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Electroless Copper Seed Layer Deposition on Tantalum Nitride Barrier Film

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Abstract

Electroless (EL) deposition is used as a seeding technology for Cu metallization in the back-end-of-line semiconductor fabrication process. In this work, effect of deposition time and annealing treatment on the properties of electroless copper seed layer are reported. It is found that all seed layers exceeding 2-minute deposition possess a (111) texture. The grain size, morphology and resistivity of the electroless Cu vary with deposition time. The largest grain size obtained by current work is around 70 nm. This corresponds to the lowest resistivity of 4.30 μΩcm. The surface roughness of as-deposited Cu films ranges from 36.6 nm to 51.9 nm. Annealing results in the growth of copper grains and improvement in surface roughness and film conductivity. The annealing treatment does not change the existing texture.

***Keywords**:* Electroless plating; Tantalum nitride; Copper metallization; Resistivity

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1. Introduction

As the density of electronic devices increases, Cu has been increasingly used as the interconnect material. However, the successful development of Cu metallization requires efficient diffusion barriers. TaN is so far one of the most promising barrier materials. Its advantages include high thermal stability, acceptable conductivity and chemical inactivity with copper at elevated temperatures [1, 2]. It also has good adhesion to both Cu and inner metal dielectrics [3, 4].

The dual-damascene process has to be used to fabricate multilevel Cu interconnect since Cu can not be dry-etched easily [5, 6]. A proper Cu electrolytic plating process is preferred to increase the reliability of the resulting damascene Cu structure. Prior to the electrolytic plating, a seed layer of Cu needs to be laid down first to conduct the plating current.

The Cu seed layer can be plated by CVD [7, 8], PVD [9, 10] or electroless (EL) plating technique [11, 12]. Comparing with PVD, electroless Cu technique enjoys high aspect ratio filling capability. Its advantages over CVD are its simplicity in the bath chemistry and low processing temperature [13]. There has been so far little work on electroless Cu deposition on TaN surface compared with TiN surface.

This paper discusses the effect of deposition time and annealing on the properties of electrolessly plated Cu. The microstructure of Cu thin films has been the subject of much recent work because of the influence of microstructure attributes, such as grain size, surface morphology and crystallographic texture, on a film's mechanical and physical properties [14,

15]. Good microstructure and morphology of Cu seed layer are desirable for the reliability of the subsequent electrolytic Cu film.

2. Experiment

The substrates used in this study were 25 nm TaN deposited on Si wafers with 500 nm SiO_2. The deposited wafer was cut into pieces of 20 mm × 20 mm. The sample was soaked in acetone solution with an ultrasonic agitation at room temperature for 10 minutes in order to remove contaminants. Pd activation was carried out before the Cu deposition since the Pd nuclei act as catalysts to decrease the activation energy and increase the deposition rate. Native oxides were reported to cause Pd agglomeration and hence inhibit the uniformity of Cu plating [16]. To remove the native oxides, the samples were etched with solution containing $HF/HNO_3/ H_2O$ = 1:1:4 (by volume) for 1 minute.

After etching, the sample was immersed into diluted HF (HF/H_2O = 1:100) to clean the chemicals and metal residues. It was then placed in the activation solution, which is composed of HF, HCl and $PdCl_2$, for 3 minutes. The activated sample was again cleaned.

Electroless Cu plating was done in a solution which contains cupric sulphate ($CuSO_4.5H_2O$), ethylene diamine tetraacetic acid (EDTA), Triton X-100, tetra-methyl-ammonia-hydroxide (TMAH) and formaldehyde (HCHO). The plating time was chosen to be 10 s, 20 s, 30 s, 1 min, 2 min, 3 min, 4 min, 5 min, 6 min, 7 min and 8 min. The pH of electroless Cu solution was adjusted by TMAH to 12.8 prior to the addition of formaldehyde; while the temperature of the bath was maintained at 60–62 ℃. Annealing was carried out only on samples that were plated 5

minutes. This treatment was done at 200 ℃, 300 ℃ and 400 ℃ in nitrogen ambient for 150 minutes.

Field emission scanning electron microscopy (FESEM, JEOL JSM-6340F) was used to observe the surface morphology and surface coverage. Composition analysis was conducted using the energy dispersive X-ray (EDX) analysis attached to the FESEM. The spot size of the EDX analysis is around 1 μm. Atomic force microscope (AFM) was employed to obtain the roughness of the film. Crystal orientation and grain size estimation were done by Shimadzu X-Ray Diffractometer-6000. Four-point resistivity probe (CDE ResMap 168) was employed to measure the sheet resistance of Cu seed layer. Thickness of Cu film was measured via surface profiler (Alpha-Step 500).

Apparent crystallite size was determined from the broadening of diffraction peak from the (111) planes. Mean grain size can be calculated from Scherrer's equation [17]:

$$d_{mean} = 0.94 \times \lambda_{Cu} / (W_{eff} \times \cos 2\theta) \qquad (1)$$

where λ_{Cu} = wavelength of CuK_{α} = 0.1542 nm, W_{eff} = effective full width at half maximum, and θ = diffraction angle. The effective full width, W_{eff} was determined from the Gaussian distribution function of the (111) peak, curve-fitted from experimental measurement. Instrumental broadening was calibrated before applying equation (1) for the grain size calculation.

3. Results and Discussion

3.1 Effect of plating time

As shown in Figure 1, the TaN substrate is covered with fine spherical Pd nuclei after 3 minutes activation. This duration provides uniformly distributed fine Pd seeds, leading to successful Cu plating [5].

Topography of samples obtained from different deposition time is shown in Figures 2-4. When the deposition time is 10 seconds (Figure 2), the nodule size becomes bigger than the one of Pd seeds (Figure 1). Energy dispersive X-ray (EDX) detects the existence of both Cu and Pd. From the fact that the nodule density and distribution are very similar, it is reasonable to believe that these light spots are Cu nodules covering the Pd nuclei. Therefore for as short as 10 seconds, Cu is deposited as a result of Pd reaction with folmaldehyde, donating ions to Cu reduction [18]. As observed in Figure 2 and Figure 3, the number of Cu nodules and Cu coverage increase as the deposition time increases. This is due to the self catalytic effect of electroless Cu plating [18].

When the deposition time increases to 5 minutes, as shown in Figure 4, full surface coverage is obtained. This is very critical for subsequent electroplating process. If the surface coverage is not 100%, electric field will not be evenly distributed and plating voids may form in the recessed areas [12]. As a result, device may fail easily.

A trend of increasing grain size with deposition time is shown in Table 1. Grain size of 65.1 nm is obtained at 8 minutes deposition time. Since the electroless Cu layer is used as a seed layer for subsequent electrolytic Cu plating, the grain size is likely to be inherited by the subsequent plating. In this sense, larger grain size is desirable since larger grain-sized Cu line is known to be more resistant to electromigration failure.

The texture information is obtained by the intensity ratio between (111) plane and (200) of the XRD data. For randomly oriented Cu powders, the I(111) / I(200) ratio is 2.17. It is found that as the deposition exceeds 2 minutes, the ratio is around 2.44 - 2.95, indicating a mild (111) texture. This is close to the value of 2.8 reported by Z. Wang *et al* [19]. The cause of texture formation has been discussed elsewhere [20], where minimization of surface energy and strain energy was correlated to the texture formation. It was argued that when the film is thin, (111) plane is preferred, and with the film growth, there will be a point that total energy is lower with (100) plane.

The (111) texture in the Cu seed layer can be adopted by subsequent electroplating of Cu and is preferred for two reasons. As (111) is the slip plane of Cu FCC structure, having (111) planes aligned on the Cu film plane directions will improve the yield strength of Cu film. Elasticity modulus in [110] directions, which lie on (111) plane, is higher than [100] directions. Therefore the mechanical properties of (111) textured Cu film is improved. Moreover, (111) textured microstructures suppresses grain boundary and interfacial diffusion of metal atoms. It was reported that the mean time to failure increases with proportion to the I(111) / I(200) ratio [21]. Due to the epitaxial effect, the subsequent electroplated film will adopt the texture of the seed layer. Thus, a (111) texture is preferred for improved electromigration and mechanical performance.

It is clearly showed in Table 1 that resistivity of the electroless Cu film decreases with the plating time. Before the full coverage of the TaN by Cu film, the improvement is very significant with the elimination of noncovered surfaces. After full-coverage is achieved, the

resistivity decrease is slow and is attributed to the increase of grain size. Similar findings have been reported on Cu film plating on TiN [20] and TiSiN [22] barrier films.

Table 1 also shows that the surface roughness of the plated films ranges from 30.2 nm to 51.9 nm. This range is comparable with the work by Ng *et al* [18] which shows a roughness from 20.73 nm to 42.72 nm with deposition time up to 60 s.

3.2 Effect of annealing

Since sample with deposition time at 5 minutes provides satisfying result in terms of surface morphology, crystal orientation and resistivity, 5 minutes deposition time was selected to study the effect of annealing on characteristics of electroless Cu film.

Table 2 summarizes the effect of annealing on the film properties. The as-deposited grain size of 51.8 nm increases to 70.1 nm after annealing for 150 minutes at 400°C. The grain size increase in clearly caused by coarsening during annealing. All annealed samples retain the preferred (111) orientation, which indicates that no major microstructural rearrangement has occurred in the specimens after annealing process. Resistivity is further reduced (e.g. 4.3 μΩ-cm after annealing at 300 ℃). This decrease can be attributed to the increase of grain size. Surface roughness is found to have slightly improved after annealing treatment. The lowest roughness obtained is ~ 29.4 nm corresponding to annealing at 400°C.

It has been shown in this work that for plating time of 5 minutes, a fully dense Cu film of ~300 nm thick can be achieved on TaN surface with reasonably low resistivity. Further increase in the plating time sees improvement of film conductivity due to grain size coarsening. However, the surface roughness starts to increase at 7 and 8 minutes, which is undesirable for subsequent Cu metalization. Therefore for the choice of plating process parameters, compromise may have

to be made depending on the specific requirement. Further improvement in conductivity and surface roughness can be made through heat treatment.

4. Conclusion

It was found that with proper etching and cleaning treatment, Cu film with full surface coverage can be obtained on $TaN/SiO_2/Si$ with 5 minutes deposition time. The properties of electroless Cu film on TaN have been characterized in terms of surface morphology, surface roughness, grain size, crystal orientation and electrical resistivity. Preferred orientation of Cu grains in (111) plane has been observed for all samples exceeding 2 minutes deposition. The grain size of Cu is a function of deposition time, with largest grain size of 65.1 nm obtained at longest deposition time of 8 minutes. Surface roughness of as-deposited electroless Cu film ranges from 30.2 nm to 51.9 nm.

Samples after annealing retain preferred orientation achieved in the as-deposited samples. Grain growth is observed in all the annealing conditions with the largest grain size of 70.1 nm found in the sample annealed at 400 ℃. The resistivity of annealed samples is also reduced from 7.69 μΩ-cm to 4.30 μΩ-cm.

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Figure. 2 Surface morphology of electroless Cu deposited after 10 seconds deposition on Pd activated TaN. The light spots are confirmed to be nodules of Pd and Cu.

Figure. 3 Surface morphology of electroless Cu after 30 seconds deposition on Pd activated TaN. The Cu nodules scattered on TaN uniformly. However, the Cu has not yet fully covered the surface.

Figure. 4 Surface morphology of electroless Cu after 5 minutes deposition on Pd activated TaN. A continuous copper seed layer is formed.

Deposition time	1min	2 min	3min	4min	5min	6min	7min	8min
Mean grain size (nm)	25.6	37.1	42.9	44.8	51.8	58.8	62.4	65.1
I(111) / I(200)	1.97	2.64	2.56	2.44	2.56	2.95	2.80	2.86
Resistivity (μΩ.cm)	607.23	20.74	10.10	8.54	7.69	5.81	5.39	5.59
Thickness (nm)	149.0	179.0	246.4	284.7	298.1	403.9	532.9	637.2
Roughness (nm)	36.6	36.6	30.2	35.0	35.9	35.4	44.5	51.9

Table 1

Annealing temperature	As- deposited	200 ℃	300 ℃	400 ℃
Mean grain size (nm)	51.8	63.3	69.5	70.1
I(111) / I(200)	2.56	2.54	2.72	2.44
Resistivity (μΩ.cm)	7.69	5.23	4.30	4.87

Table 2

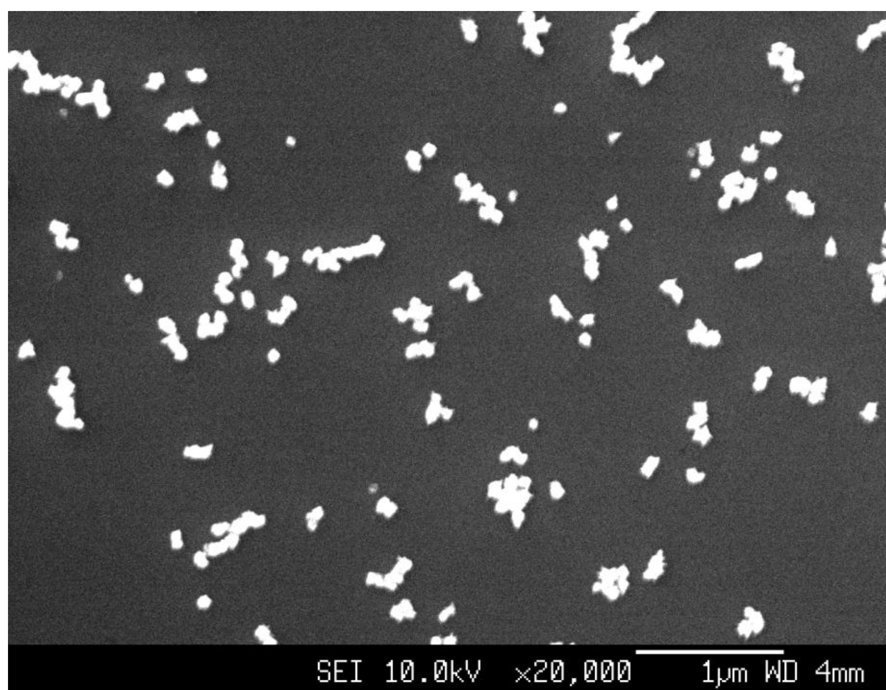

Figure 1

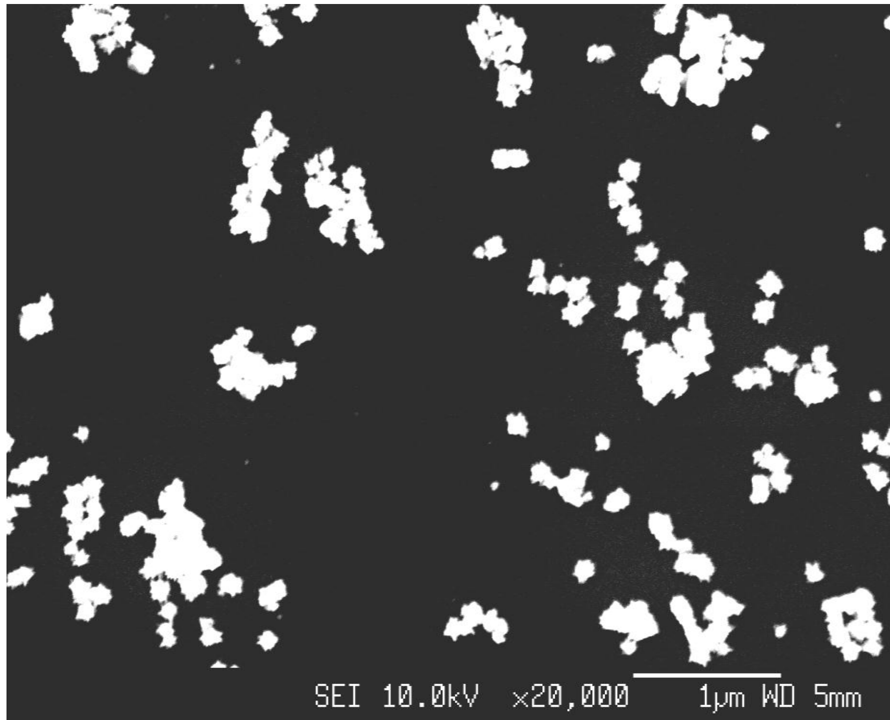

Figure 2

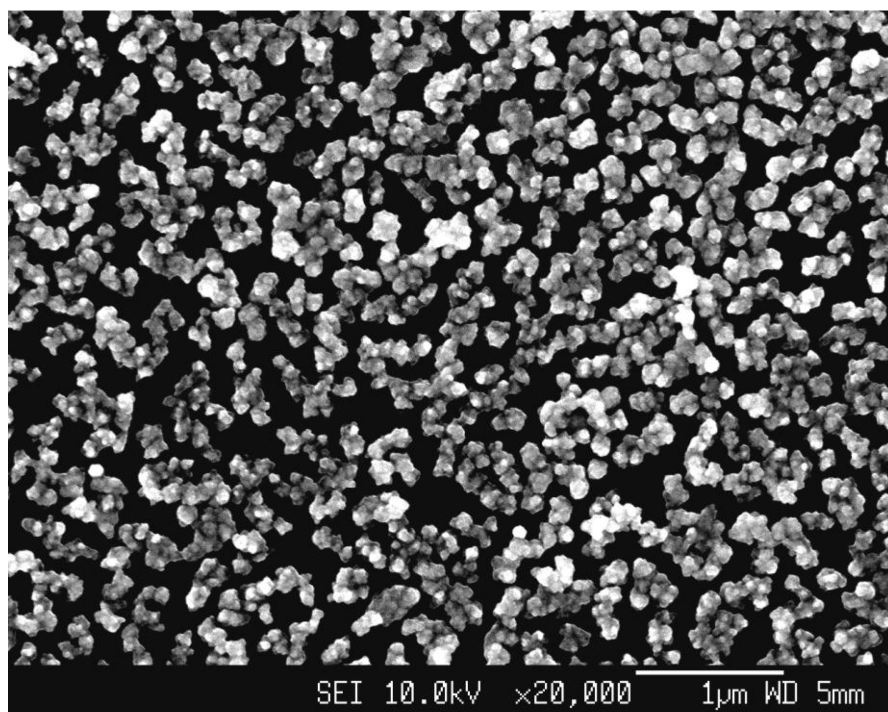

Figure 3

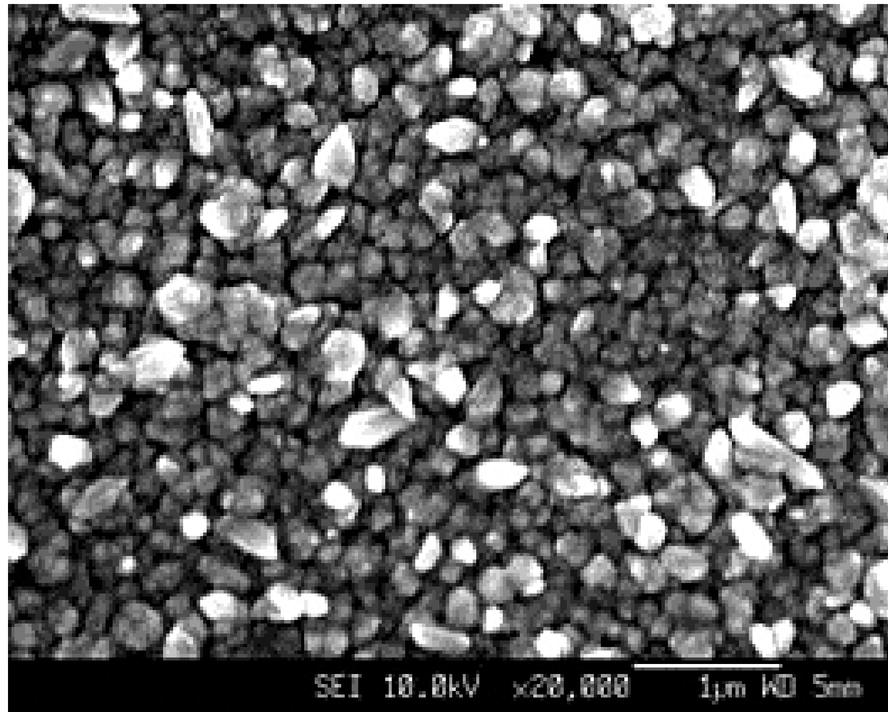

Figure 4