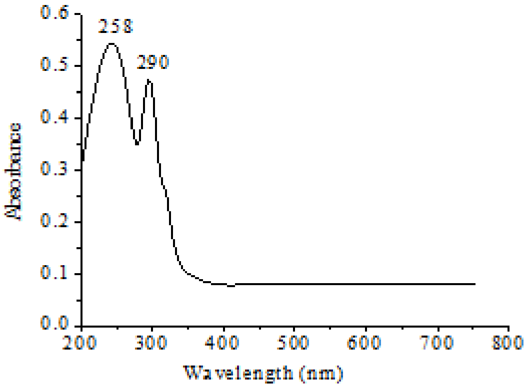

Figure 2: Electrtonic Spectrum of Copper (II)bisdiethanolaminedithiocarbamate

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.

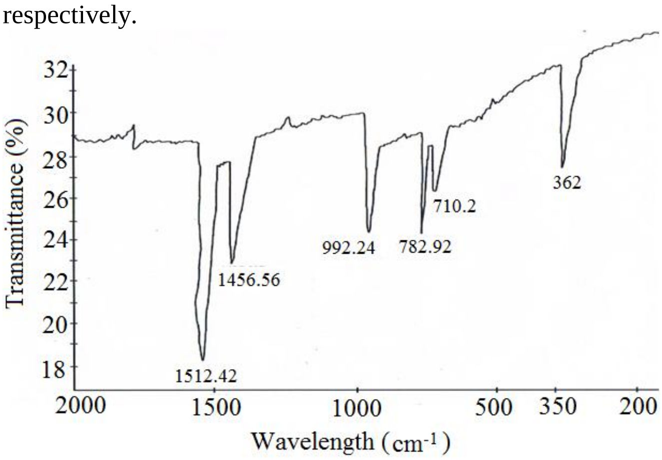

Figure 3: IR Spectrum of Copper (II)bisdiethanolaminedithiocarbamate

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.

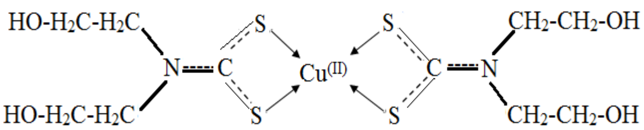

Figure 4: Structure of bisdiethanolaminedithiocarbamate complex of Copper (II)

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.

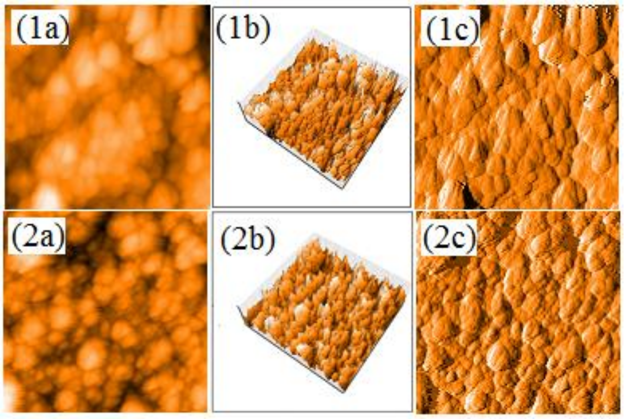

Figure 5 : AFM images of copper deposits on methanesulphonate bath (a) topography of copper deposits (b) 3-D image and (c) surface area; (1a,1b,1c) - DEADTC plain bath, (2a,2b, 2c) - xylitol with 1 ppm of DEADTC bath.

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.

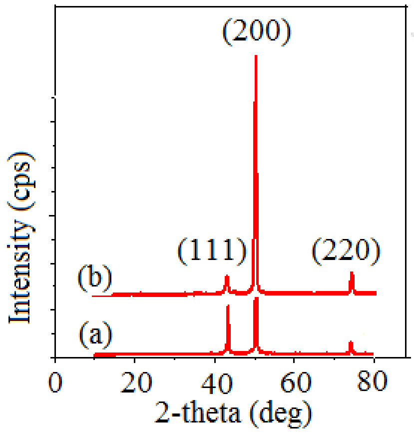

Figure 6: XRD pattern of copper deposits on methanesulphonate bath (a) DEADTC plain bath (b) xylitol with 1 ppm DEADTC bath

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.

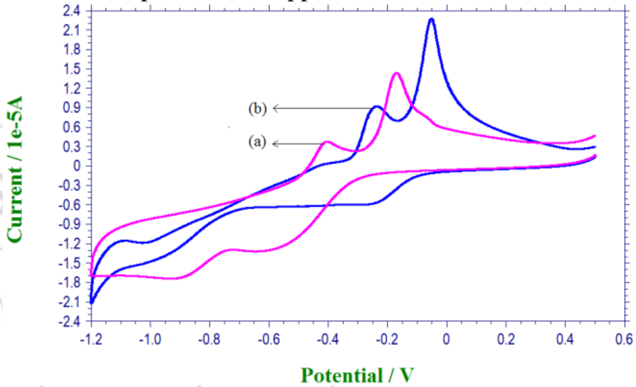

Figure 7: Cyclic voltammograms for electroless copper methanesulphonate bath (a) DEADTC plain bath, (b) xylitol with 1 ppm DEADTC bath

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.

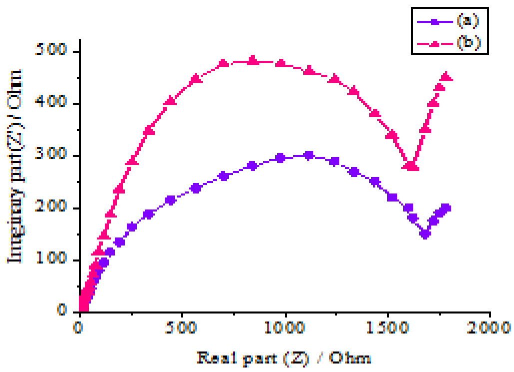

Figure 8: Nyquist diagram of electroless copper methanesulphonate bath (a) xylitol with 1 ppm DEADTC bath (b) DEADTC plain bath

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 ($C \times 10^{-3}$)	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.

References

[1] Day. M.C and Selbin. J, (1969), Theorical inorganic chemistry, second edition, pp. 391.
[2] Delephine. M, (1907), Metallic salts of dithiocarbamic acids; preparation of aliphatic isothiocyanates, Compt. Rend., Vol. 144, pp. 1125.
[3] Guy. H.G., (1936), Thiuram sulfides as repellents to leaf-feeding insects. *J. Ecom., Entomol.*, Vol. 29, pp. 467.
[4] Gordon. R.M., (1942), Observation on the treatment of scabies. *Brit. Med. J.*, pp. 685.
[5] McMullan.R.D., (1959), Insecticidal activity of the ethylenebisdithiocarbamates, *Nature*, Vol. 184, pp.1338.
[6] Harrington. G.E., (1941), Thiuram sulfide for turf diseases. *Science*, Vol. 93, pp. 311.
[7] Vander kerk.G.J.M., (1953), The fungicidal action of dithiocarbamates and bisdithiocarbamates, *Chem. Weekblad*, Vol. 49, pp. 329.
[8] Ludwig. R.A., and G.D. Thorn, (1960), Chemistry and mode of action of the dithiocarbamates fungicides, in Advanced in Pest Control Research, Vol-3, interscience publications, Inc, New York.
[9] McCallan.S.E.A., Dithiocarbamate fungicides, *Agr. Chem.*, Vol. I, pp. 15, 1946.
[10] Tisdale W.H., and A.L.Flenner, (1942), Derivatives of dithiocarbamic acid as pesticides, *Ind. Eng. Chem.*, Vol. 34, pp. 501.
[11] Brenner A.R., and Riddell G.E.,(1946), Nickel plating on steel by chemical reduction, *J. Res. Natl. Bur.*, Vol. 37, pp. 31-34.
[12] Brenner A., (1959), History of the electroless plating process. Symposium on electroless nickel plating', *ASTM special technical publication*, No. 265, pp. 1-2.
[13] Cahill. A.E (1957), American electrochemical society proceedings, Vol.44, pp. 130.
[14] Wein S., (1959), Silvering process and materials US 2871139.
[15] Saubestre E.B., (1962), Electroless plating today, *Metal Finish.*, Vol. 60, pp. 17.
[16] Zeblisky R.J., McCormack J.F., Williamson J.D., and Shneble F.W. (1963), U.S. Patent 3,095,309.
[17] Lukes R.M, (1964), The chemistry of the autocatalytic reduction of copper by alkaline formaldehyde, *Plating*, Vol. 51, pp. 1066-1068.
[18] Goldie W., (1964), Electroless Copper Deposition, *Plating*, Vol. 51, pp. 1069-1074.
[19] Debye P., and Scherrer P., (1916), Interference of irregularly oriented particles in x-rays, *Phys. Ziet.*, Vol. 17, pp.277-283.
[20] Debye P., and Scherrer P., (1917), X-ray Interference produced by irregularly oriented particles (III) x-rays, *Phys. Ziet.*, Vol. 18, pp. 291- 301.
[21] Yong-An Kim, Jong-Wan Park., (Effects of Surfactant Addition on Crystal Orientation in Alkaline-Free Electroless Copper Plating, *J. Kore Phy Soc.*, Vol. 33, pp. S138-S141.
[22] Junginger R, and Elsner G., (1988), 'On the texture of electroless copper films', *J. Electrochem. Soc.*, Vol. 135, pp. 2304-2308.
[23] Balaramesh P., Rekha S., Venkatesh P., and Shanmugan S., (2014), Electroless copper deposition using saccharose containing copper methanesulphonate bath with thiourea as stabilizer, *Chem sci transa.*, Vol. 3, pp. 1214-1220.
[24] Balaramesh P, Venkatesh P, and Rekha S, (2014), The effect of stabilizers on electroless copper plating from saccharose containing methanesulphonate baths', *Asian J. of sci and techn.*, Vol.5, pp. 276-280.
[25] Balaramesh P., Venkatesh P., and Rekha S. (2014), Influence of imidazole and benzotriazole on electroless copper plating, *Surf engi.*, Vol. 30, pp.552-556.