



Electrochemical Study of the Mechanism of Ag(W) Electroless Deposition

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We present an electrochemical study of the mechanism of silver-tungsten, Ag(W), thin film electroless deposition from the solutions that are used for micro-systems-metallization applications. Ag(W) electroless films were deposited on palladium-activated surface of thin silicon dioxide layers on silicon substrates from ammonia-acetic or benzoate silver complex based solutions at room temperature using hydrazine hydrate as a reducing agent. These solution compositions have been investigated. The adsorption mechanism of tungsten incorporation into Ag coating on the positively charged silver surface was proposed and its co-deposition with silver due to interfacial catalytic interaction between tungsten and silver ions in form of $\text{Ag}_2\text{W}_2\text{O}_7$ was shown. The kinetics of the Ag(W) electroless deposition process was analyzed by mixed potential theory. It was shown that the anodic charge-transfer reaction for ammonia-acetic solution and the diffusion of reduced silver ions to substrate for benzoate complex have controlled this process.

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Application of silver (Ag) for ultralarge scale integration (ULSI) metallization looks very promising due to its lowest specific bulk resistivity of all the metals ($\rho = 1.59 \mu\Omega \text{ cm}$),¹ and suitable conductivity, which was reported for sputtered^{2,3} and electroplated⁴ Ag thin films. Furthermore, previous studies⁵⁻⁸ have shown that the drawbacks of silver for ULSI (low conductivity in thin films, corrosion in air, and diffusion in SiO_2) may be avoided by using a binary system of silver-tungsten [Ag(W)] instead of pure Ag. Certainly, barrierless silver metallization will offer higher effective conductivity than copper metallization especially at strong scaling decreasing requested for ULSI.

Electroless thin film deposition technology is highly selective, relatively simple, and low cost compared to most other methods. It also offers valuable solutions to industrial and research issues and, therefore, is a matter of interest of both practical and theoretical aspects.

Conventional models of electroless plating assume a reducing agent that donate electrons on the activated surface while at the same time the metal ions are reduced to metal atoms that are being adsorbed to the surface. In the Ag(W) bath that is described here, hydrazine-hydrate (N_2H_4) in alkaline aqueous solution is assumed to support the anodic part of the electroless plating mechanisms.

According to mixed-potential theory,⁹ oxidation of reducing agent and reduction of metal occur simultaneously and at separate locations on a substrate. As the substrate potential becomes more negative, the rate of reaction oxidation decreases, while that of reaction reduction increases. In the steady state, at mixed potential, the rates of the two reactions are equal. Therefore, reduction of silver by hydrazine in alkaline solution occurs by



The electroless baths composition for Ag(W) film preparation was developed⁵ and material properties of such films were widely studied.⁶⁻¹⁰ Nevertheless, the mechanism of W co-deposition with Ag has not been studied yet. To solve this problem, and to receive more information about the electroless deposition kinetics, the electrochemical method of study of the oxidation-reduction reactions was applied.

Experimental

We have studied electroless Ag and Ag(W) films from two different silver-complex solutions that are given in Table I. These solutions are based on those previously used to demonstrate the viability of electroless Ag(W) deposition for microelectronic applications.¹¹ This is the main reason for more detailed investigation of such electrolytes in the present work.

The electrochemical experiments were performed in a conventional three-electrode cell under ambient conditions. Current-potential curves were obtained from linear sweep voltametric measurements using EG&G Princeton Applied Research model 273A potentiostat/galvanostat controlled via computer for automated measurement. All potentials are referred to the Ag/AgCl saturated reference electrode (SSE). Pt wire electrodes (XM110 made by Radiometer analytical) were used as working and counter electrodes. The working electrode (0.3 cm^2 in area) was predeposited by Ag or Ag(W) from the corresponding silver or silver-tungsten solution at the potential -0.7 V vs SSE for 30 s before each measurement to reproduce the electrode surface with constant activity.

The thickness of the electroless deposits was measured by an Alpha-step 500 profilometer. Ag(W) thin films composition was studied by X-ray photoelectron spectroscopy (XPS) (Physical Electronics PHI 590) and differential scanning calorimetry (DSC). High-resolution scanning electron microscopy (HRSEM) (JSM-6300) and high-resolution transmission electron microscopy (HRTEM) (FEI Tecnai F30-UT operated at 300 kV) were used to observe the film microstructure and morphology.

In this work, we assume that silver reduction and tungsten co-deposition do not depend on the presence/absence of reducing agent or its breakdown products. We also assume that oxidation of hydrazine hydrate is independent of metal concentration in solution and is allowed by catalytic properties of the electrode material. Therefore, to simulate partial cathodic or anodic reactions the investigation of the electrolytes in the absence of either the reducer or the metal ions was performed.

Results and Discussion

The introduction of tungsten into silver due to electroless deposition from solutions I and II was shown in our previous publications.^{5,10,11} To understand the mechanism of its inclusion in deposition is one of the goals of this investigation. Co-deposition of metals with such different redox-potentials as silver and tungsten ($E_{\text{Ag}(\text{NH}_3)_2^+/\text{Ag}}^0 = +0.373 \text{ V}$ and $E_{\text{WO}_4^{2-}/\text{W}}^0 = -1.05 \text{ V}$) by electrolysis of water solution is highly unlikely. Note that standard potentials for most other organic complexes of Ag, except cyanide, are close to this value. Moreover, our attempt to co-deposit Ag with W by electrolysis of cyanide and succinimide complex solutions was not successful and no W incorporation into Ag was observed for a wide range of current densities and solution compositions. Taking also into account that W as a metal or compounds of its reduced form in electroless Ag(W) films were not determined,^{7,12,13} from our point of view the adsorption way of tungsten incorporation into the deposits

without WO_4^{2-} participation in the current-forming reaction is more probable. Because the point of zero charge of silver is at potential $-(0.7-0.8)$ V,¹ the silver surface in working range of potentials $-(0-0.5)$ V has an appreciable positive charge that promotes absorption of anions. This is confirmed by the changes of cathodic polarization (Fig. 1) and by dependence of the tungsten content in the deposit on its concentration in electrolyte (Fig. 2).

The rise of cathodic polarization on about 50 mV in ammonia-acetate bath at the negligible change of equilibrium potential (E_0) (Fig. 1a) corresponds with a significant drop of the film deposition rate due to Na_2WO_4 concentration increase in solution, observed in our previous work.¹⁰ Moreover, a character of this dependence absolutely conforms with that for W content in the film (Fig. 2). This saturation of W content in the deposit obtained from ammonia-acetate electrolyte (Fig. 2) can be explained by maximum filling of the surface by adsorbed WO_4^{2-} ions. The presence of a large quantity of CH_3COO^- ions known for their high adsorption ability allows us to assume that specific adsorption of WO_4^{2-} anions is unlikely in this case. Nevertheless, because the acetate anions are the main component of ammonia-acetate solutions and their concentration remains constant for all bath compositions, a slight shift of cathodic potential in presence of WO_4^{2-} ions was attributed to their adsorption on the electrode surface. Contrary to that, for benzoate solution due to adsorption of WO_4^{2-} ions cathodic polarization decreases (Fig. 1b), which usually results from specific adsorption of anions.¹⁴ We assume that for this bath in the absence of high adsorption ability organic anions specific adsorption of WO_4^{2-} ions takes place. Because concentration of such ions in solution is high, this adsorption causes charge exchange of the electrode surface. In this case, electrostatic attraction of positive Ag^+ ions to the cathode allows their easy diffusion from the volume of electrolyte to electrode surface that facilitates reduction of silver ions significantly. This results in the cathodic polarization to decrease (Fig. 1b). The W introduction into the coating (Fig. 2) fully corresponds with the film deposition rate dependence on Na_2WO_4 content in solution.¹⁰ This can be explained by catalytic activity of tungstate ions, which initiate the Ag reduction on the cathode surface fully covered by WO_4^{2-} . In fact, the compact silver deposits were not obtained by electroless from WO_4^{2-} -ion-free benzoate bath absolutely.

Note that for both processes each additive's influence on the cathodic process was studied separately. Because no impact on W incorporation into the deposit was observed, in Fig. 1 we present a common (mixed additives) curve corresponding to the full bath composition (Table I). At the same time, the cathodic polarization is reduced when additives are added in solution (Fig. 1). This results in significant changes of deposit morphology and its properties.^{5,7,15,16} Depolarization of cathodic process for benzoate solution is higher than that for ammonia-acetate one. Because the main additive in our

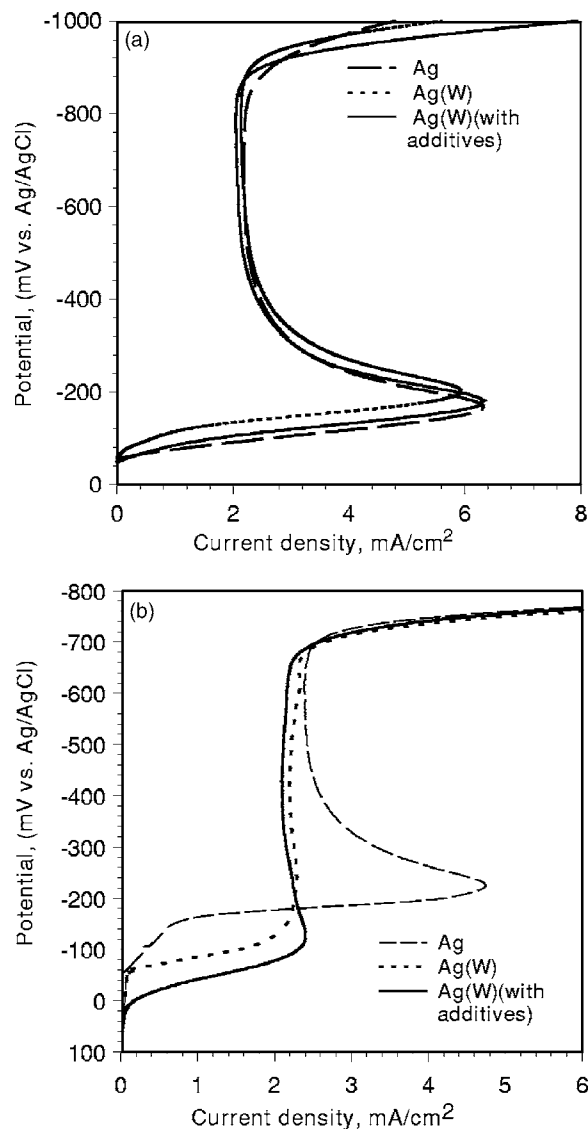


Figure 1. Cathodic reduction of silver and Ag(W) from ammonia-acetic (a) and benzoate (b) solutions. Scan rate 20 mV/s.

Table I. Silver-tungsten deposition solutions.

Description	Ammonia-acetic solution (I)	Benzoate solution (II)
	Component (concentration)	Component (concentration)
Source for Ag	AgNO_3 (0.03 M)	AgNO_3 (0.03 M)
Source for W	Na_2WO_4 (0.03 M)	Na_2WO_4 (0.015 M)
Complexing agents	Ammonia (NH_4OH) (1 M)	Benzoic acid ($\text{C}_7\text{H}_6\text{O}_2$) (0.33 M)
Reducing agent	Acetic Acid (CH_3COOH) (0.5 M)	Hydrazine hydrate (N_2H_4) (0.09 M)
Additional complexing agents	Hydrazine-hydrate (N_2H_4) (0.03 M)	Ammonium acetate ($\text{NH}_4\text{CH}_3\text{COO}$) (0.26 M)
Additives	Ethylenediaminetetraacetic acid (disodium salt dihydrate), EDTANA ($\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$) (0.017 M)	
	Sodium saccharin (0.004 M),	
	Sodium dodecyl sulfate, SDS (0.001 M)	
	Polyethyleneglicole, PEG (6×10^{-6} M)	
pH	11.1–11.4	9.15–9.2

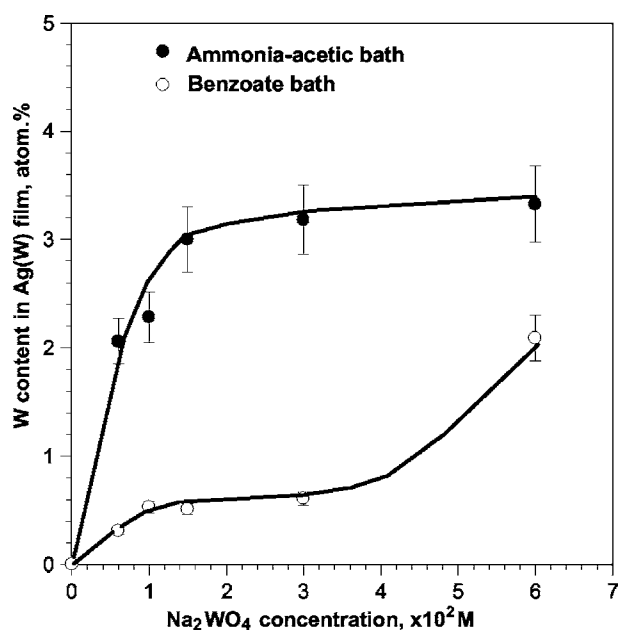


Figure 2. Tungsten atomic content in electroless Ag(W) film as a function of the sodium tungstate molar concentration in the ammonia-acetic (solid symbols) and benzoate (open symbols) solutions.

case is an additional complexing agent (ammonium acetate and EDTANA, respectively) this phenomenon can be explained, obviously, by easy reduction of silver-ammonia complex in comparison with silver-EDTA one.

The mixed potential (E_{mix}) and corresponding current density (i_{dep}) for Ag(W) electroless process were determined from Tafel current-potential dependence as the intersection point of cathodic and anodic curves (Fig. 3).

As can be seen in Fig. 3, the hydrogen evolution from both analyzed solutions takes place at more negative potentials than the corresponding E_{mix} ; therefore, its reduction during Ag(W) electroless deposition is unlikely. Assuming 100% current efficiency and taking into account that i_{dep} is constant during electroless plating, the deposition rate (R) was calculated from i_{dep} using Faraday's law $R[\text{mg h}^{-1} \text{cm}^{-2}] = i_{\text{dep}}[\text{mA cm}^{-2}] \times 4.025$ or $R[\text{nm/s}] = i_{\text{dep}}[\text{mA cm}^{-2}] \times 1.065$.

These values were calculated as 1.04 and 2.24 nm/s for ammonia-acetic and benzoate solutions, respectively, in comparison with 1.5 and 2.2 nm/s obtained from the experimental film thickness measurements. This data shows satisfactory agreement of theoretical, calculated, and experimental deposition rates for both solutions.

As concluded above, full coverage of the surface by WO_4^{2-} ions is needed to initiate cathodic reaction in benzoate electrolyte. In the case of electroless deposition, the time required for the coverage correlates with the incubation period. Therefore, to obtain the experimental value of average deposition rate for benzoate bath this incubation time has been estimated from previous measurements ("film thickness-deposition time" dependence, shown in Ref. 16) and taken into account in this present investigation. Opposed to this, silver reduction from amino-complex by so strong a reducing agent as hydrazine-hydrate is easy and occurs even on nonactivated surface and in a volume of the solution.^{11,15} In this case the experimental deposition rate was obtained counting the time of deposition from the moment of substrate immersion into solution since the incubation period is very short. This value is higher than the theoretical one and results from unstable and time-variable film deposition rate¹² that makes Faraday's law inapplicable. Note that direct measurement of the potential of Ag(W) electroless deposition in our systems is impossible because the film deposition was made on di-

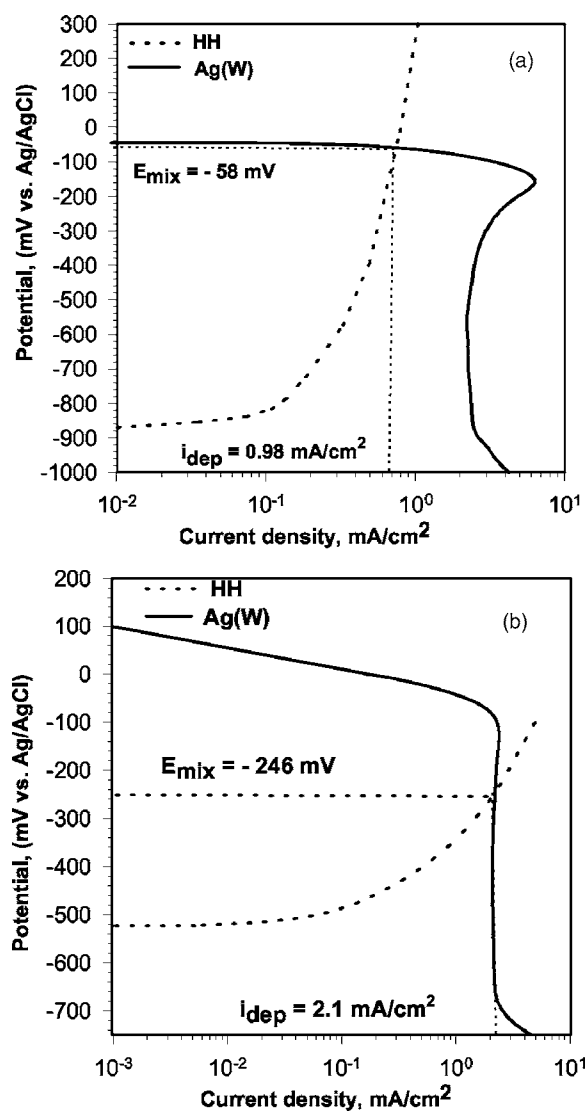


Figure 3. Tafel plots for cathodic reduction of silver (Ag(W)) and anodic oxidation of hydrazine-hydrate (HH) from ammonia-acetic (a) and benzoate (b) solutions. Scan rate 20 mV/s.

electric SiO_2 surface. However, it was done on Pd-activated silicon substrate and experimental values of potential were compared with E_{mix} obtained from polarization curves. A good agreement in potential values was observed for both baths: 50 and 58 mV for ammonia-acetic solution, 255 and 246 mV for benzoate one.

The metal electroless deposition is a heterogeneous reaction that takes place at the interface of covered surface solution. Overall deposition rate is controlled by the rate of the slowest limiting step. In our case, the Ag(W) electroless deposition rate for ammonia-acetic solution is controlled by anodic charge-transfer reaction rather than by chemical reaction, reducing agent mass transport, or desorption of products (Fig. 3a), and depends on the reaction ability of the reducing agent. It is in good agreement with our previous experiments where attempts to use such strong-less reducing agents as sodium hypophosphite or sugar was unsuccessful. On the other hand, because reduction of silver from benzoate complex occurs on diffusion current (Fig. 3b), the diffusion of its ions to the substrate is the limiting step. The significant dependence of the film deposition rate on the solution stirring and on the temperature in the absent one^{8,16} confirms this mechanism. Such differences in the mechanism of silver reduction from two investigated electrolytes results in discrepancies of Ag(W) films morphology^{10,11} and their properties.^{7,8,11,15,16}

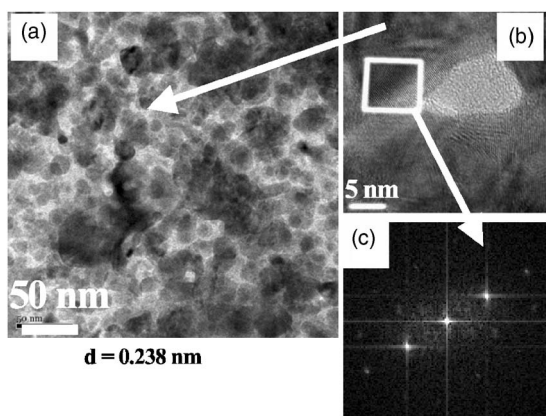


Figure 4. (a and b) XRTM images and (c) micro-diffraction pattern of a thin ligament between grains in 50 nm electroless Ag(W) film deposited from ammonia-acetic solution. The film was separated from SiO₂/Si substrate using gelatin replica.

XRD and HRTEM analyses have not shown W incorporation into the deposit as a metal for both solutions. Using HRTEM lattice imaging and FFT micro-diffraction it was found that due to electroless deposition, Ag and W form the triple compound of Ag₂W₂O₇ (Fig. 4), which is introduced into Ag films. In addition, some lattice parameters of silver oxides (AgO, Ag₂O) were determined.¹² The availability of Ag₂O and Ag₂W₂O₇ in electroless Ag(W) deposit is confirmed also by DSC data where endothermic peaks corresponding to decomposition of silver oxide (~300°C) and proper silver tungstate (~100°C) were observed.¹³ Moreover, the film has slightly yellow color, evidently due to the brown Ag₂O. After vacuum annealing at (300–400)°C the coatings become white. Based on absorption mechanism of W inclusion, such compound can be obtained due to chemical reaction of the simple silver ions with absorbed tungstate ions or with the products of their chemisorptions



Most likely, Ag⁺ ions are produced in the double layer as a result of the silver-complex ion dissociation. Moreover, a strong catalytic activity of fresh deposited silver surface confirms that Reaction 2 is very likely to occur.

Conclusion

The electroless silver-tungsten, Ag(W), films were deposited on SiO₂/Si substrate from ammonia-acetic and benzoate silver complex based solutions at room temperature using hydrazine hydrate as a

reducing agent. The absorption mechanism of tungsten incorporation into Ag coating was proposed. Using HRTEM it was shown that the tungsten is co-deposited with silver in the form of Ag₂W₂O₇.

An electrochemical nature of Ag(W) electroless deposition process was proposed and its kinetics was studied by mixed potential theory. Relatively close values of calculated and experimental deposition rate for both baths confirm this assumption. The mechanism of silver reduction from two investigated electrolytes was proposed and explained.

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