Studies on Diethanolaminedithiocarbamate as Metal Complex, Complexing Agent and Stabilizer in Copper Methanesulphonate Bath

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Abstract: ***We report a study on the use of diethanolaminedithiocarbamate (DEADTC) as complexing agent during electroless deposition of copper. For this, we study the nature and structure of the coordination complex between DEADTC and copper and the electrochemistry of the system. The properties of the complex are studied by UV and IR spectroscopy techniques. We then analyze the effect of adding DEADTC as complexing agent in electroless copper methanesulphonate baths. Its use as a stabilizer in ecofriendly xylitol based methanesulphonate baths is also studied and DEADTC is found to be a good inhibitor. Compact and finer deposits are observed in an optimized bath at pH 13.25 at 28 ± 2 °C with 1 ppm addition. The stabilization properties are determined by the AFM, CV, XRD and impedance techniques.***

Keywords: complexing agent, ecofriendly, electrochemistry, inhibitor, stabilizer

1. Introduction

Since the discovery of dithiocarbamates (DTC), a class of organosulphur compounds in the middle of the 18th century [1]. There have been many pioneering studies by researchers such as Delepine [2], Guy [3], Gordon [4], McMullan [5], Harrington [6] to synthesize several metal complexes for application in a range of fields such as rubber chemistry, agriculture and industrial, biological and medicinal sciences. DTC is used in treating metal-bearing waste streams for lowering metal concentrations in effluents. Diethanolaminedithiocarbamate (DEADTC) has been recognized as an effective accelerator, antioxidant, insecticide, bactericide, microbicide and fungicide in many research articles and reviews [7-10]. Commercial applications and theoretical basis of electroless copper deposition process has been studied by many workers [11-18]. The ability of DTC and DEADTC to coordinate with metal ions makes it a promising complexing agent and stabilizer in electroless plating baths. Despite the promise, a literature survey shows that not much work has been carried out yet to understand and optimize the use of DEADTC in electroless bath. This work fills this gap and establishes the applicability of DEADTC as a stabilizer in copper methanesulphonate electroless bath

2. Experimental

2. 1. Chemicals and solutions

The following chemicals and reagents were procured from various sources and used as such without further purification. The electroless Cu deposition was performed on a Cu sheet (2.0 x 2.0 x 0.1 cm) in a 100 mL beaker.

1. Absolute ethanol
2. Ammonia solution
3. Carbon- disulphide
4. Copper sulphate
5. Diethanolamine
6. Dry ether
7. Methanesulphonic acid
8. Para-formaldehyde
9. Potassium hydroxide
10. Xylitol

2.2. Spectrometer

Electronic spectra data were obtained with (Hitachi 210 model) using a regular quarts cuvette 10 mm path length. Infrared spectra were recorded on a (Hitachi 210 model) 200-4000 cm^{-1} using KB pellet.

2.3. Calculations of rate, thickness and activation energy of copper deposits

The rate of the electroless copper deposit was calculated using the following equation.

$$Rate\ of\ deposition\ (\mu m/h)\ =\ Thickness\ /\ Deposition\ time \quad (1)$$

From the weight of the deposit, total plated area and density of the copper, thickness was calculated as follows.

$$Thickness(\mu m) = \frac{W \times 10^4 \times 60}{A \times D} \quad (2)$$

Depending upon the nature of the electroless copper bath, the activation energy was calculated by the following equation.

$$Ea = slope \times 2.303 \times R \quad (3)$$

2.4 Characterization of coating surface

Atomic force microscope (AFM) (NanoSurf Easy Scan2, Switzerland) was used to analyze the surface roughness of the Cu deposits. X-ray diffraction, (X'Pert-Pro, P-analytical) was used to identify the structural properties of the copper deposits. The Debye-Scherrer [19, 20] (1916 &1917) equation for calculating the particle size is given by

$$D = K\lambda / \beta \cos\theta \qquad (4)$$

Specific surface area of the copper deposits is determined by the formula

$$S = \frac{6\times10^{3}}{d\,\rho} \qquad (5)$$

2.5 Electrochemical Studies

Cyclic voltammetric curves were obtained using a standard electrochemical analyzer - CHI-600D Austin USA. The copper methanesulphonate solution was deaerted with nitrogen gas. The counter electrode was platinum wire and reference electrode was Ag/AgCl with saturated KCl solution. The voltammograms were recorded at room temperature 28±2 ˚C in 0.1 M Na_2SO_4 as supporting electrolyte. Standard glassy carbon electrode was used as working electrode and the voltammograms were recorded in the range from - 1.2 to + 0.5 V at potential scanning rate 50 mVs^{-1}. The following electrical equivalent circuit was found to match the system where,

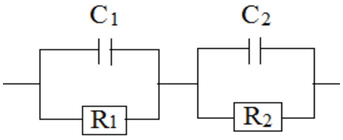

Figure 1: Electrical equivalent circuits for electrochemical impedance spectroscopy

C_1 & C_2 - Double layer capacitances
R_1 & R_2 - Charge transfer resistances

$$\frac{C_1}{R_1} + \frac{C_2}{R_2} \qquad (6)$$

Nyquist diagram {Im (Z) Vs Re (Z')}

$$fc_1 = \frac{1}{2\pi R_1 C_1} \quad and \quad fc_2 = \frac{1}{2\pi R_2 C_2} \qquad (7)$$

Order $C_1 < C_2$

Depending upon the shape of the EIS spectrum, a circuit description code and initial circuit parameters were used to find the charge transfer resistance and double layer capacitance value.

2.6 Preparation of dietanolaminedithiocarbamate

78 ml of diethanolamine (0.81) moles and 200 ml of concentrated (28%) aqueous ammonia were added to a 500ml beaker equipped with a magnetic stirrer and thermometer. The reaction mixture was cooled in an ice bath to below 10 °C then, 60 ml of ethanol containing 60 ml (0.99) moles of CS_2 were added drop wise to the reaction mixture at such a rate that the temperature did not rise above 18 °C. After the addition was complete the solution was stirred for 30 minutes and a yellowish precipitate formed. Then 100 ml of ethanol was added and stirred for additional 10 minutes. The precipitate was filtered washed with ether and dried in air. The yellow colour disappeared on drying.

2.7 Preparation of Cu (II)bisdiethanolaminedithiocarbamate

Cu (II)bisdiethanolaminedithiocarbamate chelate was prepared by mixing an aqueous solution of copper sulphate and DEADTC in a ratio of 1:2. Cu (II) sulphate was added drop wise to the DEADTC solution with hot and stirring. The *p*H of the above reaction was maintained at 2.5 since the yield was found to be better at this *p*H. The reaction resulted in the formation of a brown precipitate, which was filtered and dried.

3. Results and Discussions

The results and discussion are divided into two major parts:
Part-1: The study of formation of diethanolamine-dithiocarbamate copper complex.
Part-2: The effects of uncomplexed diethanolamine-dithiocarbamate as complexing agent and stabilizer in electroless copper methanesulphonate bath. The optimized bath was prepared and used for further physical and electrochemical investigation.

Table 1: Bath composition of copper methanesulphonate DEADTC plain bath and xylitol with 1 ppm DEADTC stabilizer

Bath contains	Complexing agent	Stabilizer
CuMS (II) ion contacting salt	3 g/L	3 g/L
Xylitol	-	20 g/L
Diethanolamine-dithiocarbamate	20 g/L	1 ppm
HCHO	10 g/L	10 g/L
KOH (*p*H)	13.00	13.25
Temperature	28 ± 2 ºC	28 ± 2 ºC

3.1 Physio-chemical analysis

The diethanolaminedithiocarbamate complex of Cu (II) was brown and water soluble because of the hydrophilic carbamate moiety in the structure of the complex. DEADTC melts along with decomposition between 82-348 ºC and there is no sharp melting point observed. Decomposition products include thiocyanate, sulphides and non-stoichimetric sulphides of various compositions. The elemental analysis shows that the structure $[Cu^{(II)}(deadtc)_2]$ complex to be covalent and bichelate in nature.

3.2. Spectral analysis

The brown colored complex, $[Cu^{(II)}[(deadtc)_2]$ showed two peaks with λ_{max} at 258 nm and 290 nm. These shifts in λ_{max} values in the UV region correspond to the ligand moiety and may be due to the effect of complex formation. The observed two peaks may be due to π-π* transition of (S=C=N) and (S=C=S) chromophore in the complex.

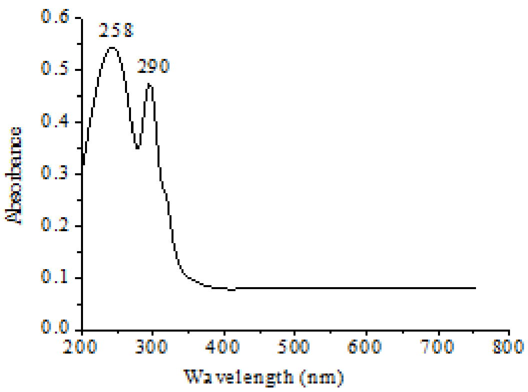

Figure 2: Electrtonic Spectrum of Copper (II)bisdiethanolaminedithiocarbamate

Spectral data from Figures 2 and 3 clearly indicate characteristic peaks of DEDTC in copper complex. A partial double bond character between the carbon and nitrogen in thioureide is confirmed by the observation of a band γ (C=N) in between 1456.56 cm^{-1} and 1512.42 cm^{-1}. Bands corresponding to 992.24 cm^{-1} at γ (C=S), δ (C=S) and (S=C=S) are observed at 710.2 cm^{-1} and 782.92 cm^{-1} respectively.

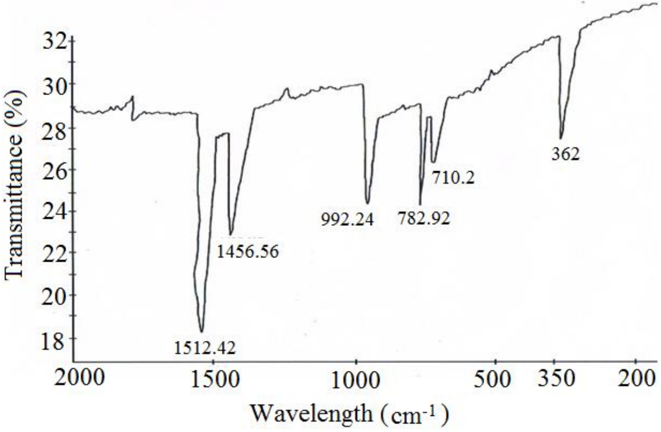

Figure 3: IR Spectrum of Copper (II)bisdiethanolaminedithiocarbamate

A strong band of metal-sulphur linkage is seen at 362 cm^{-1} and this confirms the formation of a complex. The structure of complexes of copper (II) metal ion with diethanolaminedithiocarbamates is given below.

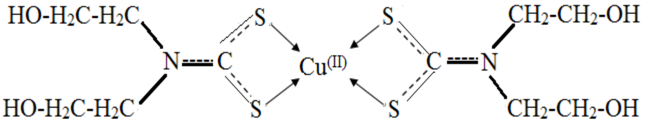

Figure 4: Structure of bisdiethanolaminedithiocarbamate complex of Copper (II)

3.3 Deposition rate and thickness of copper deposits Part-2

The effect of diethanolaminedithiocarbamate acts as complexing agent and stabilizer in electroless copper methanesulphonate. The influence of DEADTC on electroless plating using methanesulphonate bath was studied. KOH solution was used to increase the *p*H of the baths. The deposition was found to commence at a *p*H of 12 and, the rate of deposition increased initially and then decreased with further increase in *p*H. Through iterative experiments, the bath composition was optimized; the bath containing 3 g/L of copper methanesulphonate and 10 g/L of p-formaldehyde was taken as the optimum formulation. The DEADTC bath showed an optimum deposition rate of 3.02 µm/h at *p*H 13.00 and was called 'DEADTC plain bath'. Another ecofriendly xylitol based bath composition was also optimized; the bath containing 3 g/L of copper methanesulphonate and 10 g/L of p-formaldehyde was taken as the optimum formulation. The xylitol bath showed an optimum deposition rate of 3.23 µm/h and thickness of 193.8 µm at *p*H 13.25 named 'xylitol plain bath'.

The inhibiting or accelerating properties of the stabilizers were compared in terms of the deposition rate (µm/h) of the electroless plating with plain bath. When the rates of deposition values were lower than in plain bath, the stabilizers may be considered inhibitors and when greater than plain baths as accelerators or enhancers. The thickness of deposition increases on increasing plating time duration of electroless copper plating. Thus, as seen in table. 2, DEADTC used as the stabilizer in xylitol plain bath was good inhibitor at 28 ± 2°C with 1 ppm addition because it shows a deposition rate of 2.84 µm/h and thickness of 170.4 µm at *p*H 13.25.

3.4 Activation energy by Arrhenius formula

The activation energy is another marker to understand the nature of the electroless copper bath. The activation energy is inversely proportional to the rate of copper deposition. In xylitol bath, presence of DEADTC results in higher activation energy than the plain bath. It may be postulated that increasing the interactions on the metal surface results in reduction of deposition rate due to reduction in catalytic sites on the metal surface. The activation energy of the DEADTC plain bath was calculated to be 72.2 kJ/mol. The activation energy of xylitol containing methanesulphonate plain bath is 70.4 kJ/mol. Adding DEADTC as stabilizer to the xylitol bath increased the activation energy to 76.7 kJ/mol, thus confirming the inhibiting effect.

3.5 Surface morphologies of coating surface

AFM and XRD techniques were used to investigate the nature of the coated copper deposits on substrate. An increase in roughness value indicates a reduction in smoothness of the deposits. The xylitol plain bath produced maximum roughness value of 303 nm. On using DEADTC plain bath, the roughness values decreased due to steric factors. Use of DEADTC as stabilizers in the xylitol bath resulted in lower roughness values than xylitol plain bath.

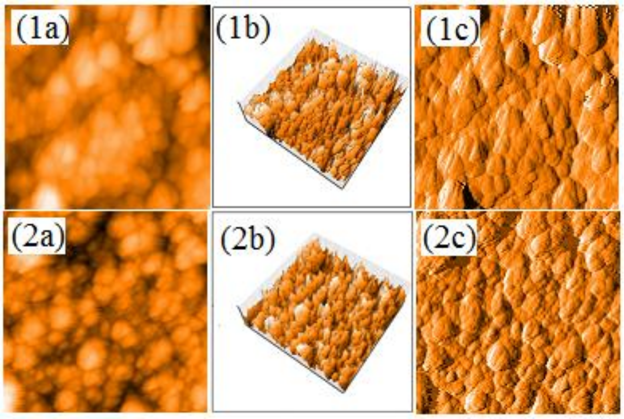

Figure 5 : AFM images of copper deposits on methanesulphonate bath (a) topography of copper deposits (b) 3-D image and (c) surface area; (1a,1b,1c) - DEADTC plain bath, (2a,2b, 2c) - xylitol with 1 ppm of DEADTC bath.

Crystallite size and specific surface area were determined by the XRD technique. Crystallite sizes are proportional to the inhibiting efficiency. Literature survey shows that the face-centered-cubic (FCC) and (111) plane in Cu are a closed packed plane in FCC structures. The texture of deposits may correspond to polarization effects because the (111) plane has the lowest surface energy plane for Cu in electroless plating [21, 22].

In this work, we added small volume biodegradable methanesulphonic acid (MSA). MSA's superiority over other bath liquids arises from its excellent metal salt solubility, stability, excellent conductivity, and ease of effluent treatment. Addition of small amounts of MSA has been reported to produce uniform and high quality coatings [23-25]. Because of high conductivity and solubility of copper methanesulphonate, the deposits of copper oriented in the (200) plane. Crystallite sizes of the copper were found to be 128 and 126 nm for DEADTC and xylitol plain baths. On adding DEADTC as a stabilizer in xylitol bath, crystallite sizes increased to 136 nm. The presence of functional groups, molecular area, and molecular weight also played a vital role in the crystal structure of the elecrtroless copper deposits.

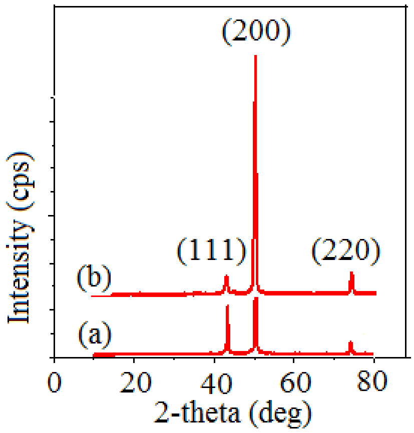

Figure 6: XRD pattern of copper deposits on methanesulphonate bath (a) DEADTC plain bath (b) xylitol with 1 ppm DEADTC bath

3.6 Quality and quantity of ecofriendly bath

Cyclic voltammetric studies and impedance tests were performed to characterize the electroless copper bath. Anodic peak potential value and anodic peak current values were analyzed to understand the quality and yield of this electroless copper bath. Charge density, appearance of peak, and inductive effects were found to alter the potential and current values. In DEADTC plain bath, E_{Pa-1} and I_{Pa-1} were found to be -0.2314 V and 8.392 × 10^{-5} A. In xylitol plain bath, E_{Pa-1} and I_{Pa-1} were found to be -0.2275 V and 5.924 × 10-6 A. When DEADTC was used as a stabilizer in xylitol bath, E_{Pa-1} and I_{Pa-1} were -0.3470 V and 3.643×10^{-6}. The high anodic peak current value also indicates that the stabilizer inhibits the deposition of copper.

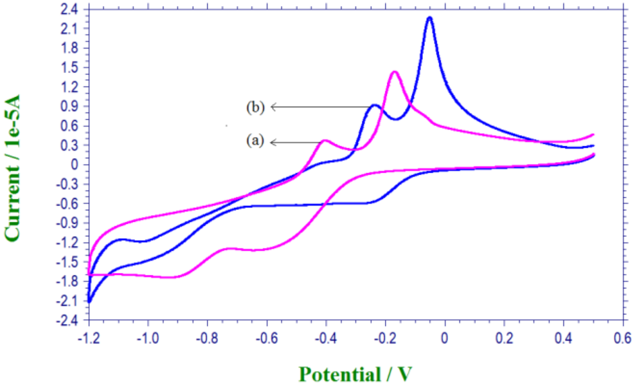

Figure 7: Cyclic voltammograms for electroless copper methanesulphonate bath (a) DEADTC plain bath, (b) xylitol with 1 ppm DEADTC bath

The Electrochemical characteristics of the corrosion process on the surface were studied by impedance spectroscopy (EIS). Interfacial charge transfer between the solid conductor (the working electrode, WE) and the electrolyte was determined. The inhibiting property of DEADTC as stabilizer was confirmed by the results of double layer capacitance and charge transfer resistance was determined with DEADTC and xylitol plain baths. Depending upon the shape of the EIS spectrum, a circuit description code and initial circuit parameters were used to find the charge transfer resistance and double layer capacitance value. Table 2 shows the influence of various surface morphologies when DEADTC was used as complexing agent and stabilizer.

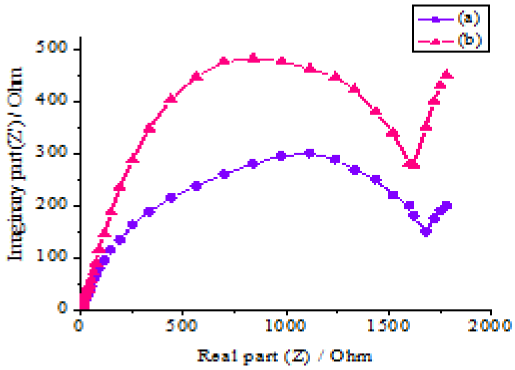

Figure 8: Nyquist diagram of electroless copper methanesulphonate bath (a) xylitol with 1 ppm DEADTC bath (b) DEADTC plain bath

Table 2: Influence of various surface morphologies of DEADTC as complexing agent and stabilizer on electroless copper bath

Surface morphologies	Diethanolaminedithiocarbamate	
	Complexing agent	Stabilizer
Activation energy (kJ/mol)	72.2	76.7
Anodic current value (Ipa-1) (A)	8.392 × 10^{-5}	3.643 × 10^{-6}
Anodic potential value (E_{pa-1}) (V)	-0.2314	-0.347
Charge transfer resistance (R_t)	33.74	59.86
Crystallite size (nm)	128	136
Deposition rate (µm/h)	3.02	2.84
Double layer capacitance (C × 10^{-3})	0.1659	0.4301
Roughness value (nm)	216	126
Specific surface area (m^2/g)	5.214	4.924
Thickness (µm)	181.2	170.4

4. Conclusion

Electrochemical and IR spectral analyzes were conducted to understand the role of DEADTC on electroless copper baths. The studies show that DEADTC formed stable complexes with copper metal, and the brown complex was water soluble, covalent and bichelate in nature. Stable DEADTC containing methanesulphonate electroless copper baths were formulated and optimized at *p*H 13.00 with addition of KOH. Another ecofrienfdly xylitol bath was prepared and optimized at *p*H 13.25 without stabilizers, which was called the xylitol plain bath. 1 ppm concentration of DEADTC was used stabilizer in this xylitol plain bath. Physical and electrochemical experimental techniques were used to characterize the texture of deposited copper and the tests confirmed the stable chelating and stabilizing properties of DEADTC. Roughness value, crystallite size and specific surface area of the copper deposits were analyzed by AFM and XRD techniques. Anodic potential and current values were determined by CV techniques. Capacitance and resistance values were determined by EIS techniques. Physical and electrochemical experimental results show DEADTC to be a good metal complexing agent and stabilizer in copper methanesulphonate bath.

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