

Electrochemical and Quantum Mechanical Aspects of Electroless Copper Plating Process

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Abstract: The influence of substituents of thiourea on the stabilization effect of copper deposition has been studied by chemical and electrochemical methods. The stabilization action of the N-phenyl thiourea and N,N' diphenyl thiourea were screened by Anodic, cathodic polarization, and impedance measurements. 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.

Key words: Electrochemical, Quantum Mechanical Aspects, Electroless Copper Plating Process.

Introduction:

Thiourea and its derivatives are some of the potential additives commonly employed in plating, batteries and corrosion inhibitors¹⁻¹⁰. A thorough study on literature clearly indicates that very few investigations have been done with aid of thiourea, Cystene and thiophenol as additives for electroless copper plating process¹¹⁻¹³. The stabilization effect of N-phenyl thiourea (PTU) and N, N'-diphenyl thiourea (DPTU) has not been reported so far. The present study discusses the stabilization action of thiourea derivatives and the performances of the compounds on the rate of electroless copper plating have been demonstrated through chemical and electrochemical methods.

Experimental details

The bath used in the present study had the following composition of AR.grade chemicals.

| | | |
|------------------------------|---|----------------------|
| 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 |

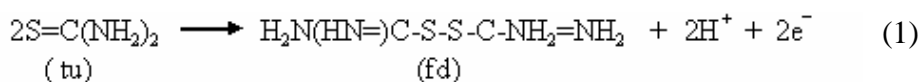
Experiments were performed with various additives in the concentration ranges of 0.1 ppm, 0.5 ppm and 1 ppm. Each experiment was repeated minimum three times to get reproducible results. The rate of deposition was calculated using the following formula as described earlier¹³. Deposition rate (micron) = $\frac{\text{Mass} \times 10^4}{\text{Density} \times \text{Area} \times \text{time (in hours)}}$.

The measurement was made with BAS-100A, Electrochemical analyser. The working electrode was 10mm² copper plated steel substrate, while auxiliary electrode and the reference electrode used were of platinum plate of 40 mm² area and Hg/Hg₂Cl₂/saturated KCl. The capacity of bath solution was 100ml which is taken in a 250ml beaker. No stirring was given during plating. 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 ± 300 mV 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.

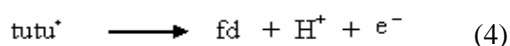
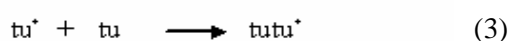
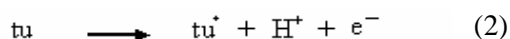
Results and discussion:

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. The results indicated that the performance of the compounds is determined by the formation of an intermediate, formamidine disulphite (fd) due to the oxidation of para formaldehyde and thiourea as given below.



The oxidation reaction takes place via intermediates



It was reported that faster the formation of fd, faster will be the rate of deposition. DPTU stabilizes lesser than PTU. This can be ascribed to the presence of biphenyl group in DPTU which shows -I effect. The biphenyl groups favour desorption of DPTU, by reducing the charge density at nitrogen atom and facilitates the formation of reaction (2) to take place i.e., [SC(=NH)NH₂] intermediate easily compared with PTU having one phenyl ring. Hence the rate of deposition is higher for DPTU than PTU. The order of stabilization effect of the additives is given below: PTU > DPTU

Table 1. Weight gain studies of electroless copper plating

| Stabilizers in mg/l | Rate of deposition ($\mu\text{m/hr}$) | | |
|---------------------|---|-----|-----|
| Plain bath | 3.2 | | |
| Concentration | 0.1 | 0.5 | 1 |
| PTU | 4.1 | 4.5 | 4.9 |
| DPTU | 4.3 | 4.8 | 5.4 |

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 1cm² area of copper electrode at a fixed scan rate of 10mV/s. The results are shown in figures 1-2. For each compounds 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.

Cathodic polarization studies:

Cathodic partial polarization was performed to investigate the function of DPTU &PTU (accelerators / stabilizers) on the reduction of Cu²⁺ ions. Figure 3-4 indicated the cathodic plots carried out using the bath-containing thiourea derivatives. No reducing agent was used. According to this study, the compounds have not encouraged the reduction of Cu²⁺ ions directly in the absence of reducing agent. Similar observations has been made by Han et al¹⁴ for the electroless deposition of nickel.

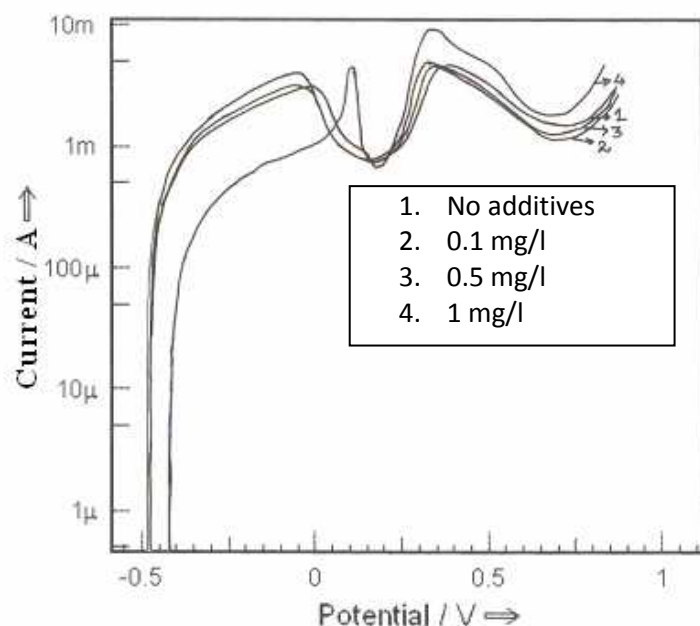


Figure 1 : Anodic polarization curves of electroless copper bath in the presence of PTU

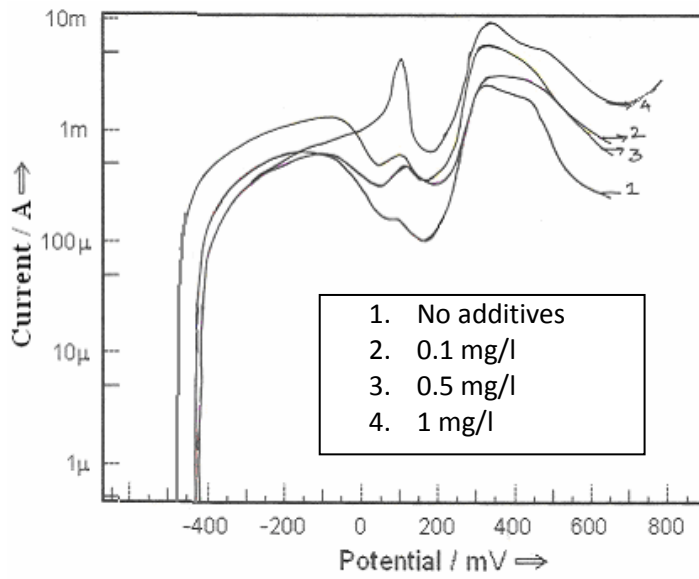


Figure 2. Anodic polarization curves of electroless copper bath in the presence of DPTU

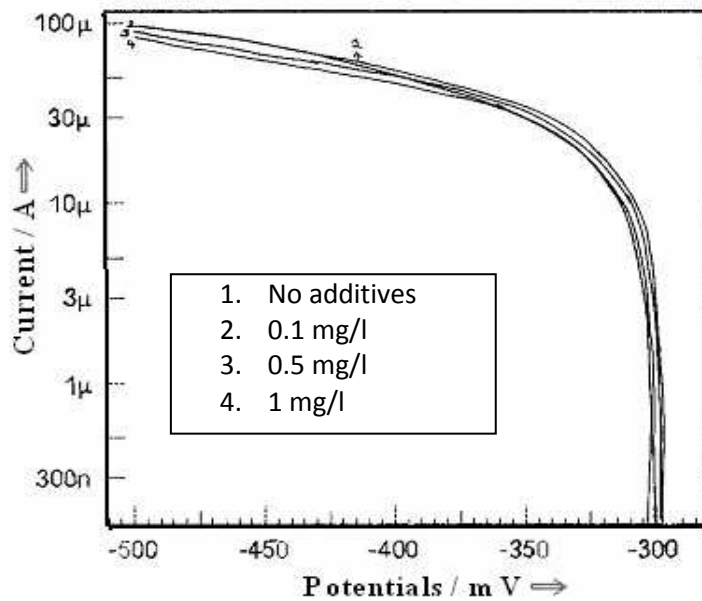


Figure 3. Cathodic polarization curves of electroless copper bath with PTU

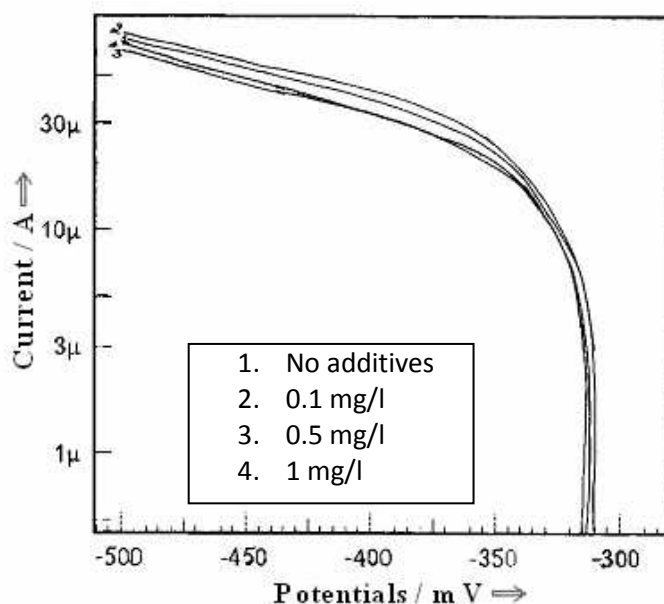


Figure 4. Cathodic polarization curves of electroless copper bath in the presence of DPTU

Impedance studies:

Nyquist results 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 increased as compared with plain bath for PTU and DTU indicate that these compounds hinder the reduction of Cu^{2+} . In the case of DPTU (at 1ppm), R_t values are fetched down and C_{dl} values are enhanced than PTU, indicating the acceleration of Cu^{2+} reduction process. 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) | $C_{dl} \times 10^{-4}$ (F/cm ²) |
|------------|------------------------------|--|
| Plain bath | 7.119 | 7.6 |
| PTU | 8.108 | 17 |
| DPTU | 5.566 | 10.45 |

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

| Stabilizer | LUMO (eV) | HOMO (eV) | ΔE (Cal.Mol ⁻¹) | Moment of dipole (Debye) |
|------------|-----------|-----------|-------------------------------------|--------------------------|
| PTU | -0.7148 | -8.5124 | 7.7976 | 4.3 |
| DPTU | -0.8888 | -8.2892 | 7.4004 | 4.0 |

Quantum mechanical studies:

The effective adsorption of the stabilizers on the metal surface was justified from quantum mechanical studies and the results are presented in table 3. The parameters like highest occupied molecular orbital, Lowest unoccupied molecular orbital, energy gap during adsorption and moment of dipole values are of important to this study. Figure 5 indicates the quantum parameters for DPTU, it is ascertained that highest occupied molecular orbital were found to be completely oriented on $-\text{NH}-\text{C}=\text{S}$ and no orientation on phenyl groups of DPTU. In the case of PTU, E_{HOMO} can be visualized on phenyl ring of PTU confirming its adsorption on metal surface through phenyl group¹⁵⁻¹⁸. The higher value of ΔE for DPTU indicates that the compound has not inhibited the deposition process effectively. However, ΔE value for PTU is lower than DPTU, demonstrates that

the former may hinder the electroless deposition of copper. It has been well established that, larger the values of dipole moment, better will be the adsorption of compounds on metal surface¹⁹. The dipole moment (μ) of PTU is higher than DPTU indicating that PTU adsorbs strongly on metal surface and slowdown the plating process to considerable extent as efficient stabilizer²⁰⁻²².

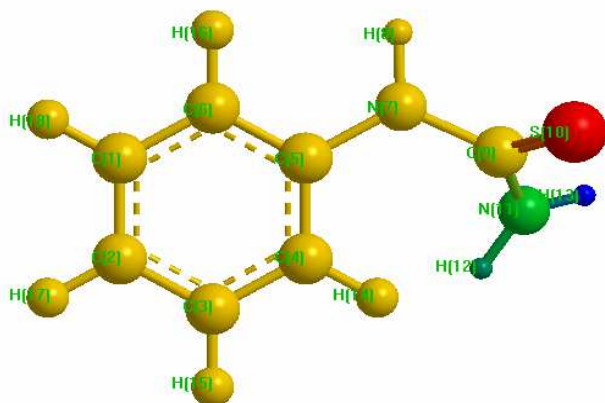


Figure 5.a.Optimized structure of phenyl thiourea

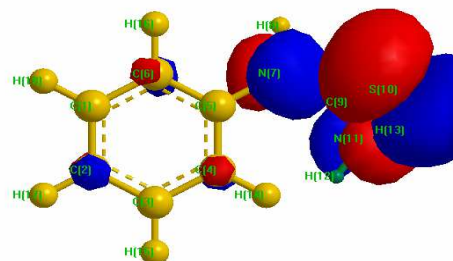


Figure 5b. HOMO of PTU

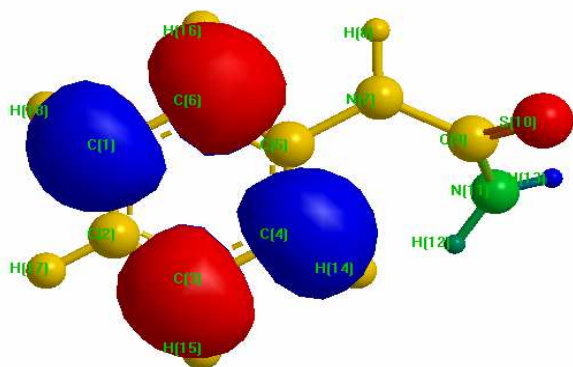


Figure 5c.LUMO of PTU

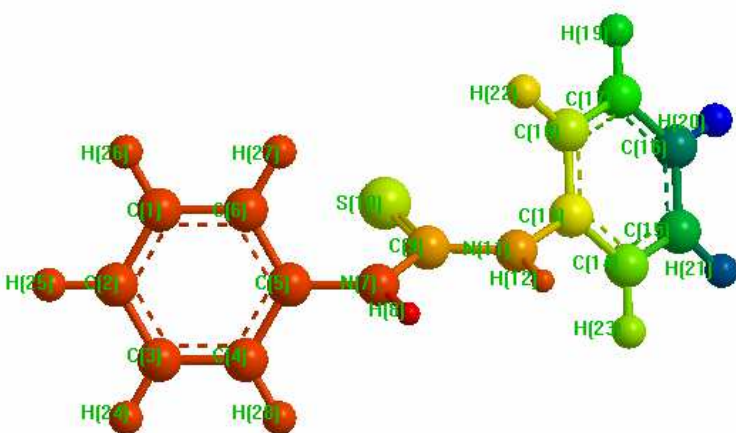
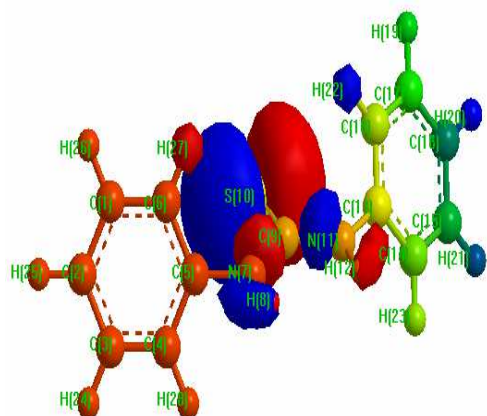
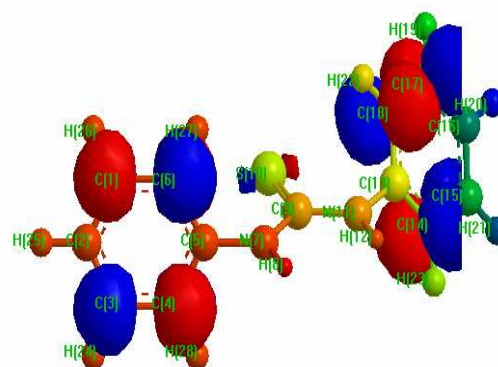


Figure 6.a.Optimized structure of DPTU

**Figure 6b. HOMO of DPTU****Figure 6c. LUMO of DPTU**

Conclusions:

N-Phenyl Thiourea retarded the rate of electroless copper deposition by virtue of its adsorption on metal surface than DPTU. The stabilization mechanism have been explained through the formation of an intermediate. The quantum mechanical parameters substantiate the mere adsorption of compounds on metal surface being responsible for stability of the electroless copper plating bath.

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