Indian Journal of Chemical Technology
Vol. 21, May 2014, pp. 188-198

Corrosion protection of copper by self assembled nano film of 4-amino-3-(octadecylthio)-6-methyl-1,2,4-triazinone

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Received 18 September 2012; accepted 10 October 2013

Self-assembled nano film of 4-amino-3-(octadecylthio)-6-methyl-1,2,4-triazinone (AOTMT) has been developed on fresh copper surface at ambient temperature. The optimum conditions for the formation of AOTMT nano film have been established through electrochemical impedance and quartz crystal nanobalance studies. The AOTMT film on copper surface is characterized by contact angle measurement, X-ray photoelectron spectroscopy (XPS), reflection absorption FTIR spectroscopy and atomic force microscopy. It is inferred that the formation of AOTMT film is through chemisorption of AOTMT on copper surface due to the nitrogen and subsequent complex formation between AOTMT and Cu^+ ions. Corrosion protection ability of AOTMT nano film is evaluated in dilute aqueous HCl environment using impedance, potentiodynamic polarization, cyclic voltammetry (CV), weight-loss and XPS studies. The results show that AOTMT nano film affords excellent corrosion protection to copper in HCl environment. The CV studies show good stability of AOTMT nano film. Potentiodynamic polarization studies reveal that the AOTMT nano film functions as a cathodic inhibitor. The mechanistic aspects of corrosion protection of copper by AOTMT nano film are also discussed.

Keywords: 1,2,4-triazinone, Copper, Electrochemical impedance, Impedance, Quartz crystal nanobalance, Self-assembled nano film, X-ray photoelectron spectroscopy

Though gold and aluminium have been the metals of choice in microelectronic packaging[1], the advantage of lower electrical resistance of copper has established copper as an alternative to gold and aluminium in microelectronic packaging[2,3]. Low cost, improved reliability of the monometallic system and improved device speed are the primary reasons for the emergence of Cu–Cu processes[4]. But, copper readily undergoes corrosion in atmosphere. Corrosion protection of copper is a very important concern in microelectronic packaging. Self assembled monolayers (SAMs) are used as barriers to protect copper against corrosion. These are dense and ordered monolayers[5]. SAM formed from octadecanethiol has been studied for protection of copper in 0.5 M Na_2SO_4 solution and an inhibition efficiency of 80.3% was reported[6]. Quan *et al.*[7,8] reported that the SAMs formed from Schiff bases are effective in protection of copper surface from corrosion in 0.5 M NaCl environment. Alkanethiol SAMs were found to be good inhibitors of copper corrosion in atmosphere[9]. Feng *et al.*[10] studied the corrosion inhibition properties of alkanethiol nano film on copper surface in chloride environment.

So far, only a few studies have been reported on corrosion protection of copper using SAMs of heterocyclic organic compounds containing long alkyl chains. Appa Rao *et al.*[11-12] reported the corrosion protection of copper using the SAMs of 2-(octadecylthio)-benzothiazole and of 5-methoxy-2-(octadecylthio)-benzimidazole. It was of interest to study the corrosion protection efficiency of the SAM of heterocyclic compound of a different moiety namely 4-amino-3-(octadecylthio)-6-methyl-1,2,4-triazinone (AOTMT). The reasons for choosing the AOTMT compound are as follows. The AOTMT molecule consists of six active sites namely four nitrogens, one sulfur and one oxygen, which facilitate chemisorption on copper surface and chelation with copper ions to form a protective nano film. It also consists of a long hydrocarbon chain to make the film hydrophobic. A survey of literature also reveals that triazinone moiety based molecules have not been studied so far as corrosion inhibitors for copper. Hence, the present study of corrosion protection of copper surface using AOTMT self-assembled nano film in 0.02–0.20 M HCl (aq.) solutions has been carried out and the results are discussed in this paper.

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Experimental Procedure

Materials

AOTMT (4-amino-3-(octadecylthio)-6-methyl-1,2,4-triazinone) was synthesized as per the procedure reported in the literature[13]. All the chemicals were of A.R. grade and were purchased from Qualigens Chemicals, India. Differential scanning calorimetry and ^1H NMR techniques were used for characterization of AOTMT. 102 mg of AOTMT was dissolved in methanol to get a 2.5 mM solution. Different concentrations in the range 1.0–2.0 mM were prepared by dilution from the 2.5 mM solution. Polycrystalline copper specimens of different dimensions were made from a copper sheet of 99.9% purity. For electrochemical impedance, potentiodynamic polarization and cyclic voltammetric (CV) studies, the copper specimens of the dimensions of 4.0 × 1.0 × 0.2 cm were used and only 1cm^2 area was exposed to the electrolyte, while the remaining area was insulated with epoxy resin. For surface analytical studies, 1.0 × 1.0 × 0.2 cm specimens were used. For weight-loss studies, 4.0 × 1.0 × 0.2 cm specimens were used. All the specimens were polished to mirror finish using 1/0, 2/0, 3/0, 4/0 grade emery papers and alumina slurry on a rotating disk and then degreased with acetone. The specimens were washed with double distilled water and dried in nitrogen atmosphere for 20 min. For studies using electrochemical quartz crystal nanobalance, copper quartz crystals of 0.20 cm^2 area were used.

Formation of self-assembled nano film

Solubility of AOTMT was tested in the organic solvents such as acetone, chloroform, methanol, ethyl acetate and *n*-hexane. It was found that AOTMT is soluble to a small extent only in methanol. Therefore, methanol was chosen as solvent for formation of AOTMT nano film on copper surface. The polished copper specimens were etched with 7 M nitric acid for 30s, washed first with triple distilled water and then with methanol. The specimens were immediately immersed in different concentrations of AOTMT solution in methanol for various immersion periods.

Electrochemical studies

Electrochemical impedance studies were first carried out in order to establish the optimum conditions for the formation of a protective AOTMT nano film on copper surface. The impedance studies were carried out in a three-electrode cell assembly (in accordance with ASTM specifications) using an electrochemical workstation model IM6e ZAHNER elektrik, Germany. The impedance studies were carried out at open circuit potentials (OCP) in the frequency range from 60 kHz to 10 mHz under excitation of sinusoidal wave of ±5 mV amplitude. The bare copper specimen or copper specimen covered with AOTMT nano film was used as the working electrode. A platinum electrode was used as the counter electrode and the reference electrode was a Ag/AgCl/1.0 M KCl electrode. The impedance studies were also carried out in order to investigate the corrosion protection ability of the AOTMT nano film in an aggressive environment, viz. HCl in the concentration range of 0.02–0.20 M at various immersion periods (0.5–24 h) and temperatures (30–60°C). Potentiodynamic polarization studies were carried out in the same three-electrode cell assembly at different concentrations of HCl (0.02–0.20 M) using the same electrochemical workstation used for impedance studies. The polarization curves were recorded in the potential range from –0.500 V to +0.200 V *vs.* Ag/AgCl/1.0 M KCl at a scan rate of 1 mV s^{-1}. Correction of the curves for IR-drop compensation was not required because of the high electrical conductivity of the aggressive corrosive environment[14]. The reference electrode was kept very near to the working electrode. The cyclic voltammetric studies of bare copper and copper electrode modified with AOTMT nano film were carried out in 0.02 M HCl in the potential range from –0.400 V to + 0.350 V *vs.* Ag/AgCl at three different sweep rates, namely 30, 60 and 120 mVs^{-1} for two cycles at each sweep rate. The CV experiments were also carried out for 15 cycles at a constant sweep rate of 30 mV s^{-1} in the same potential range in order to test the stability of the nano film. Electrochemical quartz crystal nanobalance system, model Elchema EQCN-700 and an AT–cut copper quartz crystal with 10 MHz nominal frequency were used in the studies. The copper quartz crystal was immersed in the AOTMT solution in methanol solvent and the mass change as a function of time was recorded during the formation of nano film on the copper crystal. The quartz crystal nano balance was also used to determine the corrosion rate of copper covered with AOTMT nano film in the corrosive environment, viz. 0.02 M HCl for an immersion period of 24 h.

Contact angle measurements

Contact angle measurements for bare copper and copper covered with AOTMT nano film were made by sessile water drop method using a contact angle measuring system, model G10, Kruss, Germany. The measurements were carried out at about 30°C in air.

Surface analytical techniques

Reflection absorption FTIR spectra for bare copper and copper covered with AOTMT nano film were recorded in single reflection mode using FTIR spectrometer, model Thermo-Nicolet Nexus 670 of the Thermo Electron Corporation, USA in the spectral range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. This FTIR instrument has KBr window and XT-KBr beam splitter, and the lowest possible wavenumber is 400 cm^{-1}. Bare copper and copper covered with AOTMT nano film were mounted on the reflection accessory and the plane polarized light was incident at a grazing angle of 85° from the surface normal. The sample compartment was continuously purged with nitrogen during the measurement. The surface analysis of bare copper and copper covered with AOTMT nano film was also carried out using the X-ray photoelectron spectrometer, ESCA Kratos model AXIS-165, with Mg Kα radiation (1253.6 eV) and energy resolution of 0.1 eV. Computer deconvolution was applied to detect the elemental peaks of copper, oxygen, carbon, nitrogen and sulfur present in the nano film. XPS studies were also used to analyze the nature of the surface films in the presence of a corrosive environment, i.e. 0.02 M HCl. Veeco Nanoscope IV multimode AFM was used for studying the morphology of copper surface covered with nano film. The AFM was used in the contact mode between a silicon nitride tip attached to a micro cantilever and the surface of the sample. The Z motion of the tip was monitored in height mode by mounting the sample on an X-Y-Z piezoelectric tube scanner.

Weight-loss studies

The bare copper specimens and the copper specimens covered with AOTMT nano film were immersed in 0.02 M HCl solution for a period of 3 days. The weights of the specimens before and after immersion were recorded by using an electronic balance with a readability of 0.01 mg. From the weight loss data, the corrosion rates and inhibition efficiencies were calculated.

Quantum chemical calculations

Quantum chemical calculations were carried out using semi-empirical AM1 molecular orbital method in the MOPAC program using Chem3D Ultra Molecular Modelling and Analysis software. E_{HOMO}, E_{LUMO}, ΔE, net atomic charges on each of the elements of AOTMT and the total ring charge were obtained from these calculations.

Results and Discussion

Optimum conditions for formation of AOTMT nano film

The best immersion time was reported to be more than 20 h to obtain a dense and stable nano film by Quan *et al.*[7] in their studies on formation of nano film of Schiff base on copper. In the present study also, it is found that an immersion period of 24 h is necessary to form a protective film. Therefore, an immersion period of 24 h and four different concentrations of AOTMT in the range, 1.0–2.5 mM (highest solubility) are used for the study of formation of AOTMT nano film in methanol solvent. Bode plots of copper modified with AOTMT nano film at different concentrations of AOTMT (1–2.5 mM) are recorded in 300 ppm chloride solution and the plots are shown in the Fig.1.

With increase in concentration of AOTMT, the phase angle maximum is increased and shifted towards higher frequency region. It is interesting to note that at a concentration of 2.5 mM AOTMT, the phase angle maximum is 90° and shifted towards much higher frequency region beyond 60 kHz, the highest frequency available with the instrument. This result reveals that the AOTMT nano film formed on copper surface behaves as a capacitor. At all concentrations, the phase angle maximum shows two time constants. The maximum in the high frequency domain relates to charge transfer resistance by the AOTMT film[15] and the second maximum in mid frequency region relates to a porous oxide film on the alloy surface[16]. Thus, the Bode plots reveal that the protective surface film is a combination of oxide film and AOTMT film. The

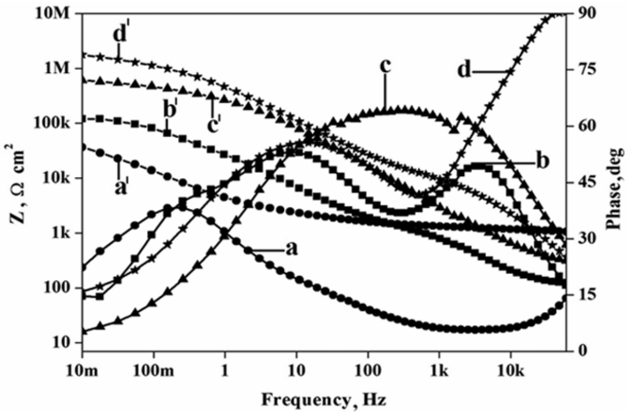

Fig. 1—Bode plot of copper covered with AOTMT nano film formed at different concentrations of AOTMT (a,a^{l}-1.0 mM, b,b^{l}—1.5 mM, c,c^{l}-2.0 mM and d,d^{l}-2.5 mM) [Environment 300 ppm chloride (NaCl), Temperature 30 °C]

physical model of the system, therefore, consists of metal/protective surface film/electrolyte and the equivalent circuits used in the case of copper covered with AOTMT film are shown in Figs 2b and c. The circuit shown in Fig 2c, which contains Warburg element, is used in the case of AOTMT film covered copper, where the Warburg impedance is seen.

In these circuits, double layer capacitance is replaced by constant phase element, because the film formed in an electrochemical system does not behave as an ideal capacitor. CPE can thus be regarded as non-ideal capacitance[17]. The CPE is a special element, whose value is a function of the angular frequency (ω) and whose phase is independent of the frequency. Its admittance and impedance are, respectively, expressed as follows:

$$Y_{\mathrm{CPE}} = Y_0\,(\mathrm{jw})^{-\mathrm{n}} \qquad \ldots (1)$$

$$Z_{\mathrm{CPE}} = 1/Y_0\,(\mathrm{jw})^{-\mathrm{n}} \qquad \ldots (2)$$

where Y_0 is the magnitude of the CPE; ω, the angular frequency; and *n*, the exponential term of the CPE[18]. The *n* value is used to account for the roughness of the electrode. The lower the value of *n*, the rougher is the electrode surface. The value of *n* is also related to the inherent physical and chemical heterogeneous nature of the solid surface[19], the presence of porous corrosion product layer[20] and non-uniform distribution of current density on the surface[18].

The impedance parameters of the present studies are given in Table 1. The R_{ct} value is found to be 1942 kΩ cm^2 for copper covered with AOTMT nano film formed in 2.5 mM concentration of AOTMT solution. The '*n*' value is also increased to 0.84. Therefore, the optimum concentration for formation of AOTMT film is established as 2.5 mM AOTMT.

The Bode plots are then recorded for copper modified with AOTMT film at 2.5 mM concentration to optimize the immersion period. It is evident from the plots that at an immersion period of 24 h, the phase angle maximum is increased to 90^0. The /Z/ *vs.* f curve shows that the total impedance is also increased. The impedance parameters are given in Table 2. The R_{ct} and R_{film} values are found to be high at 24 h immersion period. Both the n_1 and n_2 values are increased. From all these observations, it is found that 24 h immersion period is the optimum immersion period to form AOTMT nano film on copper surface.

Table 1–Impedance parameters of copper covered with AOTMT nano film formed at different concentrations of AOTMT

[Environment: 300 ppm chloride (NaCl), immersion period 0.5 h and temperature 30°C]

AOTMT conc., mM	R_{ct} kΩ cm^2	CPE_1 μF/cm^2	n_1	R_{film} kΩ cm^2	CPE_2 μF/cm^2	n_2
1.0	54.65	1.994	0.57	1.057	0.35	0.43
1.5	144.2	0.48	0.78	5.756	0.23	0.58
2.0	345.4	0.01	0.78	6.193	0.51	0.72
2.5	1942	0.01	0.84	7.522	0.01	0.73

Table 2 –Impedance parameters of copper covered with AOTMT nano film formed at different immersion periods in 2.5 mM concentrations of AOTMT

[Environment: 300 ppm chloride (NaCl), immersion period 0.5 h and temperature 30°C]

Immersion Period, h	R_{ct} kΩ cm^2	CPE_1 μF/cm^2	n_1	R_{film} kΩ cm^2	CPE_2 μF/cm^2	n_2
3	44.64	0.67	0.48	0.54	0.38	0.60
6	80.77	0.44	0.52	2.521	0.45	0.65
12	448.4	0.15	0.64	5.658	0.08	0.68
24	1942	0.01	0.84	7.522	0.01	0.73

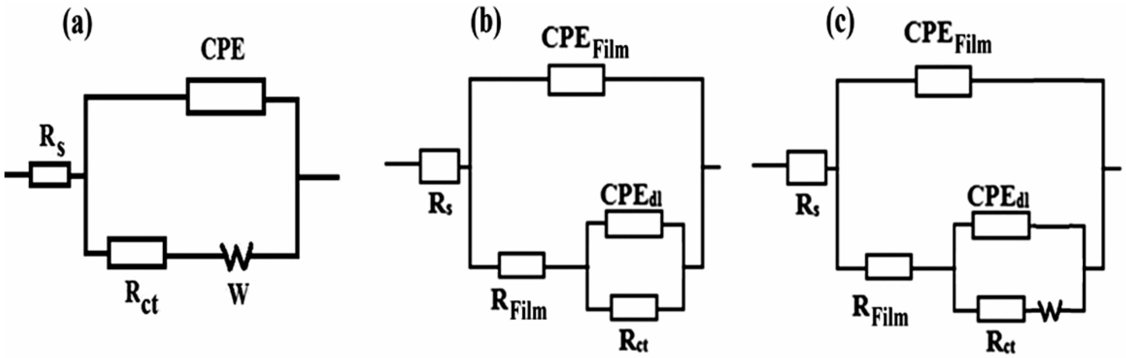

Fig. 2— Equivalent circuits used in impedance measurements of (a) bare copper electrode, (b) copper electrode covered with AOTMT nano film and (c) copper electrode covered with AOTMT nano film with Warburg [R_{ct}— charge transfer resistance, R_{film}— film resistance, CPE— constant phase element, CPE_{film}— constant phase element of film, W—Warburg impedance, CPE_{dl}— constant phase element of double layer and R_s—solution resistance]

The plot of mass change *vs*. time obtained from the EQCN experiment shows an increase in mass in the first 80 min followed by a tendency towards saturation with a further increase in time up to 140 min. The increase in mass is due to the formation of nano film of AOTMT on the copper surface. It is known that the formation of the nano film on copper surface occurs in two steps[21]. In the first step, AOTMT molecules are adsorbed on the copper surface, and in the second step, they rearrange to form an ordered nano film. Obviously, the first step involving chemisorption takes relatively less time and the second step involving the rearrangement of the organic molecules in the film takes relatively longer time. This can be clearly understood by a large increase of charge transfer resistance when the AOTMT nano film formation is allowed up to 24 h.

Characterization of AOTMT nano film

Contact angle measurements

The contact angle values for bare copper and copper covered with AOTMT nano film are found to be 78° and 90° respectively. A larger contact angle for the copper covered with AOTMT nano film indicates the hydrophobic nature of the nano film. The degree of hydrophobicity of AOTMT nano film is comparable to that of the SAMs formed by 4-aminobenzenethiol[22], 2-(octadecylthio)-benzothiazole[11] and 5-methoxy-2-(octadecylthio)-benzimidazole[12].

X-ray photoelectron spectral studies

In the XPS spectrum of bare copper, the peaks due to Cu $2p_{3/2}$, C 1s and O 1s electrons are detected. The Cu $2p_{3/2}$ peak at a binding energy of 932.6 eV can be attributed to Cu (I). The C 1s electron binding energy at 285.0 eV corresponds to contaminant carbon, which is likely due to cracking of vacuum oil used in the XPS instrument[23]. The O 1s peak observed at 531.1 eV is due to formation of Cu_2O on the copper surface[24], which is formed during the interval between polishing of the copper surface and the XPS analysis.

The XPS spectrum of copper modified with AOTMT nano film shows peaks corresponding to Cu $2p_{3/2}$, O 1s, C 1s, N 1s, and S 2p. Cu 2p spectrum shows peak due to Cu $2p_{3/2}$ at 932.5 eV, which is due to the initial oxidation of copper surface to Cu_2O during film formation. C 1s shows two peaks, one at 284.6 eV and the other at 286.4 eV. The intense C 1s peak at 284.6 eV occurs due to the presence of 18 carbon atoms in the alkyl chain of AOTMT[25]. The C 1s peak at 286.4 eV is due to the carbon present in the triazinone ring of AOTMT. The ratio of the intensities of C 1s peak to the Cu $2p_{3/2}$ peak in the spectrum of nano film modified copper is about 30 times higher than the corresponding ratio of intensities observed in the spectrum of bare copper. This result infers the presence of AOTMT nano film on copper surface. The O 1s spectrum shows two peaks. The peak at 531.4 eV is due to formation of Cu_2O on the copper surface during film formation. The existence of oxygen in the nano film shows that the oxygen dissolved in the solution has taken part in the self-assembly process, by oxidizing the copper surface to Cu_2O[5]. The second peak at 532.8 eV is due to the presence of oxygen in AOTMT molecule itself. N 1s spectrum also shows two peaks, one at 399.5 eV and the other at 400.9 eV, which are due to the presence of nitrogen atoms in AOTMT in two different chemical environments.

Qing *et al.*[26] studied the complexes of copper with 2-amino-4,6-dimethoxypyrimidine. They obtained two N 1s peaks at 398.2 eV and 400.1 eV and interpreted them due to nitrogen atoms present in the pyrimidine ring and amino group respectively. The ‘N’ with more negative charge is supposed to have relatively lower binding energy, when compared to the ‘N’, which has less negative charge. Kharafi *et al.*[27] studied the effect of sulfide pollution on the stability of the protective film of benzotriazole on copper surface. They obtained a single peak at a binding energy of 400 eV and interpreted the same to the three nitrogen atoms of the benzotriazole ring. In the present study the peak obtained at 399.5 eV is due to delocalization of the three nitrogen atoms present in the ring, providing negative charge to the ring and the other peak observed at 400.9 eV is due to the presence of nitrogen in the substituent amino group. The intensities of the peaks are in the ratio 3:1. The characteristic binding energy of the elemental nitrogen is reported as 398.0 eV in the literature[28]. The shift of N 1s binding energy from elemental binding energy indicates that the nitrogen atoms present in AOTMT play a vital role in complex formation between copper and AOTMT[23]. S 2p spectrum shows two peaks at 163.0 and 164.3 eV, which are due to S $2p_{3/2}$ and S $2p_{1/2}$ components respectively. There is a separation of 1.3 eV between the two peaks. In the literature[9] when SAM formation was done through a thiolate group namely RS^-, the two peaks due to S $2p_{3/2}$ and S $2p_{1/2}$ were reported at 162.5 and 163.7 eV respectively, with a separation of 1.2 eV. It must be noted that in the present study in the case of AOTMT nano film, sulfur is not present as thiolate but is found as sulfur with a lone pair of electrons and hence the slightly higher binding energy values of the two S 2p peaks are observed.

Reflection absorption FTIR spectral studies

For bare copper, the spectrum shows a peak at 489.5 cm^{-1}, which is assigned to copper oxide on the surface[29]. In the present study, the reflection absorption FTIR spectrum of copper modified with AOTMT film exhibits two bands, one at 2848 cm^{-1} and the other at 2915 cm^{-1}. These two bands are interpreted due to CH_2 symmetric and CH_2 asymmetric stretch modes respectively[30]. This indicates the aliphatic hydrocarbon chain present in the AOTMT film formed on copper surface. The reflection absorption FTIR spectrum of copper covered with AOTMT nano film also shows the appearance of C═O stretching band at 1747 cm^{-1}, C═N stretching band at 1462 cm^{-1} and C─S stretching band at 750 cm^{-1} [31]. These peaks infer the formation of a self-assembled nano film of AOTMT on the copper surface. The lowering of C═N stretching band from 1600 cm^{-1} to 1456 cm^{-1} reveals the formation of complex between AOTMT film and copper surface through nitrogen[32]. The vibration stretching band at 524 cm^{-1} is due to the copper oxide formed due to initial oxidation of copper surface during formation of nano film[29].

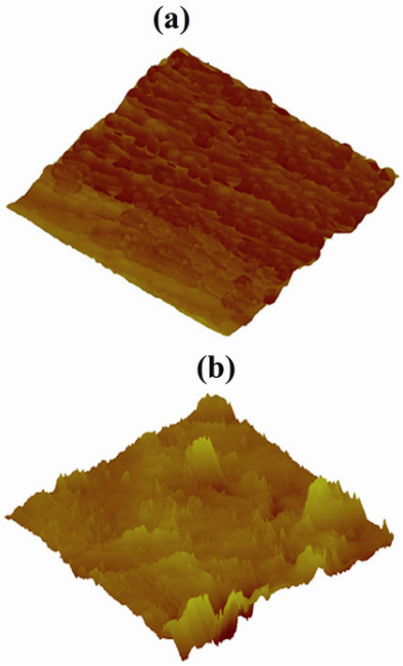

Fig. 3– AFM images of (a) bare copper and (b) copper covered with AOTMT nano film

Surface analysis by atomic force microscopy

AFM images of bare copper and copper modified with AOTMT nano film are shown in Figs 3a and b respectively. The topographical changes of copper surface as a result of formation of nano film are qualitatively characterized. The AFM image of bare copper surface shows a homogeneous film consisting of copper surface. On the other hand, the AFM image of the AOTMT nano film covered copper surface shows continuous small nodules, which cover the entire surface. This layer isolates the copper surface from the corrosive environment.

Corrosion protection of copper by AOTMT nano film

Electrochemical impedance studies in aqueous HCl environment

The Nyquist and Bode plots of bare copper in aqueous HCl solutions at different concentrations (0.02–0.20 M) are shown in Figs 4a and b respectively. The high frequency capacitive loop in Nyquist plot is so small at all concentrations. The Nyquist plots are almost shielded by a straight line in the low frequency domain. In the phase angle Bode

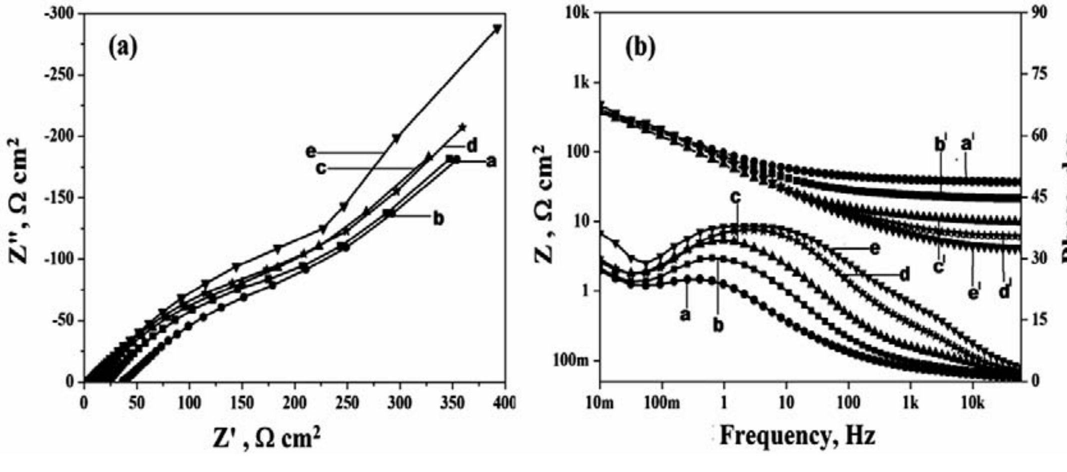

Fig. 4– (a) Nyquist and (b) Bode plots of bare copper in different concentrations of HCl at 0.5 h immersion period (HCl conc.: a,a^1-0.02 M, b,b^1-0.05 M, c,c^1-0.10 M, d,d^1-0.15 M and e,e^1-0.20 M) [Temperature 30 °C]

plot, the phase angle maximum is found to be in the range 20–35^0 and is shifted towards mid frequency region with increase in concentration of HCl. This infers the presence of oxide film on the copper surface. The */Z/ vs.* f curves show a decrease in impedance values with increase in HCl concentration. In the case of bare copper, the impedance parameters are calculated by using simple Randles circuit shown in Fig. 2a and the corresponding impedance parameters are shown in Table 3. The '*n*' values are in the range of 0.39–0.37, which indicate the roughness of the copper surface.

The Nyquist and Bode plots of copper covered with AOTMT nano film in aqueous HCl environment are shown in Figs 5a and b respectively. These Nyquist plots are quite different from those of bare copper. The Warburg impedance is disappeared at low frequencies indicating that the nano film is sufficiently densely packed to prevent the diffusion of oxygen or Cl^- ions to the copper substrate and thus inhibits the corrosion of copper.

A large depressed semicircle is observed in the region from high frequency to low frequency indicating that the charge transfer resistance is dominant in the corrosion process due to the presence of AOTMT nano film on the copper surface. This is also supported by Bode plots, in which the phase angle maxima are found to be in higher frequency domain. However, the diameter of semicircle in Nyquist plots and phase angle maximum in Bode plots are decreased with an increase in HCl concentration. It is interesting to note that even at 0.20 M HCl concentration, the phase angle maximum is found to be more than 60° and it is broadened. The impedance parameters are given in Table 3. At 0.02 M concentration of HCl, the R_{ct} value of copper modified with AOTMT nano film is found to be 50.37 kΩ cm^2, which is far higher than that in the case of bare copper (0.64 kΩ cm^2). At all concentrations, R_{ct} values of copper surface covered with AOTMT are far greater than those of bare copper. The CPE_1 value at the copper/0.02 M HCl interface is found to decrease from

Table 3 –Impedance parameters of bare copper and copper covered with AOTMT nano film at different HCl concentrations [Immersion period: 0.5 h and temperature: 30° C]

Specimen	HCl conc., M	R_{ct} kΩ cm^2	CPE_1 µF/cm^2	n_1	R_{film} kΩ cm^2	CPE_2 µF/cm^2	n_2	IE, %
Bare copper	0.02	0.64	27.37	0.39	-	-	-	-
Copper with AOTMT film	0.02	50.37	0.14	0.81	52.31	0.11	0.80	98.73
Bare copper	0.05	0.52	30.65	0.39	-	-	-	-
Copper with AOTMT film	0.05	32.94	0.15	0.79	30.55	0.12	0.71	98.42
Bare copper	0.10	0.49	42.92	0.38	-	-	-	-
Copper with AOTMT film	0.10	18.68	0.16	0.78	13.82	0.14	0.70	97.38
Bare copper	0.15	0.44	44.90	0.38	-	-	-	-
Copper with AOTMT film	0.15	18.15	0.17	0.73	11.33	0.25	0.67	97.58
Bare copper	0.20	0.42	48.66	0.37	-	-	-	-
Copper with AOTMT film	0.20	4.34	0.30	0.73	1.03	0.54	0.62	90.32

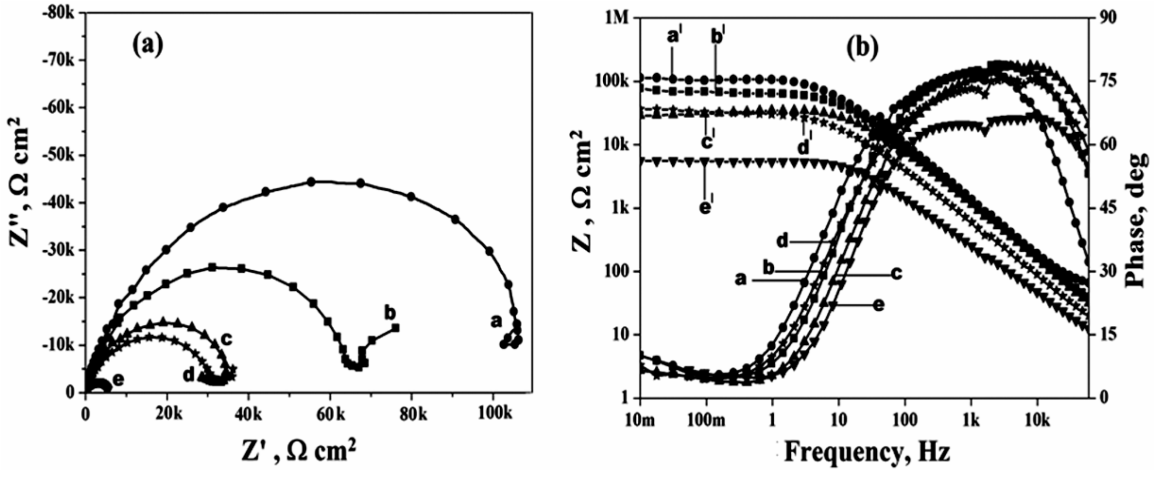

Fig. 5–(a) Nyquist and (b) Bode plots of copper covered with AOTMT nano film in different concentrations of HCl at 0.5 h immersion period. (HCl conc.: a,a^1-0.02 M, b,b^1-0.05 M, c,c^1-0.10 M, d,d^1-0.15 M and e,e^1-0.20 M) [Temperature 30 °C].

27.37 µF cm^{-2} in the case of bare copper to a very small value of 0.14 µF cm^{-2} in the case of copper surface covered with AOTMT nano film. This is because the water molecules in the electrical double layer are replaced almost completely by the organic molecules having a very low dielectric constant[5]. AOTMT nano film shows an inhibition efficiency of 90.32% evan at 0.20 M HCl environment.

It is of interest to investigate the effect of immersion period on the stability of AOTMT nano film formed on copper surface. In the case of bare copper, with the increase in immersion period, the R_{ct} values are decreased and are found to be very less. The phase angle maximum is also found to be in the range of 18^o–22^o. However, in the case of copper modified with AOTMT nano film, the diameter of semicircle is increased, when compared with bare copper. The corresponding R_{ct} values are also increased. However, with increase in immersion period, R_{ct} values are decreased slightly. The phase angle maximum at 0.5 h immersion period is found to be 78^0. It is reduced to 65^o after 24h immersion period, though broadening of phase angle maximum is retained. The impedance parameters are given in Table 4. The results reveal that even after 24 h immersion period, AOTMT nano film shows its ability to protect copper from corrosion.

Impedance studies of bare copper and copper covered with AOTMT nano film in 0.02 M HCl after immersion for 0.5 h and at different temperatures are also carried out. In the case of bare copper, the Nyquist plots show the Warburg behavior, which is increased with increase in temperature. The phase angle maximum is also decreased and shifted towards lower frequency region with increase in temperature. In the presence of AOTMT nano film also the R_{ct} values are decreased with increase in temperature. However, these values are higher than those in the case of bare copper under the same conditions. At 60^o C, the phase angle maximum is found to be 63^0 and it is somewhat shifted towards mid frequency region. Both the R_{ct} and R_{film} values are found to decrease with increase in temperature. Nevertheless, these values are still much higher in comparison to the corresponding values of bare copper. Hence, inhibition efficiencies of >93% are obtained even at 40°, 50° and 60° C. Both the CPE_1 and CPE_2 values are increased. Both the n_1 and n_2 values are decreased to some extent with increase in temperature. All these results are indicative of the deviation of double layer and also of the film from more capacitive to less capacitive behavior with an increase in temperature.

Potentiodynamic polarization studies

Potentiodynamic polarization curves for bare copper and copper covered with AOTMT nano film are obtained at HCl concentration range 0.02–0.20 M after an immersion period of 0.5 h. Compared with the bare copper, lower i_{corr} values are obtained for copper covered with AOTMT nano film in HCl solutions (Table 5).

With increase in HCl concentration, i_{corr} values are increased for both bare copper and copper covered with nano film. In the present study, the corrosion potential (E_{corr}) of the copper electrode is shifted towards more negative side after the deposition of AOTMT nano film on copper surface. The cathodic Tafel slope is shifted to a great extent in presence of the nano film on the copper surface. For example at 0.02 M HCl, the cathodic Tafel slope (b_c) is shifted from –591 mV/dec to –52 mV/dec, while the anodic shift is only 9 mV/dec in presence of AOTMT nano film on the copper surface. It may be inferred that AOTMT nano film on copper surface retards the cathodic reaction of the corrosion process. The literature reports also mentioned that SAMs of different molecules act as cathodic inhibitors[33].

Table 4 –Impedance parameters of bare copper and copper covered with AOTMT nano film in 0.02 M HCl environment at different immersion periods

[Temperature: 30 °C]

Specimen	Imm. time, h	R_{ct} kΩ cm^2	CPE_1 µF/cm^2	n_1	R_{film} kΩ cm^2	CPE_2 µF/cm^2	n_2	IE, %
Bare copper	0.5	0.64	27.37	0.39	-	-	-	-
Copper with AOTMT film	0.5	50.37	0.14	0.81	52.31	0.11	0.80	98.73
Bare copper	6	0.58	30.22	0.34	-	-	-	-
Copper with AOTMT film	6	42.10	0.17	0.80	40.72	0.24	0.79	98.62
Bare copper	12	0.51	31.74	0.35	-	-	-	-
Copper with AOTMT film	12	26.14	1.076	0.70	24.62	0.52	0.76	98.05
Bare copper	24	0.45	35.89	0.34	-	-	-	-
Copper with AOTMT film	24	10.71	1.355	0.63	9.71	0.60	0.71	95.78

Table 5 –Corrosion parameters obtained by potentiodynamic polarization studies of bare copper and copper covered with AOTMT nano film at different HCl concentrations

[Immersion period: 0.5 h, temperature: 30°C]

Specimen	HCl conc. M	E_{corr} mV	i_{corr} µA/cm^2	b_a mV/decade	b_c mV/decade	IE %
Bare copper	0.02	-42.7	13.1	46	-591	-
Copper with AOTMT film	0.02	-101.6	0.13	37	-52	99.00
Bare copper	0.05	-73.5	13.4	50	-626	-
Copper with AOTMT film	0.05	-118.8	0.25	32	-49	98.13
Bare copper	0.10	-108.5	14.1	54	-535	-
Copper with AOTMT film	0.10	-122.5	0.78	31	-57	94.46
Bare copper	0.15	-132.8	15.2	59	-523	-
Copper with AOTMT film	0.15	-128.4	1.73	25	-53	88.61
Bare copper	0.20	-144.8	16.1	62	-491	-
Copper with AOTMT film	0.20	-137.3	2.54	22	-77	84.22

Cyclic voltammetric studies

The cyclic voltammograms were recorded for bare copper in 0.02 M HCl after an immersion period of 0.5 h at different sweep rates in the potential range from -0.400 to +0.350 V *vs.* Ag/AgCl electrode. In the forward sweep only one anodic peak is observed and in the reverse sweep also only one cathodic peak is observed. It has already been reported in the literature[34] that at low concentrations and at sweep rates as high as 30 mVs^{-1}, only one peak due to oxidation of Cu to Cu^{2+} in the anodic direction and one cathodic peak due to reduction of Cu^{2+} to Cu are observed in the potential range studied. Both the anodic and cathodic peak currents are increased with increase in sweep rate from 30 mVs^{-1} to 120 mVs^{-1}. The anodic and cathodic currents are not significantly affected with the increase in number of cycles to 15.

The CV studies of the copper modified with AOTMT nano film at different sweep rates also exhibit a single anodic peak and a single cathodic peak, with much lower peak currents in comparison to bare copper. For example, at a sweep rate of 30 mVs^{-1} the anodic peak current is reduced to 35 µA cm^{-2} in case of copper covered with AOTMT nano film from 2.0 mA cm^{-2} in the case of bare copper and the cathodic current is reduced to 10.0 µA cm^{-2} from 1.1 mA cm^{-2}. Thus, the CV studies also provide evidence for the excellent protection of copper surface from corrosion by AOTMT nano film in the environment studied. The CV studies of the copper modified with AOTMT for 15 cycles bring out clear evidence that the AOTMT nano film is highly stable. This study also reveals that the AOTMT nano film is effective even upto the anodic potential of 0.600 V *vs.* Ag/AgCl without any sign of its oxidation.

X-ray photoelectron spectroscopic studies

In the XPS survey spectrum of bare copper after immersion in 0.02 M HCl environment for 3 days, Cu $2p_{3/2}$, Cu $2p_{1/2}$ and O 1s peaks are detected, along with two Cl 2p peaks at 198.2 and 199.8 eV.

The peak at 198.2 eV corresponds to Cl $2p_{3/2}$ and the one at 199.8 eV corresponds to Cl $2p_{1/2}$. The XPS spectrum of copper covered with AOTMT nano film after immersion in 0.02 M HCl environment for 3 days shows peaks corresponding to Cu $2p_{3/2}$, Cu $2p_{1/2}$, O 1s, C 1s, N 1s and S 2p. The Cl 2p peak is not found. The computer deconvolution spectra for copper, oxygen, carbon, nitrogen and sulfur are shown in Figs 6A-E respectively.

If we compare these spectra with the corresponding spectra of the copper modified with AOTMT nano film before immersion in 0.02 M HCl, a small increase in intensity of O 1s peak is observed. However, no significant change is observed in the intensities of Cu 2p, C 1s, N 1s and S 2p peaks. It is thus evident from the XPS spectra that the AOTMT nano film is stable and offers good protection to copper surface from corrosion in the environment studied.

Weight-loss studies

Results of weight-loss studies after an immersion period of three days in 0.02 M HCl environment show a corrosion rate of 0.1631 mmpy for bare copper and only 0.0064 mmpy for copper covered with AOTMT nano film. The relative standard error in corrosion rate determinations is of the order of 2% or less[35]. An inhibition efficiency of 99.4% is obtained from weight-loss studies. These results infer that the corrosion protection ability of the AOTMT nano film is quite good even after an immersion period of three days in the corrosive environment. The inhibition

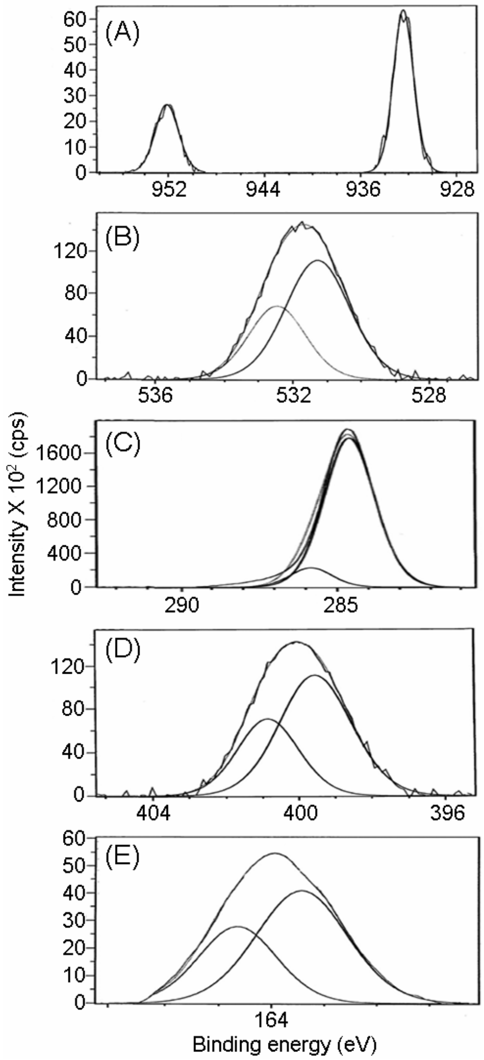

Fig. 6– XPS deconvolution spectra of different elements present on the copper covered with AOTMT nano film after immersion in 0.02 M HCl solution for a period of 3 days (A— Cu 2p, B— O 1s, C — C 1s, D — N 1s and E — S 2p).

efficiency obtained from weight loss studies is in good agreement with the values obtained from impedance studies and polarization studies though the immersion period is different in each of the methods.

Quantum chemical calculations

It has been reported that the higher the HOMO energy and negative charges of the adsorbed centres of the inhibitor, the greater is the ease of offering electrons to the unoccupied d orbital of metallic copper and the greater the chemisorption[36]. It has also been reported that inhibitors can form coordination bonds between the unshared electron pair of the N atom, π electrons of aromatic ring and the unoccupied d electron orbital of the metal[37]. The inhibition efficiency of AOTMT for copper corrosion in HCl solution can be attributed to the higher HOMO energy, lower energy gap between LUMO and HOMO and a high negative total ring charge of the AOTMT molecule. The negative charge on the two N atoms suggests the possibility of complex formation between Cu^+ ions and AOTMT through the two nitrogens present in the ring.

Mechanistic aspects of corrosion protection by AOTMT nano film

In the absence of AOTMT nano film, anodic dissolution of copper in chloride environment proceeds via following two-step oxidation process:

$$Cu + Cl^- \rightarrow CuCl + e^- \qquad \ldots (3)$$

$$CuCl + Cl^- \rightarrow CuCl_2^- \qquad \ldots (4)$$

The CuCl has poor adhesion and is unable to protect the copper surface. It transforms into the soluble cuprous chloride complex ($CuCl_2^-$)[38]. The cathodic corrosion reaction in acidic chloride environment[39] is shown below:

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \qquad \ldots (5)$$

A plausible mechanism for corrosion protection of copper by AOTMT nano film is discussed hereunder. The AOTMT molecule gets chemisorbed on the surface of copper and forms a chelate with Cu^+ ions already existing on the copper surface due to initial corrosion of copper, which occurs during the time between etching of copper surface in 7 N HNO_3 and its immersion in the AOTMT containing solution. The Cu^+ ions, which have vacant 4s and 4p orbitals accept the lone pair of electrons from nitrogen atoms of AOTMT and form [Cu^+- AOTMT] complex. The AOTMT molecules, which are essentially derived from the triazinone moiety, are considered to be oriented parallel to the copper surface. In such an orientation, the [Cu^+-AOTMT] complexation may lead to the formation of a polymeric net work on the copper surface. It may be noted that Cu^+ is known to form bidentate complexes. Besides the strong coordinate linkages between Cu^+ and N, there are van der Waal interactions between the long alkyl chains. Thus, there is formation of a [Cu^+–AOTMT] polymeric complex, which is highly protective in nature. Impedance studies show disappearance of

Warburg diffusion in case of AOTMT film covered copper. This result indicates that there is no diffusion of oxygen from solution to the copper surface. Similarly polarization studies also show that the AOTMT nano film controls the cathodic reduction of oxygen as the film acts as a barrier to the diffusion of oxygen. From these studies, it is inferred that the protective film acts as a barrier to diffusion of O_2 and hence no electron transfer occurs across the metal solution/interface. In the light of the above results and interpretations reported in the literature[22], it is proposed that in the case of the present study of self-assembly of 4-amino-3-(octadecylthio)-6-methyl-1,2,4-triazinone, there is formation of a chemisorbed polymeric nano film.

Conclusion

The optimum conditions for the formation of protective nano film of 4-amino-3-(octadecylthio)-6-methyl-1,2,4-triazinone on copper surface are (i) etching of copper surface in 7 M nitric acid for 30 s, (ii) methanol as solvent, (iii) 2.5 mM concentration of AOTMT in methanol, (iv) an immersion time of 24 h and (v) an ambient temperature of 30°C. The nano film formed by AOTMT on copper surface offers excellent corrosion protection of copper in HCl solution within the concentration range studied, i.e. upto 0.20 M at the ambient temperature 30°C. The AOTMT nano film offers good inhibition upto a temperature of 60°C in 0.02 M HCl solution. The inhibition efficiencies obtained from electrochemical impedance, potentiodynamic polarization and weight-loss studies are in good agreement with each other. AOTMT molecule functions as cathodic inhibitor. The AOTMT molecules get chemisorbed on copper surface and form a polymeric coordination complex with Cu^+ ions through nitrogen atoms.

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