Bull. Mater. Sci., Vol. 37, No. 2, April 2014, pp. 185–197. © Indian Academy of Sciences.

Self-assembled nanofilm of 1,2-dihydro-3-(octadecylthio)benzotriazine on copper for corrosion protection

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MS received 24 September 2012; revised 6 February 2013

Abstract. **The self-assembled nanofilm of 1,2-dihydro-3-(octadecylthio)benzotriazine (DOTBT) was formed on fresh copper surface obtained by etching with 7 N nitric acid at a room temperature of 30 °C. The conditions for formation of the DOTBT nanofilm have been optimized by electrochemical impedance and electrochemical quartz crystal nanobalance (EQCN) studies. The DOTBT nanofilm on copper surface was characterized by contact-angle measurement, X-ray photoelectron spectra (XPS), reflection absorption FTIR spectra and atomic force micrographs (AFM). It is inferred that formation of DOTBT film is due to chemisorption of DOTBT on copper surface through nitrogen and subsequent complex formation between DOTBT and Cu^+ ions. Corrosion protection ability of DOTBT nanofilm was evaluated in dilute aqueous NaCl solution using electrochemical impedance, potentiodynamic polarization, weight-loss and XPS studies. These studies inferred that the DOTBT film protects effectively copper from corrosion. Potentiodynamic polarization studies revealed that the DOTBT film inhibits corrosion by controlling the cathodic reaction. The mechanism of corrosion protection of copper by DOTBT nanofilm is discussed in this paper.**

Keywords. **Copper; benzotriazine; self-assembled nanofilm; impedance; EQCN; AFM.**

1. Introduction

Copper is an important metal used in microelectronics, due to its high thermal and electrical conductivity (Murarka 1997; Rose 2002). The main applications of copper in microelectronic packaging are in lead frames, inter-connection wires, foils for flexible circuits, heat sinks, wire bonding and soldering. However, the applications of copper are limited by corrosion of copper forming an oxide film. Therefore, corrosion protection of copper is of great relevance in microelectronic packaging industry.

Self-assembled monolayers (SAMs) are dense and ordered thin films (Wang *et al* 2002),which act as effective barriers and protect the metals against corrosion. It has been reported that alkanethiols adsorbed on copper surface form densely packed SAMs, which retard the oxidation of copper surface in air (Laibinis and Whitesides 1992). Corrosion protection of copper by self-assembled alkanethiol monolayer in 0·5 M NaCl solution has been reported (Feng *et al* 1997). The maximum protection efficiency of copper corrosion in 0·5 M Na_2SO_4 solution using octadecanethiol SAM was reported as 80·3% (Yamamoto *et al* 1993). Self-assembled nanofilms of Schiff bases on copper surfaces were formed by the interaction of copper with nitrogen present in the Schiff base molecules (Quan *et al* 2001, 2002). Heterocyclic compounds containing nitrogen and sulfur atoms are widely used as corrosion inhibitors (Wang *et al* 2002).

So far, only a few studies on corrosion protection of copper using SAMs of heterocyclic organic compounds containing long alkyl chains have been reported in the literature. Corrosion protection of copper using the SAMs of 2-(octadecylthio)benzothiazole (Appa Rao *et al* 2009) and of 5-methoxy-2-(octadecylthio)benzimidazole (Appa Rao *et al* 2010) has been reported. However, no studies have been reported so far on corrosion protection of copper by self-assembly of heterocyclic organic molecules containing three nitrogen atoms and one sulfur atom with a long hydrocarbon chain. Therefore, it was of interest to study the corrosion protection efficiency of the nanofilm of a heterocyclic organic molecule of a different moiety namely, 1,2-dihydro-3-(octadecylthio)benzotriazine (DOTBT), which contains three nitrogen atoms and one sulfur atom in order to facilitate chemisorption on copper surface and subsequent chelation with copper ions to form a protective film. It also consists of a long hydrocarbon chain to make the film hydrophobic. It was of interest to investigate whether the nanofilm can be formed on copper surface using this molecule and if formed, whether the film has the ability to protect copper from corrosion in an aggressive environment like aqueous NaCl solution.

2. Experimental

2.1 *Materials*

DOTBT was synthesized from equimolar amounts of 1-bromo-octadecane and benzothiazole-2-thiol as per the procedure available in the literature (Rao and Kumar 2002). All

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*Author for correspondence (boyapativapparao@rediffmail.com) the chemicals were of A.R. grade and were purchased from Qualigens Chemicals, India. Differential scanning calorimetry (DSC) and ^{1}H NMR technique were used for characterization of DOTBT. Exactly 260 mg of DOTBT was dissolved in 250 mL methanol to get 2·5 mM solution. The solutions of 1·0, 1·5 and 2·0 mM were prepared by dilution from 2·5 mM solution.

Polycrystalline copper specimens of different dimensions were made from a copper sheet of purity 99·9%. For electrochemical impedance studies and potentiodynamic polarization studies, copper specimens with dimensions of 4·0 × 1·0 × 0·2 cm were used and only 1 cm^2 area was exposed to the electrolyte, while the remaining area was insulated with epoxy resin. For weight loss studies also, the specimens of the dimensions, 4·0 × 1·0 × 0·2 cm were used. For surface analytical studies, 1·0 × 1·0 × 0·2 cm specimens were used. These specimens were polished to mirror finish using 1/0, 2/0, 3/0 and 4/0 grade emery papers and alumina powder on 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.

2.2 *Formation of self-assembled nanofilm*

Solubility of DOTBT was tested in the organic solvents such as acetone, chloroform, methanol, ethyl acetate and *n*-hexane. It was observed that DOTBT is soluble only in methanol and the solubility is very less in methanol. Therefore, methanol was chosen as the solvent for formation of DOTBT nanofilm on copper surface. The polished copper specimens were etched with 7 N nitric acid for 30 s, washed first with triple-distilled water and then with methanol. The metal specimens were immediately immersed in different concentrations of 100 mL of DOTBT solution in methanol for various immersion periods.

2.3 *Electrochemical impedance studies*

Electrochemical impedance studies (EIS) were carried out in a three-electrode cell assembly using an electrochemical workstation model IM6e ZAHNER elektrik, Germany. These studies were first carried out in order to develop the optimum conditions for the formation of protective DOTBT film on copper surface. The studies were carried out at an open circuit potential (OCP) in the frequency range from 60 kHz to 10 mHz with a sinusoidal potential perturbation of ±5 mV in amplitude. Impedance studies were also carried out in order to evaluate the corrosion protection ability of DOTBT nanofilm in aqueous NaCl environment at different concentrations (0·02–0·20 M), at different immersion periods (0·5–24 h) and at different temperatures (30–60 °C). In these studies, the bare copper specimen or copper specimen covered by DOTBT film was used as the working electrode. A platinum electrode was used as the counter electrode and the reference electrode was Ag/AgCl/1 M KCl electrode. Inhibition efficiencies were calculated from the impedance data. Potentiodynamic polarization studies were also carried out by using the same electrochemical workstation described above at different concentrations of NaCl in the range of 0·02–0·20 M. The polarization curves were recorded in the potential range of −0·500–+0·200 V vs Ag/AgCl at a scan rate of 1 mVs^{-1}. Electrochemical quartz crystal nano balance system, model Elchema EQCN-700 was used for recording mass changes during the formation of DOTBT nanofilm on AT-cut copper quartz crystal with 10 MHz nominal frequency. After the film formation was complete, mass change as a function of immersion period was recorded by immersing the nanofilm covered copper quartz crystal in 0·02 M NaCl solution.

2.4 *Weight-loss studies*

The bare copper specimens and the copper specimens covered with DOTBT nanofilm were immersed in 0·02 M NaCl 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. The studies were carried out in triplicate. The relative standard error in the corrosion rate determination is of the order of 2% or less (Freeman and Silverman 1992).

2.5 *Surface analytical studies*

Reflection absorption FTIR spectra for bare copper and copper covered with DOTBT nanofilm were recorded in single reflection mode using FTIR spectrometer, model Thermo-Nicolet Nexus 670 of the Thermo Electron Corporation, USA in the spectral range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. This FTIR instrument has KBr window and XT-KBr beam splitter and lowest possible wavenumber is 400 cm^{-1}. Bare copper and DOTBT nanofilm covered copper specimens were mounted on the reflection accessory and the plane polarized light was incident at a grazing angle of 85° from the normal surface. The sample compartment was continuously purged with nitrogen during the measurement. The surface analysis of bare copper and DOTBT nanofilm covered copper was also carried out using the X-ray photoelectron spectrometer, ESCA Kratos model AXIS-165, with MgKα 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 nanofilm. XPS studies were also used to analyse the nature of the surface films in the presence of a corrosive environment i.e. 0·02 M NaCl. Veeco Nanoscope IV multimode AFM was used for studying the morphology of copper surface covered with nanofilm. The AFM was used in the contact mode between a silicon nitride tip attached to a micro cantilever and the surface of the sample.

2.6 *Contact-angle measurements*

Contact-angle measurements for bare copper and copper covered with DOTBT nanofilm 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.

2.7 *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 DOTBT and the total ring charge were obtained from these calculations.

3. Results and discussion

3.1 *Optimum conditions for formation of DOTBT nanofilm*

The best immersion time was reported to be more than 20 h for the formation of nanofilm of Schiff base on copper surface (Quan *et al* 2001). Our results also showed that an immersion period of 24 h facilitates the formation of good protective film. Therefore, in the present study, an immersion period of 24 h was fixed initially and the concentration of DOTBT was varied from 1·0 to 2·5 mM (solubility limit).

Nyquist and Bode plots for DOTBT modified copper electrodes at different concentrations of DOTBT (1·0–2·5 mM) are obtained in 300 ppm chloride environment. Bode plots provide more valuable information than Nyquist plots. Hence, only Bode plots are presented in figure 1. Considering the phase angle vs frequency plot, with an increase in concentration of DOTBT from 1·0 to 2·5 mM, the phase angle maximum is increased from 46 to 85° and it is more broadened. This result reveals that the DOTBT nanofilm is close to capacitive behaviour. The Nyquist plots (not shown) at higher concentrations show the absence of Warburg behaviour. The corresponding impedance parameters are obtained using the equivalent circuit models shown in figure 2(a and b). The circuit shown in figure 2(a), which contains Warburg element, is used in the case of DOTBT film covered copper, where the Warburg impedance is seen. A constant phase element (CPE) was used as a substitute for the double-layer capacitance in the equivalent circuits in order to fit the impedance data more accurately (Scheider 1975; Wu *et al* 1999). The CPE is a special element, whose value is a function of the angular frequency (w), and whose phase is independent of the frequency. Its admittance and impedance are respectively, expressed as

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

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

where Y_0 is the magnitude of the CPE, j the imaginary number ($j = (-1)^{1/2}$), w the angular frequency and n the exponential term ($0 \leq n \leq 1$) of the CPE. n value indicates the roughness of the electrode. The lower the value of n, the rougher is the electrode surface. The lower value of n also relates to the inherent physical and chemical heterogeneous nature of the solid surface (Mc Cafferty 1997), the presence of a porous corrosion product layer (Touzet *et al* 1993) and the non-uniform distribution of current density on the surface (Macdonald *et al* 1982). If $n = 1$, the impedance of a CPE is identical to the impedance of the ideal capacitor.

The charge transfer resistance (R_{ct}) and the film resistance (R_{film}) throw more light on the protective nature of the nanofilm. The results given in table 1 reveal that the R_{ct} and R_{film} values are the highest and the CPE values are the lowest in the case of film formed from 2·5 mM concentration of DOTBT. Interestingly, the n value is close to 1. Therefore, 2·5 mM concentration is chosen as the optimum concentration for formation of dense and protective film.

By fixing the concentration of DOTBT solution as 2·5 mM, DOTBT nanofilms are formed on copper surface at different immersion periods in the range of 3–24 h. The Bode plots of the DOTBT modified copper electrodes at different immersion periods are obtained in 300 ppm chloride environment and are shown in figure 3. The corresponding impedance parameters are shown in table 2. The phase angle vs frequency plot reveals that at higher immersion period of 24 h, the phase angle maximum is the highest and the $|Z|$ vs f plot shows that total impedance is increased with increase in immersion period. For example, after 24 h immersion period, the R_{ct} and R_{film} values are increased to very large values of 721·3 and 70·22 kΩ cm^2, respectively. Both the n and n_{film} values are increased and CPE and CPE$_{\mathrm{film}}$ values are decreased. All these observations reveal that the optimum immersion time for the formation of protective DOTBT nanofilm is 24 h.

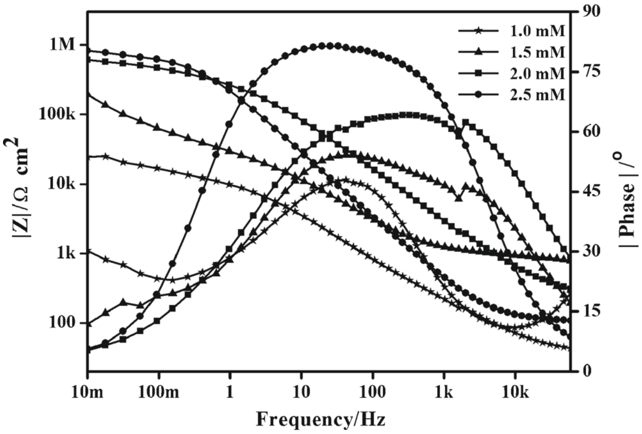

Figure 1. Bode plot of copper covered with DOTBT nanofilm formed in different concentrations of DOTBT (environment: 300 ppm chloride, temperature: 30 °C).

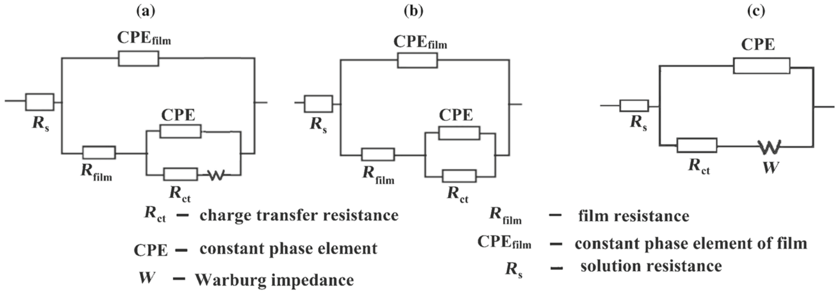

Figure 2. Equivalent circuits used in impedance measurements of (**a**) copper electrode covered with DOTBT nanofilm with Warburg, (**b**) copper electrode covered with DOTBT nanofilm and (**c**) bare copper electrode.

Table 1. Impedance parameters of copper covered with DOTBT nanofilm formed in different concentrations of DOTBT (environment: 300 ppm chloride, immersion period: 0·5 h, temperature: 30 °C).

S. no.	Concentration of DOTBT (mM)	R_{ct} (kΩ cm^2)	CPE (μF/cm^2)	n	R_{film} (kΩ cm^2)	CPE$_{film}$ (μF/cm^2)	n_{film}
1	1·0	20·26	0·514	0·55	8·13	0·769	0·64
2	1·5	40·53	0·276	0·84	20·2	0·041	0·67
3	2·0	556·1	0·034	0·89	33·6	0·017	0·70
4	2·5	721·3	0·033	0·93	70·2	0·022	0·73

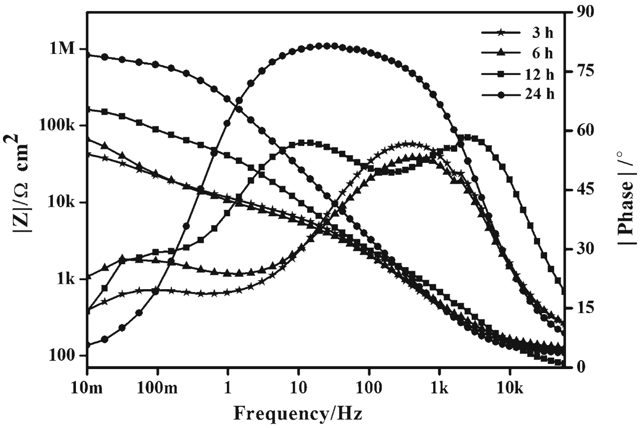

Figure 3. Bode plot of copper covered with DOTBT nanofilm formed in 2·5 mM DOTBT at different immersion periods (environment: 300 ppm chloride, temperature: 30 °C).

Figure 4(a and b) shows the mass change vs time plots obtained from the EQCN experiment in the case of blank (in methanol) and with DOTBT film, respectively. The blank curve shows negligible mass change with time, which indicates that there is not much adsorption of methanol on the copper surface. The curve with DOTBT film shows an initial increase in mass in the first 60 min followed by a tendency towards saturation with a further increase in time up to 105 min. The increase in mass of the copper quartz crystal is due to the formation of nanofilm of DOTBT on its surface. It is known that the formation of the self-assembled monolayer on copper surface occurs in two steps (Brzoska *et al* 1992). In the first step, the organic molecule chemisorbs on the copper surface and in the second step, it rearranges to form an ordered monolayer. Obviously, the first step involving chemisorption takes relatively less time and the second step involving the rearrangement of the organic molecules in the SAM takes relatively longer time. This is evidenced by the increase in charge transfer resistance of the nanofilm formed after 24 h immersion time. Therefore, an immersion period of 24 h is fixed as another optimum condition for formation of DOTBT nanofilm.

3.2 *Characterization of DOTBT nanofilm*

3.2a *Contact angle measurements*: The contact angle values for bare copper and DOTBT modified copper are found to be 78 and 93°, respectively. A relatively larger contact angle for the DOTBT covered copper surface, when compared with bare copper, indicates the hydrophobic nature of the nanofilm. The degree of hydrophobicity is higher in the case of films formed by the molecules containing long alkyl chains. The hydrophobicity of the DOTBT film is comparable to that of the SAM formed by 4-aminobenzenthiol (Tan *et al* 2006), 2-(octadecyl thiobenzothiazole) (Appa Rao *et al* 2009) and 5-methoxy-2-(octadecylthio)benzimidazole (Appa Rao *et al* 2010). However, the contact angle of DOTBT modified copper is lower than the contact angle of octadecanethiol (ODT) SAM on copper surface (Petrovic *et al* 2008). The reason is that the adsorbed DOTBT molecule is considered to be oriented parallel to the copper surface, while the ODT molecule is oriented perpendicular to

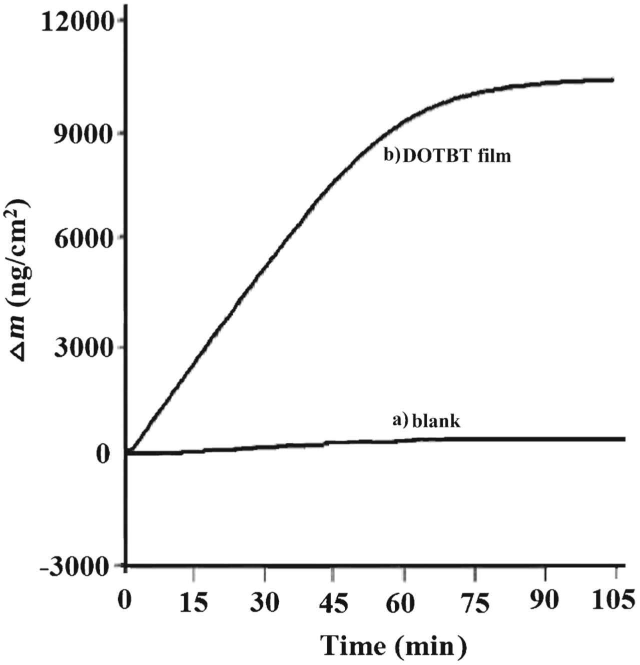

Figure 4. Mass change vs time curves obtained by quartz crystal nano balance (**a**) blank and (**b**) with DOTBT film.

copper surface and hence, a relatively larger contact angle with water drop, in case of the latter.

3.2b *X-ray photoelectron spectral studies*: In the XPS spectrum of bare copper, the peaks due to Cu $2p_{3/2}$, Cu $2p_{1/2}$, C 1*s* and O 1*s* electrons are detected. The computer deconvolution spectra for copper, carbon and oxygen are shown in the figure 5(a–c), respectively. The Cu $2p_{3/2}$ peak at a binding energy of 932·6 eV and the Cu $2p_{1/2}$ peak at 952·4 eV can be attributed to Cu (I) (Wang *et al* 2002). The C 1*s* electron binding energy at 285 eV corresponds to contaminant carbon, which is likely due to the cracking of vacuum oil used in the XPS instrument (Cicileo *et al* 1999). The O 1*s* peak observed at 531·1 eV is due to the formation of Cu_2O on the copper surface (Petkova *et al* 1998; Ye *et al* 1998), which is formed during the interval between polishing of the copper surface and the XPS analysis. In the XPS spectrum of DOTBT modified copper surface, Cu 2*p*, O 1*s*, C 1*s*, N 1*s* and S 2*p* peaks are detected and their deconvolution spectra are shown in figure 6(a–e), respectively. The peaks at 932·5 eV for Cu $2p_{3/2}$ and at 952·4 eV for Cu $2p_{1/2}$ are due to the initial oxidation of copper surface to Cu_2O during film formation. The C 1*s* spectrum shows two peaks, one at 284·7 eV and the other at 287·4 eV. The intense peak observed at 284·7 eV is due to the presence of long alkyl chain in DOTBT (Hutt and Liu 2005). The other peak at 287·4 eV is due to the carbon atoms present in the benzotriazine ring. The ratio of the intensities of the C 1*s* peak to the Cu $2p_{3/2}$ peak in the XPS spectrum of DOTBT modified copper is nearly 33 times higher than the corresponding ratio of intensities observed in the spectrum of bare copper. This result infers the presence of nanofilm of organic molecule with long alkyl chain on the copper surface. The O 1*s* peak observed at 531·8 eV is due to the initial oxidation of copper surface during film formation. The existence of oxygen in the 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 (Wang *et al* 2002). The N 1*s* spectrum shows two peaks, one at 399·0 eV and the other at 400·4 eV, which are due to the presence of two nitrogen atoms in DOTBT in two different chemical environments. The characteristic binding energy of the elemental nitrogen is reported at 398·0 eV in the literature (Beccaria and Bertolotto 1997). The shift of N 1*s* binding energy from elemental binding energy indicates that the nitrogen atoms present in DOTBT play a vital role in complex formation between copper and DOTBT. The S 2*p* spectrum shows two peaks, one at 163·1 and the other at 164·4 eV, which are due to S $2p_{3/2}$, S $2p_{1/2}$ components, respectively with a separation of 1·4 eV. This infers the presence of sulfur of DOTBT in the nanofilm formed on copper surface.

3.2c *Reflection absorption FTIR spectral studies*: Reflection absorption FTIR spectra for bare copper and the copper covered with DOTBT nanofilm are shown in figure 7(a and b), respectively. For bare copper, the spectrum shows a peak at 489·5 cm^{-1}, which is assigned to copper oxide on the surface (Papadimitropoulos *et al* 2005). The DOTBT modified copper shows peaks at 2924 and 2854 cm^{-1}, which may be interpreted due to CH_2 asymmetric and CH_2 symmetric stretching modes, respectively (Laibinis *et al* 1991; Yoshida and Ishida 1995; Silverstein and Webster 2007; Mekhalif *et al* 2008). Thus, there is a clear evidence of aliphatic hydrocarbon chain present in the DOTBT film formed on copper surface. The spectrum also shows the appearance of C=C stretching band at 1605 cm^{-1}, C=N stretching band at 1452 cm^{-1}, C–N stretching band at 1274 $cm^{-1}$and C–S stretching band at 749 cm^{-1} (Lalitha *et al* 2005). The lowering of C=N stretching band from 1600 to 1456 cm^{-1} (Baba *et al* 1997) reveals the formation of complex between DOTBT and copper surface through nitrogen. The vibration stretching band at 530 cm^{-1} is due to the copper oxide formation because of initial oxidation of copper surface during film formation (Papadimitropoulos *et al* 2005). These peaks clearly infer the presence of DOTBT nanofilm on copper surface.

3.2d *Surface analysis by atomic force microscopy*: AFM images of bare copper and DOTBT-modified copper are shown in figure 8(a and b), respectively. A homogenous thin film of copper oxides is observed on the surface of the bare copper. AFM image of the DOTBT covered copper surface shows continuous nodules covering the whole surface. This layer prevents copper surface from corrosion.

Table 2. Impedance parameters of copper covered with DOTBT nanofilm formed at 2·5 mM concentration of DOTBT at different immersion periods (environment: 300 ppm chloride, immersion period: 0·5 h, temperature: 30 °C).

S. no.	Immersion period for formation of DOTBT film (h)	R_{ct} (kΩ cm^2)	CPE (μF/cm^2)	n	R_{film} (kΩ cm^2)	CPE$_{film}$ (μF/cm^2)	n_{film}
1	3	24·98	0·326	0·82	7·10	0·055	0·53
2	6	40·24	0·256	0·83	9·48	0·099	0·53
3	12	143·8	0·213	0·86	42·24	0·058	0·65
4	24	721·3	0·033	0·93	70·22	0·022	0·73

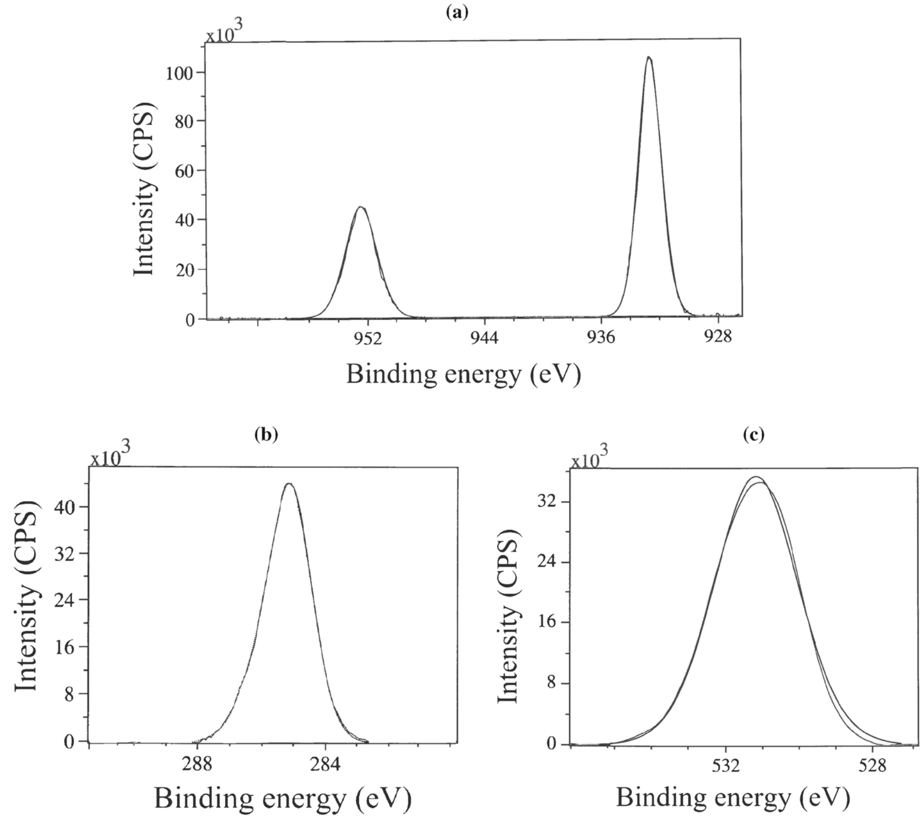

Figure 5. XPS deconvolution spectra of different elements present on the surface of bare copper (**a**—Cu 2p, **b**—C 1s, **c**—O 1s).

3.3 *Corrosion protection of copper by DOTBT nanofilm*

3.3a *Electrochemical impedance studies*: The Bode plots of bare copper and copper covered with DOTBT film are obtained in different concentrations of NaCl solutions (0·02–0·20 M) at constant immersion period of 0·5 h and are shown in figure 9(a and b). The corresponding impedance parameters are shown in table 3. The EIS data of bare copper in NaCl solution are best fitted by using the equivalent circuit shown in figure 2(c), whereas for the copper electrode covered with DOTBT film, the EIS data are best fitted with the equivalent circuit shown in figure 2(b).

The Bode plots of bare copper exhibit a phase angle maximum of 45° and a slope of –1/2 for log $|Z|$ vs log f in the medium frequency region. This is the characteristic of Warburg impedance indicating diffusion effect (Gracias 2005). In the Bode plots of DOTBT-modified copper, the phase angle maximum is increased to 80° and is shifted towards higher frequency side. This result indicates that it is closer to capacitive behaviour. The total impedance is increased to a much higher value after the film formation. The CPE values are decreased, the n values are increased and R_{ct} values are enormously increased in presence of DOTBT film on the copper surface. For example, in 0·02 M NaCl environment, the R_{ct} value has enormously increased from 2·60 kΩ cm^2 in case of bare copper to 401·4 kΩ cm^2 for copper covered with DOTBT film in the same environment. The CPE decreased from 4·00 to 0·15 μF/cm^2 and n value has increased from

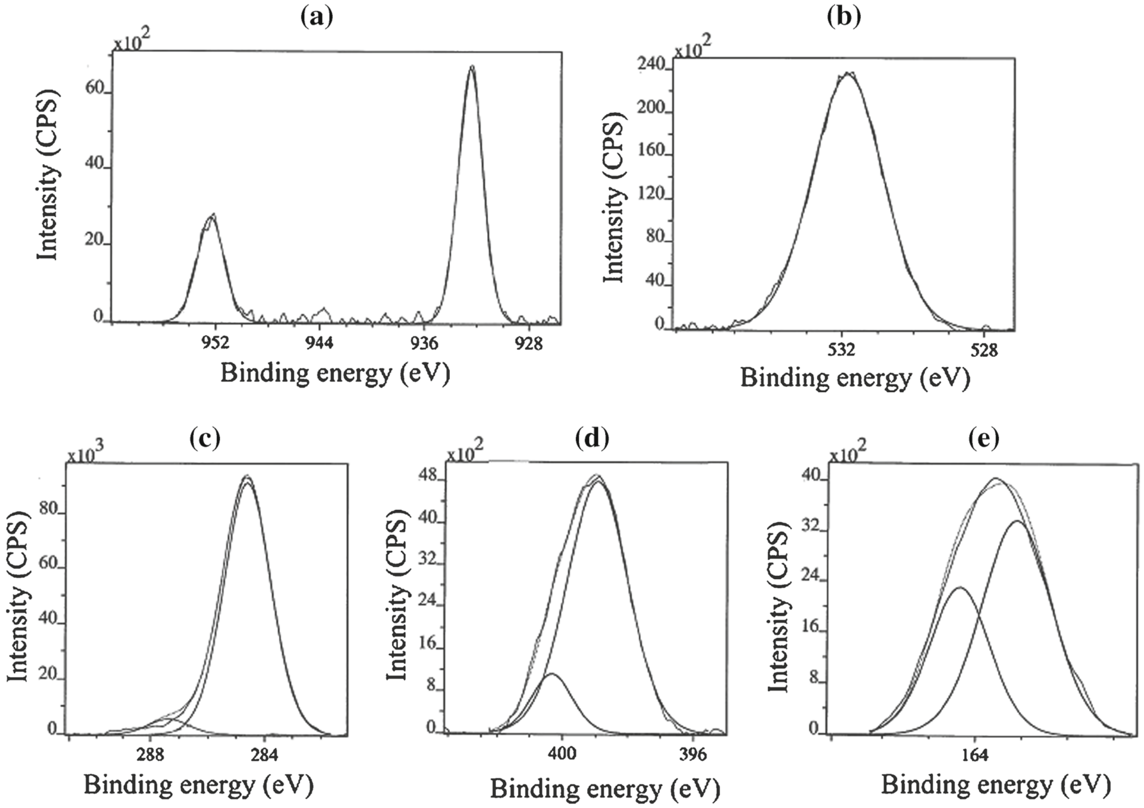

Figure 6. XPS deconvolution spectra of different elements present on the surface of copper covered with DOTBT nanofilm (**a**—Cu 2*p*, **b**—O 1*s*, **c**—C 1*s*, **d**—N 1*s*, **e**—S 2*p*).

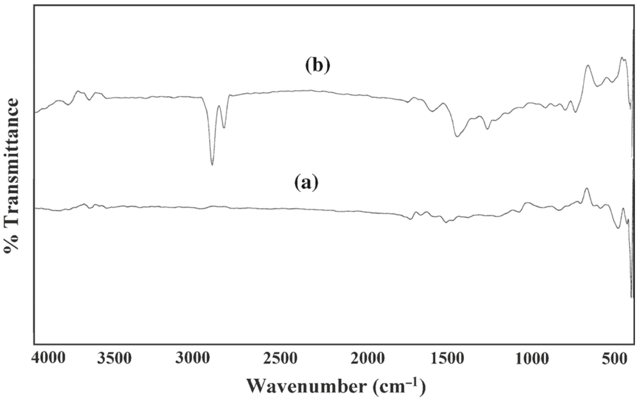

Figure 7. Reflection absorption FTIR spectra of (**a**) bare copper and (**b**) copper covered with DOTBT nanofilm.

0·46 to 0·84. The increase in *n* value indicates that the surface becomes smoother after the formation of the DOTBT film. Inhibition efficiencies are found to be in the range of 99·4–96·2% within the concentration range studied.

The Bode plots of bare copper and copper covered with DOTBT film are obtained in 0·02 M NaCl solution at different immersion periods (0·5–24 h) and are shown in figure 10(a and b). The corresponding impedance parameters are shown in table 4. The R_{ct} values of DOTBT-modified copper are much higher than those of bare copper at all immersion periods studied. The value of *n* at various immersion periods has not changed much. This shows that the homogeneity of the protective film is maintained even after an immersion period of 24 h. Inhibition efficiencies are in the range of 99·4–97·3% in 0·02 M NaCl environment within the range of immersion times studied.

The Bode plots of bare copper and DOTBT-modified copper are obtained in 0·02 M NaCl solution at different temperatures (30–60 °C) and at a constant immersion period of 0·5 h and are shown in figure 11(a and b). The corresponding impedance parameters are shown in table 5. With increase in temperature, R_{ct} values decreased for both bare copper and DOTBT-modified copper. From the literature reports, it has been inferred that with increase in temperature, corrosion rate increases in absence and presence of inhibitors (Dafali *et al* 2002). For the DOTBT-modified copper, the R_{ct} and *n* values slightly decreased with an increase in temperature. The corrosion protection efficiencies of the films are found to be in the range of 99·4–96·9% within the temperature range studied.

3.3b *Potentiodynamic polarization studies*: Potentiodynamic polarization curves for bare copper and DOTBT-modified copper are obtained in NaCl solution over a concentration range of 0·02–0·20 M after an immersion period of 0·5 h and are shown in figure 12(a and b), respectively, and the corresponding corrosion parameters are given in

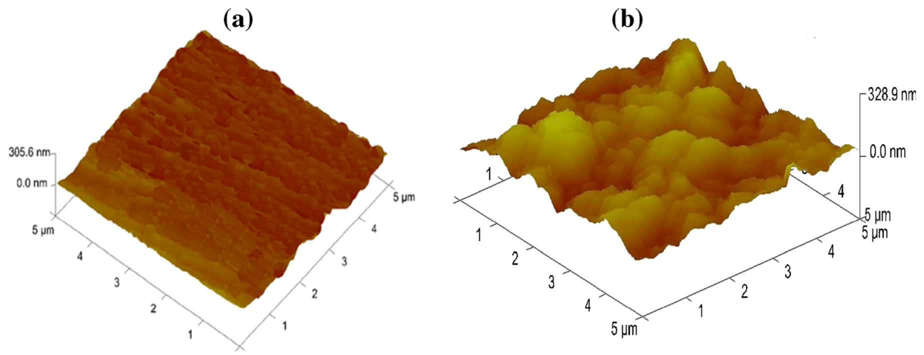

Figure 8. AFM images of (**a**) bare copper and (**b**) DOTBT nanofilm covered copper.

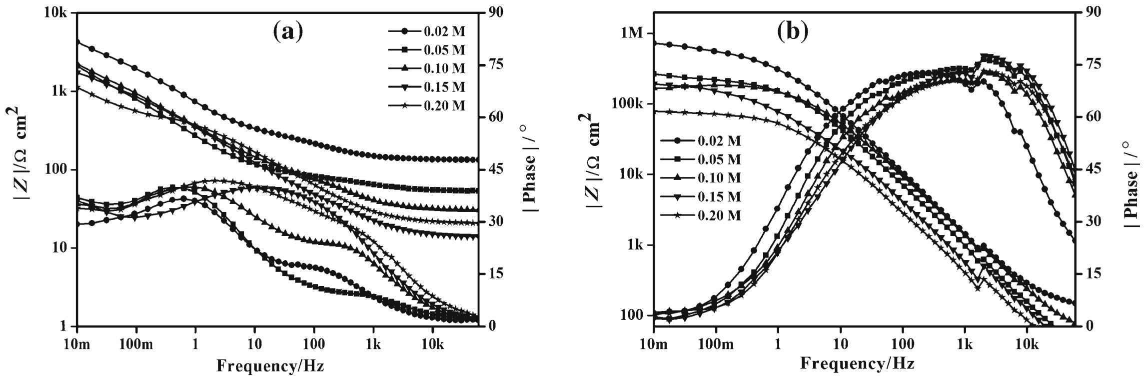

Figure 9. Bode plots of (**a**) bare copper and (**b**) DOTBT film covered copper in different concentrations of NaCl (immersion period: 0·5 h, temperature: 30 °C).

Table 3. Impedance parameters of bare copper and copper covered with DOTBT nanofilm in NaCl environment at different concentrations (immersion period: 0·5 h, temperature: 30 °C).

S. no.	Specimen	Conc. (M)	R_{ct} (kΩ cm^2)	CPE (μF/cm^2)	n	R_{film} (kΩ cm^2)	CPE$_{film}$ (μF/cm^2)	n_{film}	IE (%)
1	Bare copper	0·02	2·60	4·00	0·46	–	–	–	–
2	Copper with DOTBT film	0·02	401·4	0·14	0·84	218·3	0·095	0·64	99·4
3	Bare copper	0·05	2·27	5·91	0·46	–	–	–	–
4	Copper with DOTBT film	0·05	136·7	0·12	0·85	98·83	0·147	0·61	98·3
5	Bare copper	0·10	2·01	8·58	0·42	–	–	–	–
6	Copper with DOTBT film	0·10	112·4	0·11	0·83	77·08	0·080	0·62	98·2
7	Bare copper	0·15	1·96	8·04	0·38	–	–	–	–
8	Copper with DOTBT film	0·15	98·25	0·13	0·84	48·44	0·020	0·60	98·0
9	Bare copper	0·20	1·89	11·16	0·38	–	–	–	–
10	Copper with DOTBT film	0·20	50·14	0·15	0·80	25·10	0·156	0·60	96·2

table 6. At all the concentrations, the i_{corr} values are found to decrease in case of DOTBT-modified copper, when compared with bare copper. The corrosion potential is shifted towards negative side, after formation of film on copper surface. The cathodic Tafel slope (b_c) is shifted to a greater extent than anodic Tafel slope (b_a), after formation of nanofilm on copper surface. For example, in 0·02 M NaCl, the b_c value is shifted from −433 to −62 mV/dec, whereas, b_a value is shifted from 80 to 69 mV/dec only. From these observations, it is inferred that the cathodic reaction of corrosion process is controlled more effectively by the DOTBT film on copper surface in NaCl solutions. It is evident from the literature reports that the nanofilms formed on copper surface inhibit cathodic reaction more significantly than the anodic reaction (Ma *et al* 2003; Bereket *et al* 2007). Corrosion inhibition efficiencies are calculated from i_{corr} values and are found to be in the range of 99·7–93·3% within the concentration range studied.

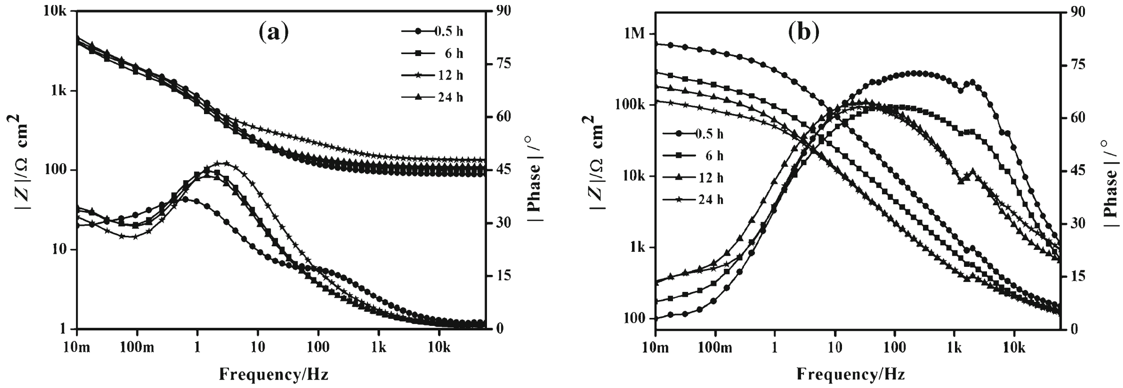

Figure 10. Bode plots of (**a**) bare copper and (**b**) DOTBT film covered copper in 0·02 M NaCl at different immersion periods (temperature: 30 °C).

Table 4. Impedance parameters of bare copper and copper covered with DOTBT nanofilm in 0·02 M NaCl environment at different immersion periods (temperature: 30 °C).

S. no.	Specimen	Immersion time (h)	R_{ct} (kΩ cm^2)	CPE (μF/cm^2)	n	R_{film} (kΩ cm^2)	CPE$_{film}$ (μF/cm^2)	n_{film}	IE (%)
1	Bare copper	1	2·60	4·00	0·46	–	–	–	–
2	Copper with DOTBT film	1	401·4	0·14	0·84	218·3	0·095	0·64	99·4
3	Bare copper	6	2·58	6·81	0·46	–	–	–	–
4	Copper with DOTBT film	6	163·6	0·18	0·74	119·4	0·223	0·50	98·4
5	Bare copper	12	2·46	7·30	0·45	–	–	–	–
6	Copper with DOTBT film	12	139·1	0·31	0·72	41·2	0·374	0·44	98·2
7	Bare copper	24	2·42	8·93	0·45	–	–	–	–
8	Copper with DOTBT film	24	89·8	0·30	0·70	8·4	0·53	0·42	97·3

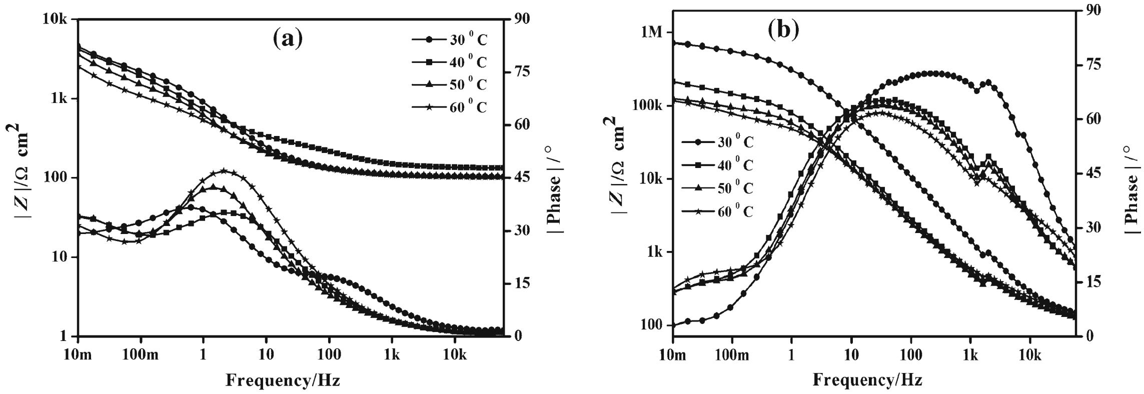

Figure 11. Bode plots of (**a**) bare copper and (**b**) DOTBT film covered copper in 0·02 M NaCl after 0·5 h immersion period at different temperatures.

3.3c *Results of studies using electrochemical quartz crystal nanobalance*: Figure 13(a and b) show the mass change vs time curves obtained from EQCN experiment for the bare copper quartz crystal and DOTBT covered copper quartz crystal in 0·02 M NaCl environment. After immersion up to 24 h, a mass change of -17 μg/cm^2 is observed for bare copper quartz crystal. The film covered copper quartz crystal showed a very less mass change of $-0{\cdot}35$ μg/cm^2 and the inhibition efficiency of the DOTBT-modified copper is found to be 97·9%. These results infer that the DOTBT nanofilm is protective in nature in NaCl environment.

3.3d *X-ray photoelectron spectral studies*: In the XPS survey spectrum of bare copper after immersion in 0·02 M NaCl environment for 3 days, Cu $2p_{3/2}$, Cu $2p_{1/2}$ and O $1s$ peaks are detected, along with Cl $2p$ peak at 199·8 eV. The

Table 5. Impedance parameters of bare copper and copper covered with DOTBT nanofilm in 0·02 M NaCl environment at different temperatures (immersion period: 0·5 h).

S. no.	Specimen	Temperature (°C)	R_{ct} (kΩ cm^2)	CPE (μF/cm^2)	n	R_{film} (kΩ cm^2)	CPE$_{film}$ (μF/cm^2)	n_{film}	IE (%)
1	Bare copper	30	2·60	4·00	0·46	–	–	–	–
2	Copper with DOTBT film	30	401·4	0·14	0·84	218·3	0·095	0·64	99·4
3	Bare copper	40	2·50	5·79	0·45	–	–	–	–
4	Copper with DOTBT film	40	126·6	0·25	0·72	63·64	0·052	0·60	98·0
5	Bare copper	50	2·44	7·71	0·45	–	–	–	–
6	Copper with DOTBT film	50	85·6	0·28	0·70	44·06	0·121	0·60	97·2
7	Bare copper	60	2·40	8·84	0·41	–	–	–	–
8	Copper with DOTBT film	60	77·2	0·20	0·64	18·97	0·188	0·55	96·9

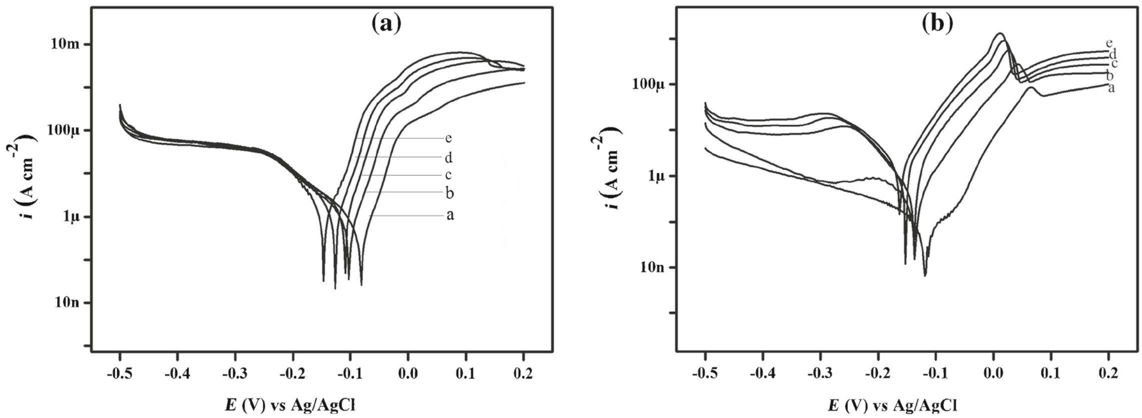

Figure 12. Potentiodynamic polarization curves of (**a**) bare copper and (**b**) DOTBT nanofilm covered copper in different concentrations of NaCl (**a**—0·02 M, **b**—0·05 M, **c**—0·10 M, **d**—0·15 M, **e**—0·20 M and (immersion period: 0·5 h, temperature: 30 °C).

Table 6. Corrosion parameters obtained by potentiodynamic polarization studies of bare copper and copper covered with DOTBT nanofilm in NaCl environment at different concentrations (immersion period: 0·5 h, temperature: 30 °C).

S. no.	Specimen	NaCl conc. (M)	E_{corr} (mV)	i_{corr} (μA/cm^2)	b_a (mV/decade)	b_c (mV/decade)	IE (%)
1	Bare copper	0·02	−83·4	11·9	80	−433	–
2	Copper with DOTBT film	0·02	−118·5	0·04	69	−62	99·7
3	Bare copper	0·05	−99·6	14·1	64	−442	–
4	Copper with DOTBT film	0·05	−135·9	0·16	34	−64	98·9
5	Bare copper	0·10	−108·6	16·0	52	−456	–
6	Copper with DOTBT film	0·10	−139·6	0·44	29	−66	97·3
7	Bare copper	0·15	−128·7	17·2	56	−419	–
8	Copper with DOTBT film	0·15	−152·9	0·81	32	−69	95·3
9	Bare copper	0·20	−147·0	19·6	60	−427	–
10	Copper with DOTBT film	0·20	−160·6	1·31	46	−68	93·3

peaks due to Cu 2*p* and O 1*s* are similar to those shown in figure 5(a and b) (before immersion in 0·02 M NaCl). The peaks infer the formation of Cu_2O. The computer deconvolution spectrum for Cl 2*p* is shown in figure 14. This peak is due to the formation of $CuCl_2$ on copper surface.

The XPS spectrum of the copper covered with DOTBT nanofilm after immersion in 0·02 M NaCl environment for 3 d shows peaks related to Cu 2*p*, O 1*s*, C 1*s*, N 1*s* and S 2*p*. The Cl 2*p* peak is absent. The computer deconvolution spectra are shown in figure 15(a–e), respectively. These spectra are compared with the corresponding spectra shown in figure 6(a–e), for the DOTBT-modified copper substrate before immersion in the said corrosive environment. The intensities of C 1*s* and O 1*s* peaks have not changed. Cu 2*p*,

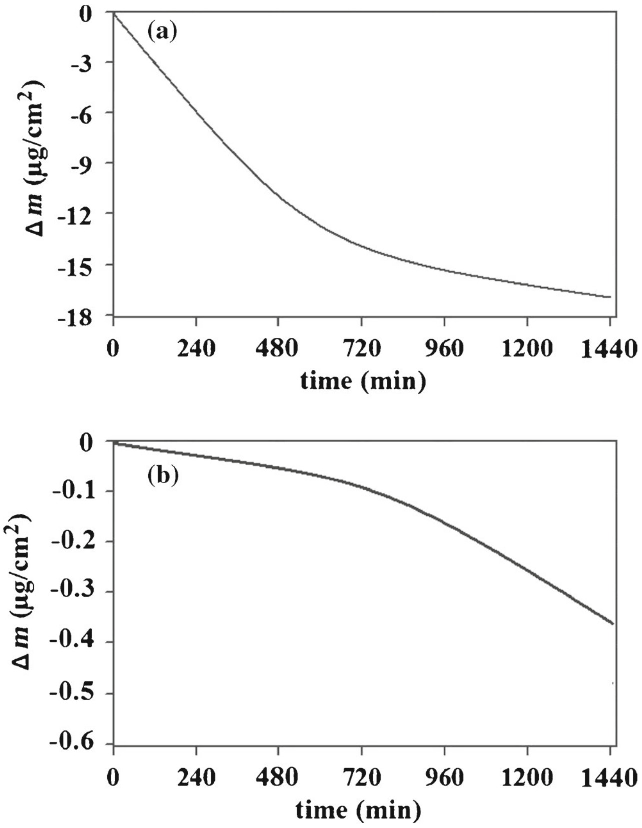

Figure 13. Mass change vs time curve on copper quartz crystal in 0·02 M NaCl. (**a**) Bare copper and (**b**) DOTBT nanofilm covered copper.

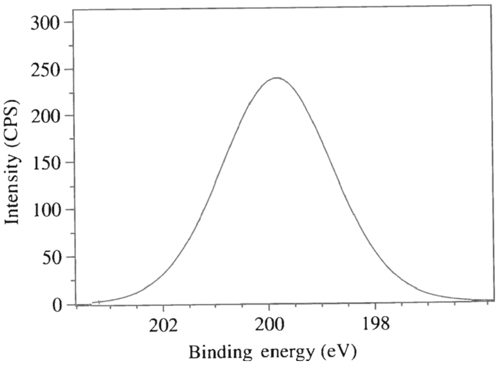

Figure 14. XPS deconvolution spectrum of Cl 2*p* present on the surface of the bare copper after immersion in 0·02 M NaCl solution for a period of 3 days.

N 1*s* and S 2*p* peak intensities have slightly decreased. These studies infer that the DOTBT nanofilm is stable on copper surface even after 3 d immersion period in 0·02 M NaCl environment.

3.3e *Results of weight-loss studies*: In 0·02 M NaCl environment after an immersion period of 3 d, corrosion rates of 0·0641 mm/yr for bare copper and of 0·0036 mm/yr for copper covered with DOTBT film are obtained. An inhibition efficiency of 94·3% is obtained from the data. These results show that the corrosion prevention of copper by DOTBT nanofilm is excellent in the NaCl environment, even after an immersion period of 3 d.

3.3f *Results of quantum chemical calculations*: Inhibitors can form coordinate bonds with metal atoms through the unshared electron pair present on the nitrogen atom and also with π electrons of the aromatic ring. The higher the negative atomic charges on the adsorbed centre, the more easily it can donate its electrons to the unoccupied orbital of the metal (Wang *et al* 2003). Chemisorption of DOTBT molecules on copper surface can be explained in terms of higher HOMO energy (−6·841 eV), small energy gap (5·005 eV) between LUMO and HOMO and a high negative total ring charge (−1·640) of the DOTBT molecule.

4. Mechanistic aspects of corrosion protection by DOTBT nanofilm

In the absence of DOTBT nanofilm, anodic dissolution of copper in chloride environment proceeds via a two-step oxidation process (Scheider 1975).

$$\mathrm{Cu} + \mathrm{Cl}^- \rightarrow \mathrm{CuCl} + e^-, \tag{3}$$

$$\mathrm{CuCl} + \mathrm{Cl}^- \rightarrow \mathrm{CuCl}_2^-. \tag{4}$$

The CuCl has poor adhesion and is unable to protect the copper surface and transforms into the soluble cuprous chloride complex, CuCl_2^- (Yan *et al* 2000). The cathodic corrosion reaction in acidic chloride environment (Zhang *et al* 2005) is

$$4\mathrm{H}^+ + \mathrm{O}_2 + 4e^- \rightarrow 2\mathrm{H}_2\mathrm{O}. \tag{5}$$

A plausible mechanism for corrosion protection of copper by DOTBT nanofilm is discussed subsequently. The DOTBT molecules get chemisorbed on the copper surface and form a chelate with Cu^+ ions on the surface as shown in figure 16. One of the reasons for relatively lower contact angle value of DOTBT SAM in comparison with ODT SAM is that the DOTBT molecules are oriented parallel to the metal surface. The DOTBT molecules get chemisorbed on the copper surface and form a monolayer. The subsequent layers are formed due to secondary forces of attraction such as hydrogen bonding and π-stack interactions between the DOTBT molecules. Thus, there is a definite possibility of formation of multilayer at least at certain locations as evidenced by AFM. There is also a possibility of pinhole distribution, which is a general feature of any SAM. The large negative charge of the ring favours the formation of a coordinate linkage between DOTBT and Cu^+ ions available on the copper surface, through the nitrogen atoms present in the triazine ring. Thus, there is formation of a [Cu^+–DOTBT] polymeric complex, which is highly protective in nature.

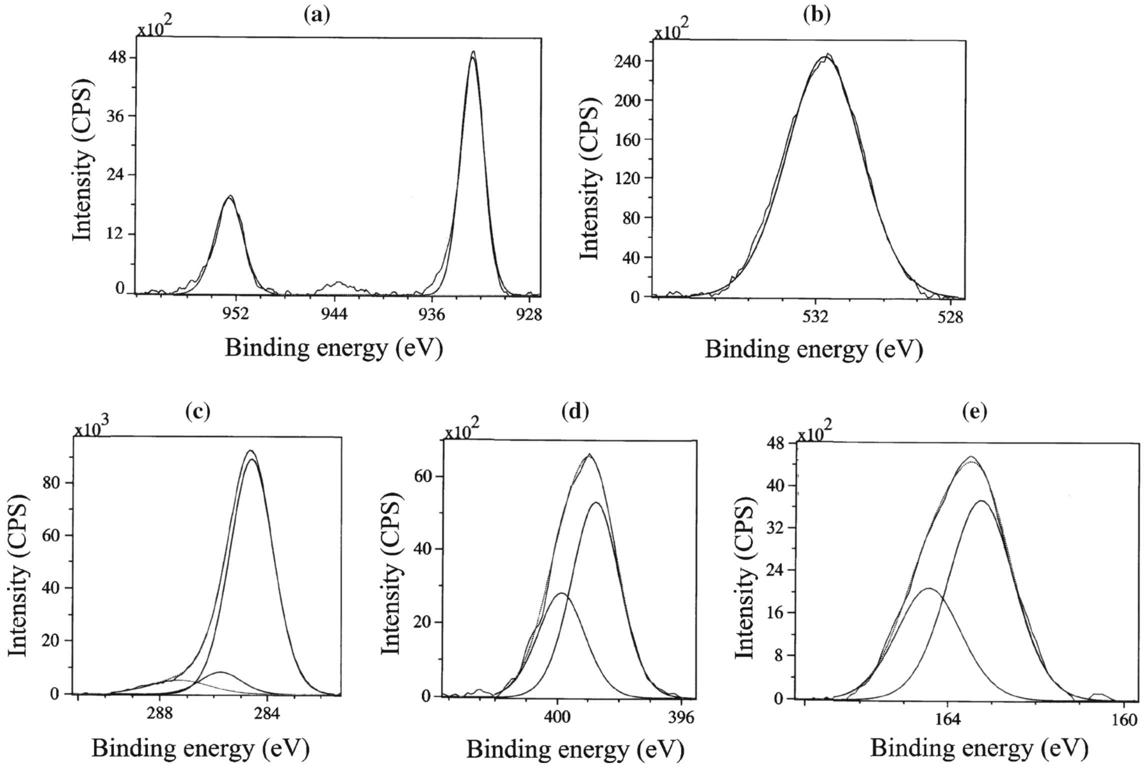

Figure 15. XPS deconvolution spectra of different elements present on the copper covered with DOTBT nanofilm after immersion in 0·02 M NaCl solution for a period of 3 days (**a**—Cu 2*p*, **b**—O 1*s*, **c**—C 1*s*, **d**—N 1*s*, **e**—S 2*p*).

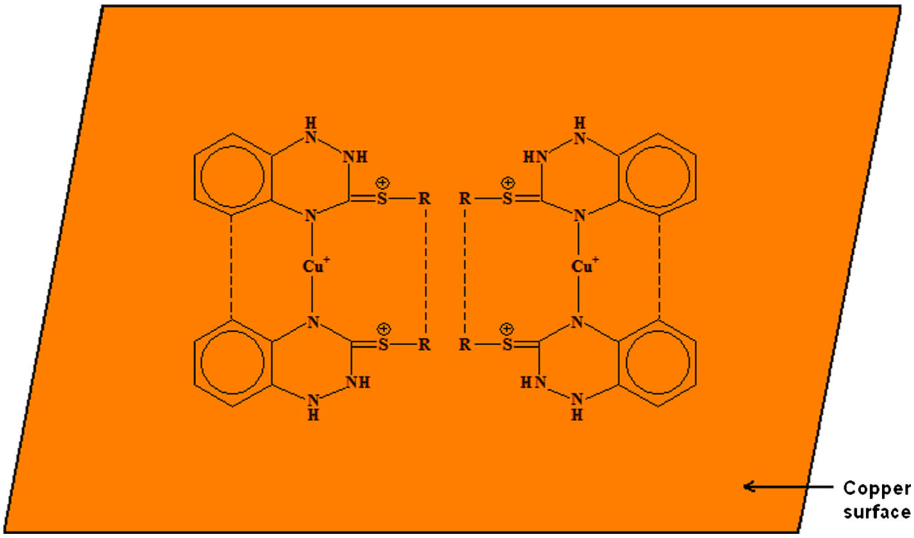

Figure 16. Schematic of formation of protective nanofilm by DOTBT on copper surface. Complex formation between Cu$^+$ ions and DOTBT molecules oriented parallel to copper surface is shown.

5. Limitations of SAMs

(I) Some problems arise when molecules are self assembled on continuously changing surfaces or metals covered with unstable, porous oxides. This causes disordering of the adsorption layers and consequently defects in SAMs.

(II) Choice of metal substrate to form SAM is limited.

(III) SAMs are sensitive to temperature.

(IV) SAMs may not be stable in all corrosive environments.

6. Conclusions

The optimum conditions for the formation of protective nanofilm of 1,2-dihydro-3-(octadecylthio)benzotriazine on copper surface are (i) etching of copper surface in 7 N nitric acid for 30 s, (ii) methanol as solvent, (iii) 2·5 mM concentration of DOTBT in methanol, (iv) immersion time of 24 h and (v) ambient temperature of 30 °C. The nanofilm formed by DOTBT on copper surface offers excellent corrosion protection of copper in NaCl solution within the concentration range (0·02–0·20 M), immersion period (0·5–24 h) and temperature range (30–60 °C) studied. The inhibition efficiencies obtained from weight-loss studies, electrochemical impedance studies, polarization studies and quartz crystal nano balance studies are in good agreement with each other. The DOTBT molecules get chemisorbed on copper surface and form a polymeric coordination complex with Cu^+ ions through nitrogen atoms.

Acknowledgement

The authors are thankful to the National Institute of Technology Warangal, India, for providing necessary facilities for carrying out this research work.

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