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Effect of Anodic Mass Transfer in the Electro Winning of Copper in Presence of Organic Compounds

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The effect of anodic oxygen bubbles on the rate of mass transfer was studied by measuring the limiting current of deposition of copper from acidified $CuSO_4$ solution using parallel plate cell. Different factors studied as types of inhibitors, their concentration and temperatures. The organic additives used are cysteine, valine, alanine, phenylalanine, serine and threostine. The rate of mass transfer was found to decrease over the natural convection value by an amount ranging from 17.40-54.34 % depending on the types of additives and its concentration. Thermodynamic parameters were also given.

Key Words: Electrodeposition, Corrosion inhibition, Limiting current, Thermodynamic parameters, Amino acids.

INTRODUCTION

Copper is the metal of choice, replacing aluminum in integrated circuit interconnections[1]. This switch are emerged and simulated due to copper advantage characteristics, such as low resistively and high immunity to electro migration, which in turn results in greater circuit reliability and markedly higher clock frequency. Copper Dual Damascene technology includes two main electrochemical steps. First step is copper electrochemical deposition[2-7] (or copper electroplating) into trenches and vias. Second electrochemical step utilizes chemical mechanical polishing.

In electro winning of metals usually an insoluble anode is used where oxygen evolution takes place. Anodic oxygen evolution consumes a considerable portion of the electrical energy provided to the cell and also could adversely affect the performance of the cell by increasing the Ohmic drop[8-10] and distributing the uniformity of current distribution[11-14]. On the other hand, anodic oxygen bubbles were found to enhance the rate of mass transfer at the cathode[15-20] to the modest degree in vertical parallel electrode cells to a modest degree. In an attempt to maximize the electricians effect of counter electrode, gases bubbles, different cell designs were proposed where the working electrodes was placed up steams of the gas evolving counter electrode; an enhancement in the rate of mass transfer to 600 % over the natural convection values obtained. The object of the present work is to study the effect of different amino acids which are represented in Fig. 1 on the rate of electrodepositing of copper using cathode and lead as anode.

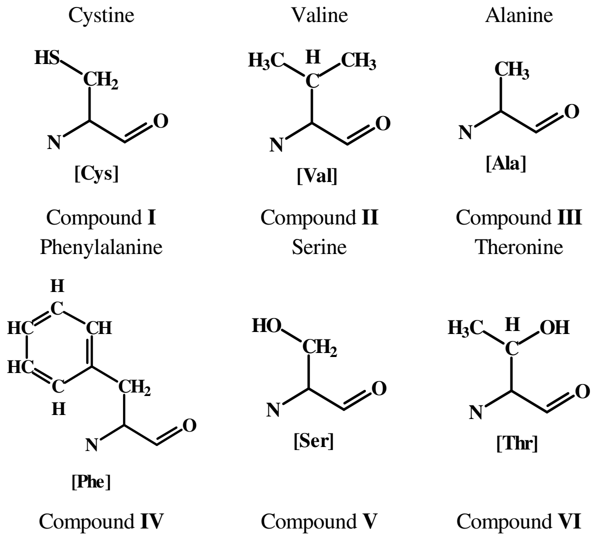

Fig. 1. Structures of amino acids

EXPERIMENTAL

The amino acids were AnalaR grade. Chemically pure H_2SO_4, analar copper sulphate, double distilled water were used to prepare 1.5 M H_2SO_4.

The cell and the circuit used in the present work are given in Fig. 2. It consisted of a rectangular plastic container having the dimensions 5.1 cm × 5 cm × 10 cm with electrodes covering the whole cross section. The cathode was a rectangular sheet of 10 cm height and 5 cm width of copper, the anode being

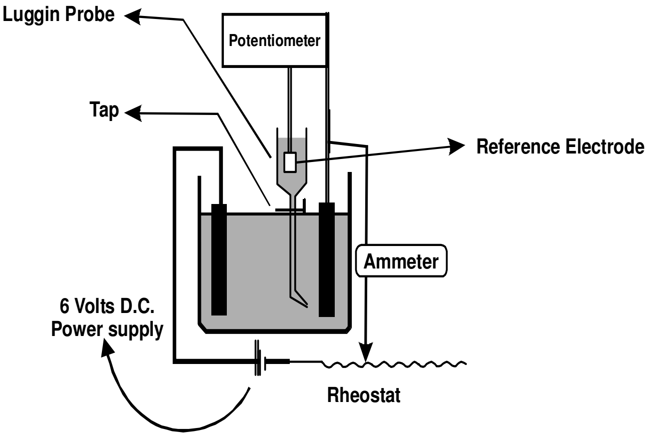

Fig. 2. Electrolytic cell and the electrical circuit

a lead sheet of similar dimensions and the electrode separation was 5 cm. The cell, placed in a 3 L plastic container having the electrolyte. The electrical circuit consisted of a 6 V d.c. power supply connected in a series with the cell and ammeter. A potentiometer is connected in parallel with the cell.

Polarization curves, (from which the limiting current was determined) was constructed by increasing the current stepwise and measuring the steady state cathode potential against a copper reference electrode placed in the cup of luuggin tube containing the solution of the cell.

The limiting current was measured potentially using a fresh solution with lead as anode. The galvanstatic and the potentiostatic methods have almost the same limiting current. Before electrolysis the cathode and anode were masked with epoxy resin except at the contact with the feed wires. Limiting current was measured for different copper sulphate solutions using pretreated electrodes. $CuSO_4$ concentrations corresponding to 0.10, 0.15, 0.20, 0.25, 0.30 and 0.40 M in 1.5 M H_2SO_4 were employed. Physical properties of the solutions (η, ρ, D) used to correlate the present data taken from the literatures. Each experiment was repeated twice using a fresh solution. Cu^{2+} concentration was estimated using iodometry.

RESULTS AND DISCUSSION

Fig. 3 shows a typical current-potential curve in presence and in absence of compounds at 25 °C. It is seen that the limiting current decreases with the increase of concentration of organic acids. Fig. 4 shows typical current-potential curves for different amino acids at constant concentration. It is seen that, the decrease in limiting current depend on the type of amino acids and its structure.

These polarization curves are served to determine the limiting current from which the mass transfer coefficient was calculated according to the equation:

$$K = \frac{I_l}{ZFC_b}$$

where K = mass transfer coefficient, I_l = limiting current densities under natural convection, Z = number of electrons involved in the reaction and C_b = initial concentration of copper ions.

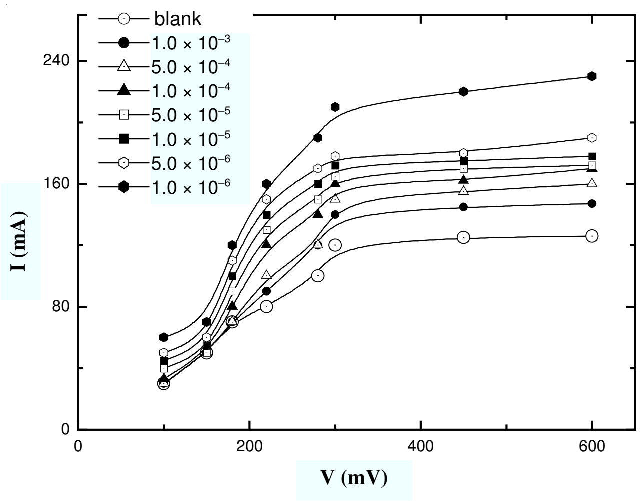

Fig. 3. Relation between I (mA) and V (mV) in presence of different concentration of valine

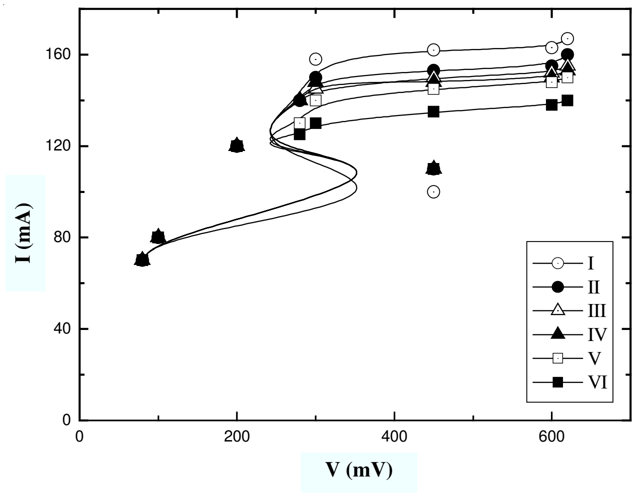

Fig. 4. Relation between I (mA) and V (mV) in presence of different organic compounds

Fig. 5 shows that in the absence of amino acids the blank data when we used lead anode fits well into equation which agrees with the earlier finding[21] derived from the hydrodynamic boundary layer theory:

$$J = 1.096(RE\cdot Fr)^{-0.176}$$

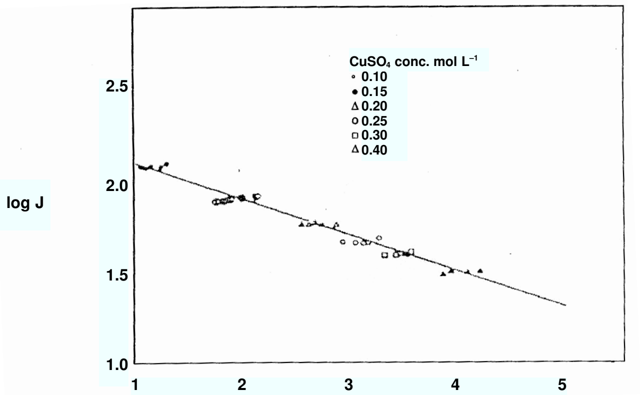

Fig. 5. Overall mass transfer correlation at vertical plates

The gas discharge velocity V used in calculating J, Re and Fr was calculated the equation:

$$V = \left(\frac{IRT}{4FP}\right)$$

Ahmed *et al.*[22] predicted that $K \propto V^{0.18}$ in absence of amino acids. But in presence of amino acids, the following relation well obtained $K \propto V^{n}$. Where b is constant depends on the amino acids. The values of constant b for various amino acids are given in Table-1.

TABLE-1
VALUES OF (b) FOR DIFFERENT AMINO ACIDS AT 25 °C USING LEAD ANODE

Amino acids	b	Amino acids	b
Valine	1.21	Theronine	1.25
Cysteine	1.22	Serine	1.26
Alanine	1.24	Phenylalanine	1.24

Plot log k against log V for different amino acids, gave a good straight line. Figs. 6 and 7 are the example for this relation when we used cysteine and valine as example.

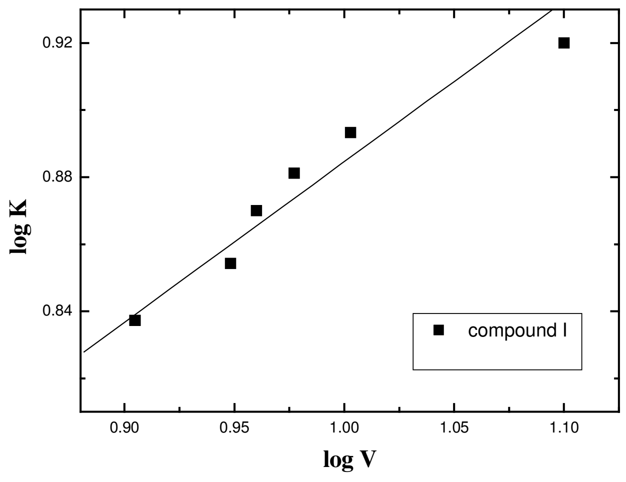

Fig. 6. Relation between log K and log V at 25 °C for cystine

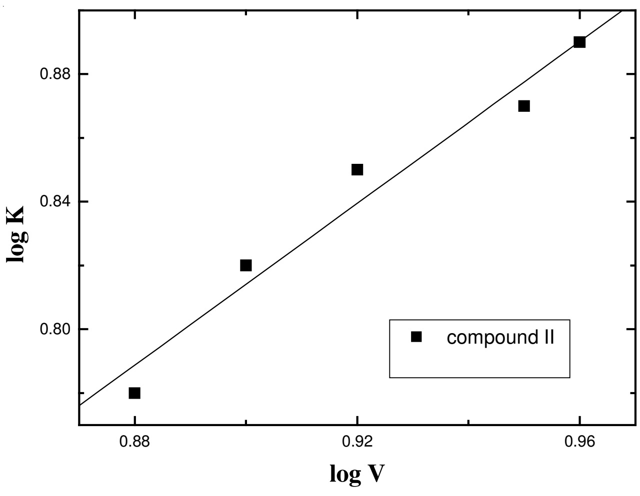

Fig. 7. Relation between log K and log V at 25 °C for valine

Table-2 shows that as we added small amount of amino acids, the rate of deposition as well as discharge velocity decreases.

TABLE-2
EFFECT OF TEMPERATURE ON THE LIMITING CURRENT IN PRESENCE OF COMPOUNDS (**I-VI**)

Organic compounds	Conc. 10^6	25 (°C)	30 (°C)	35 (°C)	40 (°C)
Blank	0	230	240	255	270
Cystine (compound **I**)	1	190	210	225	245
	5	175	190	210	225
	10	172	180	195	210
	50	170	172	180	195
	100	166	170	176	183
	500	147	160	170	178
	1000	126	145	160	170
Valine (compound **II**)	1	155	163	168	175
	5	147	155	165	170
	10	145	147	155	160
	50	133	142	150	158
	100	126	133	140	150
	500	120	126	132	140
	1000	110	120	128	135
Alanine (compound **III**)	1	170	178	190	200
	5	160	170	180	196
	10	150	160	170	180
	50	140	150	160	170
	100	130	140	150	160
	500	125	132	140	150
	1000	120	125	130	140
Phenylalanine (compound **IV**)	1	165	175	183	193
	5	158	165	173	180
	10	149	155	160	170
	50	140	148	155	160
	100	135	140	147	155
	500	130	135	140	147
	1000	128	130	135	140
Serine (compound **V**)	1	140	145	150	160
	5	135	140	145	150
	10	130	135	140	145
	50	125	130	135	140
	100	120	125	130	136
	500	110	115	122	130
	1000	105	110	117	122
Theronine (compound **VI**)	1	165	175	183	193
	5	158	165	173	180
	10	149	155	160	170
	50	140	148	155	160
	100	135	140	147	155
	500	130	135	140	147
	1000	128	130	135	140

Effect of amino acids on the limiting current: If the limiting current in absence of organic compounds (I_b) and in presence of organic compounds (I), the percentage inhibition can be calculated from the equation:

$$\text{Inhibition } (\%) = \left(\frac{(I_b - I)}{I_b}\right) \times 100$$

Table-3 shows the relation between percentage inhibition and concentration of amino acids at 25 °C.

Fig. 8 shows that the percentage inhibition caused by amino acids ranges from 17.40-54.34 % depending on the type of amino acids and their concentration. The order of decreasing the limiting current is as follows: cysteine > alanine > phenylalanine > theronine > valine > serine.

TABLE-3
RELATION BETWEEN (%) INHIBITION AND CONCENTRATION OF AMINO ACIDS AT 25 °C

10^6 Conc. (mol L^{-1})	I_l (mA)	Inhibition (%)
Cystine (compound **I**)		
1	190	17.40
5	175	23.90
10	172	25.22
50	170	26.01
100	166	27.03
500	147	30.10
1000	126	45.21
Valine (compound **II**)		
1	155	32.6
5	147	36.10
10	145	37.10
50	133	42.17
100	126	45.10
500	120	47.82
1000	110	52.17
Alanine (compound **III**)		
1	170	26.01
5	160	30.43
10	150	34.78
50	140	39.13
100	130	43.47
500	125	45.10
1000	120	47.82
Phenylalanine (compound **IV**)		
1	165	29.20
5	158	32.17
10	149	34.10
50	140	39.13
100	135	41.30
500	130	43.47
1000	128	44.34
Serine (compound **V**)		
1	140	39.13
5	135	41.30
10	130	43.47
50	125	45.11
100	120	47.82
500	110	52.17
1000	105	54.34
Theronine (compound **VI**)		
1	165	29.20
5	158	32.17
10	149	34.10
50	140	39.13
100	135	41.30
500	130	43.47
1000	128	44.34

The decrease in mass transfer coefficient as well as discharge velocity is attributed to: (1) Adsorption of organic substance on the cathode surface where they screen a part of cathode[23] thus is reducing the active cathode area with consequent reduction in the limiting current. (2) The adsorbed organic substance increases the local solution viscosity at the cathode surface with consequent decrease in the diffusivity of copper ions, resulting in a decrease of the mass transfer coefficient k and the limiting current $k = \frac{D}{\delta}$. (3) The adsorbed substances molecules hinder the natural convection flow arising from the density difference between the bulk solution and the electrode surface. This effect arises as a result of the fact that one end of organic molecules is attached to the electrode while the other end is attached to the solution. (4) The organic substance decrease the velocity[24-26] coalescence of O_2 bubbles evaluated at the lead anode with a consequent decrease in their ability to enhance the rate of mass transfer at cathode[27].

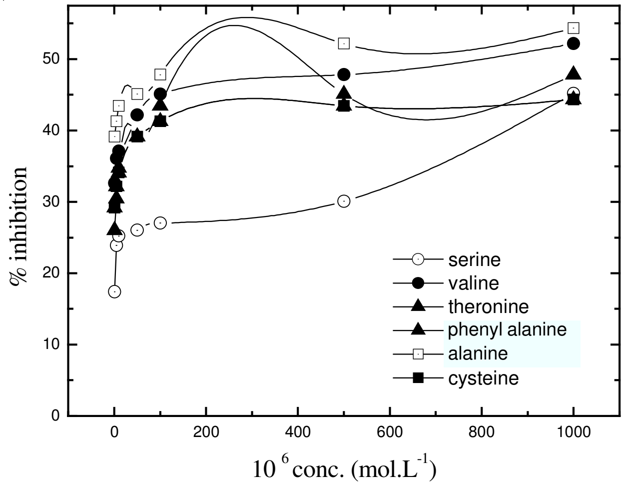

Fig. 8. Relation between percentage inhibition and concentration for amino acids at 25 °C

Thermodynamic treatment of the reaction: From the integrated form of Arrhenius equation:

$$\ln(I) = \frac{-E}{RT} + \ln(A)$$

where R = gas constant, E = activation energy and A = frequency factor. The values of E are given in Table-3. But the values for enthalpy of activation, $\Delta H^{\#}$, entropy of activation $\Delta S^{\#}$ and free energy of activation $\Delta G^{\#}$, can be obtained by using the following equations:

$$\Delta H^{\#} = Ea - RT$$

$$\frac{\Delta S^{\#}}{R} = \ln A - \ln\left(\frac{\alpha Te}{h}\right)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

where α = Boltzmann constant, e = 2.718 and h = Plank's constant.

Although the change in the free energy of activation, $\Delta G^{\#}$ with the amino acids concentration for all used acids is only small, Table-4 and variation occur in the enthalpy of activation $\Delta H^{\#}$ and entropy of activation $\Delta S^{\#}$ with acid concentration where in all these cases $\Delta H^{\#}$ and $\Delta S^{\#}$ compensate each other to produce little changes in $\Delta G^{\#}$.

However all the values of $\Delta S^{\#}$ are highly negative values, indicating a more ordered system and non-random distribution of amino acids in the electrode these values are independent on the type of amino acids and the number of subsistent present in each compound.

In general, it is found that the values of Ea and $\Delta H^{\#}$ decrease as the amino acids concentration decrease as shown in Table-4 which maybe attributed to that the amino acids increase the local solution viscosity at the copper surface with a consequent decrease in the diffusivity of Cu^{2+} ion, the amino acids molecules decrease the natural convection flow arising

TABLE 4
ACTIVATION ENERGIES AND THERMODYNAMIC PARAMETERS FOR AMINO ACIDS

10^6 conc.	1	5	10	50	100	500	1000
Blank solution							
Ea	8.407 ± 0.504						
$\Delta H^{\#}$	5.928 ± 0.504						
$\Delta S^{\#}$	-1790.86 ± 1.65						
$\Delta G^{\#}$	59.554 ± 0.997						
Phenylalanine (compound **IV**)							
Ea	12.92 ± 0.567	13.27 ± 0.570	10.52 ± 0.926	7.06 ± 1.75	5.07 ± 0.431	9.87 ± 0.855	15.52 ± 1.79
$\Delta H^{\#}$	10.44 ±0.567	10.79 ± 0.570	8.07 ± 0.926	4.58 ± 1.75	2.59 ± 0.431	7.39 ± 0.855	13.04 ± 1.79
$\Delta S^{\#}$	-166.22 ± 1.85	-165.20 ± 3.03	-175.2 ± 3.03	-186.98 ± 5.7	-193.74 ± 1.4	-178.52 ± 2.8	-160.8 ± 5.89
$\Delta G^{\#}$	60.00 ± 1.120	60.28 ± 1.83	60.28 ± 1.83	60.33 ± 3.46	60.35 ± 0.852	60.62 ± 1.69	60.98 ± 3.55
Valine (compound **II**)							
Ea	6.13 ± 0.377	7.75 ± 0.673	5.40 ± 0.831	8.88 ± 0.245	8.91 ± 0.510	7.900 ± 0.365	10.56 ± 0.730
$\Delta H^{\#}$	3.64 ± 0.377	5.27 ± 0.673	2.92 ± 0.831	6.40 ± 0.245	6.43 ± 0.510	5.421 ± 0.365	80.81 ± 0.730
$\Delta S^{\#}$	-190.7 ± 1.23	-185 .7 ± 2.2	-193.8 ± 2.72	-182.75 ± 0.833	-183.14 ± 1.67	-186.0 ± 1.19	-178.66 ± 0.238
$\Delta G^{\#}$	60.51 ± 0.745	60.64 ± 1.33	60.70 ± 1.64	60.89 ± 0.503	61.04 ± 1.008	61.15 ± 0.721	61.35 ± 1.144
Theronine (compound **VI**)							
Ea	8.58 ± 0.426	8.89 ± 0.069	9.44 ± 0.083	10.05 ± 0.101	10.75 ± 0.124	9.39 ± 0.457	7.77 ± 0.982
$\Delta H^{\#}$	6.102 ± 0.426	6.419 ± 0.069	6.965 ± 0.083	7.57 ± 0.101	8.274 ± 0.124	6.921 ± 0.457	5.29 ± 0.982
$\Delta S^{\#}$	-181.77 ± 1.39	-181.17 ± 0.226	-179.88 ±0.2746	-178.42 ± 0.332	-176.6 ± 0.406	-181.59 ± 1.49	-187.41 ± 3.21
$\Delta G^{\#}$	60.30 ± 0.842	60.43 ± 1.36	60.597 ± 0.165	60.95 ± 0.200	60.95 ± 0.245	61.06 ± 0.904	61.17 ± 1.94
Alanine (compound **III**)							
Ea	7.99 ± 0.253	6.81 ± 0.130	6.62 ± 0.711	6.947 ± 0.516	7.189 ± 0.491	6.28 ± 0.386	4.751 ± 0.618
$\Delta H^{\#}$	5.51 ± 0.253	4.33 ± 0.130	4.14 ± 0.711	4.469 ± 0.516	4.71 ± 0.491	3.807 ± 0.368	2.27 ± 0.618
$\Delta S^{\#}$	-183.94 ± 0.831	-188.28 ± 0.427	-189.44 ± 2.33	-188.79 ± 1.69	-188.37 ± 1.6	-191.69 ± 1.2	-197.00 ± 2.02
$\Delta G^{\#}$	60.36 ± 0.501	60.47 ± 0.258	60.62 ± 1.406	60.75 ± 1.019	60.87 ± 0.970	60.96 ± 0.728	61.00 ± 1.22

Ea (Kj/mol), $\Delta H^{\#}$ (Kj/mol), $\Delta S^{\#}$ (J K^{-1} mol^{-1}) and $\Delta G^{\#}$ (Kj/mol).

from the density difference between the bulk solution and the solution at the electrode surface due to repulsion force between Cu^{2+} and NH_4^+ group of the amino acid leading to decrease the rate of deposition.

Conclusion

The electrode processes on copper in acidified $CuSO_4$ were finding to depend on the amino acids as well as their concentrations. They also depend on the type of the cathode and temperature. The activation energy proves that the reaction is diffusion controlled. The overall mass transfer correlation proves that the electroplating reaction is natural convection, which is in accordance with our previous studies.

List of symbols

I_l : the limiting current density, A cm^{-2}
K : the mass transfer coefficient, cm s^{-1}
z or n : the number of the transferred electrons = 2 in case of Cu^{2+} ions
F : Faraday's constant = 96485 A s mol^{-1}
j : the mass transfer rate, mol cm^{-2} s^{-1}
C_o or C_b : is the bulk concentration, mol cm^{-3}
U : the electrode peripheric velocity or characteristic flow velocity, cm s^{-1}, U = ωr, cm rad s^{-1}
ω : the angular velocity, rad s^{-1}
r : the radial distance, cm
Fr : Froude number, $Fr = V^2/hg$
V : the oxygen gas discharge velocity, cm s^{-1}
h : the electrode height, cm
g : the acceleration gravity, cm s^{-2}
ΔH^* : the enthalpy of activation, kJ mol^{-1}
ΔS^* : is the entropy of activation, J mol^{-1} K^{-1}
ΔG^* : the net free-energy change, kJ mol^{-1}
R : the universal gas constant = 8.314 J mol^{-1} K^{-1}
T : the absolute temperature, K
Ea : the activation energy, kJ mol^{-1}
A : the Arrhenius constant
B : Boltzmann constant
h : Blank's constant
P : pressure atmosphere
Re : Reynolds number, Re = Ud/ν
ν : the kinematic viscosity, cm^2 s^{-1}

REFERENCES

1. S.P. Muraka, I.V. Verner, R.J. Gutman, Copper-Fundamentals Mechanisms for Microelectronic Applications, John Wiley & Sons. Inc., N.Y., p. 337 (2000).
2. A.S. Sethuraman, J.F. Wang and L.M. Cook, *J. Electron. Mater.*, **25**, 1617 (1996).
3. G.B. Shinn,V. Korthuis, A.M. Wilson, in eds.: Y. Nishi and R. Doering, Chemical-Mechanical Polishing, Handbook of Semiconductor Manufacturing Technology, Marcel Dekker, Inc., New York, p. 415 (2000).
4. S.H. Li and R. Miller, Chemical Mechanical Polishing in Silicon Processing, Semiconductor and Seminals, Academic Press, New York, Vol. 63 (2000).
5. P.B. Zantya, A. Kumar and A.K. Sikder, *Mater. Sci. Eng.: R*, **45**, 89 (2005).
6. J.M. Steigerwald, S.P. Muraka and R.J. Gutman, Chemical Mechanical Pilnarization of Microelectronic Materials, John Wiley & Sons, Inc., New York (1997).
7. C.L. Borst, W.N. Gill and R.J. Gutmann, Chemical-Mechanical Polishing of Low Dielectric Constant Polymers and Organosilicate Glass, (2002).
8. H. Hine and K. Murakami, *J. Electrochem. Soc.*, **129**, 292 (1980).
9. H. Vogt, *Electrochem. Acta*, **263**, 1311 (1981).

10. S. Sides and C.W. Tobias, *J. Electrochem. Soc.*, **129**, 2715 (1982).
11. C.W. Tobias, *J. Electrochem. Soc.*, **106**, 833 (1959).
12. J.E. Funk and J.F. Thorpe, *J. Electrochem. Soc.*, **116**, 48 (1969).
13. P.A. Damma, *J. Electrochem. Soc.*, **121**, 567 (1974).
14. S. Mohanta and T.Z. Fahidy, *J. Appl. Electrochem.*, **7**, 235 (1977).
15. V.A. Eltel, B.V. Tilak and A.S. Gendron, *J. Electrochem. Soc.*, **121**, 867 (1974).
16. L. Sigtist, O. Dossenbach and N. Ibel, *Int. J. Heat Mass Transfer*, **22**, 1343 (1979).
17. M.G. Fouad, F.N. Zein and M.I. Ismail, *Electrochim. Acta*, **16**, 1477 (1971).
18. G.H. Sedahmed, S.S. Iskander, L.A.S. Mansour and M.A. Fawzy, *Surface Tech.*, **11**, 67 (1980).
19. A.M. Ahmed and H.M. Faid-Allah, *Bull. Electrochem.*, **3**, 255 (1987).
20. A.-M.M. Ahmed, A.A.-H. Abdel-Rahman and A.F. El-Adl, *J. Disp. Sci. Technol.*, **31**, 343 (2010).
21. M. Eisenberg, C.W Tobias and C.R. Wilk, *J. Electrochem. Soc.*, **103**, 423 (1959).
22. A.M. Ahmed, E.A. Hamed, A.A. El Bardan and E.F. Saad, *Alex. Eng. J. Univ.*, **26**, 578 (1989).
23. C.R. Wilk, M. Eisenberg and C.W. Tobias, *J. Electrochem. Soc.*, **100**, 513 (1953).
24. G.H. Sedahmed, *J. Appl. Electrochem.*, **17**, 746 (1987).
25. L.J.J. Jansen and J.G. Hoogland, *Electrochim. Acta*, **18**, 543 (1973).
26. H. Brandt, M. Fisher and K. Schwabe, *Corros. Sci.*, **10**, 631 (1970).
27. J.E.N. Thomas, Proc. 5th Eur. Symp On Corrosion Inhibitors, Ferrara, Annale University of Ferrara, p. 452 (1981).