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Electrocrystallization and electrodeposition of silver on titanium nitride

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Abstract

The electrocrystallization and electrodeposition of silver on TiN substrates in $AgNO_3$ + KSCN solutions were studied by electrochemical methods and scanning electron microscopy. The description of Ag electrocrystallization is given in terms of instantaneous, progressive or mixed nucleation models. The parameters of electrocrystallization were determined and the fractional area covered by silver was estimated. A two-step procedure was used for forming a continuous silver film on a TiN substrate. During the first step, a seed layer was deposited on TiN by applying either high negative potential or cathodic current density in 0.011 M $AgNO_3$ + 2.5 M KSCN solution. The applied cathodic current density was higher than the limiting diffusion current in the solution. During the second step, a bulk silver film was deposited galvanostatically from a 0.22 M $AgNO_3$ + 2.5 M KSCN solution at a cathodic current density lower than the limiting current density.

1. Introduction

Currently, the most common materials used for interconnects in large scale integration (LSI) circuits are aluminium and its alloys. Materials, such as copper and silver, which possess lower electrical resistivity than Al, are ideal materials for interconnects for ultralarge scale integration (ULSI) devices; in practice, ULSI devices have been designed and produced which utilize copper interconnects. Silver possesses even lower electrical resistivity than copper; however, silver is difficult to deposit in the sub micrometric geometries required for ULSI devices by chemical vapour deposition (CVD) and sputtering techniques [1, 2].

Titanium nitride (TiN) is widely used as an adhesion layer and/or diffusion barrier in ULSI devices. Because TiN is conductive silver may be deposited electrolytically onto TiN substrates. The aim of the present work is to study the electrodeposition of silver on TiN substrates from thiocyanate solutions, with particular emphasis on the electrocrystallization of the silver films. $AgNO_3$ + KSCN solutions were selected for silver deposition because [3–8]: (i) these solutions are stable; (ii) current efficiency of the deposition is close to 100%; (iii) previous studies have shown that electrolytic silver deposits from these solutions produce good coatings (on copper substrates); and (iv) these solutions contain sufficiently high concentrations of Ag(I) required for relatively high electrodeposition rates.

2. Experimental procedure

The electrodeposition of silver onto TiN from $AgNO_3$ solutions, ranging from 0.0011 to 0.22 M concentration, was studied. The solutions contained 2.5 M KSCN as a complexing agent. Analytical grade chemicals and distilled water were used to prepare solutions. Measurements were performed at a temperature of 20 °C.

An EG&G Applied Research potentiostat/galvanostat (model 273A) connected to an IBM compatible PC was used for data collection. All electrochemical experiments were performed in a three-electrode glass cell. The TiN electrode was a flat round piece about 0.7 cm in diameter. A Teflon shielded copper wire was attached to the rear side of the electrode for electrical contact and the electrode was then mounted in epoxy. The silver electrode was made from an Ag wire pressed into a Teflon tube. The working part of this electrode was the top surface of a rod (area 0.196 cm^2). The counter electrode was platinum mesh. The reference electrode was a saturated calomel electrode (SCE). Electrode potentials are reported against the saturated calomel electrode scale (SCE).

Before each experiment, the surfaces of the TiN and Ag electrodes were mechanically polished with 2400 grit silicon carbide paper and rinsed in ethanol and distilled water. The silver films on the TiN electrode after a previous experiment were removed by applying a potential +0.500 V for a period of 2 min in the investigated electrolyte. After electrodeposition, the microstructure of the silver film was examined using a Zeiss DSM-960 scanning electron microscope.

3. Results and discussion

3.1. *Linear sweep voltammetry*

Cyclic voltammograms for TiN in 2.5 M KSCN revealed a relatively large overpotential for water decomposition, and TiN was not electrochemically active between +0.85 and −1.25 V. Addition of $AgNO_3$ to 2.5 M KSCN changed the cathodic portion of the cyclic voltammograms as illustrated in Figure 1. As shown, electroreduction of silver complexes onto the TiN electrode begins at more negative potentials than for electroreduction of silver complexes onto the Ag electrode (electroreduction at the TiN electrode starts at about −0.37 V, whereas, at the Ag electrode electroreduction starts at −0.25 V). During reverse polarization, both materials show similar values of current above −0.6 V. This indicates that both electrodes have similar surface properties. Also, the voltammogram for the TiN electrode showed a crossover on the cathodic branches at about −0.4 V. This indicated a slow three-dimensional nucleation of silver on TiN during electrodeposition [9–13].

3.2. *Potentiostatic current transients*

Potentiostatic current transients were studied in 2.5 M KSCN containing $AgNO_3$ at concentrations of 0.011 M, 0.003 M and 0.05 M. The shapes of the potentiostatic current transients with one maximum current were similar to each other regardless of Ag(I) concentration (Figures 2 and 3).

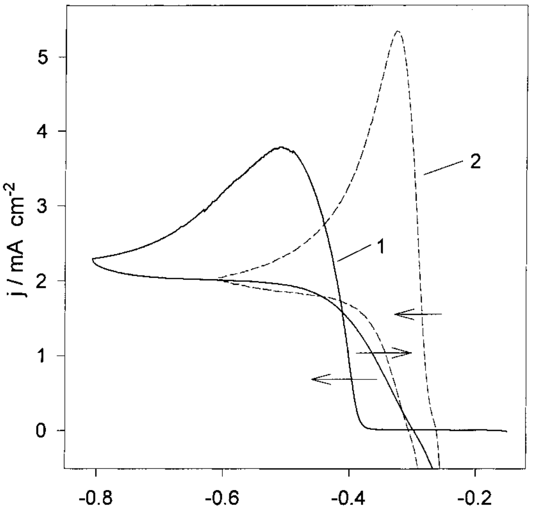


Fig. 1. Linear sweep voltammograms for silver deposition onto TiN (1) and Ag (2) electrodes in 0.05 M $AgNO_3$ + 2.5 M KSCN at scan rate 20 mV s^{-1}. Arrows indicate a potential scan direction.

To describe the nucleation of silver two models proposed by Scharifker et al. [11–12, 14] were used. One model assumes pure instantaneous nucleation and the other pure progressive nucleation. As was shown by Sluyters-Rehbach et al. [15] and Heerman and Tarallo [16], these models predict current transients correctly if electrocrystallization is not in the limit of very short times.

To recognize the two nucleation models, the equation derived in [11, 12] can be used. Thus,

$$\left(\frac{j}{j_m}\right)^2 = a\left(\frac{t}{t_m}\right)^{-1}\left[1 - \exp\left(-b\frac{t}{t_m}\right)\right]^2 \qquad (1)$$

where a and b are constants; j_m is the maximum current and t_m is the time at maximum current. When $a = 1.9542$ and $b = 1.2564$ pure instantaneous nucleation reaction takes place at the electrode; when $a = 1.2254$ and $b = 2.3367$ pure progressive nucleation occurs.

Each of the j/j_m against t/t_m curves was fitted to Equation 1 using nonlinear curve fitting operations to determine the nucleation mechanisms for silver deposits on the TiN electrode. In the 0.05 M $AgNO_3$ + 2.5 M KSCN solution, pure instantaneous nucleation of Ag onto the TiN electrode occurred at overpotentials ranging from 0.085 to 0.355 V. In the 0.011 M $AgNO_3$ + 2.5 M KSCN solution, instantaneous nucleation occurred at overpotentials ranging from 0.51 to

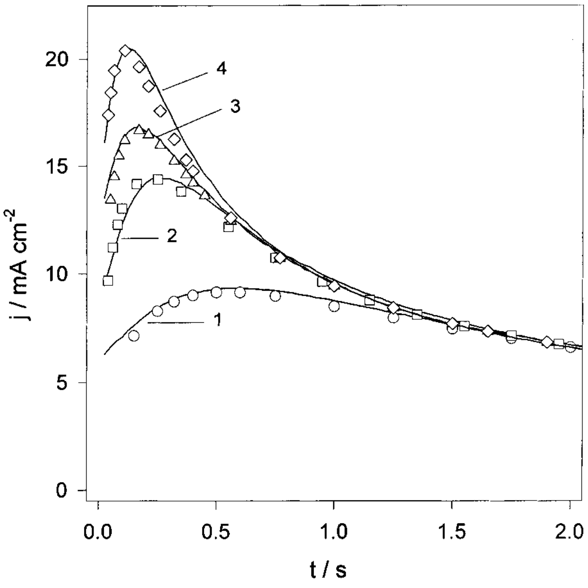


Fig. 2. Comparison between experimental current transients obtained in 0.05 M $AgNO_3$ + 2.5 M KSCN (solid lines) and calculated by Equation 2 (transparent points). Key: (1) $\eta = 0.155$ V ($N = 554\ 600$ cm^{-2}); (2) $\eta = 0.255$ V ($N = 1\ 293\ 200$ cm^{-2}); (3) $\eta = 0.305$ V ($N = 1\ 861\ 000$ cm^{-2}); (4) $\eta = 0.355$ V ($N = 2\ 682\ 700$ cm^{-2}). $D = 1.20 \times 10^{-5}$ cm^2 s^{-1}.

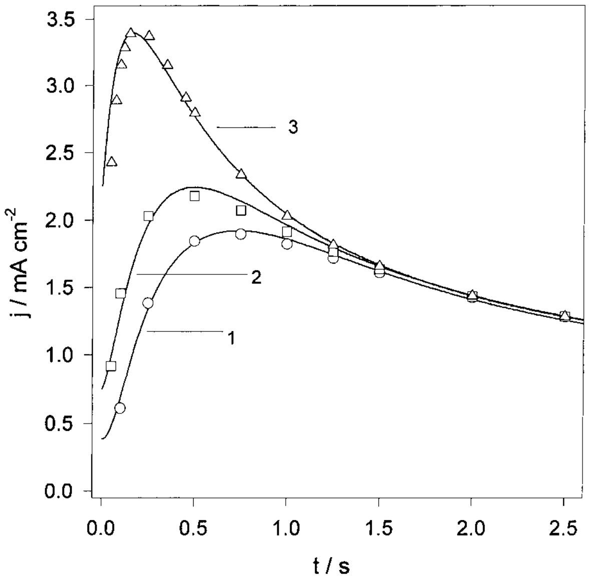


Fig. 3. Comparison between experimental current transients obtained in 0.011 M $AgNO_3$ + 2.5 M KSCN (solid lines) and calculated by Equation 3 (transparent points). (1) $\eta = 0.31$ V ($N_0 = 1\ 305\ 460$ cm^{-2}, $A = 11.18$ s^{-1}); (2) $\eta = 0.41$ V ($N_0 = 1\ 511\ 800$ cm^{-2}, $A = 85.28$ s^{-1}); (3) $\eta = 0.51$ V ($N_0 = 3\ 800\ 000$ cm^{-2}, $A = 135.00$ s^{-1}). $D = 1.15 \times 10^{-5}$ cm^2 s^{-1}.

0.690 V and pure progressive nucleation occurred in a relatively narrow overpotential range from 0.235 to 0.310 V.

For instantaneous nucleation, the nucleation parameters can be determined by

$$j(t) = zFc\left(\frac{D}{\pi t}\right)^{1/2}[1 - \exp(-N\pi kDt)] \qquad (2)$$

where $k = (8\pi cM/\rho)^{1/2}$; M and ρ are the molecular weight and density of the deposited metal, respectively; c is the bulk concentration of silver complexes; zF is molar charge of electrodepositing species; D is the diffusion coefficient; t is the deposition time; and N is the number density of growing centres. Equation 2 was used to calculate the current transients for different overpotentials in 0.05 M $AgNO_3$ + 2.5 M KSCN. The calculated current transients were in good agreement with the experimental current transients, as shown in Figure 2.

Figure 4 shows the dependence of number density of growing centres N as a function of cathodic overpotential, η. The number of growing centres increased with increasing overpotential in 0.05 M $AgNO_3$ + 2.5 M KSCN and 0.011 M $AgNO_3$ + 2.5 M KSCN. The overpotential values for which the numbers of growing centres were determined are lower in 0.05 M $AgNO_3$ + 2.5 M KSCN than those in 0.011 M $AgNO_3$ + 2.5 M KSCN.

When either the pure instantaneous or pure progressive models cannot describe the nucleation process, the nucleation parameters can be determined by the Scharifker–Mostany model [17]. According to this model the entire current transients are described by the equation:

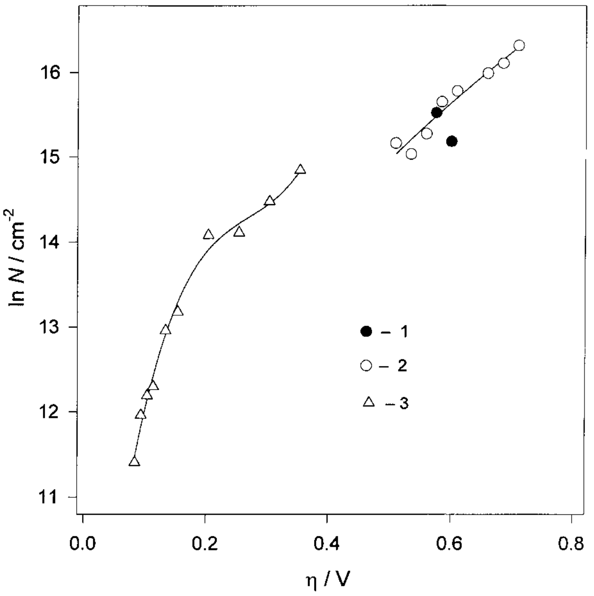


Fig. 4. Dependencies of N on potential of TiN electrode in x M $AgNO_3$ + 2.5 M KSCN, where (1) $x = 0.003$, (2) $x = 0.011$ and (3) $x = 0.050$.

$$j(t) = zFc\left(\frac{D}{\pi t}\right)^{1/2}\left\{1 - \exp\times\left[-N_0\pi kD\left(t - \frac{1 - e^{-At}}{A}\right)\right]\right\} \qquad (3)$$

where N_0 is the number density of active sites for nucleation and A is the nucleation rate per active site.

An analysis of the j/t curves indicates that the Scharifker–Mostany model is valid for all solutions at any overpotential applied to the TiN electrode. As an example, Figure 3 shows experimental and theoretical current transients for the instantaneous (0.51 V), mixed (0.41 V), and progressive (0.31 V) silver nucleation mechanisms on TiN. The experimental data are in good agreement with the theoretical data obtained by the j/t curve fittings to Equation 3.

Calculations of the diffusion coefficient, $D_{Ag(I)}$, using Equations 2 and 3 resulted in similar values. Using Equation 2 (for the mixtures containing 0.011 M and 0.05 M $AgNO_3$) gave a value $D_{Ag(I)} = (1.20 \pm 0.05) \times 10^{-5}$ cm^2 s^{-1}, and using Equation 3 (for the mixture containing 0.003 M $AgNO_3$) gave a value $D_{Ag(I)} = (1.40 \pm 0.05) \times 10^{-5}$ cm^2 s^{-1}.

The values for the nucleation centres (N_0) as a function of overpotential in the 0.011 M $AgNO_3$ + 2.5 M KSCN and 0.003 M $AgNO_3$ + 2.5 M KSCN solutions are shown in Figure 5. In the 0.011 M $AgNO_3$ + 2.5 M KSCN solution, there are two overpotential regions where N_0 increases; between 0.16 and 0.26 V and at values higher than 0.4 V. At overpotential values higher than 0.51 V, nucleation became instantaneous. In the 0.003 M $AgNO_3$ + 2.5 M KSCN solution, the N_0 values are similar to those obtained in the 0.011 M $AgNO_3$ + 2.5 M KSCN solution. For the case of the instantaneous nucleation of Ag on TiN, the values of N_0 determined using Equation 3 did not

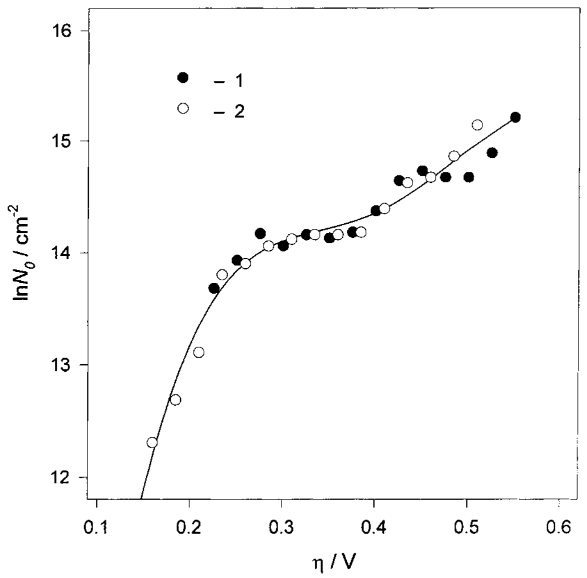


Fig. 5. Dependencies of N_0 on overpotential of TiN electrode in x M AgNO$_3$ + 2.5 M KSCN, where (1) $x = 0.003$ and (2) $x = 0.011$.

exceeded the values of N determined using Equation 2 by about 10%.

The nucleation rate, A, of Ag depends on the concentration of Ag(I) and the overpotential of TiN (Figure 6). In 0.05 M + 2.5 M KSCN, the rate of silver nucleation is very high and, therefore, the nucleation process is instantaneous. Since, experimental ln A against η dependencies are rectilinear, it is possible to determine the number of atoms in the critical silver nucleus (n_k) based on the values of slopes and the atomistic theory of nucleation [12]. Using a value for the charge transfer coefficient, α, of 0.28 for thiocyanate solutions [18], the number of atoms in the critical silver nucleus that deposits on TiN is calculated as 0 (zero). The slope ($d\ln A/d\eta = 12.5$) for the deposition of silver on TiN from the investigated solutions was found to be less than previously reported values for silver deposition on vitreous carbon from AgNO$_3$ solutions or ammonia baths [12, 19], and, assuming $\alpha = 0.5$, results in calculation of n_k values that are negative and unreal.

It is known [14], that the number density of growing centres, N, is associated with the size of the fractional area covered by the diffusion zones, Θ, as a function of time, t, according to the following equation:

$$\Theta = 1 - \exp(-N\pi kDt) \tag{4}$$

Figure 7 shows the dependence between Θ and t at different applied overpotentials in 0.05 M AgNO$_3$ + 2.5 M KSCN. Θ reaches a value of 1 within 1 s for overpotentials higher than 0.5 V. A slow increase of Θ with time is observed for 0.33 and 0.35 V. This slow increase of Θ explains the difference between the cyclic voltammograms for the TiN and Ag electrodes (Figure 1).

3.3. *Coverage of substrate by deposited metal*

During the deposition process, the size of the fractional area covered by a deposited film is one of the important parameters. In the case of the instantaneous nucleation of silver on the TiN substrate, the fractional area covered by metal, Θ_M, is a sum of the areas under the hemispheric nuclei. The radius of the hemispheric nucleus as a function of time is given by [17]

$$r_0(t) = \left(\frac{2DcMt}{\rho}\right)^{1/2} \tag{5}$$

where $r_0(t)$ is the radius of hemispheric nuclei.

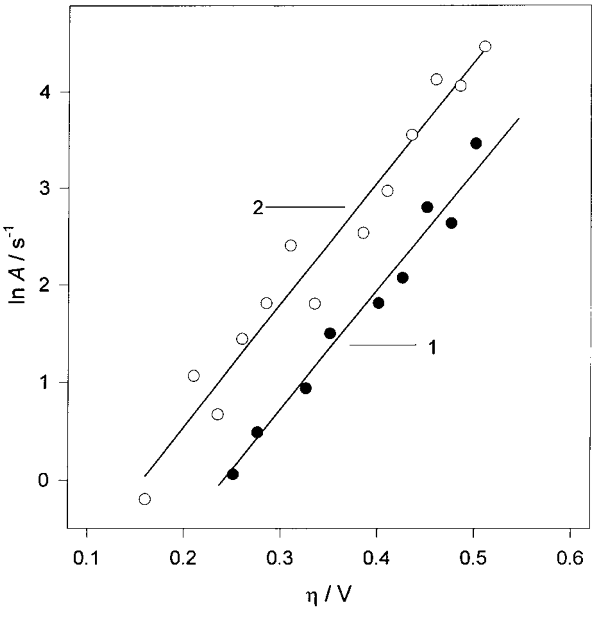


Fig. 6. Nucleation rate per site (A) as a function of overpotential of TiN electrode in x M AgNO$_3$ + 2.5 M KSCN, where (1) $x = 0.003$ and (2) $x = 0.011$.

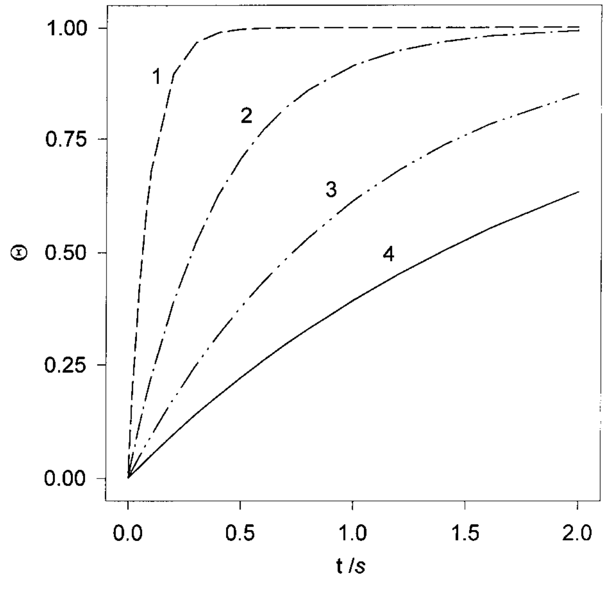


Fig. 7. Fraction of area covered by diffusion zones (Θ) as a function of time in 0.05 M AgNO$_3$ + 2.5 M KSCN at overpotentials: (1) 0.355, (2) 0.155, (3) 0.105 and (4) 0.085 V.

Under the assumption that all nuclei are growing at the same rate, the fractional area covered by the deposit can be expressed as

$$\Theta_{\mathrm{M}} = N\pi[r_0(t)]^2 = 2N\pi\left(\frac{DcMt}{\rho}\right) \tag{6}$$

According to Equation 6, Θ_{M} against time shows a linear dependence. This indicates that values for Θ_{M} vary between 0 and infinity. For $\Theta_{\mathrm{M}} < 1$, nuclei do not overlap each other, whereas, the nuclei overlap when $\Theta_{\mathrm{M}} > 1$.

For the silver nucleation on TiN, the time required for Θ_{Ag} to reach 1 is shown in Figure 8. It was found that in all solutions, *t* decreases with increasing overpotential. In 0.05 M, $AgNO_3$ + 2.5 KSCN, the relatively long time required for Θ_{Ag} to reach 1 at overpotentials higher than 0.4 V is a result of the small number density of growing centres on TiN, whereas, in 0.003 M $AgNO_3$ + 2.5 KSCN, the long time required for $\Theta_{\mathrm{Ag}} = 1$ is a consequence of the low concentration of Ag(I).

3.4. *Two-step electrodeposition of silver on TiN*

Usually, electrodeposition of bulk silver films is performed at current densities lower than the limiting current density. Otherwise, the deposit quality is poor due to powder formation. Acceptable deposition rates can be achieved in silver salt baths containing at least 0.05 M of Ag(I). To form continuous films within a relatively short period of time, it is necessary to increase the number density of growing centres to a maximum. If the number density of growing centres is too small, only partial coverage of TiN by silver occurs, as shown in Figure 9.

Therefore, a two-step deposition was considered to form a continuous silver film on TiN. During the first step, a high negative potential was applied for a short period of time. Under such conditions, a continuous silver layer, approximately 40–100 nm thick, was formed on the TiN surface. This layer is called a seed layer. Then, the bulk silver film was deposited at a current value lower than the limiting diffusion current density in the investigated electrolyte. The data in Figure 8 indicate that the time required for full coverage of the TiN electrode with silver depends on the Ag(I) concentration in the solution and the potential of the TiN electrode.

SEM investigations of the seed layer deposited in 0.05 M $AgNO_3$ + 2.5 M KSCN revealed the formation of large silver grains on TiN in comparison to fine grains formed in 0.011 M $AgNO_3$ + 2.5 M KSCN and 0.003 M $AgNO_3$ + 2.5 M KSCN. However, the use of extra diluted Ag(I) solutions (e.g., 0.003 M) is not practical due to rapid depletion of Ag(I) from the bath. Thus, the optimal composition of the solution for the Ag seed layer deposition is 0.011 M $AgNO_3$ + 2.5 M KSCN. This electrolyte, facilitates a high number density of growth centres for the nucleation, and a short time period for full coverage of TiN by the silver seed layer.

The SEM micrographs in Figure 10 show the films formed from seed layers deposited at different potentials. The time required for depositing a seed layer with approximately the same quantity of Ag varied for each applied potential. The second step was performed under galvanostatic control in another solution containing a higher concentration of Ag(I), that is, 0.22 M $AgNO_3$ + 2.5 M KSCN at current density 5 mA cm^{-2}. The average thickness of the bulk silver films was 1 μm. It is evident that the entire thin film forms during 50–100 s if the potential value for the first deposition

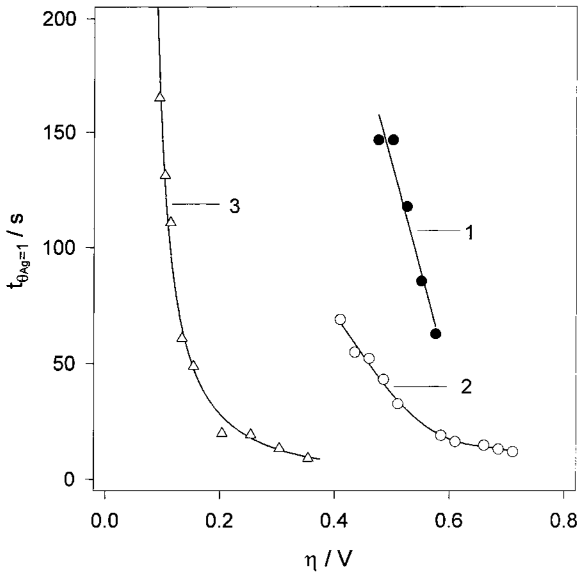


Fig. 8. Estimated times $t_{\theta \mathrm{Ag}=1}$ for silver deposition on TiN from *x* M $AgNO_3$ + 2.5 M KSCN as a function of applied overpotential, where (1) $x = 0.003$, (2) $x = 0.011$ and (3) $x = 0.050$.

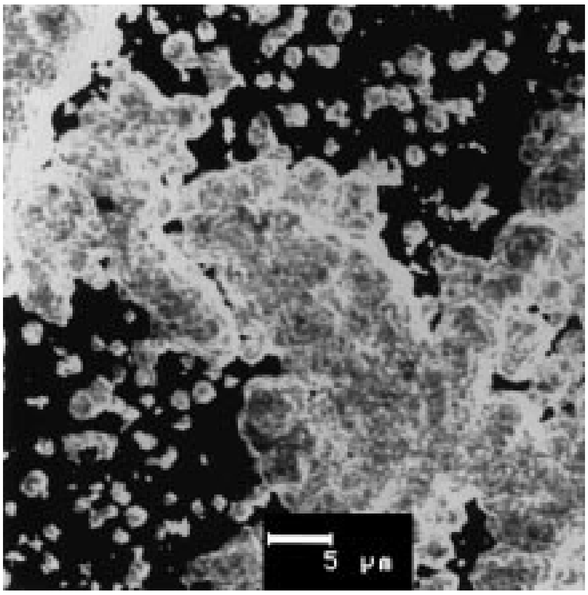
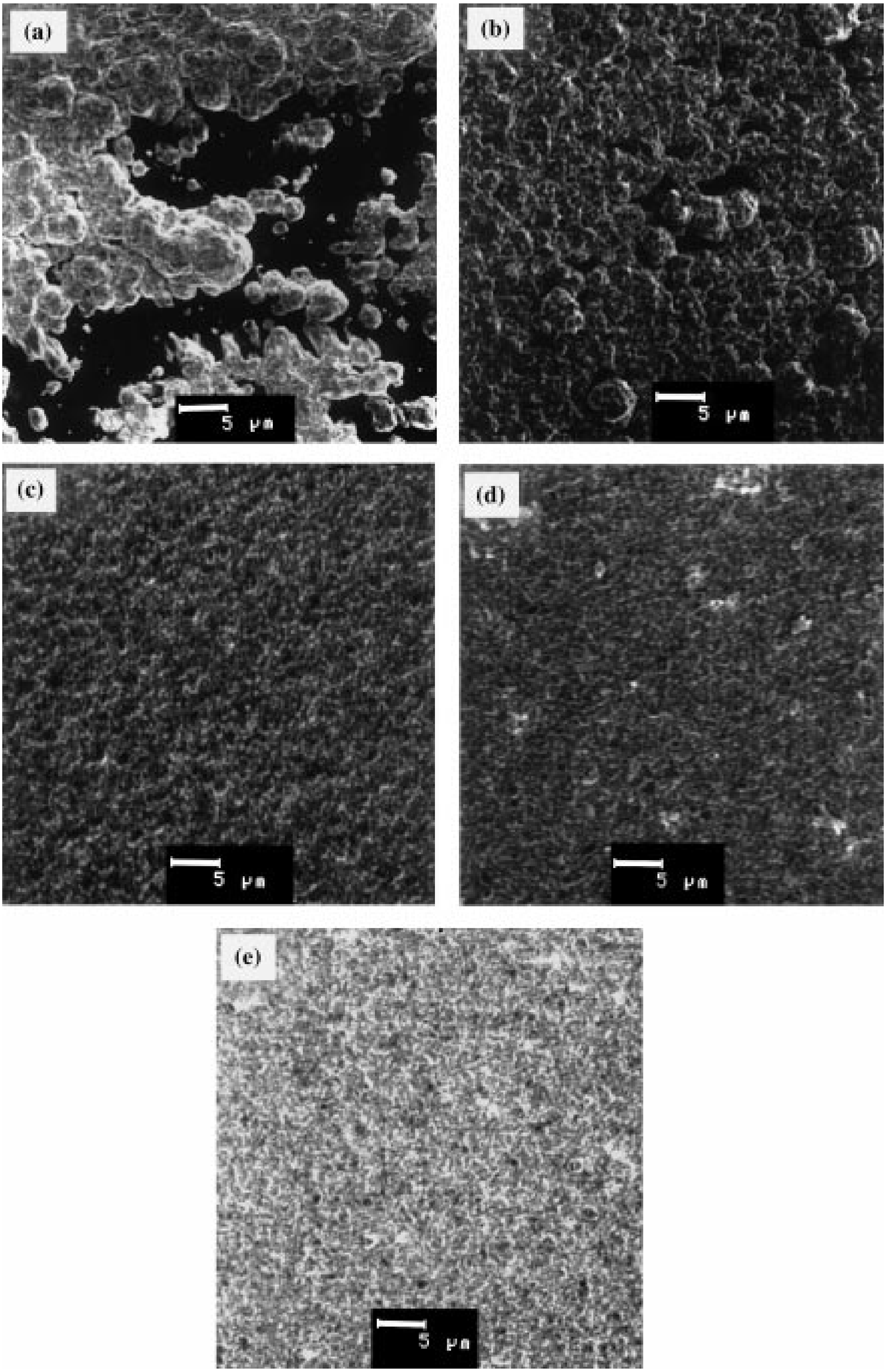


Fig. 9. Characteristic SEM image of Ag coating obtained on TiN in a one galvanostatic step mode from 0.22 M $AgNO_3$ + 2.5 M KSCN at current density 5 mA cm^{-2}; average thickness of deposit 1 μm.


(a)
5 μm
(b)
5 μm
(c)
5 μm
(d)
5 μm
(e)
5 μm

◄

Fig. 10. Effect of potential value for the seed layer deposition on TiN from 0.0011 M $AgNO_3$ + 2.5 M KSCN on the SEM images: (a) $E = -0.475$ V (deposition time 150 s); (b) $E = -0.7$ V (deposition time 135 s); (c) $E = -0.9$ V (deposition time 100 s); (d) $E = -1.4$ V (deposition time 75 s); (e) $E = -1.6$ V (deposition time 50 s). The bulk silver coatings (second step) were deposited under galvanostatic control from 0.22 M $AgNO_3$ + 2.5 M KSCN at current density 5 mA cm^{-2}; average thickness of deposit 1 μm.

step is more negative than −0.9 V. At this potential, the number density of growth centres is 3×10^6 cm^{-2}. However, the finest grains of silver films were obtained when the seed layers were deposited at −1.4, −1.6 V. In this case the growth centres are formed instantaneously.

Similar results were also obtained under galvanostatic conditions. For these conditions, current density values of 2–10 mA cm^{-2} for the seed layer deposition were applied to generate deposition potentials more negative than −1.4 V. The seed layers were formed within 50–150 s. The bulk silver film was then deposited as before, that is, galvanostatically in 0.22 M $AgNO_3$ + 2.5 M KSCN. An example of such a film is shown on Figure 11.

4. Conclusions

The results of the cathodic cyclic voltammetry of TiN in KSCN + $AgNO_3$ show that the nucleation process of silver on TiN undergoes three-dimensional electrocrystallization.

Theoretical analyses of the potentiostatic current transients show that the Ag nucleation process can be described by the models developed by Scharifker et al. Depending on the silver concentration in the solution and the applied potential, the nucleation process can be instantaneous, progressive, or mixed.

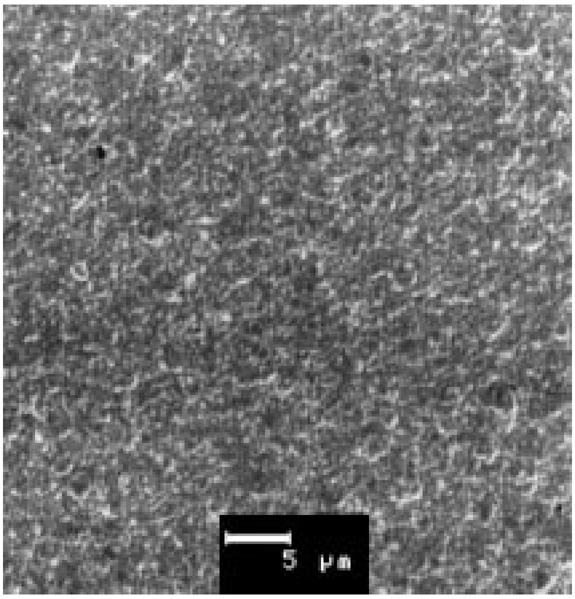


Fig. 11. SEM image of Ag deposit onto TiN. The seed layer was deposited for 100 s under galvanostatic control at current density 7 mA cm^{-2} in 0.0011 M $AgNO_3$ + 2.5 M KSCN. Then the bulk silver coating (second step) was deposited from 0.22 M $AgNO_3$ + 2.5 M KSCN at current density 5 mA cm^{-2}; average thickness 1 μm.

A continuous silver film, 40–100 nm thick, is formed on TiN within 50–100 s when the number density of growth centres is (3–5) $\times 10^6$ or higher. This is accomplished at potentials more negative than −0.9 V. At these potentials, the silver nucleation process can be described by the instantaneous nucleation model.

Applications of potential values more negative than −0.9 V for deposition of relatively thick Ag films (bulk silver) resulted in a powder deposit. This difficulty was overcome in a two-step deposition. Seed layers of silver were deposited in 0.011 M $AgNO_3$ + 2.5 M KSCN either under potentiostatic control, for example, −1.4 V, −1.6 V or galvanostatic control 2–10 mA cm^{-2} (the first step). Then, bulk silver films were deposited from the solution with higher concentration of Ag(I), for example, 0.22 M $AgNO_3$ + 2.5 M KSCN, at current density 5 mA cm^{-2} (the second step). In these two-step depositions, silver films of 1 μm in thickness were obtained. The SEM investigations showed high quality Ag films regardless of the experimental conditions for the seed layer deposition.

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