature of deposition. Figure 3-7 shows the average surface roughness (RMS) as a function of deposition temperature for the Cu films deposited for 10 min on TaN and TaSiN substrates. The surfaces of the Cu films on the TaSiN substrate generally have a slightly larger roughness than that on the TaN substrate at a given deposition temperature; this may be attributed to the smoother surface of TaN substrate than the TaSiN substrate, as shown in Fig.3-8. Moreover, it is notable that the surface of the Cu films deposited at 240℃ became much rougher, either on TaN or TaSiN substrate; this is presumably due to the fact that the Cu CVD at 240℃ was in the mass-flow-controlled region, which features a deposition of poor comformality.

3.3.4 Crystal Structure of Cu film

In deep submicron regime of integrated circuits, electromigration (EM) is a key reliability issue of the interconnection metal. It has been reported that the resistance to electromigration is sensitive to the texture of Cu films, with (111) being the preferred texture [29, 41-42], and the XRD intensity peak ratio of Cu(111) to Cu(200) reflection is an important indicator. Figure 3-9 shows the XRD spectra for the Cu films deposited at various temperatures on TaN and TaSiN substrates, while the intensity peak ratio of Cu(111) to Cu(200) reflections versus deposition temperature is illustrated in Fig.3-10. The peak ratio of Cu(111) to Cu(200) reflections for the Cu films deposited on TaSiN substrate is higher than that deposited on TaN substrate. Since it was reported that the TaSiN film is more amorphous-like than the TaN film [34], we may presume that the more amorphous-like TaSiN substrate would enhance layer growth of Cu film, leading to more (111) preferred film formation, because there is no specific crystal-lattice-matching restriction between a film and substrate that obstructs stable (111) two-dimensional island formation [43]. Moreover, the peak ratio of Cu(111) to Cu(200) reflections increases with increasing deposition temperature; this is presumably because the Cu atoms or Cu species have a better-migrated capability at higher temperatures, resulting in the Cu atoms or Cu species to arrive at the Cu(111) sites of the lowest potential energy [44].

3.4 Effect of Post-deposition Thermal Annealing

Figure 3-11 and Fig.3-12 illustrate the SEM micrographs showing surface morphology of CVD Cu films deposited on TaN and TaSiN substrates thermally annealed at 400℃ for 30min in N_2 ambient. Compared to the as-deposited Cu films shown in Fig.3-2 and Fig.3-3, we found that the 400℃-annealed films all exhibit larger grain size and feature fluid-like or milky morphology with the exception of the film deposited at the temperature of 240℃, which was in the

mass-flow-controlled region. Figure 3-13 shows the film resistivity versus deposition temperature for the Cu films deposited on TaN and TaSiN substrates with a furnace annealing at 400℃ for 30min in N_2 ambient; the data for the as-deposited films are also induced for a comparison. The film resistivity was reduced after the thermal annealing. This maybe attributed to the decrease in grain boundary density, defects healing and the impurity out diffusion from inner of the Cu films.

Figure 3-14 and Fig.3-15 show, respectively, the AFM 3D images of the Cu films deposited on TaN and TaSiN substrates thermally annealed at 400℃ for 30min in N_2 ambient. The 400℃ annealing resulted in a film of smoother surface and closely contacted Cu grains; similar observation was reported in the literature for CVD Cu films annealed in Ar and Ar/H_2 ambient [44]. The comparison of the average surface roughness between the as-deposited and 400 ℃-annealed Cu films on TaN and TaSiN substrates is illustrated in Fig.3-16.

Figure 3-17 shows the XRD spectra for the as-deposited and 400℃-annealed CVD Cu films deposited at a temperature of 200℃, while the intensity peak ratio of the Cu(111)/Cu(200) reflections for the Cu films deposited at various temperatures on TaN and TaSiN substrates is illustrated in Fig.3-18. Thermal annealing resulted in the improvement of Cu(111)/Cu(200) peak ratio. We presume that the thermal annealing reduces the grain boundary and surface energy of the Cu grain, resulting in the recrystallization of Cu grains to forming the most stable (111) texture [45].

3.5 Summary

CVD of Cu films on TaN and TaSiN substrates using a liquid metalorganic compound of Cu(hfac)TMVS with 2.4wt% TMVS additive as the Cu precursor was investigated in this chapter. The activation energies of Cu CVD on TaN and TaSiN substrates at a deposition pressure of 150mtorr and at temperatures below 220℃, where Cu CVD is surface-reaction-controlled, were determined to

be 5.91 and 5.48 kcal/mole, respectively, as shown in Fig.3-1. The lowest resistivity Cu films were obtained at a deposition temperature of 160℃; the lowest film resistivity is approximately 2.15μΩ-cm either on TaN or TaSiN substrates. For the Cu films deposited at temperatures below 160℃, the film resistivity increases with decreasing deposition temperature presumably due to higher contamination of residual impurities from the reaction by-products and higher grain boundary density of the Cu films. For the Cu films deposited at temperatures above 160℃, the film resistivity increases with increasing deposition temperature presumably resulting from higher contamination of impurities in the films and porous microstructure of the Cu films. The grain size, the surface roughness, and the intensity peak ratio of Cu(111)/Cu(200) reflections all increased with increasing deposition temperature. The post-deposition thermal annealing of Cu films at 400℃ resulted in increased grain size, decreased film resistivity, reduced surface roughness and milky surface morphology, and increased peak ratio of Cu(111)/Cu(200) reflections.

Table 3-1 Major parameters and processing conditions of Cu CVD used in this study.

Substrate temperature (°C)	140~240
Operating pressure (mtorr)	150
Cu precursor flow rate (ml/min)	0.4
CEM temperature (°C)	70
Carrier gas (He) flow rate (sccm)	25
Substrate holder rotation speed (rpm)	7
Gas-injector/susceptor distance (cm)	2
Precursor's delivery line temperature (°C)	72
Reactor (reaction chamber) wall temperature (°C)	45

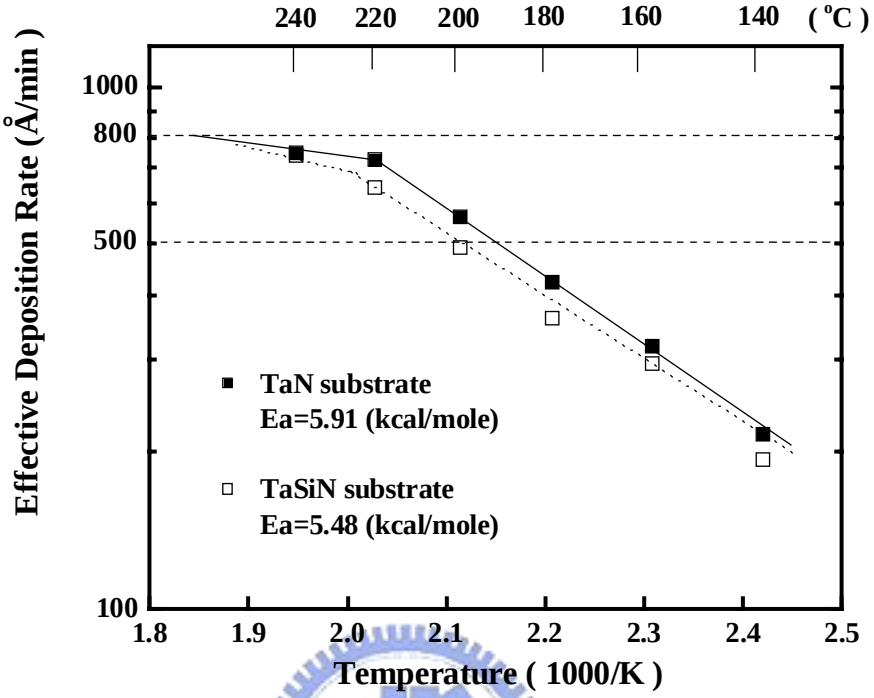
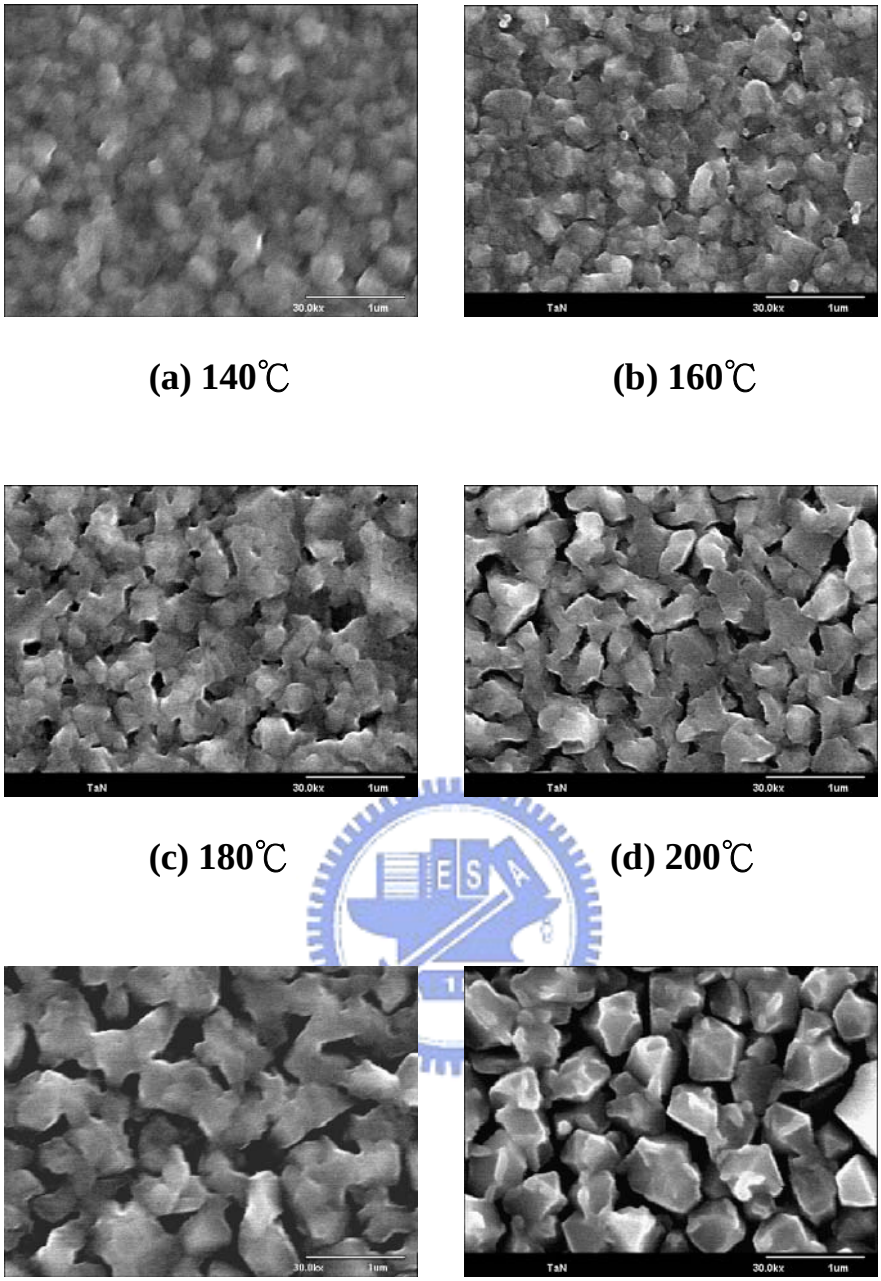


Fig.3-1 Effective deposition rate vs. substrate temperature (Arrhenius plot) for Cu films deposited on TaN and TaSiN substrates at a deposition pressure of 150mtorr.

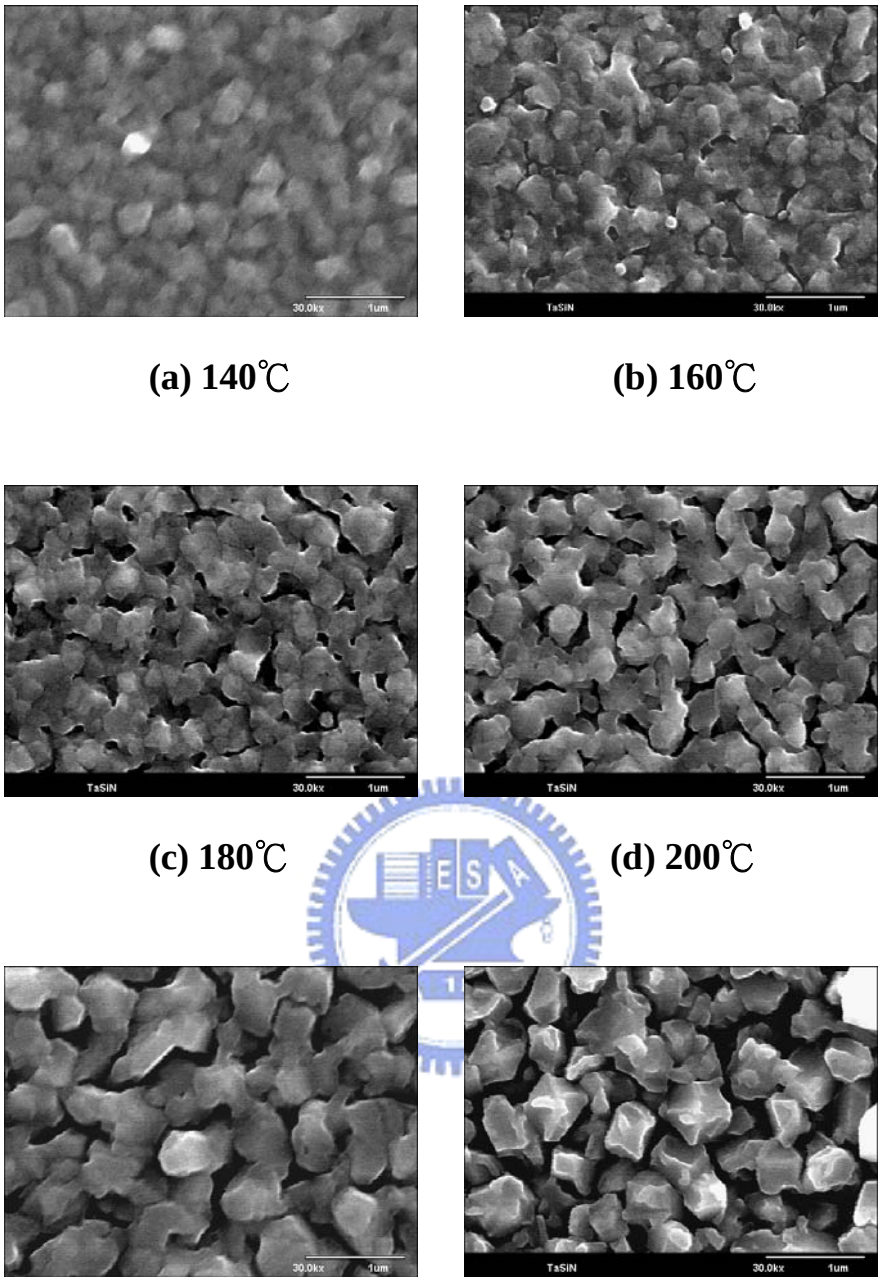


(a) 140℃ **(b) 160℃**

(c) 180℃ **(d) 200℃**

(e) 220℃ **(f) 240℃**

Fig.3-2 SEM micrographs showing surface morphology of Cu films deposited on TaN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 200℃, (e) 220℃, and (f) 240℃ with a deposition pressure of 150mtorr for a deposition time of 10min.



(a) 140℃ **(b) 160℃**

(c) 180℃ **(d) 200℃**

(e) 220℃ **(f) 240℃**

Fig.3-3 SEM micrographs showing surface morphology of Cu films deposited on TaSiN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 200℃, (e) 220℃, and (f) 240℃ with a deposition pressure of 150mtorr for a deposition time of 10min.

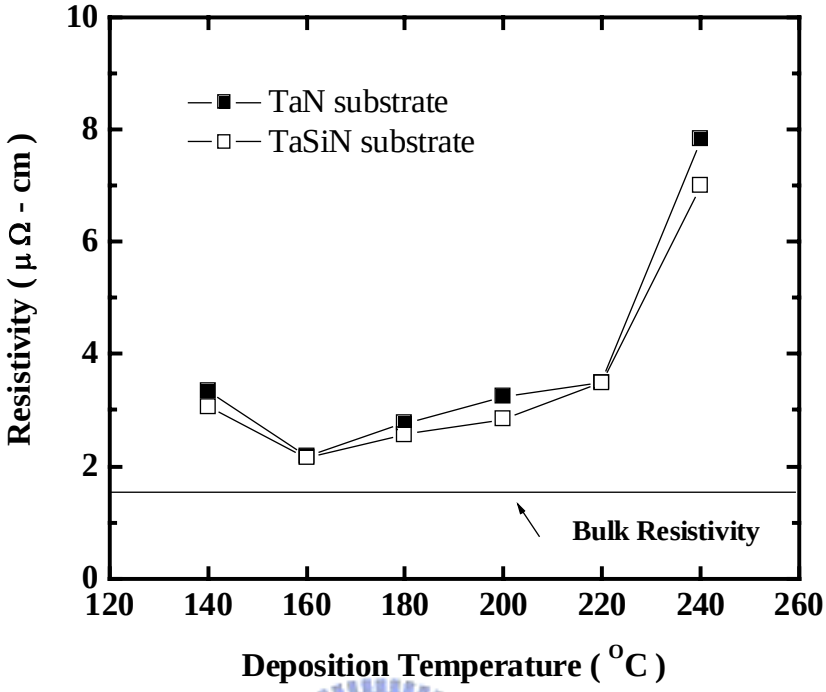
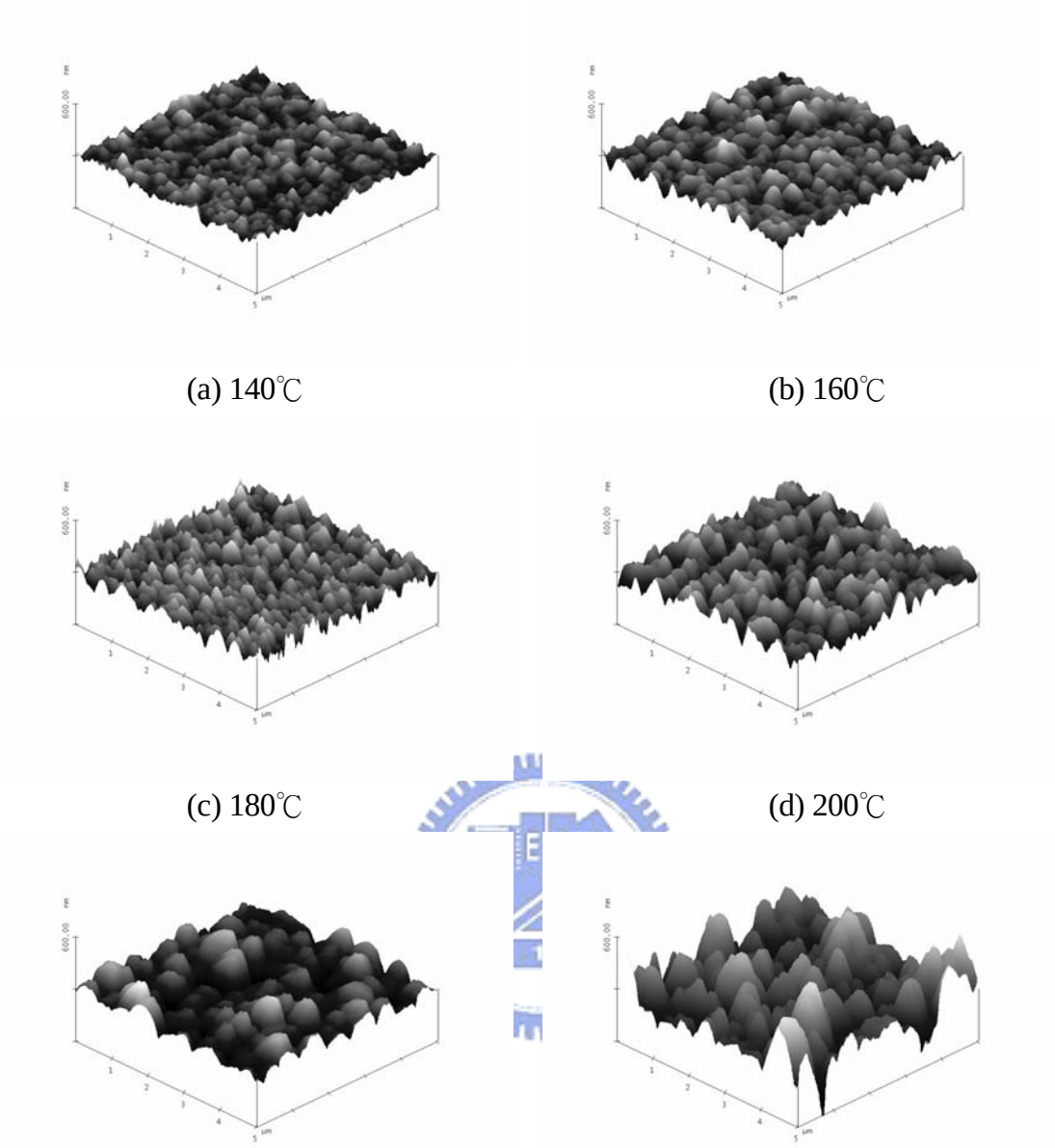


Fig.3-4 Resistivity vs. deposition temperature for Cu films deposited on TaN and TaSiN substrates at a pressure of 150mtorr for a deposition time of 10 min.

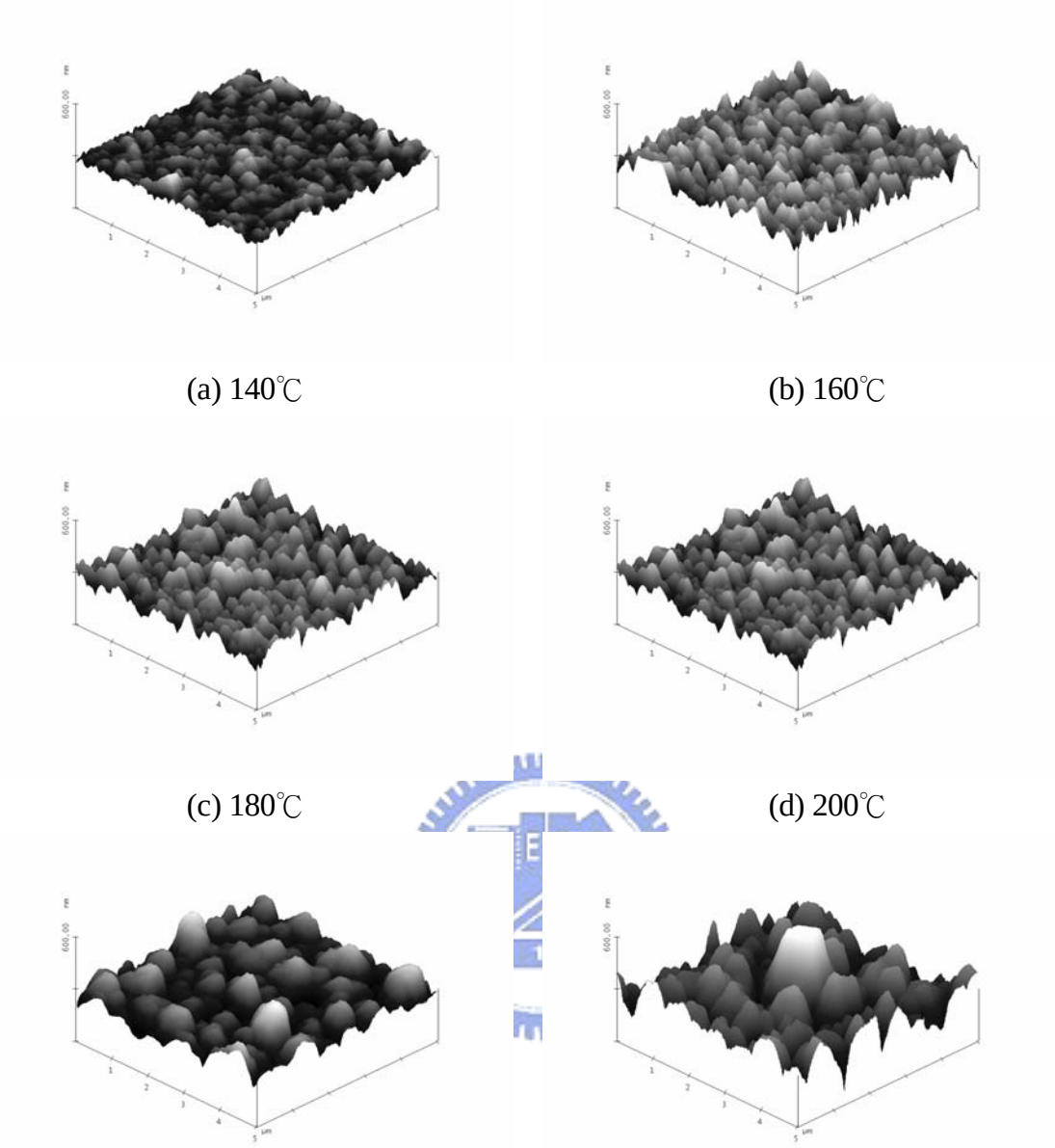


(a) 140℃ (b) 160℃

(c) 180℃ (d) 200℃

(e) 220℃ (f) 240℃

Fig.3-5 AFM 3D images showing the surface roughness of Cu Films deposited for 10min on TaN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 200℃, (e) 220℃, and (f) 240℃.



(a) 140℃ (b) 160℃

(c) 180℃ (d) 200℃

(e) 220℃ (f) 240℃

Fig.3-6 AFM 3D images showing the surface roughness of Cu Films deposited for 10min on TaSiN substrate at (a) 140℃, (b) 160℃, (c)180℃, (d) 200℃, (e) 220℃, and (f) 240℃.

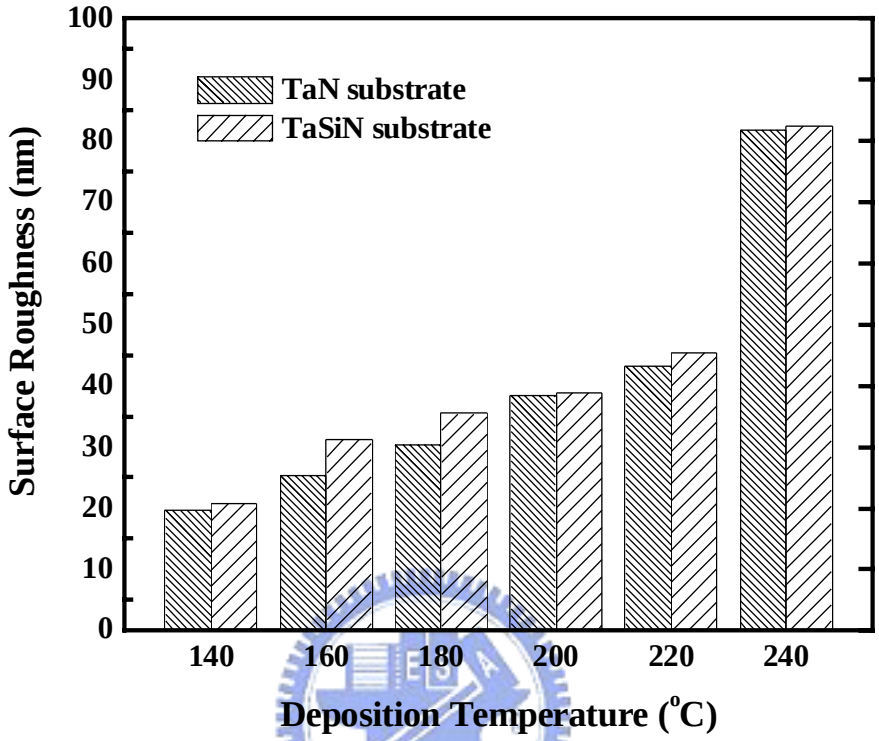
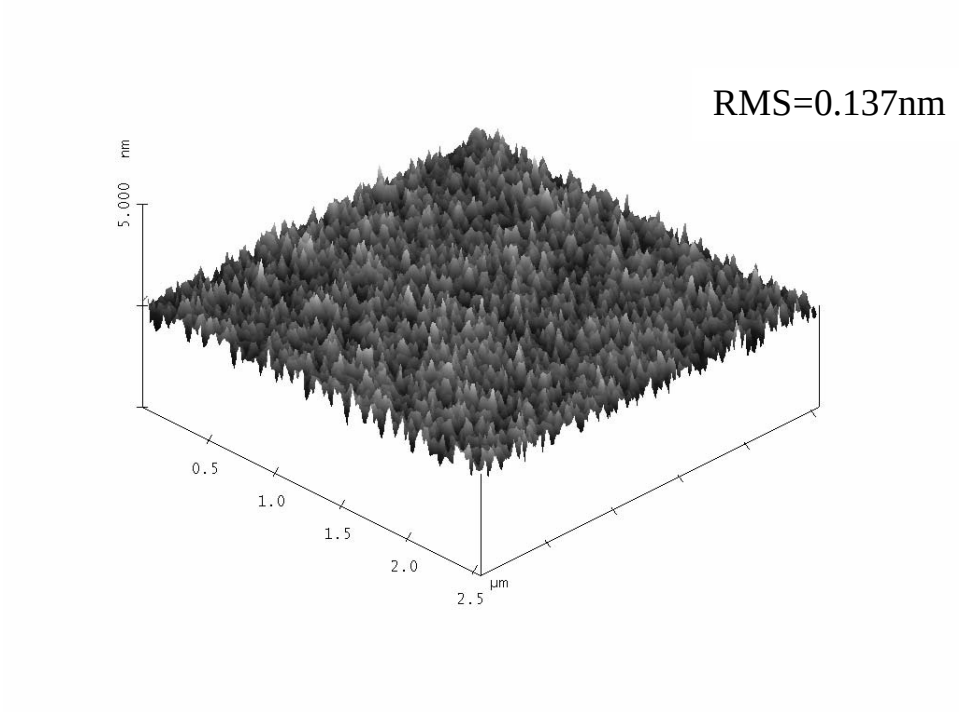
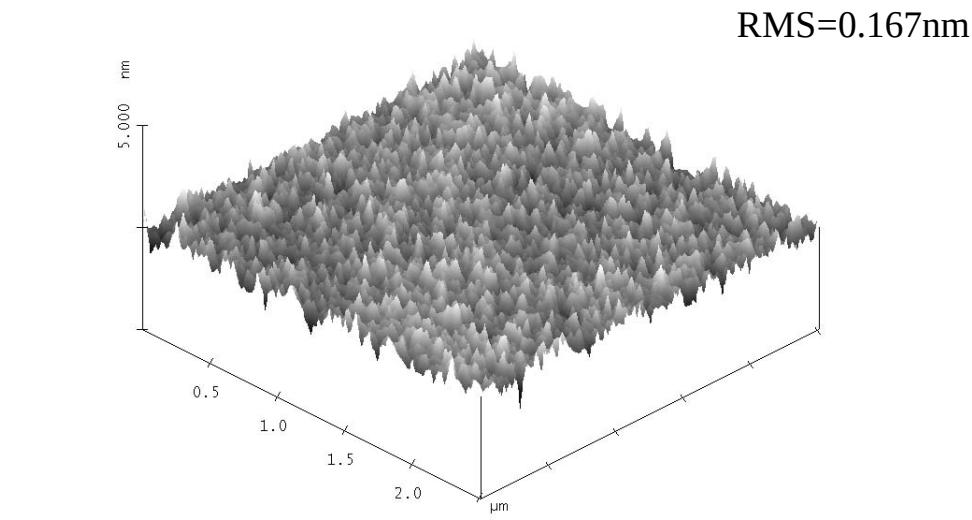


Fig.3-7 Average surface roughness (determined by AFM) vs. deposition temperature for the Cu films deposited on TaN and TaSiN substrates. The Cu films were deposited at a pressure of 150mtorr for 10min.

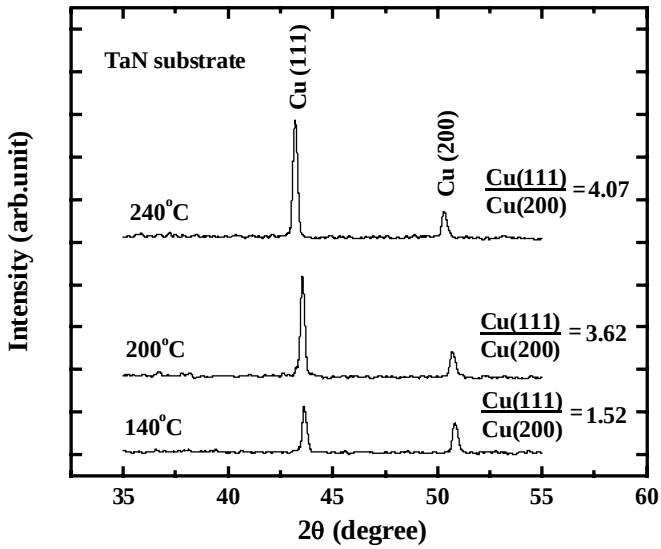


(a) TaN

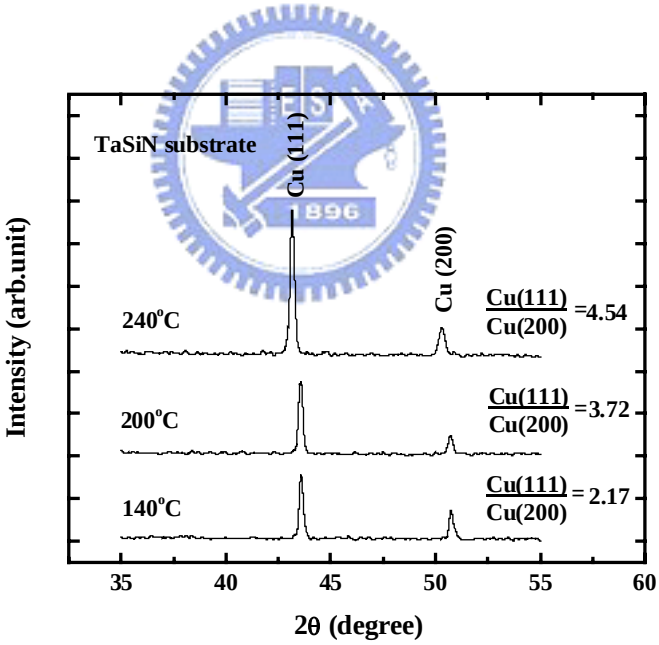


(b) TaSiN

Fig.3-8 AFM 3D images showing the surface roughness of (a) TaN and (b) TaSiN substrates.



(a)



(b)

Fig.3-9 XRD spectra for Cu films deposited on (a)TaN and (b)TaSiN substrate at various deposition temperatures.

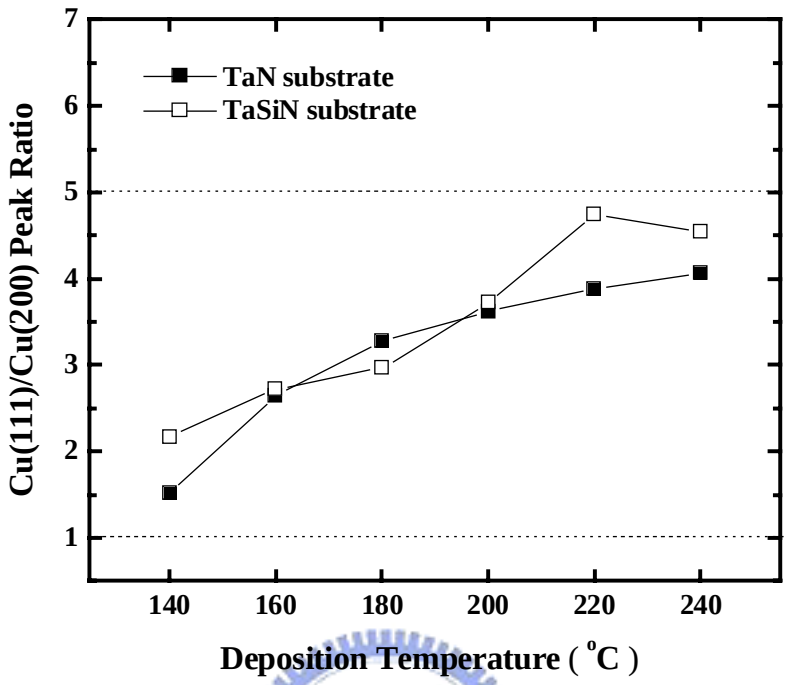
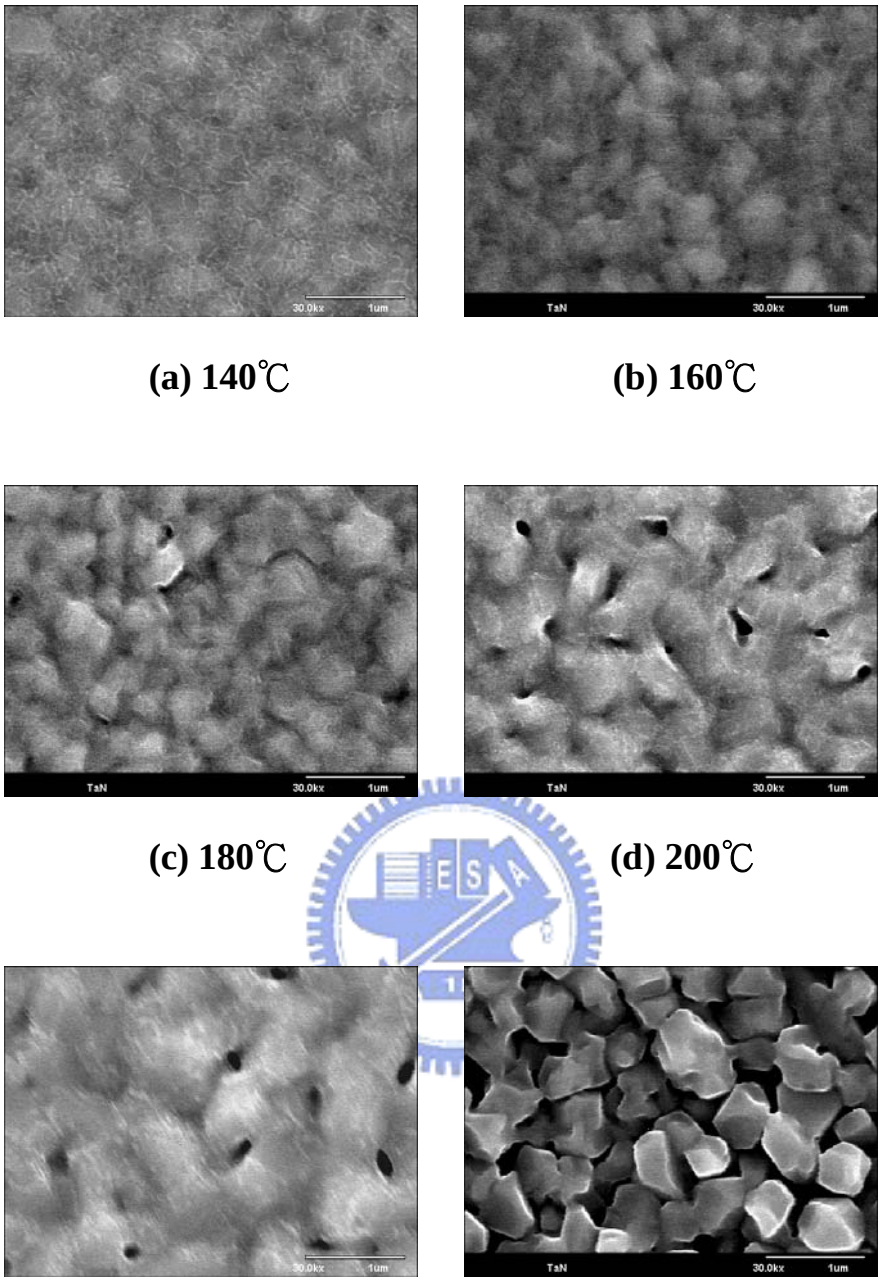


Fig.3-10 XRD intensity peak ratio of Cu(111) to Cu(200) reflections vs. deposition temperature for Cu films deposited on TaN and TaSiN substrates at a pressure of 150mtorr for 10min.

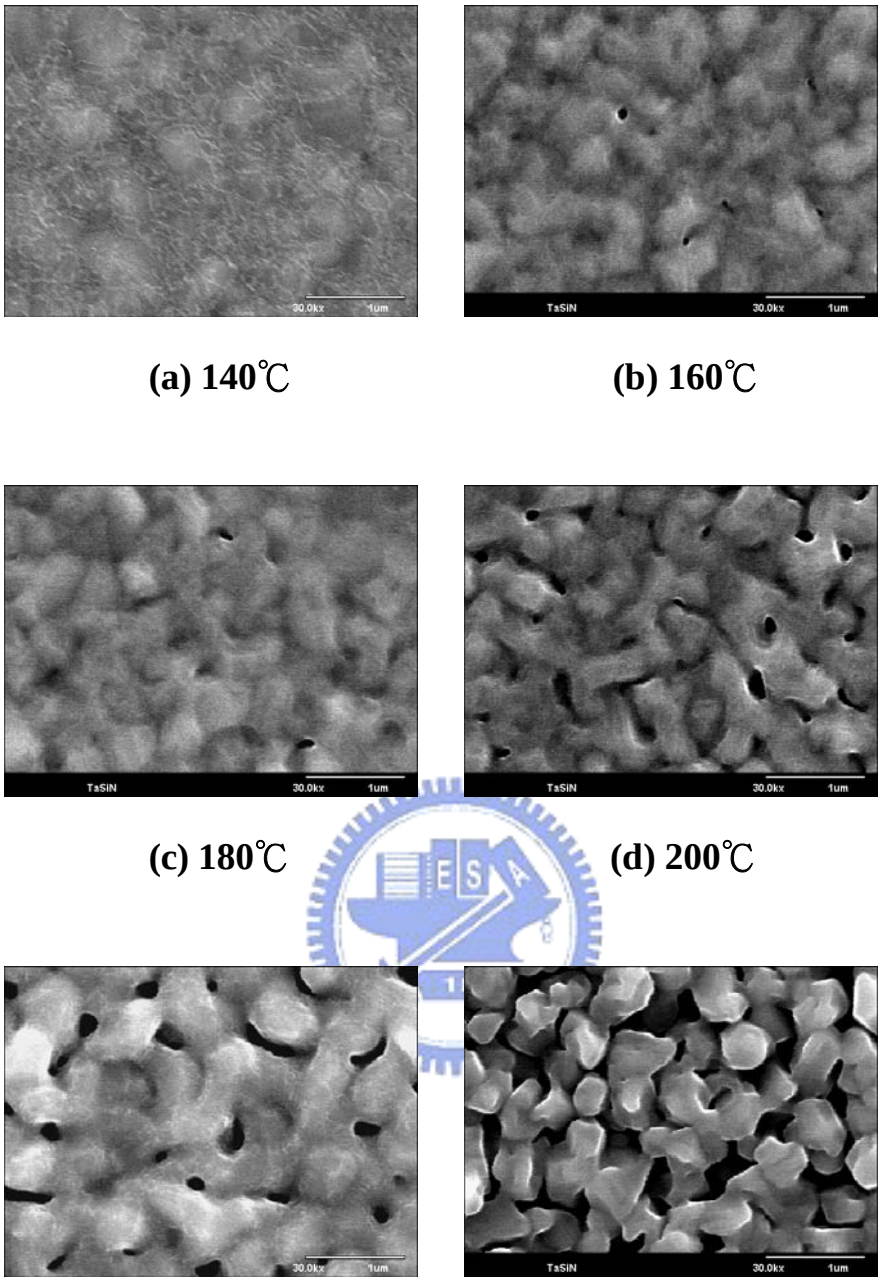


(a) 140℃ **(b) 160℃**

(c) 180℃ **(d) 200℃**

(e) 220℃ **(f) 240℃**

Fig.3-11 SEM micrographs showing surface morphology of Cu films deposited on TaN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 200℃, (e) 220℃, and (f) 240℃ for 10min with a pressure of 150 mtorr and then thermally annealed at 400℃ for 30min in N_2 ambient.

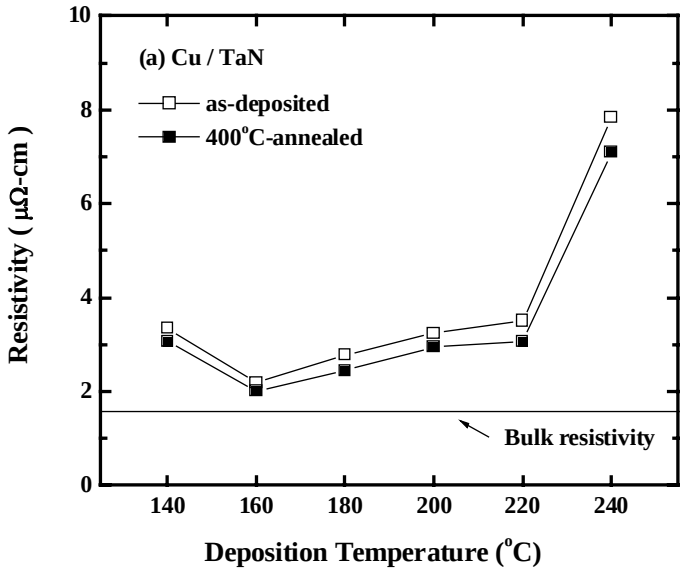


(a) 140℃ **(b) 160℃**

(c) 180℃ **(d) 200℃**

(e) 220℃ **(f) 240℃**

Fig.3-12 SEM micrographs showing surface morphology of Cu films deposited on TaSiN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 200℃, (e) 220℃, and (f) 240℃ for 10min with a pressure of 150mtorr and then thermally annealed at 400℃ for 30min in N_2 ambient.



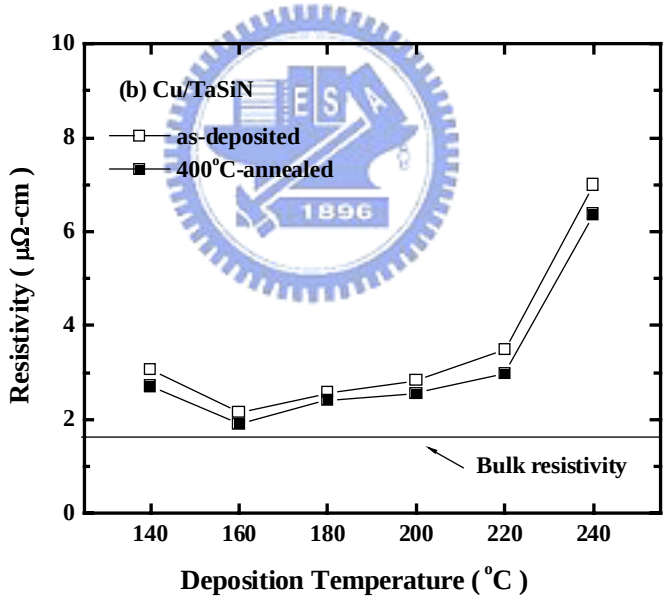
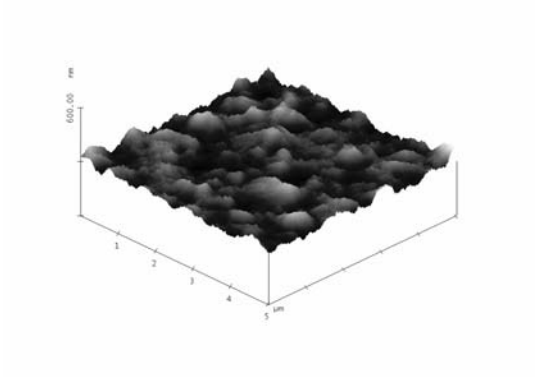
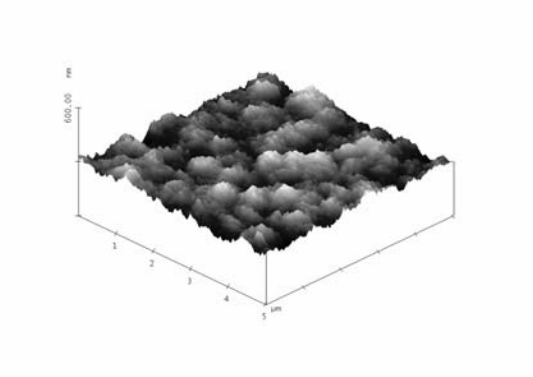


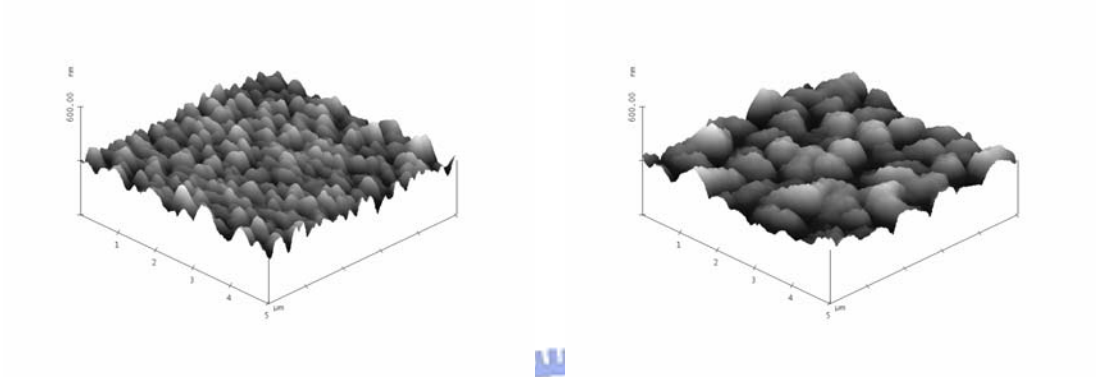
Fig.3-13 Film resistivity vs. deposition temperature for Cu films deposited on (a) TaN and (b) TaSiN substrates with and without (as-deposited) a furnace annealing at 400℃ for 30min in N_2 ambient.



(a) 140℃

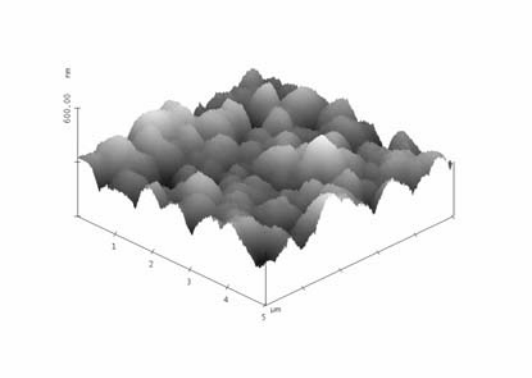


(b) 160℃



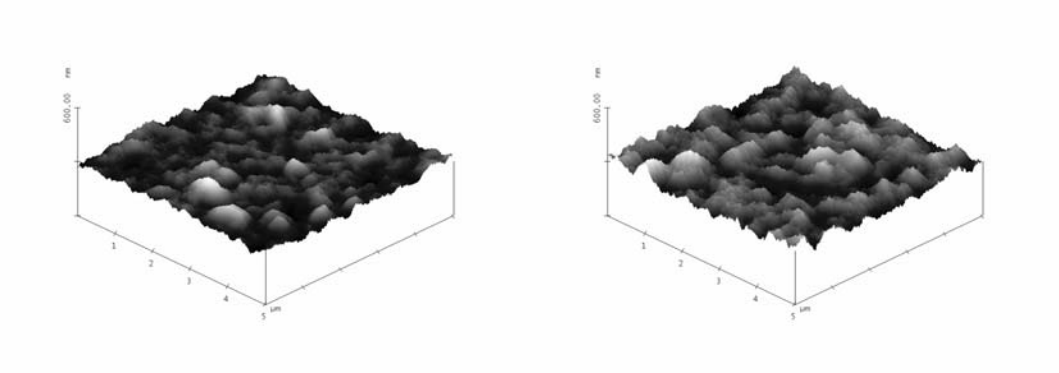
(c) 180℃

(d) 220℃

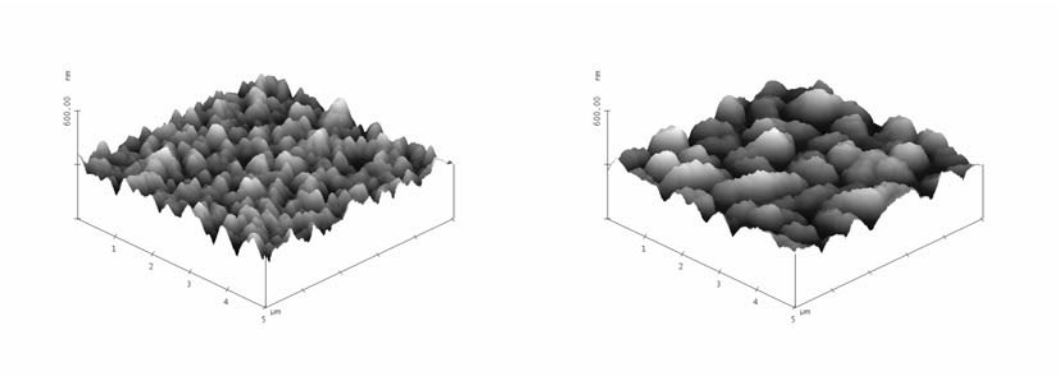


(e) 240℃

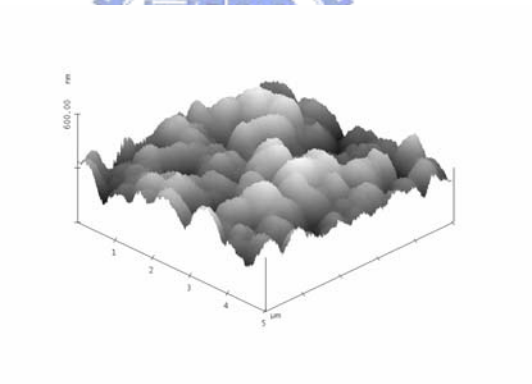
Fig.3-14 AFM 3D images showing the surface roughness of Cu Films deposited for 10min on TaN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 220℃, and (e) 240℃ thermally annealed at 400℃ for 30min in N_2 ambient.



(a) 140℃　　(b) 160℃

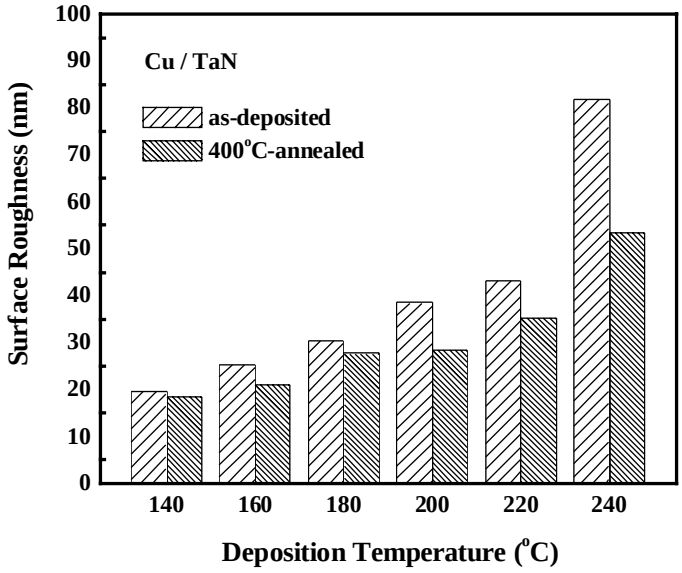


(c) 180℃　　(d) 220℃



(e) 240℃

Fig.3-15 AFM 3D images showing the surface roughness of Cu Films deposited for 10min on TaSiN substrate at (a) 140℃, (b) 160℃, (c) 180℃, (d) 220℃, and (e) 240℃ thermally annealed at 400℃ for 30min in N_2 ambient.



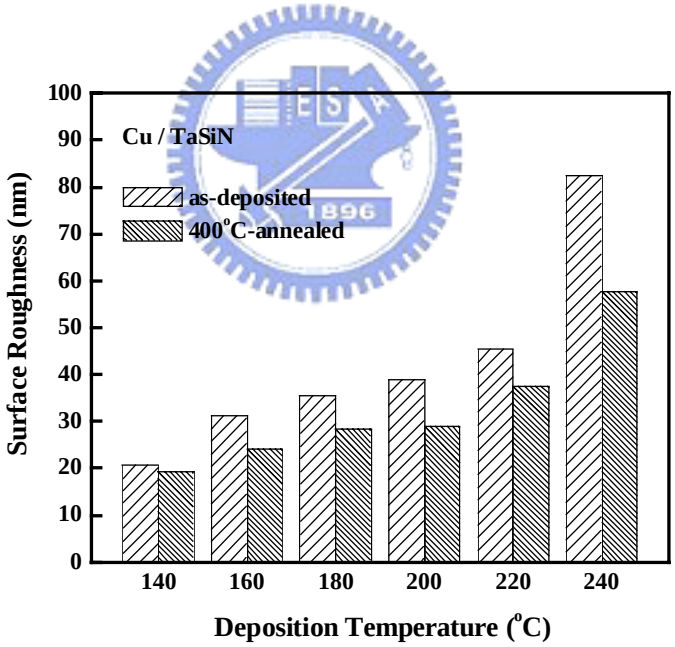
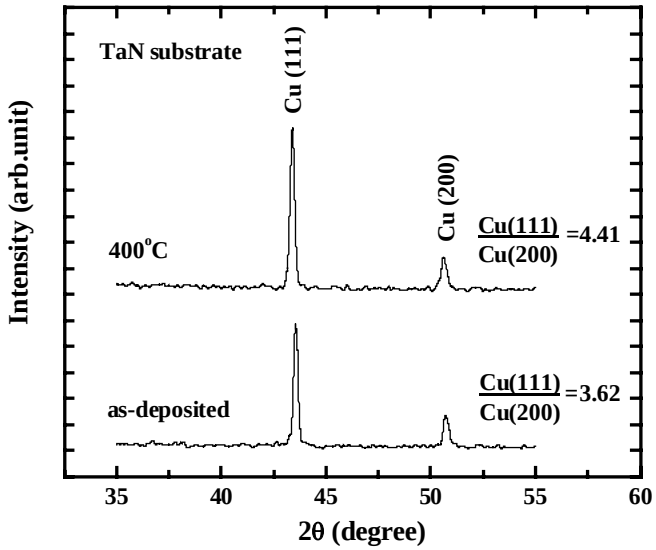
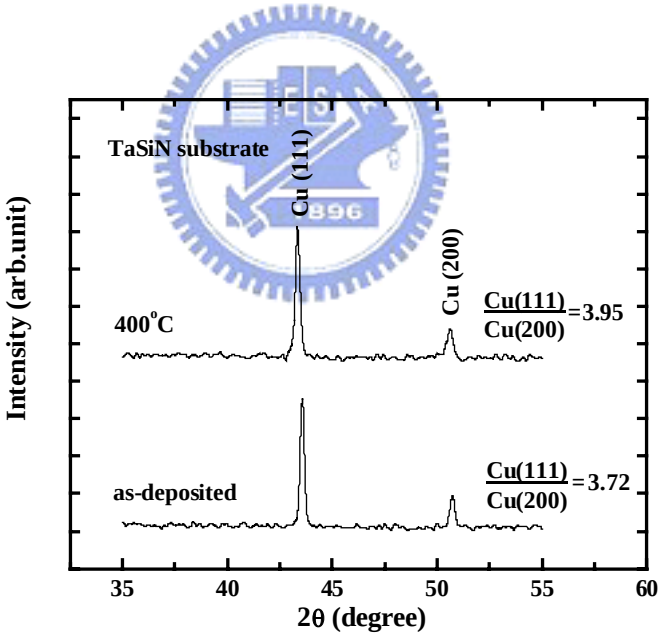


Fig.3-16 Average surface roughness (determined by AFM) vs. deposition temperature for the Cu films deposited on TaN and TaSiN substrates thermally annealed at 400℃ for 30min in N_2 ambient.

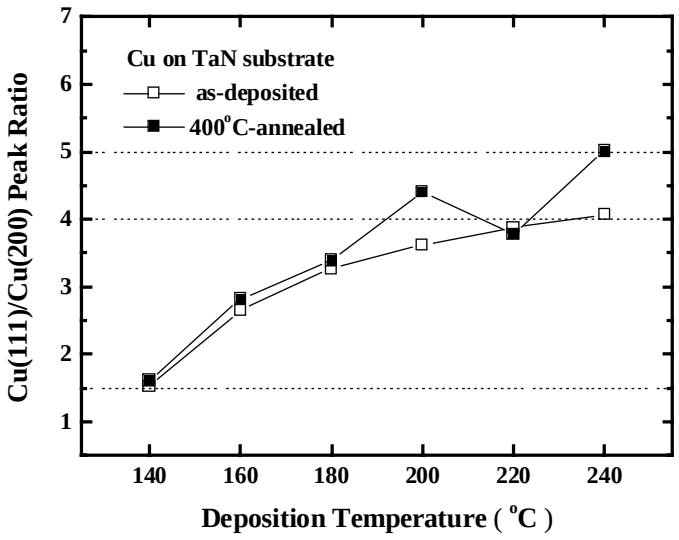


(a)

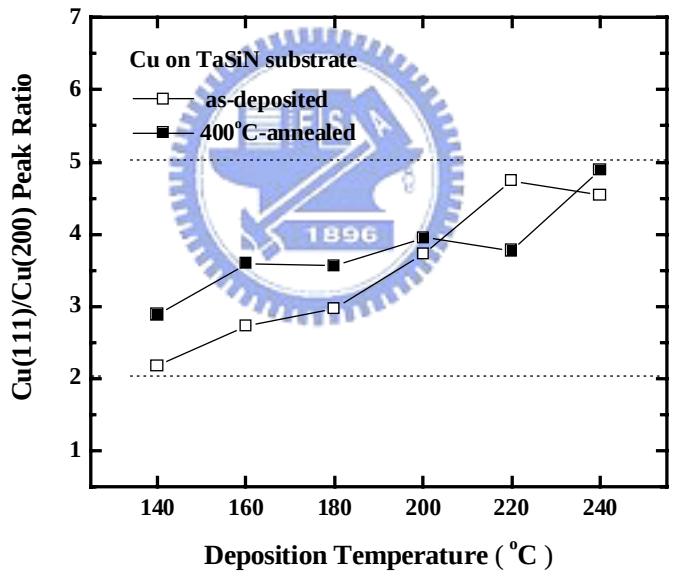


(b)

Fig.3-17 XRD spectra for as deposited and 400℃-annealed Cu films deposited at 200℃ on (a) TaN and (b) TaSiN substrates.



(a)



(b)

Fig.3-18 XRD intensity peak ratio of Cu(111) to Cu(200) reflections vs. deposition temperature for Cu films deposited on (a) TaN and (b) TaSiN substrates at a pressure of 150mtorr for 10min and then thermally annealed at 400℃ for 30min in N_2 ambient. Data for the as-deposited Cu films are also included for comparison.