Chapter 5
Effects of Substrate Plasma Treatment and Post-Deposition Thermal Annealing on CVD-Cu films

5.1 Introduction

It has been reported that the nucleation process of Cu and the microstructure of CVD-Cu film are very sensitive to the substrate surface condition [53, 54]. Moreover, plasma treatment on the substrate surface prior to the deposition of Cu film promoted the (111)-preferred texture [48, 53], because plasma treatment resulted in the modification of substrate surface energy and the removal of native oxide and/or particle contamination on the substrate surface.

In this chapter, we investigate the effects of TaN and TaSiN substrate treatment by Ar-plasma (physical sputtering) and H_2-plasma (chemical reaction) on the property of CVD-Cu films. The effects of post-deposition thermal annealing are also studied.

5.2 Experimental Details

In the study of this chapter, TaN and TaSiN are used as the substrates for the CVD of Cu films; same process as reported in chapter 3 was used for the sputter deposition of the TaN and TaSiN layers. The TaN- or TaSiN-coated substrate wafer was loaded into the multi-chamber Cu CVD system. When the pressure of the loading chamber reached 10^{-6}torr, the substrate wafer was transferred to the pretreatment chamber or reaction chamber (copper deposition chamber) via the transfer chamber depending on the process requirement of whether the plasma pretreatment on substrate was to be performed or not. In this study, Ar-plasma or H_2-plasma treatment was performed at 50W power for 10 min. The major plasma processing conditions of Ar-plasma and

H_2-plasma treatments used in the study of this chapter are the same as those used in chapter 4, as shown in Table 4-1. After the plasma treatment, the substrate sample was transferred to the reaction chamber for Cu film deposition. Prior to the Cu film deposition, the substrate sample was heated to the desired deposition temperature with the He carrier gas flowing at 25 sccm and the chamber pressure maintained at 150mtorr. Usually, it took about one hour for the substrate sample to reach the preset temperature. In this study, Cu CVD was performed at a temperature of 160℃ and a pressure of 150motrr with a precursor flow rate of 0.4ml/min and a He carrier gas flow rate of 25 sccm. The parameter and processing conditions of Cu CVD are the same as those shown in Table 3-1 used in chapter 3. At the end of Cu film deposition, the sample was cooled in the ambient of He at a pressure of 150mtorr.

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

5.3 Cu Films on Ar-Plasma-Treated Substrate

Figure 5-1 and Fig.5-2 illustrates the SEM micrographs showing the surface morphology of Cu films deposited on TaN and TaSiN substrates, respectively, with and without Ar-plasma treatment. It can been seen that the Cu films deposited on the Ar-plasma-treated TaN and TaSiN substrates appeared to have better contacted grains and contain less voids in comparison with those deposited on the as-deposited substrates. The Cu films deposited on Ar-plasma-treated substrates also exhibited a smoother surface than those deposited on the bare substrates without the plasma treatment, as shown by the AFM 3D images illustrated in Fig.5-3 and Fig.5-4. The Ar-plasma treatment on the TaN and TaSiN substrates surface also affected the texture of the deposited Cu films. Figure 5-5 shows the XRD spectra for the Cu films deposited on TaN and TaSiN substrates with and without the Ar-plasma treatment. With Ar-plasma treatment, the smoother and amorphous-like substrate surface enhanced the migration of Cu-containing adspecies to form a Cu film with more (111) preferred orientation because the (111) texture is the most stable and dense configuration [49, 50].

The resistivities of the Cu films deposited on the Ar-plasma-treated TaN and TaSiN substrates were determined to be 2.16 and 2.08μΩ-cm, respectively, which are slightly lower than the values of 2.24 and 2.15μΩ-cm measured on the Cu films deposited on the bare TaN and TaSiN substrates, respectively. The slightly lower resistivity for the Cu films deposited on the plasma-treated substrate is presumably due to the films with better contacted grains and containing less voids.

5.4 Cu Films on H_2-Plasma-Treated Substrate

Figure 5-6 illustrates the SEM micrographs showing the surface morphology of the Cu films deposited on the H_2-plasma-treated TaN and TaSiN substrates. In comparison with the corresponding Cu films deposited on the as-deposited TaN and TaSiN substrates [Fig.5-1 (a) and Fig.5-2 (a)], the Cu films deposited on the H_2-plasma-treated substrates also appeared to have better contacted grains and contain less voids. The H_2-plasma treatment on the TaN and TaSiN substrates surface also resulted in improving the (111) preferred orientation for the deposited Cu films. Figure 5-8 shows the XRD spectra for the Cu films deposited on TaN and TaSiN substrates with and without the H_2-plasma treatment.

The intensity peak ratio of Cu(111) to Cu(200) reflections was improved for the Cu films deposited on the H_2-plasma-treated substrates, either TaN or TaSiN. The resistivities of the Cu films deposited on the H_2-plasma-treated TaN and TaSiN substrates were determined to be 2.31 and 2.25μΩ-cm, respectively, which are slightly higher than the values of 2.24 and 2.15μΩ-cm measured on the Cu films deposited on the as-deposited TaN and TaSiN substrates, respectively.

5.5 Effect of Post-Deposition Thermal Annealing

Copper films deposited on the TaN and TaSiN substrates, either with or without the plasma treatment, were thermally annealed at 400℃ for 30min in N_2 ambient. Figure 5-9 and Fig.5-10 illustrate the SEM micrographs showing the surface morphology of the post-deposition thermal annealed Cu films deposited on the as-deposited and the plasma-treated TaN and TaSiN substrates, respectively. The milky and fluid-like surface morphology, as compared to the surface morphology of the Cu film before the thermal annealing, implies that the Cu surface became smoother and the film became less porous after the thermal annealing. The AFM images of the Cu films after the 400℃ thermal annealing are illustrated in Fig.5-11 and Fig.5-12, respectively, for the Cu films deposited on the TaN and TaSiN substrates. In comparison with the as-deposited Cu films [Fig.5-3, Fig.5-4 and Fig.5-7], it can be seen that the average surface roughness (RMS) of the Cu films was notably reduced as a result of the post-deposition thermal annealing. Table 5-1 compares the surface roughness (RMS) for the as-deposited and the 400℃-annealed Cu films deposited on the TaN and TaSiN substrates with and without the plasma treatment. The thermal annealing at 400℃ also resulted in the decrease in Cu film resistivity, the comparison of which is shown in Table 5-2. After the thermal annealing, the resistivity of Cu films deposited on the Ar-plasma and H_2-plasma treated TaN and TaSiN substrates all exhibited a smaller value compared to the resistivity of the corresponding as-deposited film. Moreover, thermal annealing also resulted in an increase in the intensity peak ratio of Cu(111) to Cu(200) reflections, as shown in Table 5-3. The decrease in average surface roughness and the increase in peak ratio of Cu(111)/Cu(200) reflections are presumably due to the fact that thermal annealing would reduce the grain boundary and surface energy of the Cu films, causing recrystallization of Cu grains to form the most stable (111) texture [49, 55].

5.6 Summary

This chapter investigates the effects of substrate plasma treatment on the CVD-Cu film as well as the effects of post-deposition thermal annealing of the Cu film. The Cu films deposited on Ar-plasma-treated and H_2-plasma-treated TaN and TaSiN substrates all appeared to have better contacted grains and contain less voids; they also exhibited a smoother film surface and enhanced (111)-preferred orientation compared with those deposited on the bare TaN and TaSiN substrates. The Cu films deposited on the Ar-plasma-treated substrates exhibited the lowest film resistivity among all the films studied in this thesis. Thermal annealing at 400℃ for 30 min in N_2 ambient resulted in the reduce of surface roughness and film resistivity and the increase of intensity peak ratio of Cu(111) to Cu(200) reflections. For comparison, the surface roughness, film resistivity, and intensity peak ratio of Cu(111) to Cu(200) reflections for the Cu films deposited on the as-deposited and plasma-treated TaN and TaSiN substrates, either with or without the post-deposition thermal annealing, are summarized, respectively, in Tables 5-1, 5-2, and 5-3.

Table 5-1 Surface roughness (RMS, in unit of nm) for the as-deposited and 400℃-annealed Cu films deposited on TaN and TaSiN substrates with and without plasma treatment.

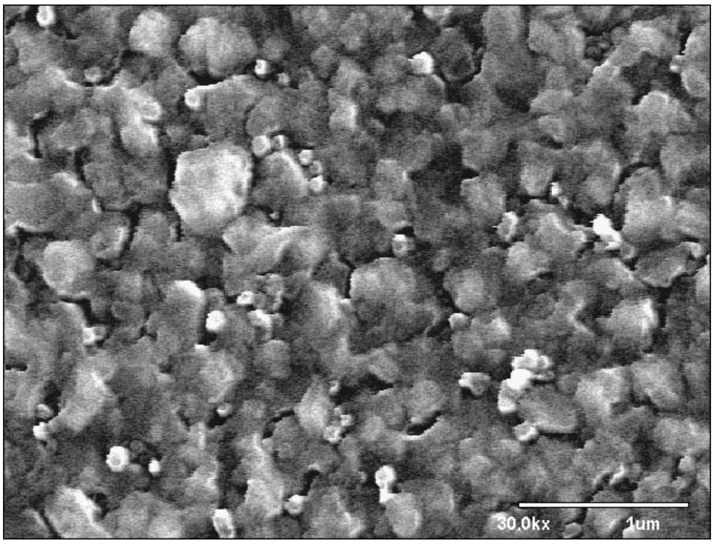
Substrate	TaN Substrate		TaSiN Substrate	
Plasma Treatment	as-deposited	400℃-annealed	as-deposited	400℃-annealed
None (as-deposited)	25.4	22.0	31.2	24.4
Ar-plasma	23.1	17.9	23.7	19.1
H_2-plasma	24.8	21.5	25.3	22.6

Table 5-2. Film resistivity (in unit of μΩ-cm) for the as-deposited and 400℃-annealed Cu films deposited on TaN and TaSiN substrates with and without plasma treatment.

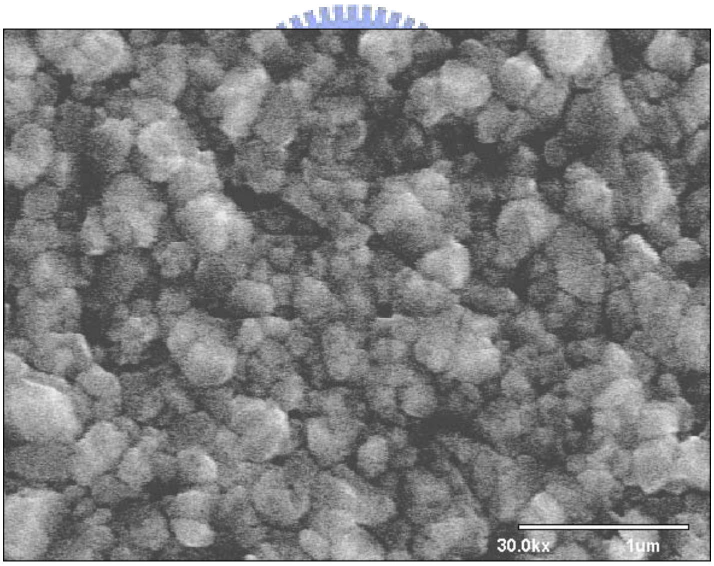
Substrate	TaN Substrate		TaSiN Substrate	
Plasma Treatment	as-deposited	400℃-annealed	as-deposited	400℃-annealed
None (as-deposited)	2.24	2.18	2.16	2.10
Ar-plasma	2.16	2.09	2.08	2.01
H_2-plasma	2.31	2.13	2.25	2.04

Table 5-3 Intensity peak ratio of Cu(111) to Cu(200) reflections for the as-deposited and 400℃-annealed Cu films deposited on TaN and TaSiN substrates with and without plasma treatment.

Substrate	TaN Substrate		TaSiN Substrate	
Plasma Treatment	as-deposited	400℃-annealed	as-deposited	400℃-annealed
None (as-deposited)	1.96	2.90	2.79	3.56
Ar-plasma	4.34	4.87	4.47	4.91
H_2-plasma	3.14	3.65	3.47	4.15

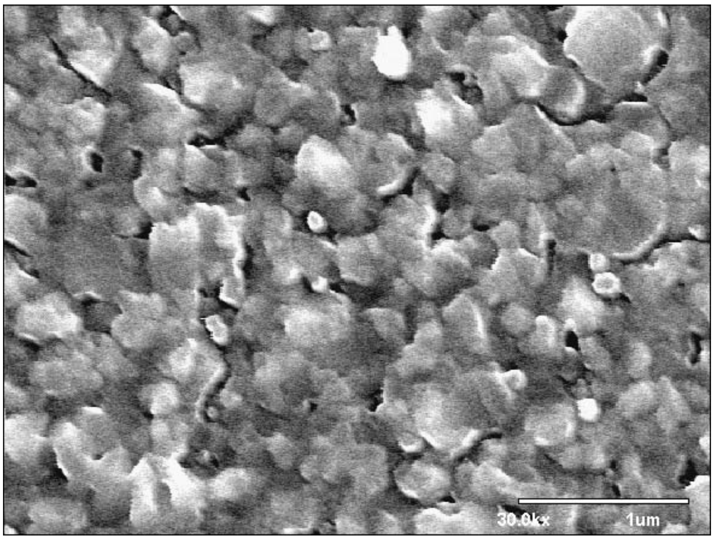


(a)

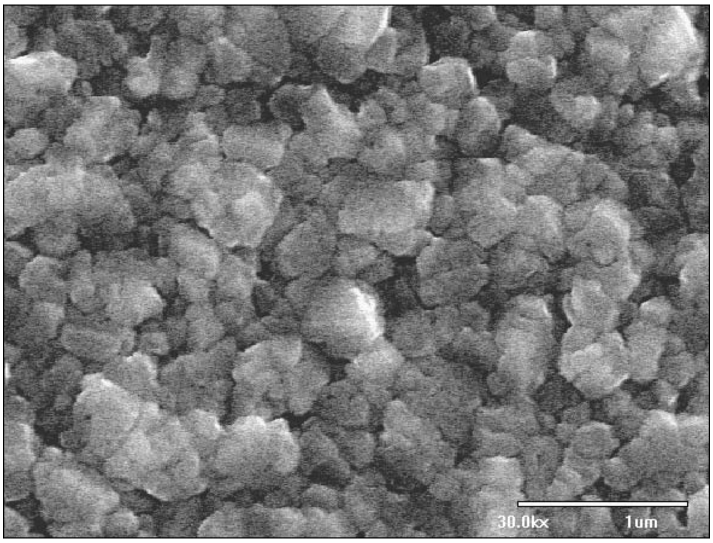


(b)

Fig.5-1 SEM micrographs showing surface morphology of Cu films deposited on (a) as-deposited and (b) Ar-plasma-treated TaN substrate. The Cu films were deposited at 160℃ and 150mtorr for 10 min.

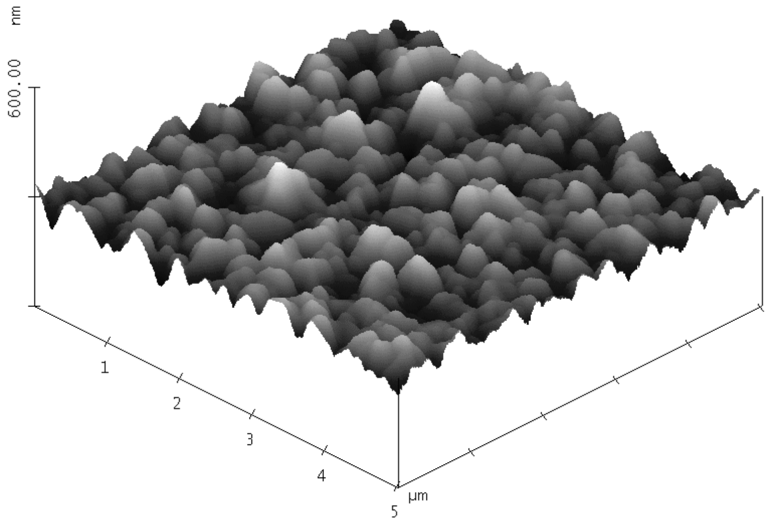


(a)

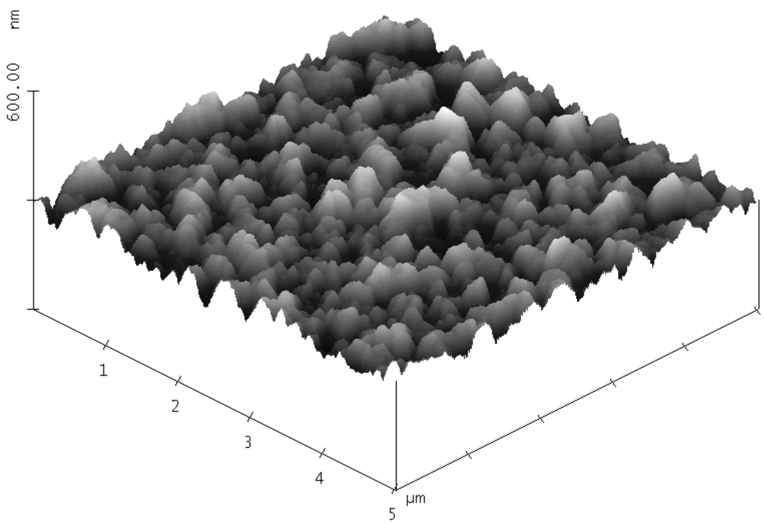


(b)

Fig.5-2 SEM micrographs showing surface morphology of Cu films deposited on (a) as-deposited and (b) Ar-plasma-treated TaSiN substrate. The Cu films were deposited at 160℃ and 150mtorr for 10 min.

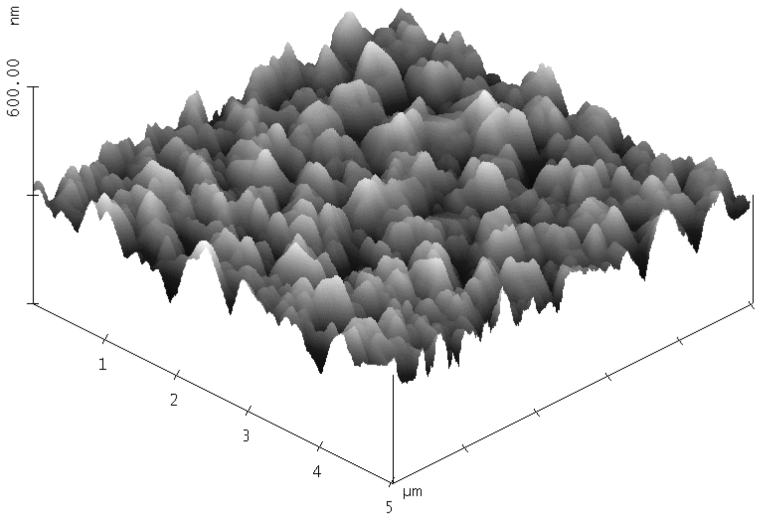


(a) RMS = 25.49nm

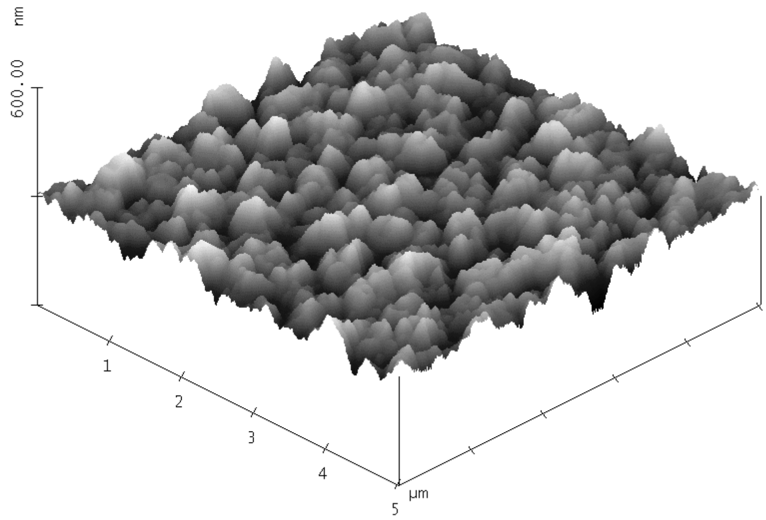


(b) RMS = 23.11nm

Fig.5-3 AFM images showing surface roughness of Cu films deposited on (a) as-deposited and (b) Ar-plasma-treated TaN substrate.

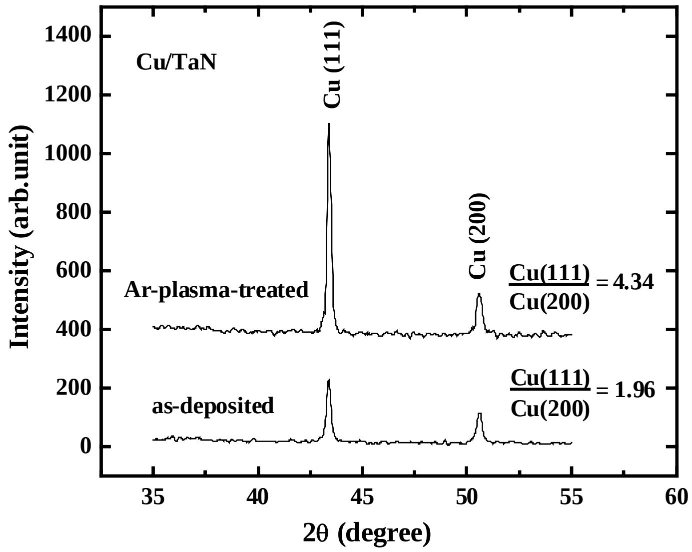


(a) RMS = 31.20nm

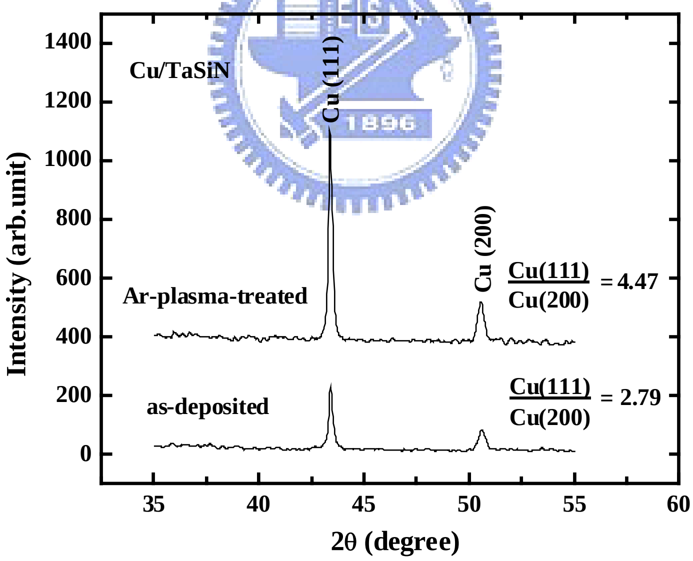


(b) RMS = 23.75nm

Fig.5-4 AFM images showing surface roughness of Cu films deposited on (a) as-deposited and (b) Ar-plasma-treated TaSiN substrate.

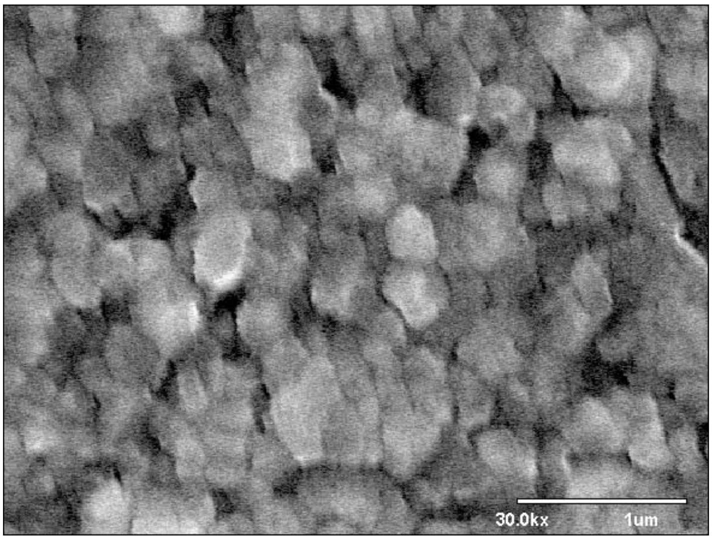


(a)

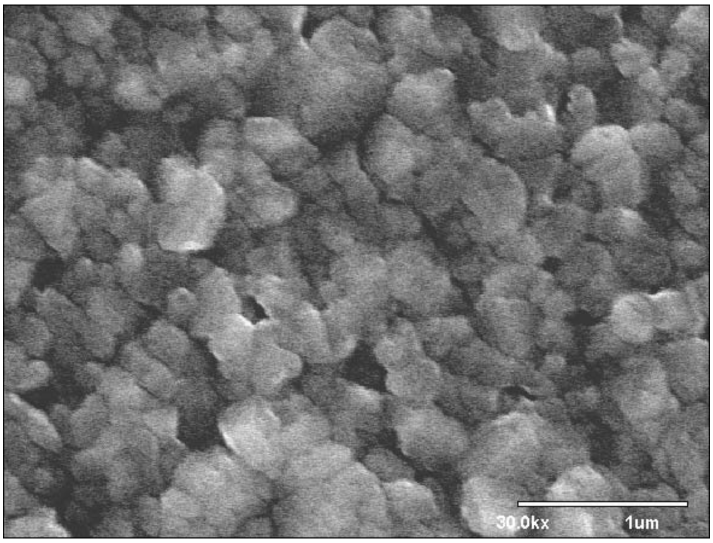


(b)

Fig.5-5 XRD spectra of Cu films deposited on as-deposited and Ar-plasma-treated (a) TaN and (b) TaSiN substrates.

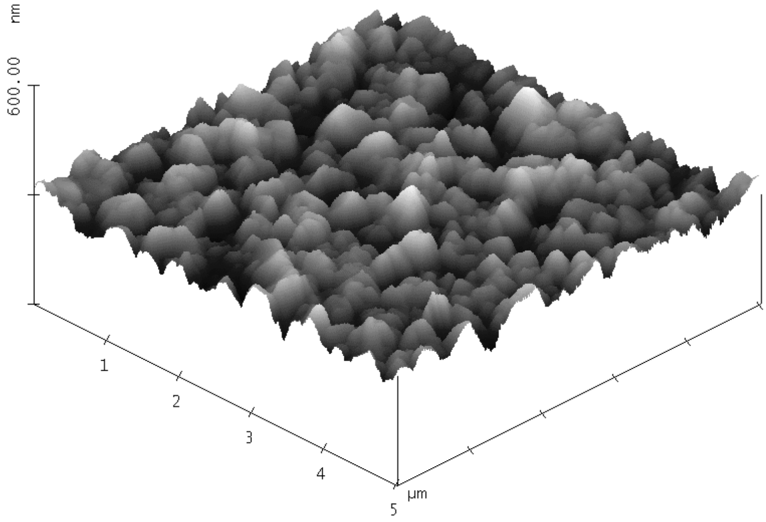


(a)

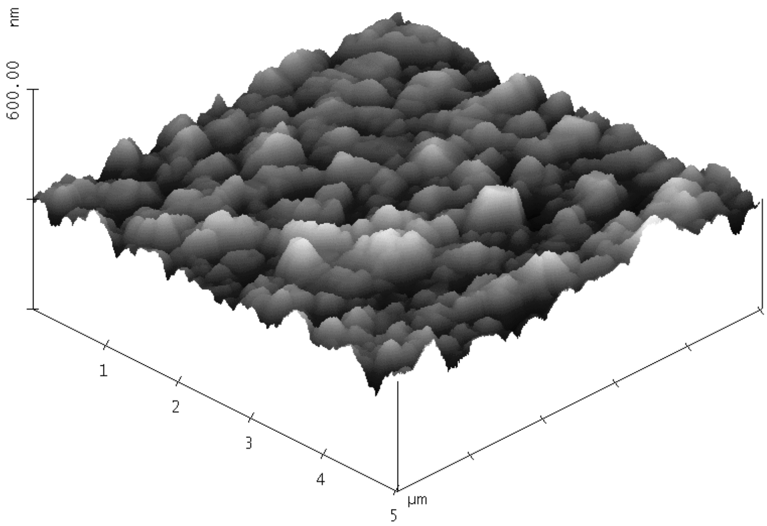


(b)

Fig.5-6 SEM micrographs showing surface morphology of Cu films deposited on H_2-plasma-treated (a) TaN and (b) TaSiN substrates. The Cu films were deposited at 160℃ and 150mtorr for 10 min.

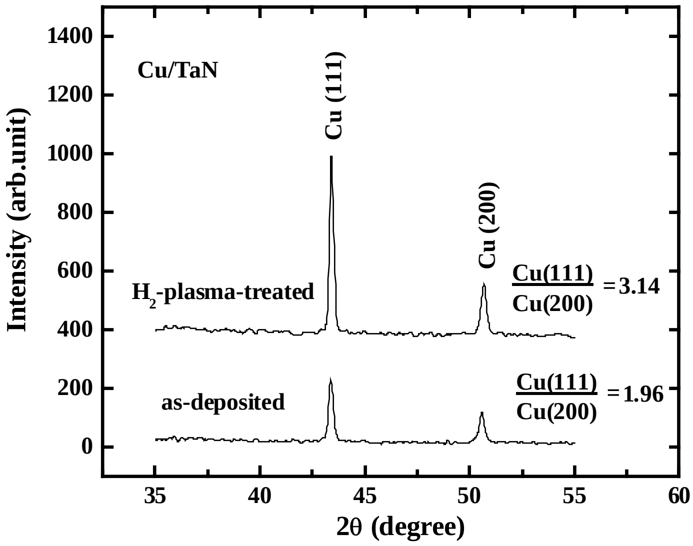


(a) RMS = 24.79nm

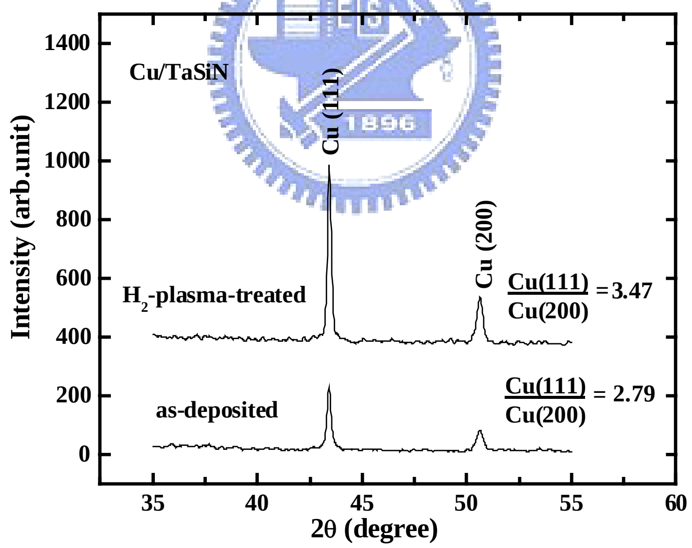


(b) RMS = 25.28nm

Fig.5-7 AFM images showing surface roughness of Cu films deposited on H_2-plasma-treated (a) TaN and (b) TaSiN substrates.



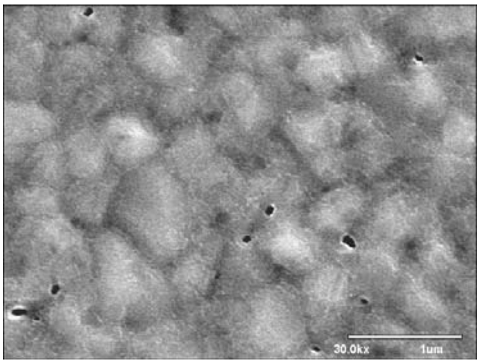
(a)



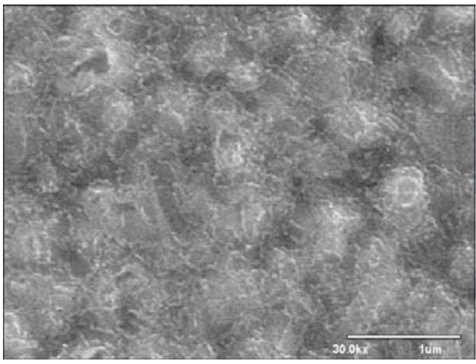
(b)

Fig.5-8 XRD spectra of Cu films deposited on as-deposited and H_2-plasma-treated (a) TaN and (b) TaSiN substrates.

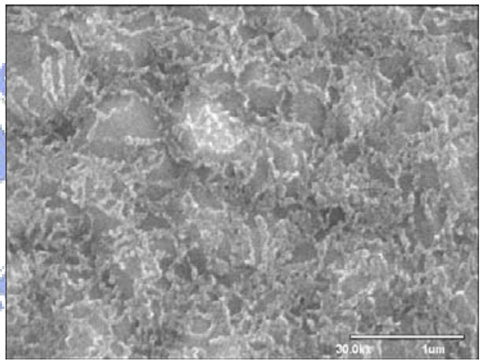
Cu/TaN



(a) as-deposited



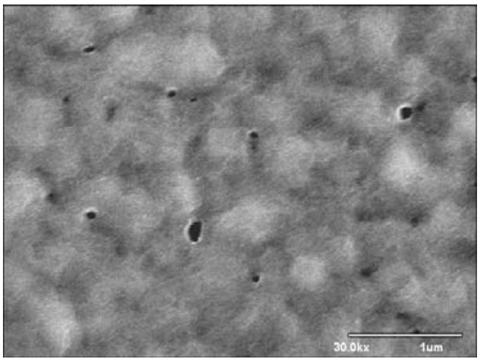
(b) Ar-plasma-treated



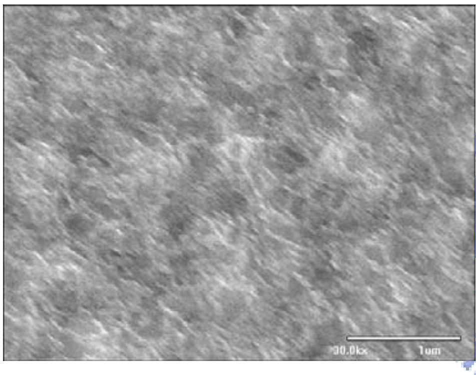
(c) H_2-plasma-treated

Fig.5-9 SEM micrographs showing surface morphology of post-deposition Thermal annealed (400℃ for 30min in N_2 ambient) Cu films deposited on (a) as-deposited, (b) Ar-plasma-treated, and (c) H_2-plasma-treated TaN substrates.

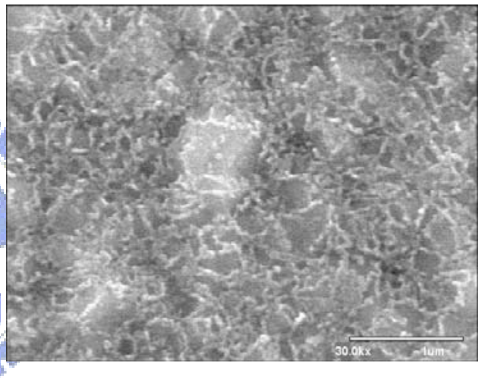
Cu/TaSiN



(a) as-deposited



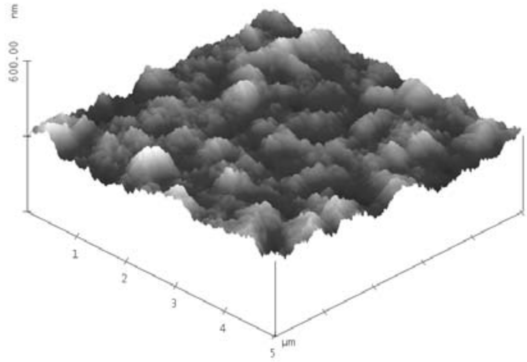
(b) Ar- plasma-treated



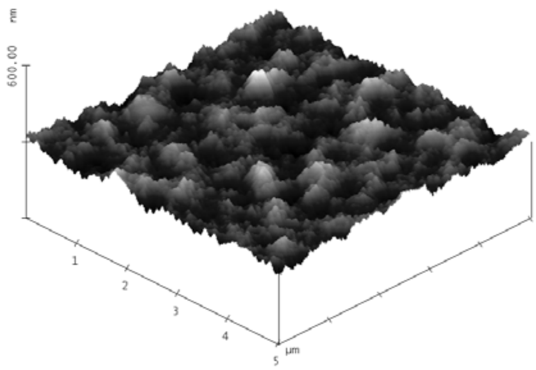
(c) H_2- plasma-treated

Fig.5-10 SEM micrographs showing surface morphology of post-deposition thermal annealed (400℃ for 30min in N_2 ambient) Cu films deposited on (a) as-deposited, (b) Ar-plasma-treated, and (c) H_2-plasma-treated TaSiN substrates.

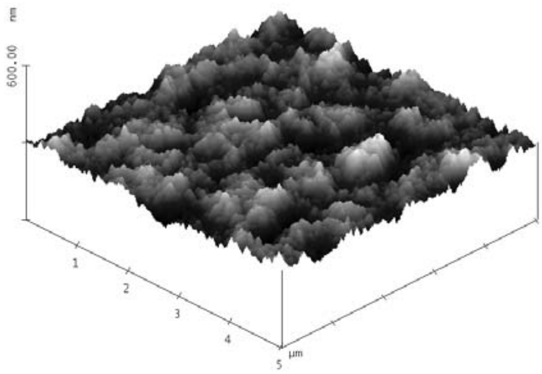
Cu/TaN



(a) RMS = 22.03nm



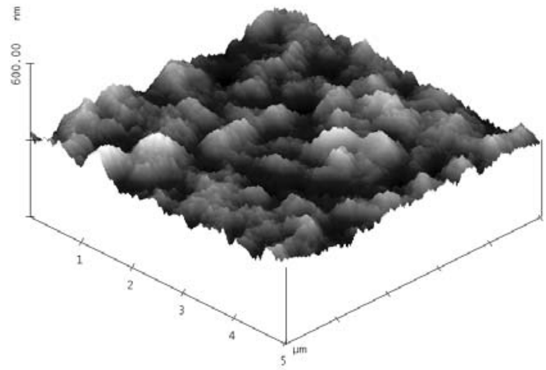
(b) RMS = 17.94nm



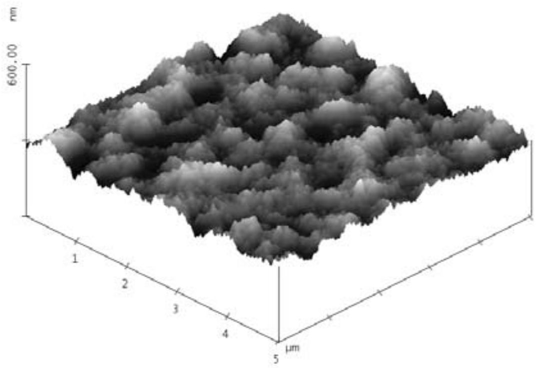
(c) RMS = 21.46nm

Fig.5-11 AFM images showing surface roughness of post-deposition thermal annealed (400℃ for 30min in N_2 ambient) Cu films deposited on (a) as-deposited, (b) Ar-plasma-treated, and (c) H_2-plasma-treated TaN substrates.

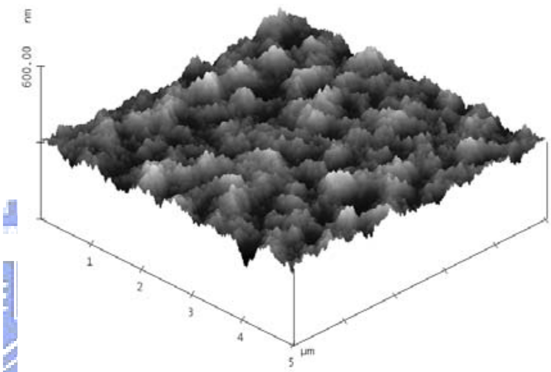
Cu/TaSiN



(a) RMS = 24.43nm



(b) RMS = 19.12nm



(c) RMS = 22.59nm

Fig.5-12 AFM images showing surface roughness of post-deposition thermal annealed (400℃ for 30min in N_2 ambient) Cu films deposited on (a) as-deposited, (b) Ar-plasma-treated, and (c) H_2-plasma-treated TaSiN substrates.