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THE EFFECT OF SURFACTANTS ON SUPERCONFORMAL DEPOSITION OF ELECTROLESS COMPOSITES IN NANOSCALE PATTERNS

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Electroless plating of metal composites has been proposed as a promising method for metallization of high aspect ratio trenches for micro- and nanoelectronics and microelectromechanical systems application. Deposition of Ag(W) electroless films was performed from ammoniate silver solution to fill deep damascene trenches. Polyethylene glycol (PEG) with molecular weight of 400, 1500 and 6000, RE-610 and Triton X-100 were studied as an additives in the plating bath for superconformal deposition. The deposition rate, resistivity, grain size and the trench filling behaviour were studied as a function of the additives concentration and deposition temperature using Scanning Electron Microscopy (SEM) cross section study. The PEG with molecular mass about 1500 was found to provide superconformal Ag(W) electroless growth in nanometre wide trenches.

Keywords: electroless deposition surfactant, microelectronics metallization, metal composite thin film.

Introduction

Superconformal metal deposition (“super-fill”) in submicron features is of a great interest for the technologies of micro size electromechanical systems, nanorobots fabrication and a new generation of integrated circuits [1]. “Super-fill” plating can fill high aspect ratio features (trenches and vias) without voids and seam [2]. Because of the “super-fill” capability, low cost and superior film properties, the plating techniques are very promising for Ultra-Large-Scale-Integration (ULSI) applications [3]. Some results on superconformal copper electroless [4], electroplating [1] and silver deposition [5] for ULSI interconnects were published. In this work we report on electroless silver deposition with the “super-fill” capability. Electroless deposition of silver-tungsten (Ag(W)) thin films with high corrosion resistance and low resistivity in the order of 3–4 10^{-6} Ω cm made such material very promising for practical applications in microelectronics [5]. In this work we present results of Ag(W) superconformal electroless deposition. The grain size and the trench filling behavior were studied as a function of the additives concentration and the deposition temperature using the Scanning Electron Microscopy (SEM) technique.

Experimental

The Ag(W) films were deposited from the ammonia acetate and benzoate electroless solutions as described in [6] on silicon dioxide (SiO_2) wafers containing 450 nm deep trenches with aspect ratio from 1:1 to 2,5:1. The structure period was kept constant at value about 0,6 mkm so the space between lines was varied. Trenches were etched in thermal SiO_2 with followed activation using citrate palladium complex solution or sputtered Cu seed. The possibility of electroless CoWP barrier/seed layer integration shows the one-tool process compatibility.

The 18 MΩ cm resistivity deionized water was used for solution preparation and samples washing. All chemicals were of chemical purity. The influence of surfactants such as RE-610 (polyoxyethylene nonylphenyl ether phosphate), Triton X-100 (polyethylene glycol octylphenyl ether

or $C_{14}H_{22}O(C_2H_4O)_n$ (n = 9–10)) and polyethylene glycol (PEG) with various molecular weights (400, 1500, 6000) on the superconformal Ag(W) deposition was investigated. The concentration of additives was about 0,01-0,015 g/l (0,01 g/l for PEG).

The grain size and the trench filling behaviour were studied as a function of the additive concentration in the solution and the deposition temperature (from 4 ºC to 40 ºC) using the Scanning electron microscope (SEM). The deposition kinetics was characterized using the profilometry and optical microscopy control. Thin films resistivity was measured by four-probe method.

Results and Discussion

The dependences of film thickness as a function of deposition time and deposition rate for ammoniate and benzoate solutions are presented in Fig.1. It's observed that deposition rate is practically the same on the conformal seed layer and activated silicon oxide (50–70 nm/min for ammoniate solution). Such 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 that run with slow rate and depends on the number of nucleation sites, the plated surface becomes a very thin continues Ag(W) layer. The followed Ag reduction and deposition runs by the autocatalytic mechanism and it's very similar to the plating of sputtered seed layer. The difference in the plating rate appears only at the beginning and depends on the catalytic activity of sublayer.

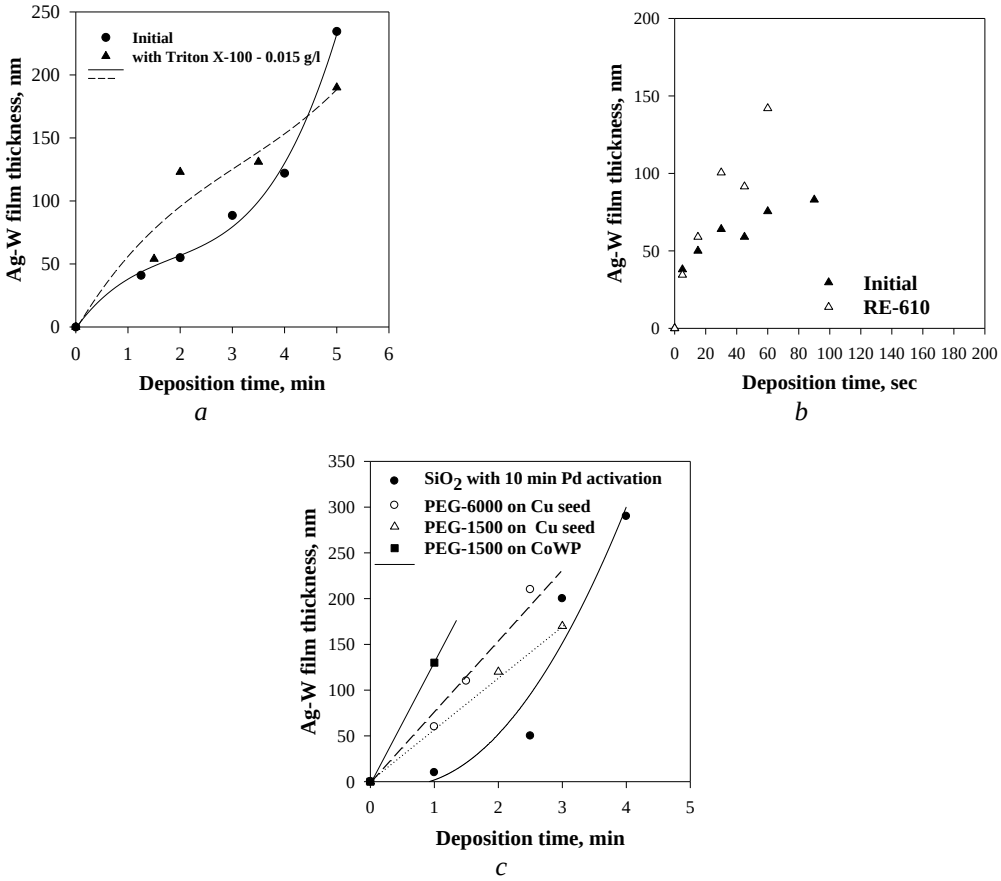


Fig. 1. Kinetics of silver-tungsten electroless deposition from solutions with different surfactant additives: *a* – Triton X-100; *b* – RE-610; *c* – PEG

For comparison, the effect of surface activation was studied on the wet Pd activated SiO_2 where activation time was 5 or 10 minutes, CoWP/Cu/SiO_2 where CoWP was electroless deposited on PVD Cu, and Cu/SiO_2 substrates.

Comparison the deposition after 5 min and 10 min Pd activation showed that fabrication of more nucleation sites by changing of surface activation procedure results in higher deposition rate and shorter induction period.

The activation procedure and quality of the seed layer mainly determine the quality of the deposits and deposition kinetic. Deposition with dry activation produces more smooth and uniform Ag(W) layers. Moreover, the induction period for deposition on thin film seed is absent that may be explained by different potential of Cu and CoWP seed in comparison to Pd activated SiO_2. Deposition on both Cu sputtered seed and CoWP electroless seed showed conformal behavior.

The surfactants do not affect significantly the deposition rate demonstrating suitable values for practical applications but its effect on electrical properties was more significant (Fig. 2). The minimal resistivity was obtained from solution with PEG additive so it was taken for the further trench filling study.

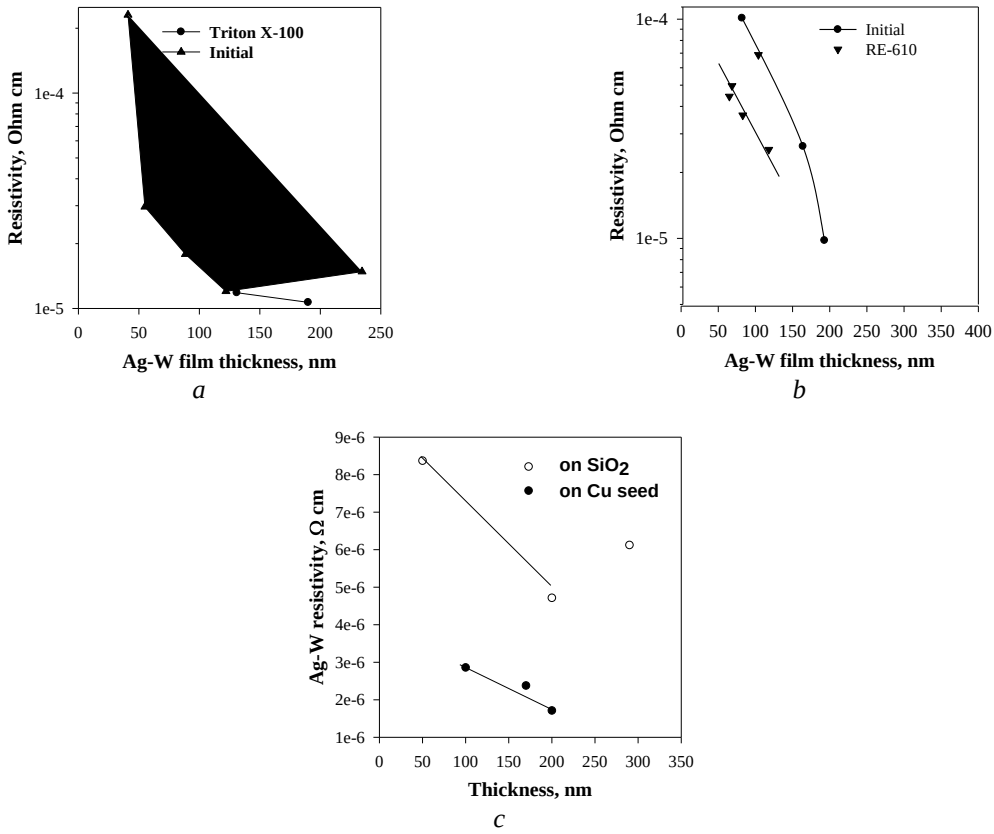


Fig. 2. Resistivity of silver-tungsten thin films electroless deposited from solutions with different surfactant additives: *a* – Triton X-100; *b* – RE-610; *c* – PEG

The obtained morphology of the Ag(W) in the trenches for different procedures of electroless deposition (composition of solutions, rate of deposition, temperature of substrate, etc.), was studied using SEM. The corresponded pictures of the filled structures are presented in Figs. 3-5. Figures present the evolution of the trench filling from the ammoniate bath.

It's shown that both solutions can be suitable for trench filling after proper modification. Ag(W) from the ammoniate solution fills the wide trenches but there is blocking for narrow. Nevertheless, the grain size and surface roughness are too large. Ag(W) deposition in submicron trenches from polyethylene glycol (PEG) free solution fails to fill high aspect ratio trenches (Fig. 3). Large grains formed at high deposition rate blocked the trenches at the initial stage of deposition and prevented further growth inside the trenches.

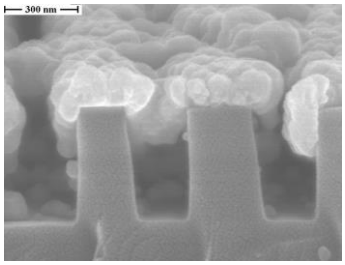
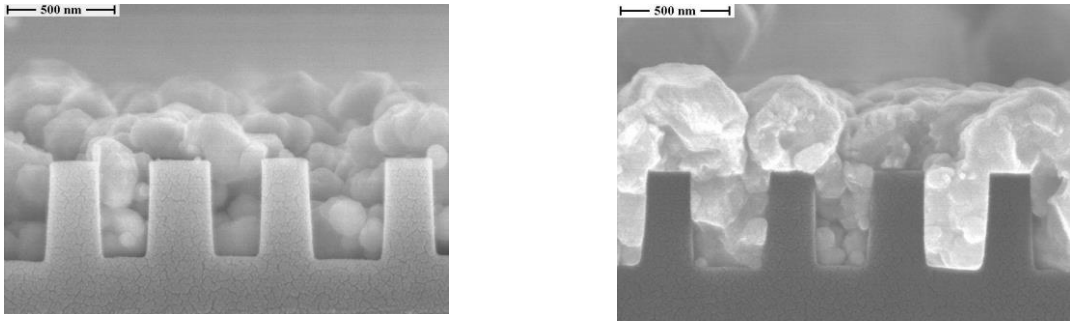


Fig. 3. SEM image of trenches filled from ammoniate solution without polyethylene glycol

Adding of the PEG surfactants helps to fill the narrow trenches. Using of stronger complexes (EDTA, BTA) reduces deposition rate and grain sizes but deposition is still non-uniform.

An addition of a small amount of PEG-400 (PEG with molecular weight of about 400 g/mol) to the electrolyte improves the Ag(W) trench filling at room temperature (Fig. 4, *a*) due to solution stabilization and surface tension reduction. However, relatively high surface roughness and many voids in the trenches were observed in the SEM image. To overcome this problem low-temperature electroless deposition from the same solution was performed. Ag(W) film deposited at temperature of 4 ºC (Fig. 4, *b*) demonstrates small grains and conformal trench coverage with low deposition rate. However, seams were observed in 2,5:1 aspect ratio trenches.



a *b*

Fig. 4. SEM image of trenches filled from ammoniate solution with PEG-400: *a* – at room temperature, *b* – at 4 ºC

The PEG-1500 (molecular weight about 1500) and PEG-6000 (molecular weight about 6000) additives were added to the plating solution and their effect on the channel filling was studied. Superconformal deposition was observed in trenches with aspect ratio of 2,5:1 (Fig. 5). No voids or seams were found at 4 ºC and room temperature when PEG-1500 was used. PEG-6000 significantly reduced the solution stability initiating homogeneous nucleation in the volume that caused deposition of fine particles.

Low temperature deposition improves the filling. The optimal composition of plating solutions for void-free trench filling was found out. It's shown that both ammonia-acetate and benzoate solutions are suitable for trench filling after optimization. The polyethylene glycol (PEG) surfactants (PEG-400 and PEG-1500) were found to be most effective for trenches "superfilling". The optimal value of surfactants molecular weight was in the range from 400 to 1500 g/mol. Using of additional complexing agents (EDTA, BTA, ammonia acetate) reduces deposition rate and grain sizes.

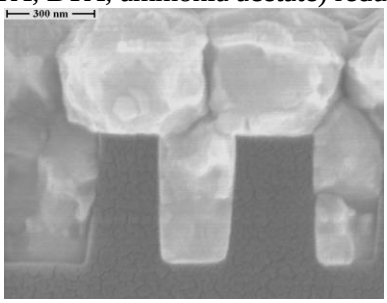


Fig. 5. SEM image of trenches filled from ammoniate solution with PEG-1500 at room temperature

The effect of PEG is not fully understood. It may act as a surfactant that reduces the surface tension and prevents silver volume nucleation improving the solution stability. PEG may also act as a suppressor (similar to Cu plating bath carrier/suppressor) with the diffusion gradient forming in the trenches during deposition, which results in bottom up according to curvature enhanced accelerator coverage model [7].

The benzoic acid based solution from the beginning provided conformal deposition but voids and seam defects took place in narrow trenches. Ag(W) from the benzoate solution fills the wide trenches without blocking and produces smaller grains due to stronger complex. Adding the PEG-400 avoids the void formation – the superfilling-like deposition obtained. Unfortunately, the grain size and surface roughness are too large. Using of BTA reduces deposition rate and grain sizes and can be concerned as one way to improve the roughness.

Conclusion

The silver-tungsten electroless deposition from ammoniate bath was performed on pattern SiO_2/Si wafers. The study of electroless Ag(W) sub 0,2 μm trench filling is presented. Electroless Ag(W) thin films show high reflection, good step coverage and adhesion to the SiO_2. The conformal deposition in sub 0,2 μm trenches was achieved. The critical role of deposition temperature and PEG additive in ammoniate bath was determined. It was shown that benzoate bath with additives produces even narrow trenches superfilling at room temperatures.

The electroless Ag(W) plating showed the full filling of 2,5 aspect ratio trenches in SiO_2 in the case of direct deposition with Pd activation. The critical effect of seeding was observed. Using of thin sputtered metal seed for dry surface activation changed the deposition nature dramatically. Filling of trenches with Cu or CoWP/Cu seed demonstrated basically conformal behavior. The Ag(W) deposition rate was found to be a function of produced nucleation sites amount. The resistivity of deposits about $2\ 10^{-6}$ Ω cm makes them promising for future microelectronic application as a conductive layers. Superconformal seam-free filling of submicrometer trenches at room temperature was achieved by using of PEG containing surfactants with molecular weight from 400 to 1500 g/mol.

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