Improved Efficiency of 3-Mercaptopropyltrimethoxysilane on Surface Protection of Copper by Hydrogen Peroxide

N. Karthik and M.G. Sethuraman

Keywords--- *MPTS, H_2O_2 and FT-IR*

I. INTRODUCTION

ORGANOFUCTIONAL silanes are hybrid organic- inorganic compounds with a general formula of R′ Si $(OR)_3$, where R′ represents an organic functional group and OR is a hydrolysable alkoxy group. It is generally believed that the hydrolysis of silane generates silanol groups, and hydrolyzed silane molecules deposit on metal surface by forming Si-O-M bonds through a condensation reaction between silanol and hydrated metal oxide surface [1,2]. At the same time silanol groups react with each other to form Si-O-Si bonds, leading to a cross linked film. The mechanism can be expressed by the following equations:

$$-SiOH + MOH \leftrightarrow -Si-OM + H_2O \quad (1)$$

$$-SiOH + -SiOH \leftrightarrow -Si-O-Si- + H_2O \quad (2)$$

Copper metal is widely used in microelectronic packaging. The advantages of copper over aluminium are lower resistance and higher reliability. But copper is an active metal and the main problem of using copper is its dissolution in aqueous solution and air [3]. MPTS have shown to form strong covalent bonds with different metals [4]. When compare to silanol groups mercapto group (–SH) have stronger affinity to bind with copper through Cu-S bonds. This action mechanism has been proved by Fourier-transform infrared spectroscopy (FT-IR) analysis [5]. The objective of the work is to investigate the effect of hydrogen peroxide into the corrosion inhibition of MPTS on copper in 1% NaCl solution by potentiodynamic polarization method.

II. MATERIALS AND METHODS

- *Pretreatment of Electrodes*

The working electrode was made from copper rod embedded in a Teflon sheath and the geometric area of surface was 1 cm^2. After successively polished with different grades of emery paper and 0.3µm alumina, the electrode was rinsed with Milli-Q water, pure acetone and treated in ultrasonic bath to remove any existed alumina particles and any carbon dioxide produced during the process of polishing.

- *Sol Preparation*

Silanic bath contains 4% v/v (MPTS) in 90% v/v (ethanol) and with varied concentrations of 30% H_2O_2 such as 600 ppm, 1000 ppm and 2000 ppm. The pH value was adjusted to 4 by adding 0.1M HCl in drop wise.

- *Electrochemical Measurements*

The MPTS were coated electrochemically on copper by using cyclic voltammetric technique and its corrosion efficiency was obtained by polarization method, PDS was carried out from cathodic potential of -0.4 V to anodic potential of + 0.2 V vs SCE/V with respect to open circuit potential. A saturated calomel electrode and platinum wire were used as reference and counter electrodes respectively. The test solution was 1% NaCl solution.

N. Karthik, Department of Chemistry, Gandhigram Rural Institute- Deemed University, Gandhigram -624 302, Tamil Nadu.
M.G.Sethuraman, Department of Chemistry, Gandhigram Rural Institute- Deemed University, Gandhigram -624 302, Tamil Nadu.
E-mail:mgsethu@rediffmail.com

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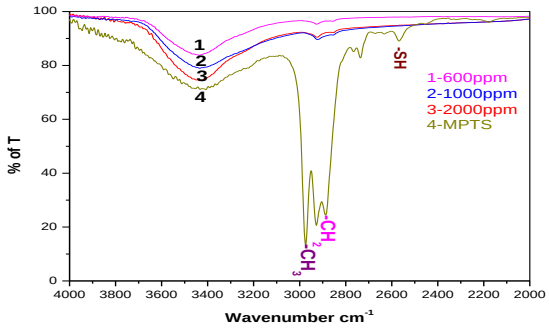
III. RESULTS AND DISCUSSION

- *IR Analysis*

FT-IR spectrum (Fig. 1a) clearly shows the disappearance of –SH peak at 2568 cm^{-1} in MPTS coated copper indicates that MPTS molecule anchored on copper via the formation of Cu-S bonds. As it shows that methylene (-CH_2) and methyl (-CH_3) stretching frequencies around 2800-3000 cm^{-1} was extensively reduced in the hydrogen peroxide mixed MPTS coated copper (Fig. 1(a).



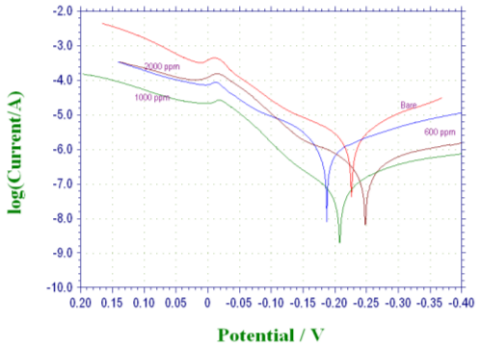


Fig. 1(a) FT-IR Spectrum of (1) MPTS (2), (3), (4) MPTS Coated Copper with Different Concentration of H_2O_2

Fig. 1(b) Polarization Curves of Bare Copper and MPTS Coated Copper with Different Concentration of H_2O_2

- *Polarization Curves*

Compared with i_{corr} (3.175 μAcm^{-2}) of the bare copper, i_{corr} for MPTS coated copper decreases with increasing hydrogen peroxide concentration. Such a decreases in i_{corr} is due to the formation of protective insulating layer. The minimum i_{corr} (0.070 μAcm^{-2}) was achieved for the electrolyte with 1000 ppm of hydrogen peroxide was evident from Fig. 1(b).

- *Mechanism*

Hydrogen peroxide as an additive into the electrolyte, on addition it lowers the deposition current as a result it may be erased the H_2 evolution, and consequently dense uniform coatings may be formed [6].

$$Cu(0) + \text{-}SH \xrightarrow{H_2O_2} Cu(1) + \tfrac{1}{2}\,H_2\uparrow$$

IV. CONCLUSION

1. It is found that hydrogen peroxide is an efficient additive for the corrosion protection of MPTS coated copper.
2. The optimum concentration of hydrogen peroxide was 1000 ppm and slightly lower efficiencies were found at 2000 ppm concentration.
3. The inhibition efficiency of MPTS in various concentration of hydrogen peroxide is in the order of 97.79 $_{(1000ppm)}$> 86.32 $_{(2000ppm)}$ > 42.17 $_{(600ppm)}$

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