The effect of surface activation on electroless Ag(W) deposition

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Electroless Ag(W) films were deposited from the ammonia-acetic silver complex solution in 450 nm deep damascene channels with aspect ratio ranging from 1 to 2.5 activated either by Pd solution or by dry sputtered metal seed. A small addition of PEG-1500 (PEG with molecular weight of about 1500) to the electrolyte and lower deposition temperature were found to be necessary to achieve the homogeneous trench filling without voids or seam creation, which may contribute to increase resistivity of interconnect metallization. The effect of activation procedure on Ag(W) film: nucleation, electrical and mechanical properties, is shown. Thin metal seed instead of wet Pd activation, leads to: decrease of the film electroless deposition incubation period, conformal trench filling and low resistivity of sub-100 nm layers. Thin 60 nm Ag(W) films with resistivity value of about 2 $\mu\Omega\cdot$cm after vacuum annealing at 350 C for 2 h were obtained that makes them promising for future ULSI microelectronic application as conductive layers.

1. Introduction

The miniaturization of electronic devices with high density of interconnect features, has requested very urgently, to develop Ultra-Large-Scale-Integration (ULSI) circuits with less than 50 nm pitches and aspect ratio of the order of 2 for the local interconnect in 2016 [1]. Entering the sub-100 nm feature sizes era challenges most of developed microelectronic technologies including, of course, the interconnect fabrication that becomes a bottleneck for future integrated circuit performance [2]. The both theoretical analysis and practical realization [2], showed possible future problems of copper metallization that result in increased resistivity and relative low reliability [3]. Therefore, an intensive search for new interconnect material as well as metallization technologies was started several years ago [4-8]. Silver has recently attracted a great interest as a potential candidate for advanced ULSI metallization [4-8], due to lowest room temperature bulk resistivity (1.59 $\mu\Omega\cdot$cm), relative high melting point and higher reliability in comparison to the Cu metallization [3]. The advantages of thin silver films and patterns were demonstrated using dc magnetron sputtering [3, 6] and e-beam deposition techniques [4].

Nevertheless, compatibility with dual damascene scheme [9] requires defect-free filling of high aspect ratio trenches that makes application of electrochemical deposition from aqueous solution as one of the most promising technologies [10]. The advantages of electroless deposition enable the possibility to fill narrow trenches and via with high aspect ratio as well as direct plating of dielectric surface, which open a potential application of this method for ULSI technology.

The silver thin film corrosion and tarnishing may be avoided by encapsulation with Ti layers [3] or using the light doping by tungsten [5]. The resistivity of Ag thin films with less than 1 at. % of W were found to be in order of 2 $\mu\Omega\cdot$cm that makes them suitable for ULSI application. Advanced corrosion stability of the Ag(W) films up to 350 C was achieved [5, 11-12].

In this work we present the surface activation influence on electroless Ag(W) deposition in 450 nm deep damascene channels with aspect ratio ranging from 1 to 2.5. The experimental data include Ag(W) deposition rate, microhardness and resistivity measurements as well as the film morphology and trench filling SEM observation.

2. Experimental details

Ag(W) deposition was performed from ammonia-acetic silver solution with sodium tungstate employed as a source of tungsten ions and hydrazine hydrate as a reducing agent. Minute quantities of additives were introduced in solution to improve Ag(W) layer brightness and trenches filling (Table 1).

It was shown that Ag(W) deposition in sub-micron trenches from polyethylene glycol (PEG) free solution fails to fill high aspect ration trenches due to blocking of deposition. A small addition of PEG with molecular weight of about 1500 to the electrolyte and lower deposition temperature were found necessary to achieve the trench filling without voids or seam creation.

Table 1. Description of Ag(W) electroless plating solution and deposition parameters.

Destination	Source	Concentration, g/l
Source Ag	AgNO$_3$	5.4
Source W	Na$_2$WO$_4$	9.9
Complexing agent	Ammonia-acetic buffer	43 of 25 % NH$_4$OH and 30 CH$_3$COOH
Reducing agent	Hydrazine hydrate	2.5
Additives	Saccharine	0-0.1
	EDTA	5
	PEG-1500	0-0.02
pH		10.65-11.44
T, C		6-25
t, min		3-20

The plated sample was a chip containing test structure of 2 cm long lines with variable width from 0.18 μm to 0.45 μm and the same depth of 0.45 μm for all trenches. Trenches were etched in thermal SiO$_2$ followed by wet or dry activation. For comparison, the effect of surface activation was studied on the wet Pd activated SiO$_2$, CoWP/Cu/SiO$_2$, where CoWP was electroless deposited on PVD Cu, Ag/W/Ti/SiO$_2$ with all metals sputtered and Cu/SiO$_2$ substrates.

A wet activation procedure included treatment by HNO$_3$ for 20 min, detergent hot solution for 10 min, 2 % hot 3-aminopropyl-3-ethoxysilane (TAPOS) for 30 min and Pd (citric complex) for 5 or 10 min that avoided SiO$_2$ etching. The dry activated samples were cleaned in the isopropanol and dipped in diluted (1:50) HCl to remove the surface contaminations.

Thickness, composition, microstructure, micro-hardness and resistivity of thin Ag(W) deposits were studied. Ag(W) films of about 80 nm thickness with ~1 at.% of W deposited on different seeds were used for microhardness measurements. Ag(W) composition was analyzed qualitatively and quantitatively by X-ray Photoelectron Spectroscopy (XPS) using a Physical Electronics PHI model 590 unit. Scanning Electron (SEM) (JSM 6700 F) and Atomic Force (Veeco's Dimension 3100 AFM with high aspect ratio silicon tips) microscopy were used to characterize trench filling kinetic, film microstructure and morphology. The thickness of the deposited Ag(W) layers was determined by an Alphastep 500. The resistivity was measured using In-line Four Point Probe made by Lucas/Signatone^{TM}. The microchardness of the deposits was measured using a standard hard-operated loading system (PMT-3) by continuous pressure using a Vickers-style indenter with a 15-s loading time. The loading pressure on the Vickers's diamond pyramid was 4.5 g, and 10 measurements were taken on each sample. Post-deposition vacuum annealing under pressure less than 2×10^{-7} Torr at 350 C for 2 h was applied to improve the deposit electrical properties.

3. Results and discussion

Previously it was shown [13] that the substrate structure defines the Ag(W) film distribution and its resistivity. The effect of activation procedure on Ag(W) layer nucleation, mechanical and electrical properties as well as trench filling was studied in present work. The morphology evolution, deposition kinetics and the trench filling behavior were investigated using high sensitivity SEM technique.

Significant change in film deposition rate (Fig. 1) and nucleation mechanism (Figs. 2-3) as a function of different activation methods was observed.
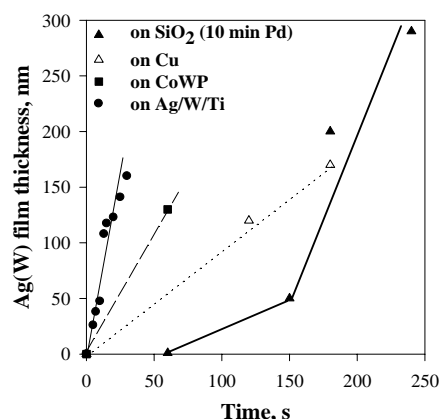

Fig. 1. The Ag(W) growth kinetics as a function of SiO$_2$ activation methods.

As seen in Fig. 1, Ag(W) deposition rate is strongly depended on the seed layer structure. It is higher on Ag in comparison with other metals. In this case less energy is needed to produce a new structure since Ag(W) film growths on the metal with similar morphology (polycrystalline Ag). This results in high deposition rate. The value of deposition rate on SiO$_2$ is obviously connected with time-limited incubation period when the silver islands on Pd catalytic sites are formed. We believe that after first stage of growing, that run with slow rate (Fig. 1) and depends on the number of nucleation sites, a plated surface becomes a very thin continues Ag(W) layer. The followed Ag deposition takes place by the autocatalytic mechanism that is very similar to the plating of sputtered Ag seed layer and occurs with the same deposition rate. The difference in the plating rate appears only at the process beginning and depends on the catalytic activity of seed layer.

The SEM images of plated trenches are presented in Fig. 2. All depositions were made at room temperature. In the case of Pd activation fabrication of more nucleation sites occurs by changing of surface activation time. This results in higher deposition rate and shorter induction period. Moreover, Ag(W) films have demonstrated larger grain size structure in comparison with ones deposited on metal seeds.

Deposition on the metal seed (CoWP and Cu) showed conformal behavior. The activation procedure and quality of the seed layer mainly determine the quality of the deposits. The dry activation produces more smooth and uniform Ag(W) layers with smaller grains (Fig. 2-3) that results in the film properties (Table 2, Fig. 4).
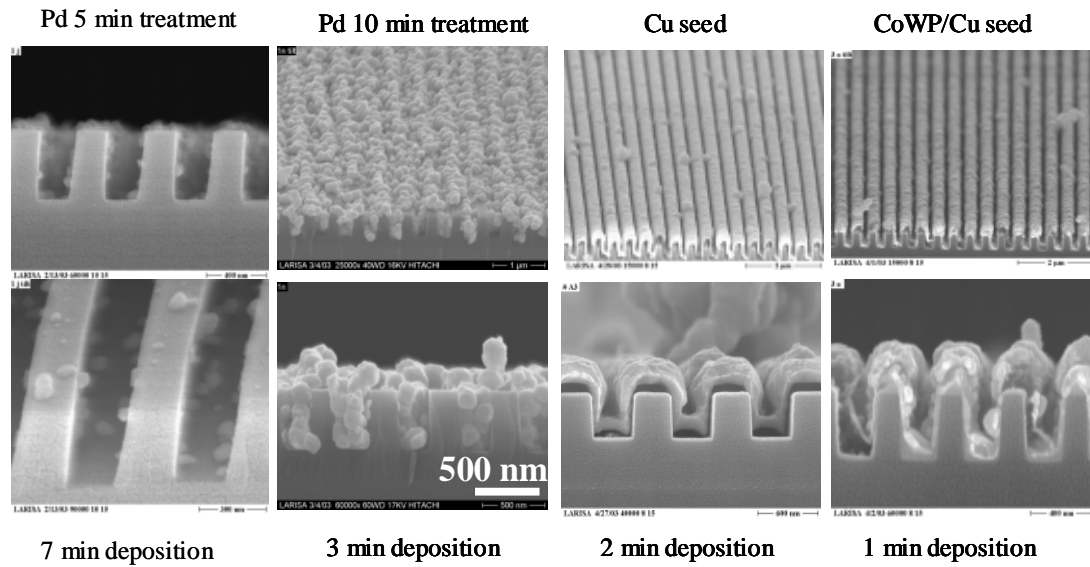
Pd 5 min treatment | Pd 10 min treatment | Cu seed | CoWP/Cu seed

7 min deposition   3 min deposition   2 min deposition   1 min deposition

Fig. 2. The effect of substrate activation on Ag(W) nucleation.
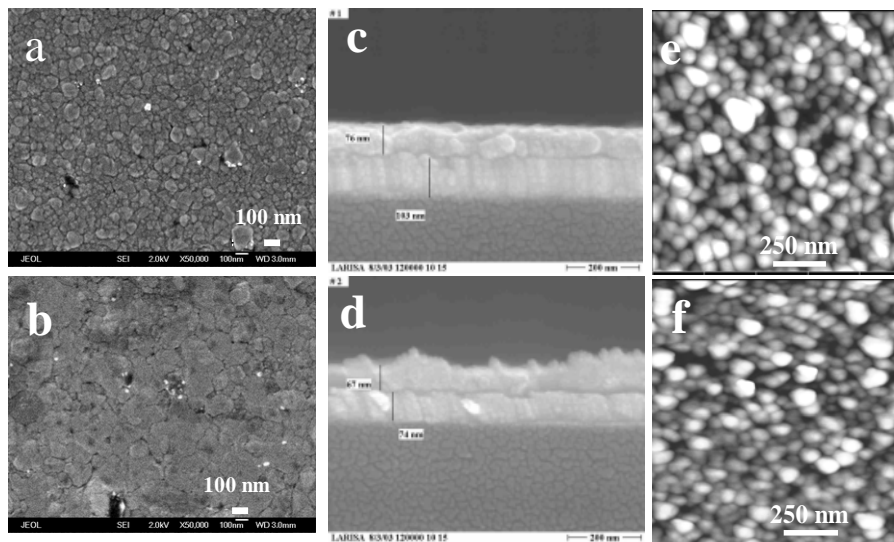

Fig. 3. HRSEM (a,b), AFM (e,f) images and cross section (c,d) of Ag(W) film on Ag/W/Ti seed in as deposited (a,c,e) and annealed (b,d.f) conditions.

Table 2. Microhardness of Ag(W) film on different seeds.

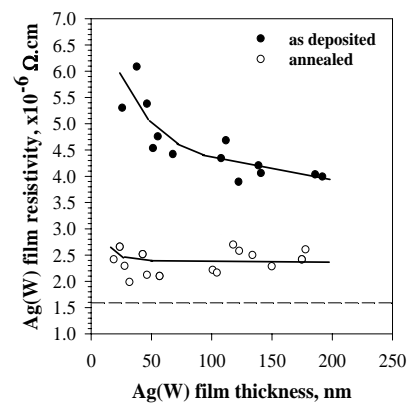| Seed	Micrichardness, GPa
Ag	0.31
Cu	0.51
CoWP	1.45
SiO$_2$	0.68

Fig. 4. The resistivity of Ag(W) films deposited on dry activated SiO$_2$ in as-deposited and annealed state.

Nevertheless, voids formation in the high aspect ratio trenches was observed, while the deposition on wet activated surface produces void-free filling of 0.18 μm wide trenches with aspect ratio about 2 (Fig. 2).

It can be noted that W content in the electroless Ag(W) film in not depended on the seed layer material but is defined only by the solution composition [12].

As seen in Table 2, Ag(W) layer deposited on CoWP substrate has demonstrated 2-5 times higher hardness in comparison with one on the other seeds. Obviously, internal pressure and structural inhomogeneous of this Ag(W) deposit, is the reason of such phenomenon. Since electrical properties of Ag(W) film deposited on SiO_2 with wet Pd activation is widely described [12, 14-15] in this work we present the electrical resistivity measurements only for deposits on metal seed (Fig. 4).

As seen in Fig. 4, all Ag(W) deposits have shown very close resistivity (ρ) values. Some scattering of ρ, 4 - 6 μΩ·cm and 2 - 3 μΩ·cm for as-deposited and annealed films, respectively, was observed. Non-uniformity of Ag(W) structure due to different deposition rate caused by the seed properties is a reason of this scattering. The resistivity decrease after vacuum annealing which improves the film structure, confirms this conclusion. It can be noted that after annealing Ag(W) films deposited on different metal seeds have demonstrated that the ρ is practically independent on the film thickness and very close to that of Ag bulk (Fig. 4). So, after post-deposition vacuum annealing at 350 C for 2 h the resistivity values of about 2.4 μΩ·cm and 4.0 μΩ·cm for 60 nm and 20 nm Ag(W) films, respectively, were obtained. Such electrical resistivity together with high corrosion stability of Ag(W) [5], make electroless Ag(W) deposits very useful for ULSI interconnect metallization technology.

4. Conclusion

The characterization of electroless Ag(W) sub 0.2 μm trench filling as a function of surface activation is presented. The electroless Ag(W) plating have shown the full filling of 2.5 aspect ratio trenches in SiO_2 in the case of direct deposition with wet Pd substrate activation. The effect of dry surface activation on Ag(W) growth was observed. It was shown that thin sputtered metal seed changes the kinetics of electroless deposition and results in improvement of the film structure. The Ag(W) deposition rate was found to be a function of produced nucleation sites amount. Filling of trenches with Cu or CoWP/Cu seed have demonstrated basically conformal behavior. Vacuum annealing influence on the electroless Ag(W) film resistivity was studied. Thin 60 nm Ag(W) films with ρ of about 2×10^{-6} Ω·cm after proper annealing were obtained that makes them promising for future microelectronic application as conductive layers.

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