Chapter 4
Cu Nucleation on Plasma-Treated TaN and TaSiN Substrates

4.1 Introduction

It is known that the nucleation and subsequent coalescence process for the growth of film can be affected by the surface energy of the substrate on which the Cu film is to be deposited [46]. It has been reported that plasma treatment on the substrate surface modified the substrate surface energy and promoted the Cu(111)-preferred texture [47-49]. There are two types of plasma treatment, the physical sputtering plasma (e.g. Ar-plasma) and the chemical reaction plasma (e.g. H_2-plasma or N_2-plasma) treatments. The physical sputtering plasma uses the negative DC bias of subsceptor to accelerate the ionized Ar ions to sputter the substrate surface for the purpose of removing native oxide and particle contamination on the substrate surface and modifying the substrate surface condition, whereas the chemical reaction plasma modifies the substrate surface condition via chemical reaction between the surface materials and the hydrogen radicals generated in H_2-plasma (or nitrogen radicals generated in N_2-plasma). In this chapter, we investigate the effects of substrate treatment by Ar-, H_2- and N_2-plasma on the nucleation process of CVD-Cu films. The substrates used in this study were TaN and TaSiN, and the wetting angle of Cu nucleation on the plasma-treated TaN and TaSiN substrates was measured.

4.2 Experimental Details

The substrate materials used in this study were TaN and TaSiN. They were sputter deposited on Si wafer (i.e. Si substrate) according to the same process as described in chapter 3. 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 (together with the substrate holder) was transferred to the pretreatment chamber via the transfer chamber to proceed with the plasma treatment. Three different plasma treatments were investigated in this study: Ar-plasma, H_2-plasma, and N_2-plasma. The processing conditions of the Ar-, H_2-, and N_2-plasma treatments are summarized in Table 4-1. After the plasma treatment, the substrate wafer was transferred to the reaction chamber (via the transfer chamber) to proceed with the Cu CVD.

4.3 Properties of Plasma-Treated Substrates

The Ar-, H_2- and N_2-plasma treatments all improved the surface smoothness of the TaN and TaSiN substrates. Figure 4-1 and Fig.4-2 illustrate the AFM images showing the surface roughness of the as-deposited and plasma-treated TaN and TaSiN substrates, respectively. The Ar-plasma treatment resulted in the greatest improvement in substrate surface smoothness. Film resistivity was measured for the as-deposited and the plasma-treated TaN and TaSiN substrates, as shown in Table 4-2. All plasma treatments resulted in slight increase in measured resistivity; among them, the N_2-plasma-treated substrate exhibited the greatest amount of increase. This may due to the nitridation of the substrate surface during the process of N_2-plasma treatment.

4.4 Cu Nucleation

4.4.1 Nucleation on TaN substrate

The nucleation process of Cu film on the TaN substrate with and without a plasma treatment was investigated using scanning electron microscopy (SEM). Figure 4-3 illustrates the top view SEM micrographs showing the surface morphology of Cu nucleation on the as-deposited TaN substrate for various durations of Cu CVD performed at 160℃. It took more than 6 min to form a continuous Cu film on the TaN substrate. Figure 4-4 illustrates the top view SEM micrographs showing the Cu nucleation on the Ar-plasma-treated and H_2-plasma-treated TaN substrates; it took only about 3 and 2 min, respectively, to form a continuous Cu film on the Ar-plasma-treated and H_2-plasma-treated TaN substrates. Moreover, Fig.4-5 illustrates the top view SEM micrographs showing the Cu nucleation on the N_2-plasma-treated TaN substrate for various durations of Cu CVD; compared to the Ar- and H_2-plasma treatment, the N_2-plasma treatment apparently resulted in prolonged incubation time, taking more than 7 min to form a continuous Cu film.

The shape of the nucleated Cu grain is dependent on the substrate surface condition. Figure 4-6 shows a schema of Cu nucleation grain and the illustration of Young's equation [49]

$$\cos\theta = \frac{\sigma_s - \sigma_i}{\sigma_c} \quad (1)$$

where θ is the wetting angle of the Cu grain, σ_s and σ_c are respectively the substrate surface energy and the Cu grain surface energy, and σ_i is the interfacial energy between the Cu grain and the substrate. Figure 4-7 illustrates the oblique view SEM micrographs for the grains of Cu nucleation on the as-deposited and various plasma-treated TaN substrates. The wetting angle (contact angle) of the nucleated Cu grain on the as-deposited TaN substrate was found to be about 63°, while they were about 42°, 46° and 84°, respectively, on the Ar-plasma-, H_2-plasma- and

N_2-plasma-treated TaN substrates. The smaller wetting angle of Cu grains on the Ar-plasma- and H_2-plasma-treated substrates implies that the Ar- and H_2-plasma treatment resulted in increased substrate surface energy and/or decreased interfacial energy, thus enhancing the Cu film growth in two dimensions (layer growth) and forming the most stable (111) closely packed configuration [49, 50].

The wetting angle of the Cu grains nucleated on the N_2-plasma-treated TaN substrate was about 84°, which is much larger than the wetting angle of 63° observed on Cu grains nucleated on the as-deposited TaN substrate without any plasma treatment. The large wetting angle of the Cu grains nucleated on the N_2-plasma-treated TaN substrate is presumably due to the nitridation of the N_2-plasma-treated TaN substrate surface. The wetting angles of Cu grains nucleated on various plasma-treated TaN substrates are summarized in Table 4-3. Both Ar- and H_2-plasma treatments on the TaN substrate prior to the Cu nucleation increased the substrate surface energy and/or decreased the interfacial energy, resulting in a smaller wetting angle. On the other hand, the N_2-plasma treatment apparently decreased the substrate surface energy and/or increased the interfacial energy, resulting in a larger wetting angle.

4.4.2 Nucleation on TaSiN substrate

The nucleation processes of Cu on the as-deposited, the Ar- and H_2-plasma-treated, and N_2-plasma-treated TaSiN substrates are illustrated in Fig.4-8, Fig.4-9 and Fig.4-10, respectively. They are all similar to the nucleation process on the corresponding TaN substrates. Figure 4-11 illustrates the oblique view SEM micrographs for the grains of Cu nucleation on the as-deposited and various plasma-treated TaSiN substrates. The wetting angles of the nucleated Cu grains on the as-deposited, and the Ar-, H_2-, and N_2-plasma-treated TaSiN substrates were found to be about 58°, 45°, 41° and 86°, respectively, as also summarized in Table 4-3. Similar to the Cu nucleation on the TaN substrate, smaller wetting angles were obtained for Cu nucleation on Ar-plasma- and H_2-plasma-treated TaSiN substrates, as compared to the Cu grains nucleated on the as-deposited TaSiN substrate without any plasma treatment. This implies that either Ar-plasma or H_2-plasma treatment on the TaSiN substrate resulted in the increase of the substrate surface energy and/or decrease of the interfacial energy. On the other hand, the wetting angle of the Cu grains nucleated on the N_2-plasma-treated TaSiN substrate became larger than that on the as-deposited TaSiN substrate, implying that the N_2-plasma treatment decreased the substrate surface energy and/or increased the interfacial energy. In this study, we found that each individual plasma treatment (Ar-, H_2-, or N_2-plasma) produced a similar effect on modifying the surface condition for TaN and TaSiN substrates.

4.5 Summary

In this chapter, we investigate the effects of substrate treatment by Ar-, H_2-, and N_2-plasma on the nucleation process of Cu on TaN and TaSiN substrates. No appreciable difference was found for Cu nucleation on TaN and TaSiN substrates with respect to the nucleation rate and the effects of substrate plasma treatment. Nonetheless, it was found that the Ar-plasma and H_2-plasma treatments resulted in increased nucleation rate, while the N_2-plasma treatment resulted in decreased nucleation rate. For the Cu CVD performed at 160℃ and 150mtorr in this study, it took about 6min to form a continuous Cu film on the as-deposited TaN or TaSiN substrate, whereas it took only about 3 and 2 min, respectively, to form a continuous Cu film on the Ar-plasma-treated and

H_2-plasma-treated TaN or TaSiN substrate, and more than 7 min was needed to form a continuous Cu film on the N_2-plasma-treated substrates.

Among the plasma treatments used in this study, both Ar-plasma and H_2-plasma exhibited positive effect in reducing the wetting angle of nucleated Cu grains presumably because these plasma treatments all resulted in increased substrate surface energy and/or decreased interfacial energy. The small wetting angle can promote the 2-D growth, resulting in the formation of the most stable (111) closely packed configuration. On the other hand, N_2-plasma treatment on the substrate surface resulted in increased wetting angle of Cu nucleation, implying that the N_2-plasma-treated substrate has a reduced substrate surface energy and/or increased interfacial energy. The lower substrate surface energy retarded the Cu nucleation and thus prolonged the incubation time.

Table 4-1 Major plasma processing conditions used in this study.

Ar plasma		H_2 plasma	
Substrate temperature (°C)	80	Substrate temperature (°C)	80
Operating pressure (mtorr)	40	Operating pressure (mtorr)	40
Ar gas flow rate (sccm)	6	H_2 gas flow rate (sccm)	15
RF power (W)	50	RF power (W)	50
Self-DC bias (V)	-192	Self-DC bias (V)	-213
Duration of plasma treatment (min)	10	Duration of plasma treatment (min)	10

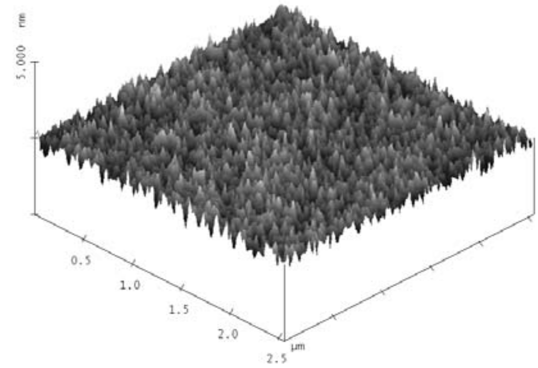
N_2 plasma	
Substrate temperature (°C)	80
Operating pressure (mtorr)	40
N_2 gas flow rate (sccm)	7
RF power (W)	50
Self-DC bias (V)	-270
Duration of plasma treatment (min)	10

Table 4-2 Film resistivity of TaN and TaSiN layers as-deposited and after various plasma treatments.

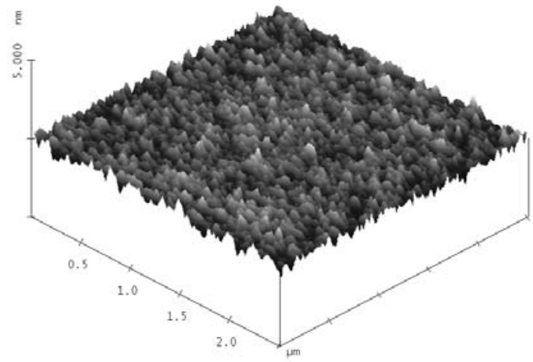
Plasma Treatment	TaN substrate (μΩ-cm)	TaSiN substrate (μΩ-cm)
None (as-deposited)	287	305
Ar-plasma	291	308
H_2-plasma	289	307
N_2-plasma	302	315

Table 4-3 Wetting angle of Cu grains nucleated on various plasma-treated TaN and TaSiN substrates

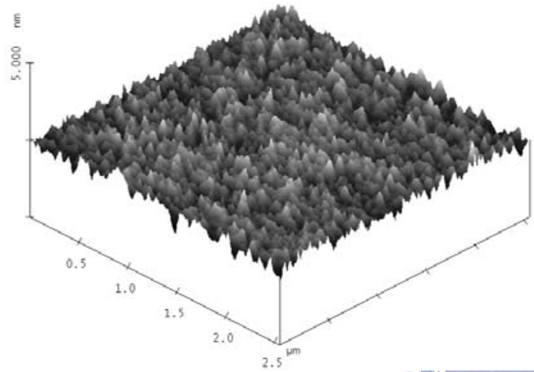
Plasma treatment	Substrate	
	TaN	TaSiN
None	63°	58°
Ar plasma	42°	45°
H_2 plasma	46°	41°
N_2 plasma	84°	86°



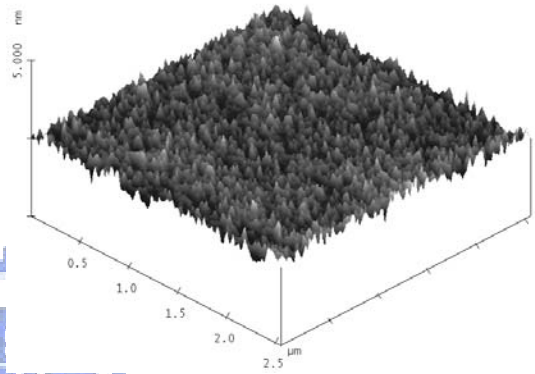
(a) As-deposited
(RMS = 0.137nm)



(b) Ar-plasma-treated
(RMS = 0.109nm)

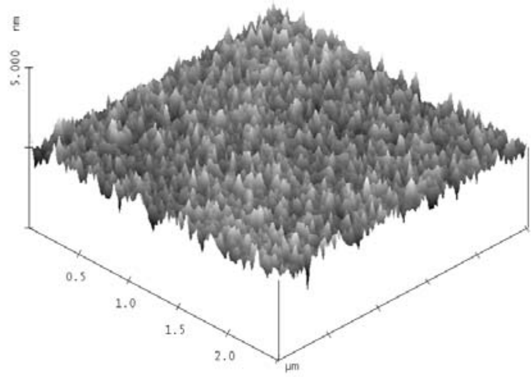


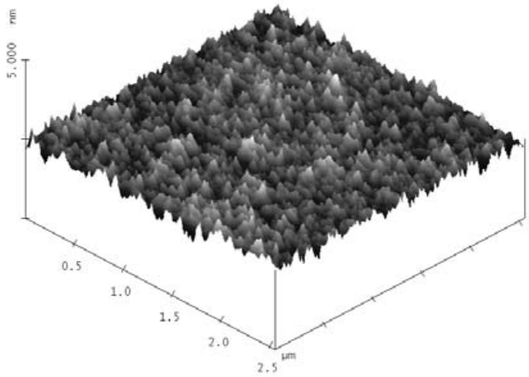
(c) H_2-plasma-treated
(RMS = 0.132nm)



(d) N_2-plasma-treated
(RMS = 0.120nm)

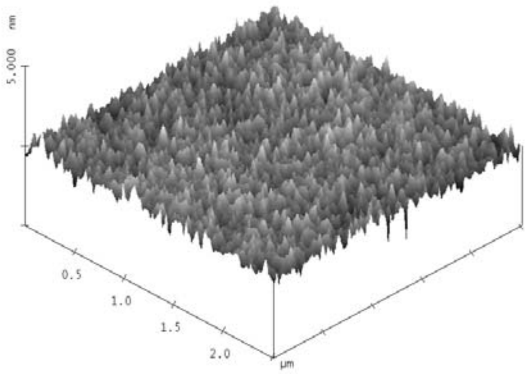
Fig.4-1 AFM images showing the surface roughness of TaN substrate (a) as-deposited, (b) Ar-plasma-treated, (c) H_2-plasma-treated, and (d) N_2-plasma-treated.

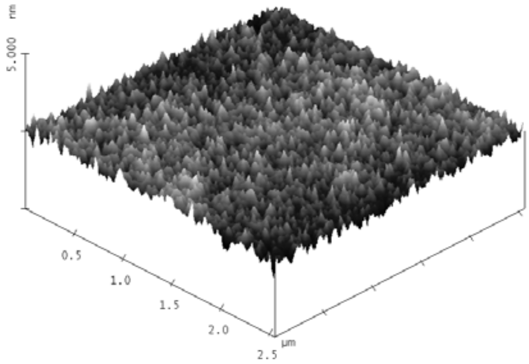




(a) As-deposited
(RMS = 0.167nm)

(b) Ar-plasma-treated
(RMS = 0.121nm)

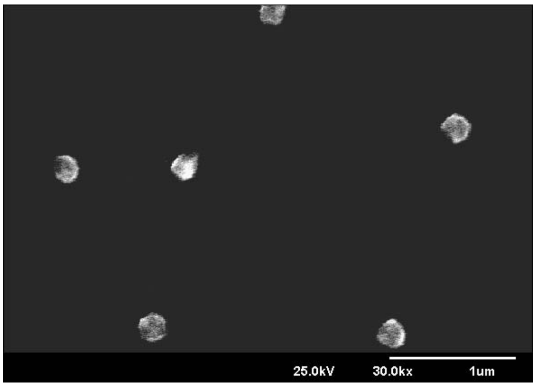




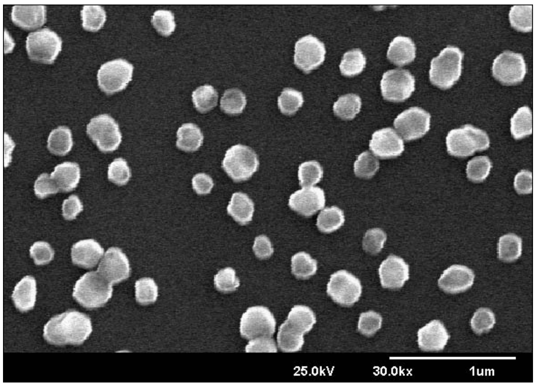
(c) H_2-plasma-treated
(RMS = 0.156nm)

(d) N_2-plasma-treated
(RMS = 0.139nm)

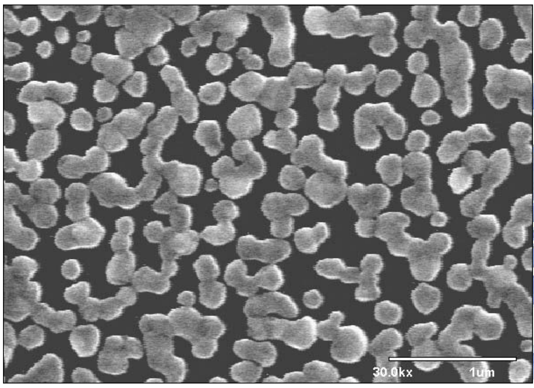
Fig.4-2 AFM images showing the surface roughness of TaSiN substrate (a) as-deposited, (b) Ar-plasma-treated, (c) H_2-plasma-treated, and (d) N_2-plasma-treated.



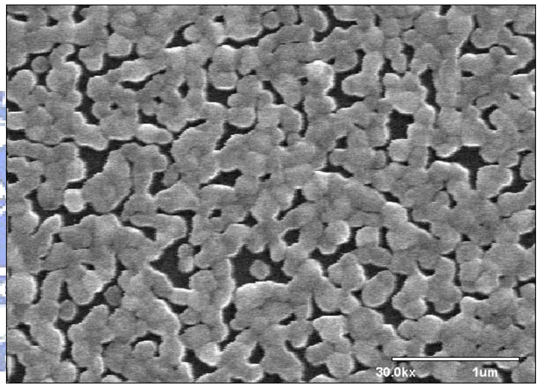
(a) 1min



(b) 2min



(c) 3min



(d) 6 min

Fig.4-3 SEM micrographs showing surface morphology of Cu nucleation on the as-deposited TaN substrate with the Cu CVD performed at 160℃ for (a) 1min, (b) 2min, (c) 3min, and (d) 6min.

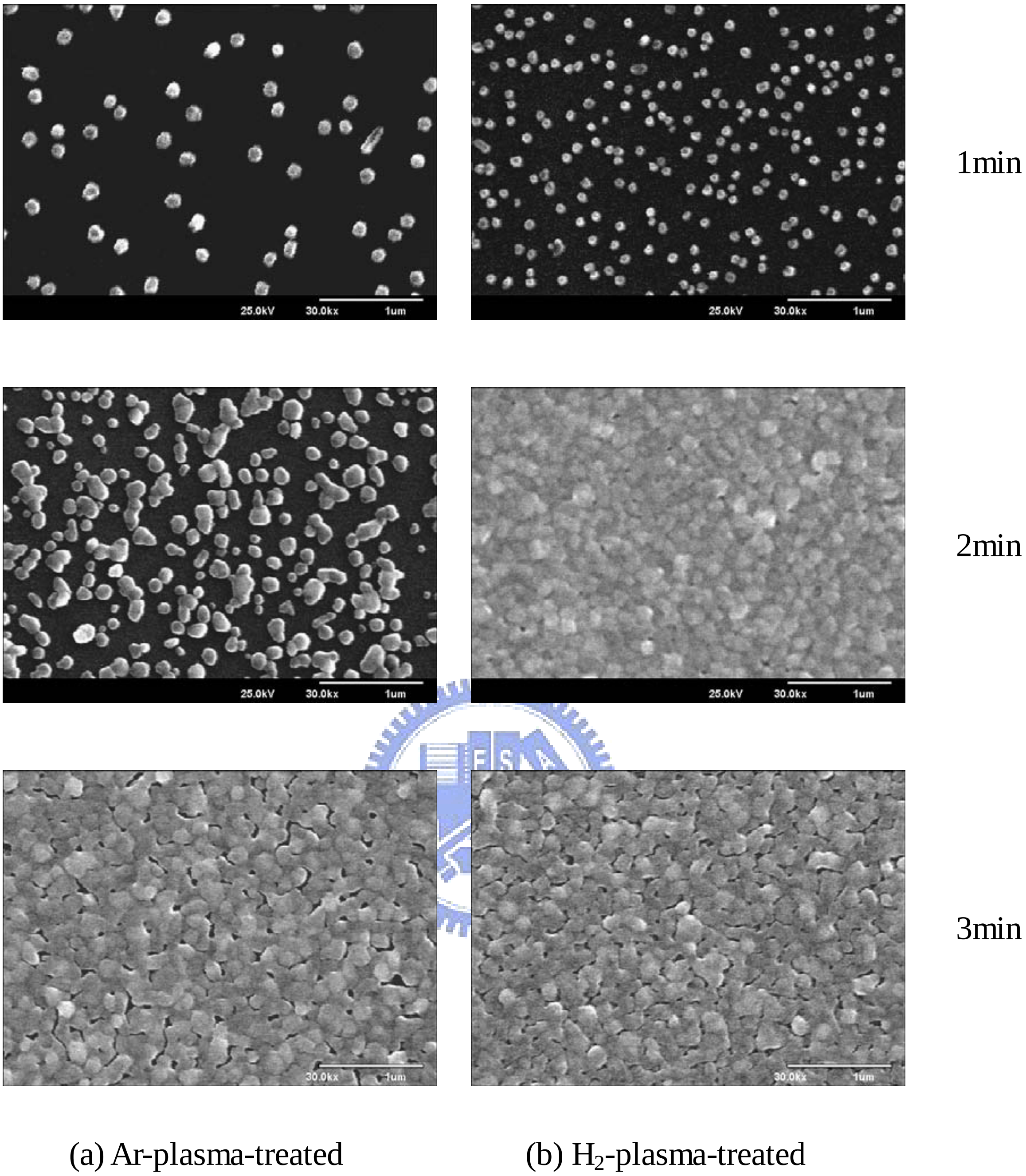
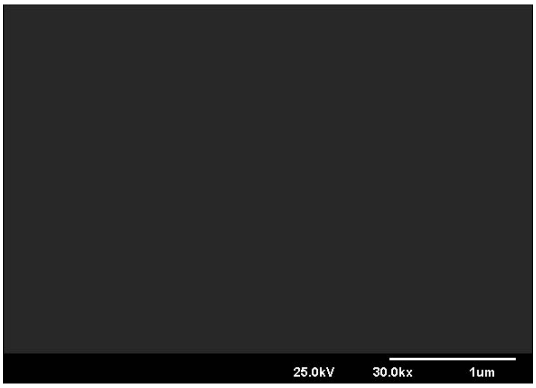
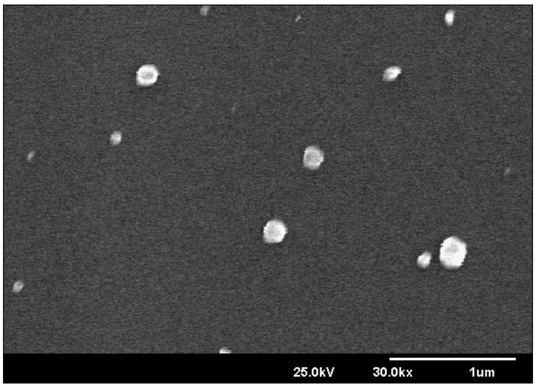


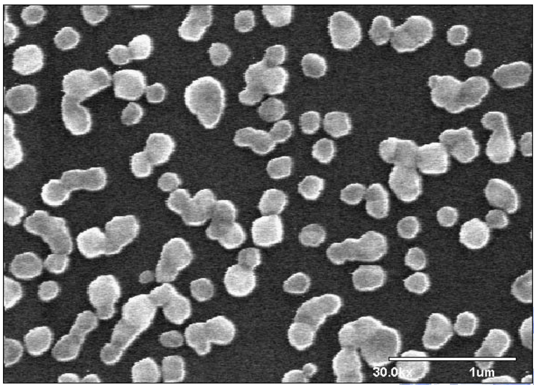
Fig.4-4 SEM micrographs showing surface morphology of Cu nucleation on (a) Ar-plasma-treated and (b) H_2-plasma-treated TaN substrates for 1 to 3 min with the Cu CVD performed at 160℃.



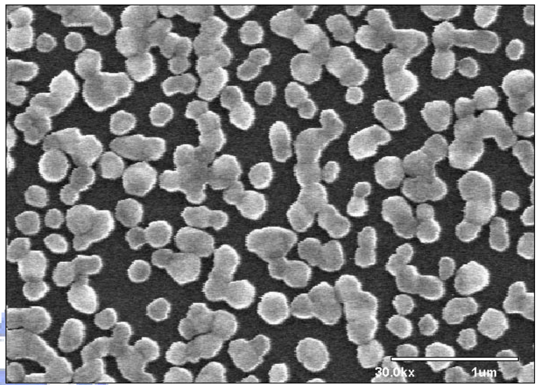
(a) 1min



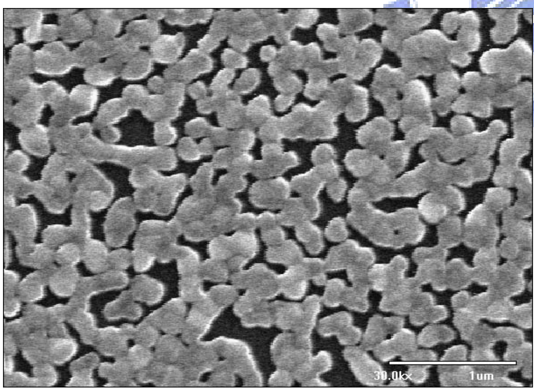
(b) 2min



(c) 3min

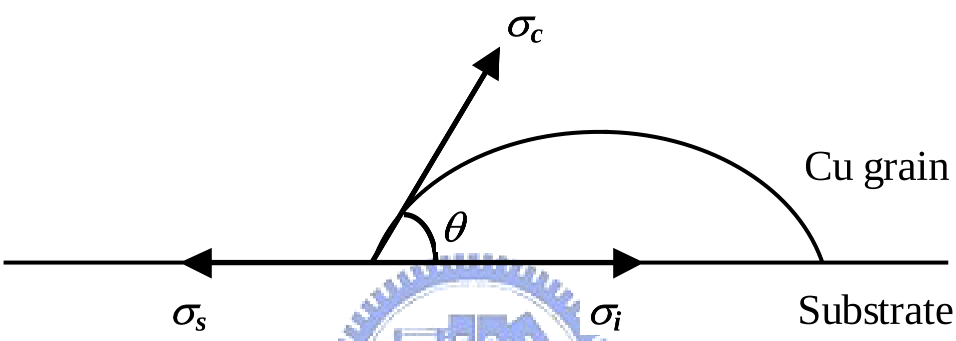


(d) 6min



(e) 7 min

Fig.4-5 SEM micrographs showing surface morphology of Cu nucleation on N_2-plasma-treated TaN substrate with the Cu CVD performed at 160℃ for (a) 1min, (b) 2min, (c) 3min, (d) 6min, and (e) 7min.



θ : wetting angle (contact angle)

σ_s : surface energy of substrate

σ_c : surface energy of Cu grain

σ_i : interfacial energy between Cu grain and substrate

Fig. 4-6 Schematic illustration of Young's equation.

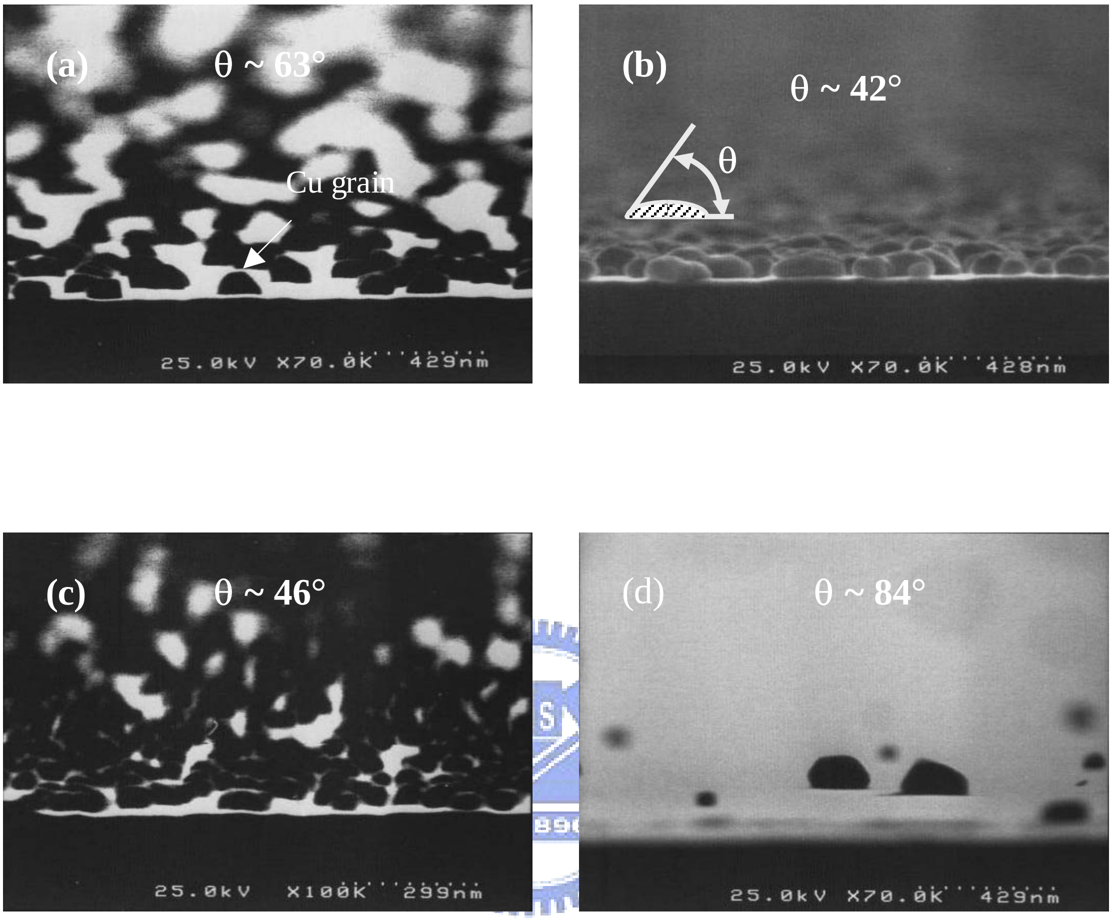
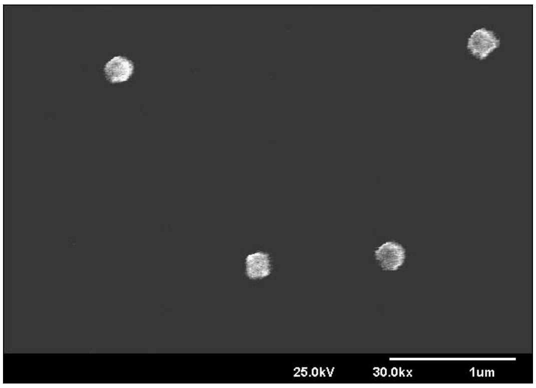
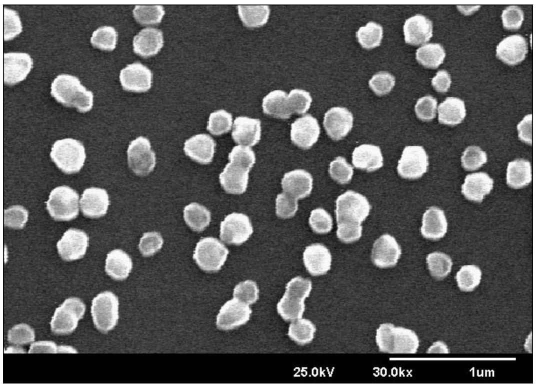


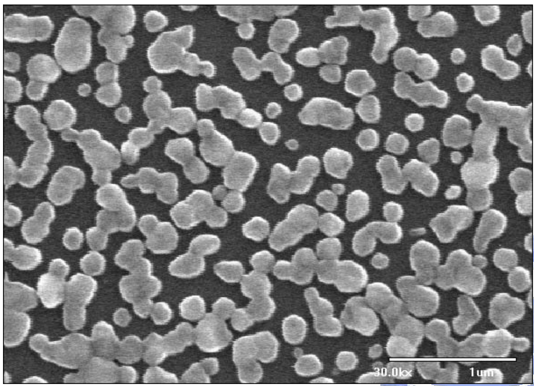
Fig.4-7 Oblique view SEM micrographs showing the nucleated Cu grains on (a) as-deposited, (b) Ar-plasma-treated, (c)H_2-plasma-terated, and (d) N_2-plasma-treated TaN substrates with the Cu CVD performed at 160℃.



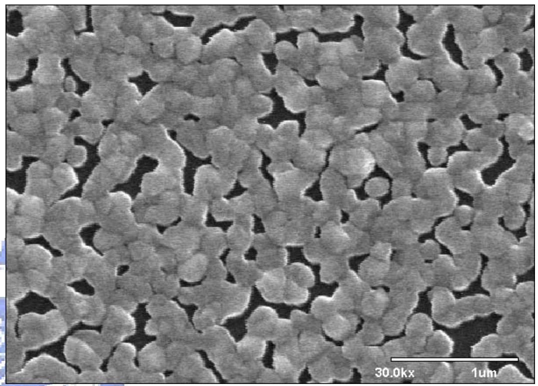
(a) 1min



(b) 2min



(c) 3min



(d) 6 min

Fig.4-8 SEM micrographs showing surface morphology of Cu nucleation on the as-deposited TaSiN substrate with the Cu CVD performed at 160℃ for (a) 1min, (b) 2min, (c) 3min, and (d) 6min.

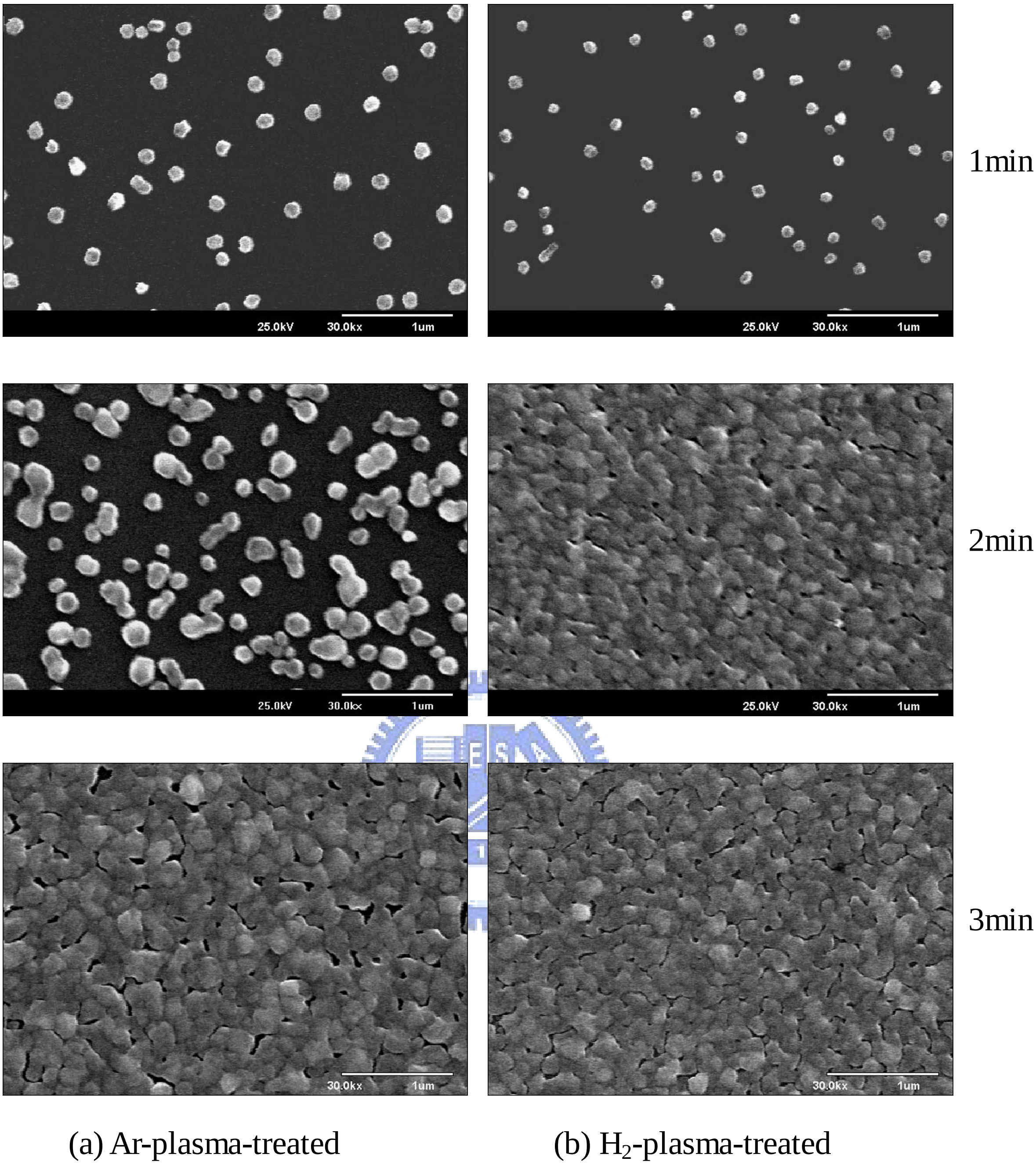
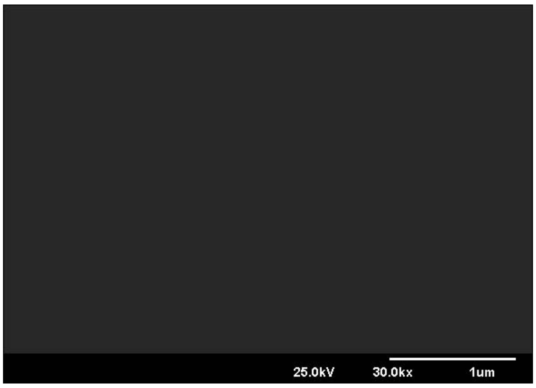
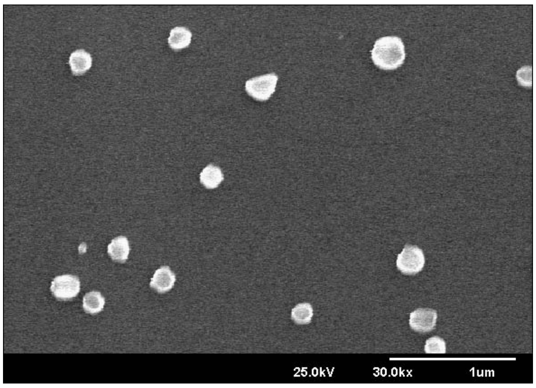


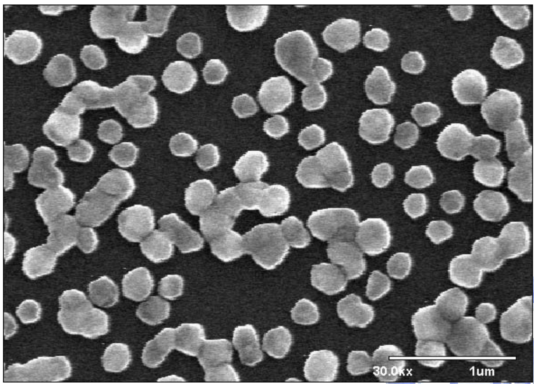
Fig.4-9 SEM micrographs showing surface morphology of Cu nucleation on (a) Ar-plasma-treated and (b) H_2-plasma-treated TaSiN substrates for 1 to 3 min with the Cu CVD performed at 160℃.



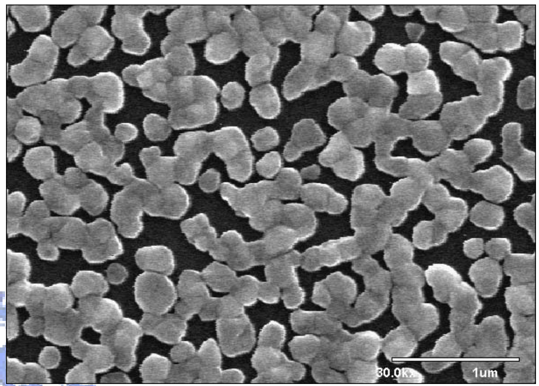
(a) 1min



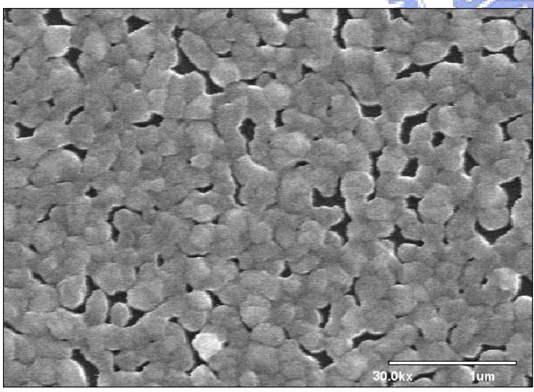
(b) 2min



(c) 3min



(d) 6min



(e) 7 min

Fig.4-10 SEM micrographs showing surface morphology of Cu nucleation on N_2-plasma-treated TaSiN substrate with the Cu CVD performed at 160℃ for (a) 1min, (b) 2min, (c) 3min, (d) 6min, and (e) 7min.

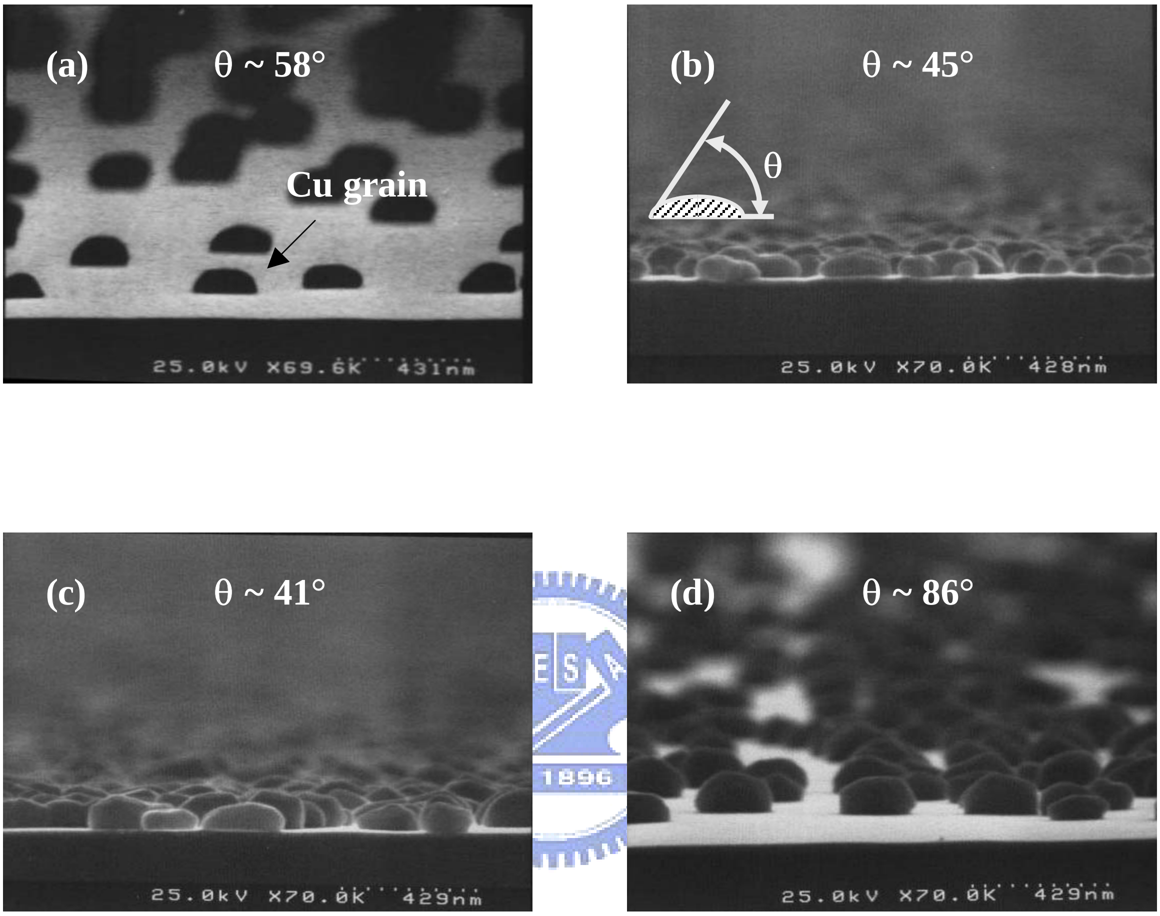


Fig.4-11 Oblique view SEM micrographs showing the nucleated Cu grains on (a) as-deposited, (b) Ar-plasma-treated, (c) H_2-plasma- treated, and (d) N_2-plasma-treated TaSiN substrates with the Cu CVD performed at 160℃.