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Electroless copper deposition: An Experimental and Theoretical approach

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Abstract: It is found on many occasions that the stability of electroless copper with formaldehyde as the reducing agent is vulnerable and so for a viable industrial process high stable plating bath is a subject of practical interest. In the present investigation, thiourea and few of its derivatives were used as stabilizers. The role of action of these compounds on the rate of electroless copper plating has been studied by weight gain, anodic & cathodic polarization and A.C impedance methods. The calculations of global reactivity indices of the additives such as the localization of frontier molecular orbital's, E_{HOMO}, E_{LUMO}, energy gap (ΔE) and dipole moment (μ) were used to substantiate the effective adsorption of the compounds on metal surface being responsible for stability of the bath.

Keywords: electroless, stability, impedance, quantum.

1. Introduction

Thiourea and its derivatives are some of the effective ingredients widely used in plating, battery electrolyte and pickling baths [1-4]. Cobley et al.[5] and Larson et al.[6] detailed reviews on electroless copper plating process with various parameters influencing the rate of deposition. Zhu[7], Schneider and their co-researchers[8] investigated the electroless copper plating process using sulphur compounds as additives and found that the compounds enhanced the plating rate. Wei et al.[9] found that use of special complexing agents could stabilize electroless cobalt-tungsten plating process. A decorative copper plating process was developed by Yuan[10] and his team members. The careful study of literature reveals that very few reports are available for thiourea, as additives for electroless copper plating process. The performance of thioureas Viz., N-methyl, N,N' ethylene and allyl thiourea as additives is still unexplored experimentally. The present study involves the role of action thiourea derivatives and the performances of the compounds on the rate of electroless copper plating have been investigated through chemical and electrochemical methods.

Experimental details

The following compounds of A.R grade were used as additives in the present study

1. N-Allyl thiourea - Merck (Germany)
2. N-Methyl thiourea - Kochlight Laboratories (England)
3. N,N' ethylene thiourea - Merck (Germany)

The bath used in the present study had the following composition.

Copper as methane sulphonate	-	3g/l
Di sodium salt EDTA	-	20 g/l
Para formaldehyde	-	10 g/l
pH	-	12.5-13
Temperature	-	28±2°C
Thiourea derivatives	-	0.1ppm, 0.5ppm, 1ppm

Experiments were performed with various additives in the concentration ranges of 0.1 ppm, 0.5 ppm and 1 ppm.. Each experiment was repeated minimum three times to get reproducible results. The rate of deposition was a calculated using the following formula.

$$\text{Rate of deposition } (\mu\ hr^{-1}) = W \times 60 \times 10^4 / DAt, \qquad (1)$$

where W = weight of the deposit (g); D = density of the deposit (g cm^{-3}); t = plating duration (min);
A = surface area of the specimen (cm^2).Mild steel specimens of compositions, C = 0.08%, P = 0.07%, Si = O%, S = 0%, Mn = 0.41% and Fe remainder, and of size 4 x 1 x 0.020 cm were used for weight gain measurements.

The polarisation studies were carried out using 1cm^2 area of electrolessly copper coated specimens as the working electrodes[11-13]. The measurement was made with BAS –100A, Electrochemical analyzer. The auxiliary electrode and the reference electrode used were of platinum plate of 4cm^2 area and saturated calomel electrode respectively. A constant quantity of 200ml of bath solution was taken in a 250ml beaker. No agitation was provided. In order to understand the effectiveness of the compounds on the stability of the bath, anodic and cathodic polarisation measurements were carried out both in the presence and absence of copper ion and paraformaldehyde in the potential range of ±300mV from the OCP under the plating condition. Quantum calculations were carried using Gaussian 03 software package. The energy of highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and Dipole moment (µ) were calculated with the above given software package.

3. Results and discussion

3.1 Weight gain studies

The results of weight gain studies for the electroless copper plating in the presence and absence of thiourea derivatives are given in table 1. NMTU stabilzes better than ATU and ETU.This can be ascribed to the presence of $-CH_3$ group in NMTU which shows +I effect greater than ATU. The presence of closed ring structure in ETU has not facilitated the adsorption of the compound on metal surface being responsible for stabilization of plating bath. The order of performance of the compounds is given below: NMTU> ATU > ETU.

Table 1. Weight gain studies of electroless copper plating

Stabilizers	**Rate of deposition (µm/hr)**		
Plain bath	**3.2**		
Concentration	**0.1 ppm**	**0.5 ppm**	**1 ppm**
NMTU	2.2	1.9	1.2
ATU	2.3	2.1	1.9
ETU	3.5	4.7	5.3

3.2 Anodic polarization measurements

Anodic polarization was carried out over a wide range of potential for the plain bath (with out additive) and with various additives with concentrations as mentioned above have been added to the bath. The working electrode is 1cm^2 area of copper electrode at a fixed scan rate of 10mV/s. The results are shown in figures 1-3. For each stabilizers and accelerators the polarization was carried out for three different concentrations. The oxidation current of p-formaldehyde is found to decrease with increase in concentration of Thiourea derivatives and also it is less than the plain bath. It is evident that these compounds inhibit the oxidation reaction even at 0.1ppm.It is envisaged that the oxidation currents of the compounds are higher than the plain bath, but it decreases as the concentration increases. As the oxidation current is higher than the plain bath, the compounds accelerate the reaction as well as stabilize the bath. Upon increasing the concentration, oxidation current is decreased taking the role of stabilizers. Hence the compounds may be classified as accelerator -stabilizer class.

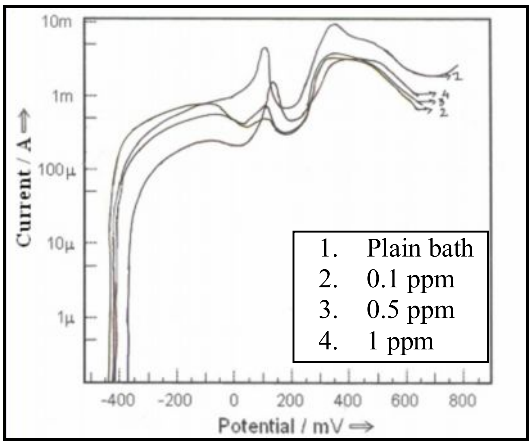

Figure 1. Anodic polarization curves of electroless copper bath in the presence of N-MeTU

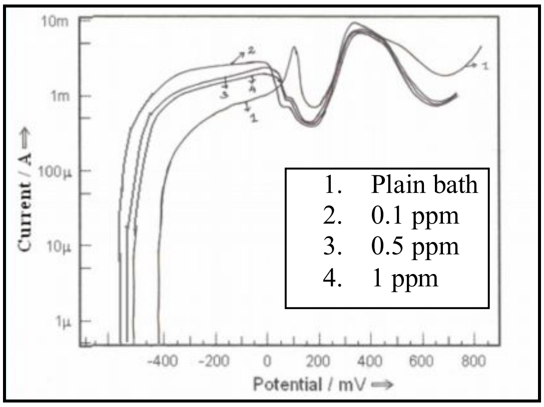

Figure 2. Anodic polarization curves of electroless copper bath in the presence of N,N'-ethylene thiourea

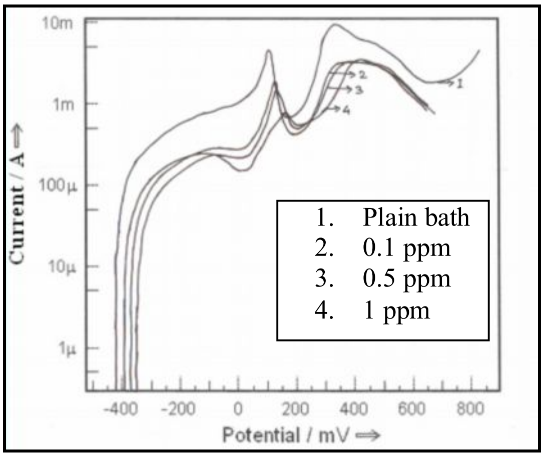

Figure 3. Anodic polarization curves of electroless copper bath in the presence of N-Allyl thiourea

3.3 Cathodic polarization studies

Cathodic partial polarization was carried out to find the role of additives (accelerators / stabilizers) on the reduction of Cu^{2+} ions. Figure 4-6 indicated the cathodic plots carried out using the bath-containing thiourea derivatives devoid of reducing agent. The compounds have not favored the reduction of Cu^{2+} ions directly in the absence of formaldehyde. A similar observation has been made by Han et al [14] for the electroless deposition of nickel.

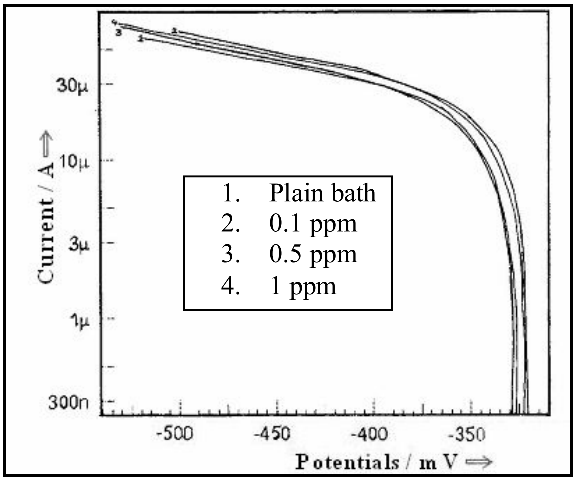

Figure 4.Cathodic polarization curves of electroless copper bath with NMTU

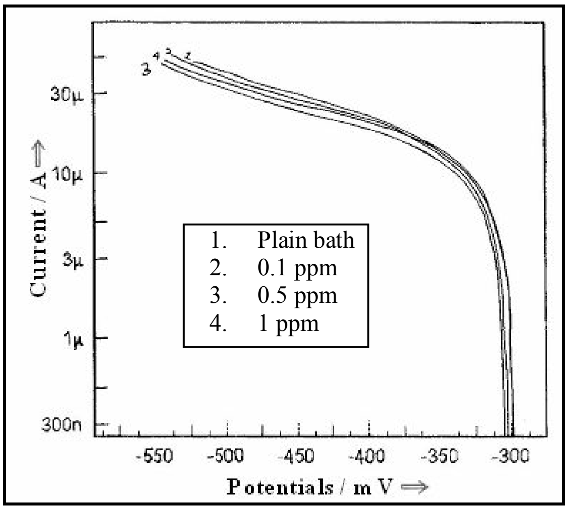

Figure 5. Cathodic polarization curves of electroless copper bath in the presence of ATU

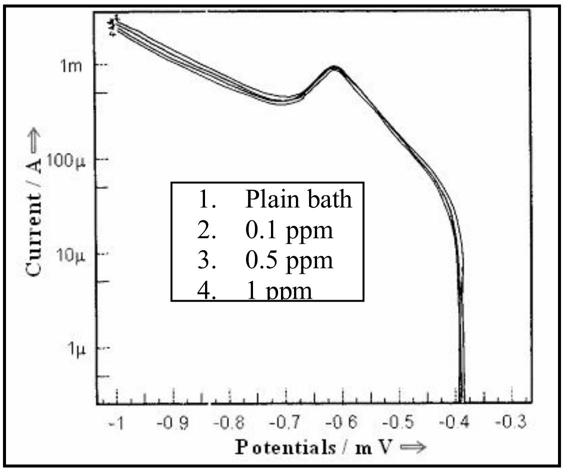

Figure 6. Cathodic polarization curves of electroless copper bath in the presence of ethylene thiourea

3.4 Impedance studies

Nyquist data for electroless plating of copper in the presence and absence of thio compounds are presented in Table 2. The charge transfer resistance value is very less for the bath demonstrated that the solution is highly conducting due to presence of methane sulphonate ions. R_t values are enhanced as compared with plain bath for ATU and NMTU indicate that these compounds hinder the reduction of Cu^{2+} . In the case of ETU (at 1ppm), R_t values are fetched down and C_{dl} values are enhanced due to the acceleration of Cu^{2+} reduction process[15-18]. These results were in good agreement with weight gain results.

Table 2: Values of charge transfer resistance and double layer capacitance obtained from the impedance measurements of electroless copper formaldehyde bath in the without and with stabilizers (1ppm)

Stabilizer	R_t (ohm/cm^2)	$C_{dl\ x\ 10^{-4}}$ (F/cm^2)
Plain bath	7.119	7.6
ATU	8.108	17
NMTU	5.758	5.28
ETU	5.566	10.45

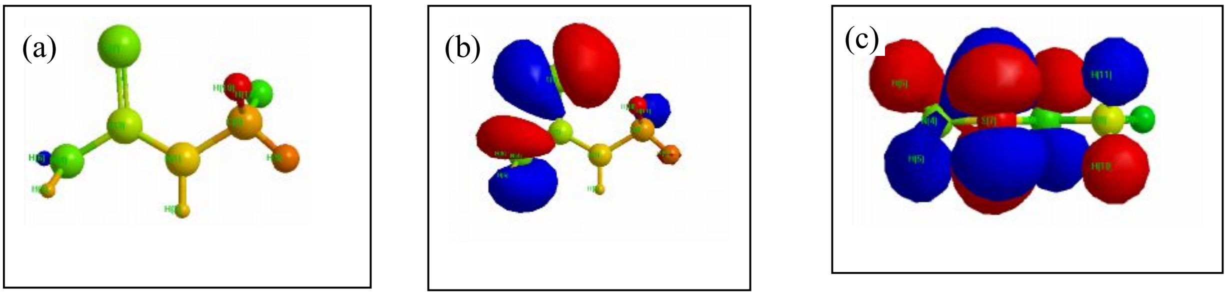

Figure 7 (a) optimized structure of NMTU (b) HOMO of NMTU (c) LUMO of NMTU

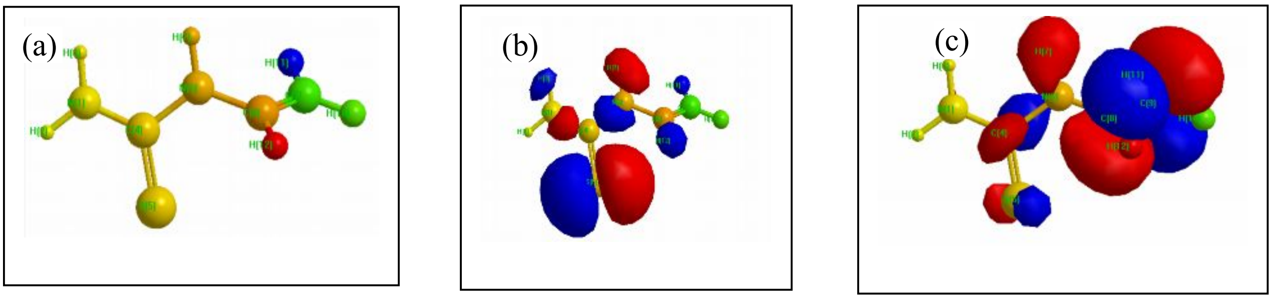

Figure 8 (a) optimized structure of ATU (b) HOMO of ATU (c) LUMO of ATU

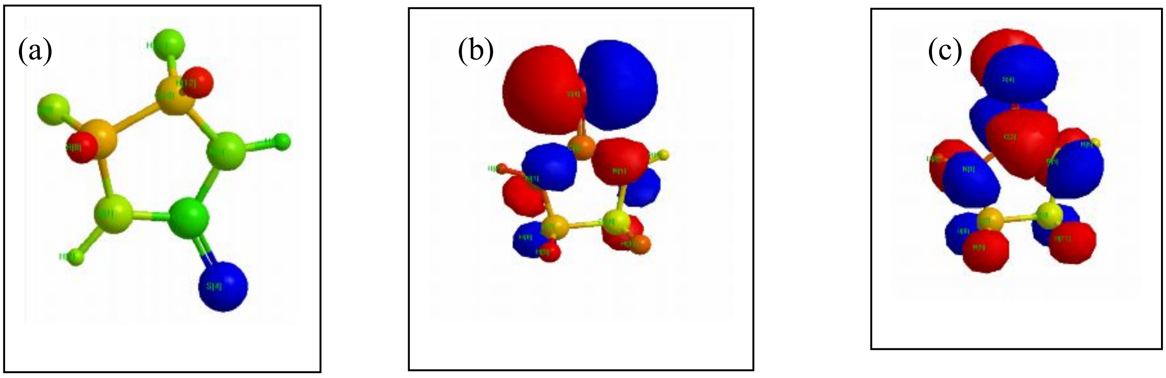

Figure 9 (a) Optimized structure of ETU (b) HOMO of ETU (c) LUMO OF ETU

From figure 7- 9, it can be observed that HOMO and LUMO energy orbital's were loftily localized on tolyl moiety and almost nil, on one $-NH_2$ group of thiourea derivatives indicating that the methyl, allyl and ethylene moiety posse good adsorption centers consolidating the opinion of several researchers that p electrons and hetero atoms are responsible for adsorption process [19-21]. The gap between HOMO–LUMO energy levels of molecules was another important parameter that needs to be considered. Smaller the value of ΔE of a compound, higher is the inhibition of reaction. The higher value of energy gap (ΔE) for ETU indicates that the compound has not inhibited the deposition

3.5 Quantum mechanical studies

The computed quantum chemical parameters like energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), LUMO- HOMO, energy gap (ΔE), dipole moment (μ), are summarized in Table 3. process effectively. However, ΔE value for NMTU is lower than ATU, demonstrates that the former may slowdown the electroless deposition of copper. It has been reported that, larger values of dipole moment will favour the adsorption of compounds on metal surface[22]. The dipole moment (μ) of NMTU is higher than ATU and ETU indicating that NMTU adsorbs strongly on metal surface and slowdown the plating process to considerable extent as compared with other two stabilizers [23].

Table 3: Quantum mechanical parameters for thiourea derivatives on the rate of electroless copper plating process.

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
NMTU	0.16733	-8.22598	8.39132	4.9
ATU	0.31633	-8.40574	8.72207	4.5
ETU	0.51789	-8.44651	8.9644	4.1

4. Conclusions

Thiourea derivatives acted as stabilizers and retarded the rate of electroless copper deposition through their effective adsorption on metal surface. The quantum mechanical parameters substantiated the mere adsorption of compounds on metal surface being responsible for stability of the electroless copper plating bath. Hence, it is recommended that the application of these findings can be extended for surface finishing industrial processes.

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