JOURNAL OF APPLIED ELECTROCHEMISTRY **11** (1981) 395–400

On the mechanism of electroless plating.
II. One mechanism for different reductants

J. E. A. M. VAN DEN MEERAKKER
Philips Research Laboratories, Eindhoven, The Netherlands

Received 22 September 1980

A mechanism is proposed for the reactions in electroless plating solutions with different reducing agents. The mechanism is based on the formation of atomic hydrogen during the oxidation of the reducing agents. The hydrogen atoms can either be oxidized or be desorbed as a gas. The mechanism accounts for both the electrochemical and the catalytic nature of the process.

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1. Introduction

Electroless deposition of metals is an electrochemical process under mixed potential control [1–5]. Experiments in which the anodic and the cathodic reactions take place in a cell with two compartments separated by a glass frit have confirmed the electrochemical nature [6–8].

The catalytic aspect of electroless processes is much less well understood. A characteristic aspect of the known electroless solutions is that they all use one of a small number of reducing agents (formaldehyde, hypophosphite, borohydride, hydrazine or dialkylamine borane). Another aspect is that hydrogen is evolved in almost all electroless reactions, albeit in different ratios with the rate of metal deposition.

Four different reaction mechanisms have been proposed to account for this hydrogen evolution (Table 1):

(a) the 'pure electrochemical' mechanism [8–11],
(b) the 'metal hydroxide' mechanism [12–14],
(c) the 'hydride ion' mechanism [15–17],
(d) the 'atomic hydrogen' mechanism [18–25].

Although all these mechanisms can explain most characteristics of the electroless solutions for which they were originally proposed, there is experimental evidence that none of them can be used to give a uniform description of electroless processes in general. Observations that the evolved hydrogen originates mainly from the reductant molecule [24–29] refute mechanism (a); the metal hydroxide mechanism cannot work in experiments in which the anodic and cathodic reactions take place in a cell with two compartments separated by a glass frit [6–8]; and, according to the last two mechanisms, hydrogen evolution should be at least equivalent to metal deposition, which is contrary to the observations of Pearlstein and Weightman [30] and Luneckas and Genutiene [31].

Nevertheless all electroless processes have so much in common that a uniform mechanism is very probable.

Table 1. Existing mechanisms

(a) *The 'pure electrochemical' mechanism [8–11]*
Anodic: $H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e$
Cathodic: $M^{n+} + ne \rightarrow M\downarrow$
$2H^+ + 2e \rightarrow H_2\uparrow$

(b) *The 'metal hydroxide' mechanism [12–14]*
$Ni(OH)_2 + H_2PO_2^- \rightarrow NiOH + H_2PO_3^- + H$
$NiOH + H_2PO_2^- \rightarrow Ni\downarrow + H_2PO_3^- + H$
$NiOH + H_2O \rightarrow Ni(OH)_2 + H$
$2H \rightarrow H_2\uparrow$

(c) *The 'hydride ion' mechanism [15–17]*
$2RH + 2OH^- \rightarrow 2ROH + 2H^-$
$M^{2+} + 2H^- \rightarrow [M + 2H] \rightarrow M\downarrow + H_2\uparrow$
$2H_2O + 2H^- \rightarrow 2H_2\uparrow + 2OH^-$
(RH is formaldehyde or hypophosphite)

(d) *The 'atomic hydrogen' mechanism [22–25]*
Anodic: $RH + OH^- \rightarrow ROH + H + e$
Cathodic: $M^{n+} + ne \rightarrow M\downarrow$
$H^+ + e \rightarrow H$
Recombination: $H + H \rightarrow H_2\uparrow$
(RH is formaldehyde, hypophosphite or borohydride)

0021–891X/81/030395–06$02.60/0

2. A uniform mechanism

The electroless process proceeds only on certain catalytic metals. These metals are known to be good hydrogenation–dehydrogenation catalysts. Poisons for hydrogenation–dehydrogenation reactions, such as thiourea and mercaptobenzothiazole, act as stabilizers in practically all electroless processes [32–35]. Another similarity between the various electroless solutions is the influence of pH on the reaction rate: a higher pH increases the deposition rate for solutions with hypophosphite [22, 36], hydrazine [37, 38], formaldehyde [39, 40] or dialkylamine borane [34, 41]. For solutions with borohydride as the reductant a reverse pH influence is observed, but this is caused by the acid-catalyzed hydrolysis of BH_4^- to BH_3OH^- [5, 41].

Studies of the anodic oxidation of hypophosphite [42], hydrazine [43] and formaldehyde [44] at a palladium membrane have shown that, when these reducing agents are oxidized at one side, hydrogen atoms diffuse through the membrane and can be oxidized at the other side. This means that these reductants are dehydrogenated at the palladium surface, and that atomic hydrogen is an intermediate in the anodic oxidation reaction. Other electrochemical measurements confirmed this for palladium as well as for other metals [45–47]. Also in the case of borohydride, dehydrogenation is found at the electrode surface during anodic oxidation [48, 49].

We propose that for all electroless plating solutions one mechanism must be valid, with the dehydrogenation of the reductant as the first step. In the 'atomic hydrogen' mechanism of Table 1 the recombination of hydrogen atoms must compete with their oxidation, as in the case of formaldehyde (see Part I of this paper).

Anodic

Dehydrogenation: $RH \xrightarrow{M} \dot{R} + \dot{H}$ (1)
Oxidation: $\dot{R} + OH^- \rightarrow ROH + e$ (2)
Recombination: $\dot{H} + \dot{H} \rightarrow H_2\uparrow$ (3)
Oxidation: $\dot{H} + OH^- \rightarrow H_2O + e$ (4)

Cathodic

Metal deposition: $M^{n+} + ne \rightarrow M\downarrow$ (5)
Hydrogen evolution: $2H_2O + 2e \rightarrow H_2\uparrow + 2OH^-$. (6)

The codeposition of phosphorus in most electroless solutions with hypophosphite as the reductant is a third cathodic reaction [50]. The codeposition of boron is probably also a cathodic process [51]. When hydrazine is the reductant ammonia can be produced cathodically [52]. The mechanisms for different reducing agents are summarized in Tables 2 and 3.

In acid media Reactions 4 and 6 become respectively:

$$\dot{H} \rightarrow H^+ + e \quad (4a)$$

$$2H^+ + 2e \rightarrow H_2\uparrow. \quad (6a)$$

2.1. *Dehydrogenation*

The dehydrogenation step determines the catalytic nature of the electroless processes. A metal that cannot start this first step for a certain reductant will be noncatalytic in electroless solutions with that reductant. This step also explains the high activation energies found for all electroless processes as the chemical bond R–H has to be broken (the values of Table 4 are high in comparison with the 6.5–7.5 kcal mol^{-1} found for solutions in which metal ions are reduced by reversible redox systems) [53].

The dehydrogenation step is slightly different in the case of dialkylamine boranes. According to Lelental [54] a dissociation into the free amine and a borane radical takes place, and this is facilitated by the metal surface.

The radicals $\dot{R}$ have also been proposed by others [46, 47, 55] as intermediates in the anodic oxidation of formaldehyde and hydrazine. Electron spin resonance measurements have shown that the corresponding radicals also participate in other reactions of borohydride and hypophosphite [56, 57].

2.2. *Oxidation of* $\dot{R}$

The oxidation of $\dot{R}$ via Reaction 2 yields the final product of the anodic process in the case of formaldehyde and hypophosphite: formate and phosphite respectively. For hydrazine, dialkylamine borane and borohydride the oxidation of $\dot{R}$ results in products which can themselves be dehydrogenated. For borohydride these products, BH_3OH^-, $BH_2(OH)_2^-$ and $BH(OH)_3^-$, are the same as those found in the acid-catalyzed hydrolysis [58].

Table 2. The anodic processes

	BOROHYDRIDE	DIALKYLAMINE BORANE	HYDRAZINE	FORMALDEHYDE	HYPOPHOSPHITE
1	$BH_4^- \xrightarrow{M} \dot{B}H_3^- + \dot{H}$				
2	$\dot{B}H_3^- + OH^- \longrightarrow BH_3OH^- + e$				
1	$BH_3OH^- \xrightarrow{M} \dot{B}H_2OH^- + \dot{H}$	$R_2NHBH_3 + OH^- \xrightarrow{M} R_2NH + \dot{B}H_2OH^- + \dot{H}$			
2	$\dot{B}H_2OH^- + OH^- \longrightarrow BH_2(OH)_2^- + e$	$\dot{B}H_2OH^- + OH^- \longrightarrow BH_2(OH)_2^- + e$			
1	$BH_2(OH)_2^- \xrightarrow{M} \dot{B}H(OH)_2^- + \dot{H}$	$BH_2(OH)_2^- \xrightarrow{M} \dot{B}H(OH)_2^- + \dot{H}$	$N_2H_4 \xrightarrow{M} \dot{N}_2H_3 + \dot{H}$		
2	$\dot{B}H(OH)_2^- + OH^- \longrightarrow BH(OH)_3^- + e$	$\dot{B}H(OH)_2^- + OH^- \longrightarrow BH(OH)_3^- + e$	$\dot{N}_2H_3 + OH^- \longrightarrow N_2H_3OH + e$		
				$HCHO + H_2O \rightleftharpoons CH_2(OH)_2$	
				$CH_2(OH)_2 + OH^- \rightleftharpoons CH_2OHO^- + H_2O$	
1	$BH(OH)_3^- \xrightarrow{M} \dot{B}(OH)_3^- + \dot{H}$	$BH(OH)_3^- \xrightarrow{M} \dot{B}(OH)_3^- + \dot{H}$	$N_2H_3OH \xrightarrow{M} \dot{N}_2H_2OH + \dot{H}$	$CH_2OHO^- \xrightarrow{M} \dot{C}HOHO^- + \dot{H}$	$H_2PO_2^- \xrightarrow{M} H\dot{P}O_2^- + \dot{H}$
2	$\dot{B}(OH)_3^- + OH^- \longrightarrow B(OH)_4^- + e$	$\dot{B}(OH)_3^- + OH^- \longrightarrow B(OH)_4^- + e$	$\dot{N}_2H_2OH + OH^- \longrightarrow N_2H_2(OH)_2 + e$	$\dot{C}HOHO^- + OH^- \longrightarrow CH(OH)_2O^- + e$	$H\dot{P}O_2^- + OH^- \longrightarrow H_2PO_3^- + e$
	$\upharpoonleft\downharpoonright$ $BO_2^- + 2H_2O$	$\upharpoonleft\downharpoonright$ $BO_2^- + 2H_2O$	$\downarrow$ $N_2\uparrow + 2H_2O$	$\downarrow$ $HCOO^- + H_2O$	
3	$\dot{H} + \dot{H} \longrightarrow H_2\uparrow$				
4	$\dot{H} + OH^- \longrightarrow H_2O + e$				
1+2+3	$BH_4^- + 4OH^- \longrightarrow$ $BO_2^- + 2H_2O + 2H_2\uparrow + 4e$	$2R_2NHBH_3 + 8OH^- \longrightarrow$ $2R_2NH + 2BO_2^- + 4H_2O + 3H_2\uparrow + 6e$	$N_2H_4 + 2OH^- \longrightarrow$ $N_2\uparrow + 2H_2O + H_2\uparrow + 2e$	$2HCHO + 4OH^- \longrightarrow$ $2HCOO^- + 2H_2O + H_2\uparrow + 2e$	$2H_2PO_2^- + 2OH^- \longrightarrow$ $2H_2PO_3^- + H_2\uparrow + 2e$
1+2+4	$BH_4^- + 8OH^- \longrightarrow$ $BO_2^- + 6H_2O + 8e$	$R_2NHBH_3 + 7OH^- \longrightarrow$ $R_2NH + BO_2^- + 5H_2O + 6e$	$N_2H_4 + 4OH^- \longrightarrow$ $N_2\uparrow + 4H_2O + 4e$	$HCHO + 3OH^- \longrightarrow$ $HCOO^- + 2H_2O + 2e$	$H_2PO_2^- + 2OH^- \longrightarrow$ $H_2PO_3^- + H_2O + 2e$

Table 3. The cathodic processes

Formaldehyde

$$M^{n+} + ne \rightarrow M\downarrow \qquad (5)$$

$$2H_2O + 2e \rightarrow H_2\uparrow + 2OH^- \qquad (6)$$

Hypophosphite

$$M^{n+} + ne \rightarrow M\downarrow \qquad (5)$$

$$2H_2O + 2e \rightarrow H_2\uparrow + 2OH^- \qquad (6)$$

$$H_2PO_2^- + e \rightarrow P\downarrow + 2OH^- \qquad (7)$$

Borohydride and dialkylamine borane

$$M^{n+} + ne \rightarrow M\downarrow \qquad (5)$$

$$2H_2O + 2e \rightarrow H_2\uparrow + 2OH^- \qquad (6)$$

$$B(OH)_4^- + 3e \rightarrow B\downarrow + 4OH^- \qquad (8)$$

Hydrazine

$$M^{n+} + ne \rightarrow M\downarrow \qquad (5)$$

$$2H_2O + 2e \rightarrow H_2\uparrow + 2OH^- \qquad (6)$$

$$N_2H_4 + 2H_2O + 2e \rightarrow 2NH_3\uparrow + 2OH^- \qquad (9)$$

According to Reaction 2 a higher pH must stimulate the anodic process. Studies of the anodic oxidation of borohydride [59], hydrazine [60] and formaldehyde [61, 62] have shown that a higher pH indeed results in higher anodic currents.

2.3. *Oxidation or recombination of* $\dot{H}$

Reactions 3 and 4 compete with each other at the metal surface. Which of the two really occurs is dependent on the properties of the metal, the pH of the solution and the mixed potential of the process. This competition influences the reducing agent efficiency of the process. This efficiency is defined as the theoretical amount of the reductant required to deposit one mole of metal divided by the actual amount consumed in the process. When Reaction 3 proceeds the overall anodic reaction is:

$$2RH + 2OH^- \rightarrow 2ROH + H_2\uparrow + 2e. \qquad (10)$$

Table 4. Activation energies of some electroless plating solutions

Plated metal	*Reductant*	*Activation energy* (kcal mol^{-1})	*Reference*
Cu	Formaldehyde	11.7	[63]
Ni–P	Hypophosphite	17.7	[19]
Ni–B	Dimethylamine borane	10.6–15.3	[64]
Au	Borohydride	19	[41]
Co	Hydrazine	15.9	[20]

Table 5. Reductant efficiencies of some electroless plating solutions

Reductant	*Plated metal*	*Efficiency* (%)	*Reference*
Formaldehyde	Cu	50	[17]
	Cu–Pt	79	[65]
Hypophosphite	Ni–P	6–45	[36]
	Ni–Re–P	52–59	[30]
	Pd	100	[31]
Borohydride	Ni–B	39	[24]
	Au	50–75	[66]
Dialkylamine borane	Ni–B	30–50	[67]
	Ni–W–B	63–78	[68]
Hydrazine	Pd	28–86	[69]

When Reaction 4 proceeds:

$$RH + 2OH^- \rightarrow ROH + H_2O + 2e. \qquad (11)$$

It is obvious that when the overall Reaction 10 proceeds the maximum efficiency can only be 50%.

In Part 1 we have shown that the percentage of Reaction 11 can be calculated, and we found that on copper only Reaction 10 occurs, while on platinum and palladium only Reaction 11 proceeds. On silver and gold both reactions can occur. This means that in electroless copper solutions the reductant efficiency cannot exceed 50%, while it is possible for the other metals. In the same way one can calculate that on nickel–phosphorus and nickel–boron only Reaction 10 will occur, while on rhenium and tungsten Reaction 11 will proceed. In Table 5 the reducing agent efficiencies of a number of electroless plating solutions are summarized. The values are taken from the cited references or calculated with the given data. It can be seen that an efficiency of more than 50% is only found for those metals on which Reaction 11 occurs.

3. Conclusions

The proposed mechanism explains the validity of the mixed potential theory and the catalytic nature and the high activation energy of electroless processes. It also accounts for the influence of pH on the deposition rate. Deuterium tracer experiments with different electroless solutions are in complete agreement with the mechanism. It also explains the fact that in electroless copper, nickel–

boron and nickel–phosphorus solutions a reducing agent efficiency of at most 50% is found, whereas this efficiency can exceed 50% when metals like platinum, rhenium and tungsten are codeposited. According to this mechanism an efficiency of 100% is possible, which is actually found in electroless palladium solutions under certain circumstances.

Acknowledgements

The author wishes to thank A. Molenaar and M. H. J. van Rijswick of these Research Laboratories for helpful discussions.

References

[1] M. Paunovic, *Plating* **55** (1968) 1161.
[2] A. V. Gorodyskii, I. A. Stepanova and A. I. Zayats, *Sov. Electrochem.* **9** (1973) 312.
[3] I. Ohno, *Surf. Technol.* **4** (1976) 515.
[4] H. Zeilmaker and E. Barendrecht, *Proc. 9th World Congress on Metal Finishing, Amsterdam* (October 1976).
[5] Y. Okinaka, *J. Electrochem. Soc.* **120** (1973) 739.
[6] A. E. Cahill, *Proc. Amer. Electroplating Soc.* **44** (1957) 130.
[7] S. M. El-Raghy and A. A. Abo-Salama, *J. Electrochem. Soc.* **126** (1979) 171.
[8] C. H. de Minjer, *Electrodeposition and Surf. Treatment* **3** (1975) 261.
[9] W. Machu and S. El-Gendi, *Metalloberfläche* **13** (1959) 97.
[10] J. Elze, *Metallogr.* **14** (1960) 104.
[11] K. Müller, *Metalloberfläche* **14** (1960) 65.
[12] P. L. Cavallotti and G. Salvago, *Electrochim. Metallogr.* **3** (1968) 239.
[13] G. Salvago and P. L. Cavallotti, *Plating* **59** (1972) 665.
[14] Z. Kovac and I. M. Croll, *Electrochem. Soc. Meeting, Montreal,* October (1968) Abstract No. 488.
[15] P. Hersch, *Trans. Inst. Metal Finishing* **33** (1955–6) 417.
[16] R. M. Lukes, *Plating* **51** (1964) 969.
[17] *Idem, ibid* **51** (1964) 1066.
[18] A. Brenner and G. E. Riddell, *J. Res. Nat. Bur. Standards* **37** (1946) 1.
[19] G. Gutzeit, *Plating* **46** (1959) 1158.
[20] D. J. Levy, *Proc. Amer. Electroplating Soc.* **50** (1963) 29.
[21] T. V. Ivanovskaya and K. M. Gorbunova, *Prot. Metals* **2** (1966) 393.
[22] A. A. Nikiforova and G. A. Sadakov, *Sov. Electrochem.* **3** (1967) 1076.
[23] F. M. Donahue, *Oberfläche* **13** (1972) 301.
[24] K. M. Gorbunova, M. V. Ivanov and V. P. Moiseev, *J. Electrochem. Soc.* **120** (1973) 613.
[25] K. A. Holbrook and P. J. Twist, *J. Chem. Soc.* A (1971) 890.
[26] W. Franke and J. Mönch, *Liebigs Ann. Chem.* **550** (1941) 1.
[27] A. A. Sutyagina, K. M. Gorbunova and M. P. Glazunov, *Russian J. Phys. Chem.* **37** (1963) 1096 and 1196.
[28] K. A. Holbrook and P. J. Twist, *J. Chem. Soc., Dalton* (1972) 1865.
[29] H. Hoyer, *Z. Naturforsch.* **4(a)** (1949) 335.
[30] F. Pearlstein and R. F. Weightman, *Electrochem. Technol.* **6** (1968) 427.
[31] A. Luneckas and I. Genutiene, *Liet. TSR, Moslu Akad. Darb., Ser. B* **4** (1975) 13.
[32] G. Gutzeit, *Plating* **47** (1960) 63.
[33] K. M. Gorbunova, M. V. Ivanov and A. A. Nikiforova, *Prot. Metals* **6** (1970) 470.
[34] F. Pearlstein and R. F. Weightman, *Plating* **61** (1974) 154.
[35] E. B. Saubestre, *ibid* **59** (1972) 563.
[36] J. P. Randin and H. E. Hintermann, *ibid* **54** (1967) 523.
[37] D. J. Levy, *Electrochem. Technol.* **1** (1963) 38.
[38] J. W. Dini and P. R. Coronado, *Plating* **54** (1967) 385.
[39] A. Molenaar, M. F. E. Holdrinet and L. K. H. van Beek, *ibid* **61** (1974) 238.
[40] J. Dumesic, J. A. Koutsky and T. W. Chapman, *J. Electrochem. Soc.* **121** (1974) 1405.
[41] Y. Okinaka, *Plating* **57** (1970) 914.
[42] S. Yu. Vereshchinskii, *Tr. Moskow Energy Inst.* **112** (1972) 93.
[43] N. V. Korovin and B. N. Yanchuk, *Sov. Electrochem.* **5** (1969) 1087.
[44] N. V. Korovin and B. N. Yanchuk, *ibid* **7** (1971) 354.
[45] S. Trasatti and A. Alberti, *J. Electroanal. Chem.* **12** (1966) 236.
[46] J. Heitbaum and W. Vielstich, *Electrochim Acta* **18** (1973) 501.
[47] R. P. Buck and L. R. Griffith, *J. Electrochem. Soc.* **109** (1962) 1005.
[48] J. P. Elder and A. Hickling, *Trans. Faraday Soc.* **58** (1962) 1852.
[49] J. P. Elder, *Electrochim. Acta* **7** (1962) 417.
[50] K. M. Gorbunova and A. A. Nikiforova, *Prot. Metals* **5** (1969) 163.
[51] M. Lelental, *J. Electrochem. Soc.* **120** (1973) 1650.
[52] V. S. Daniel'-Bek and T. N. Glazamova, *Sov. Electrochem.* **2** (1966) 1279.
[53] T. H. James, *J. Phys. Chem.* **66** (1962) 2416.
[54] M. Lelental, *J. Catalysis* **32** (1974) 429.
[55] G. V. Vitvitskaya and V. S. Daniel'-Bek, *Sov. Electrochem.* **3** (1967) 863.
[56] M. C. R. Symons, *Int. J. Radiation Phys. Chem.* **8** (1976) 381.
[57] J. R. Morton, *Molec. Phys.* **5** (1962) 217.
[58] K. N. Mochalov, V. S. Khain and G. G. Gilmanshin, *Proc. Acad. Sci., USSR* **162** (1965) 402.
[59] G. A. Sadakov, A. Ya. Ezikyan and F. I. Kukoz, *Sov. Electrochem.* **13** (1977) 1540.
[60] J. A. Harrison and Z. A. Khan, *J. Electroanal. Chem.* **26** (1970) 1.
[61] S. Sibille, J. Moiroux and J. C. Marot, *ibid* **88** (1978) 105.
[62] G. Prabhakara Rao, M. Usman and S. K. Rangarajan, *Electrochim. Acta* **22** (1977) 137.
[63] F. L. Shippey and F. M. Donahue, *Plating* **60**

(1973) 43.
[64] A. F. Schmeckenbecher, *ibid* 58 (1971) 905.
[65] J. E. A. M. van den Meerakker, unpublished results.
[66] E. A. Efimov, T. V. Gerish and I. G. Erusalimchik, *Prot. Metals* 12 (1976) 631.
[67] H. Niederprüm and H. G. Klein, *Metalloberfläche* 24 (1970) 468.
[68] G. O. Mallory and T. R. Horhn, *Plating* 66 (1979) 40.
[69] R. N. Rhoda, *J. Electrochem. Soc.* 108 (1961) 707.