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Surface analysis of Cu coated with ALD Al₂O₃ and its corrosion protection enhancement in NaCl solution: EIS and polarization

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Keywords: atomic layer deposition, copper, corrosion, electrochemical impedance spectroscopy, Kramers-Kronig, polarization

Abstract
Al₂O₃ was coated on copper substrates with a thickness of 62 nm at 473 K temperature using atomic layer deposition method. The morphology of the produced samples was obtained by scanning electron microscope and atomic force microscope while the latter instrument also provided information on the surface roughness and grain sizes formed on the surface of the samples. Energy dispersive spectroscopy was employed for obtaining abundances of different elements in the samples before and after corrosion tests. Corrosion behavior of Cu and Al₂O₃/Cu was investigated by means of electrochemical polarization and electrochemical impedance spectroscopy analyses in 3.5% (0.6 M) NaCl solution. The validity of the data obtained from the latter method is investigated by Kramers-Kronig transformations. Also simulation of this data by equivalent electrical circuits resulted in a corrosion inhibition enhancement factor of $\eta = 97.48\%$ which indicates high improvement in corrosion resistance of Cu by Al₂O₃ coating. Corrosion parameters were also obtained from the polarization curves by fitting the experimental results with Stern-Geary relation near the open circuit potential. Negative shift of corrosion potential for the Al₂O₃ coated Cu relative to uncoated Cu indicates that Al₂O₃ coating is blocking the cathodic reaction. Corrosion inhibition efficiency/yield ($PE\%$) obtained from anodic and cathodic branches of polarization curves showed high enhancement with values of 69% and 93%, respectively while the latter is consistent with the corrosion inhibition enhancement factor of $\eta = 97.48\%$ mentioned above. Results are compared with the published data and good agreements are obtained, deviation of those results from the rest is discussed considering all parameters involved in the ALD deposition.

1. Introduction

Copper is an important metal with excellent thermal conductivity, mechanical workability and resistance against corrosion and has found many engineering applications namely domestic plumbing systems, electrical power lines, heat exchange, oil industries, microelectronics, marine environments and heat transducers [1–7]. Although copper has high corrosion inhibition in pure water, but in corroding media such as chloride environment undergo corrosion and its corrosion mechanism has been studied by many researchers [8–14].

One of the protection methods against corrosion is coating of copper (metal) surface by a protective material. Different methods are proposed and used for this purpose, such as chemical vapor deposition (CVD) [15, 16], self-assembled mono-layers [17], polymers [18], plasma and electrochemical deposition [19, 20]. Recently, atomic layer deposition (ALD) is used for formation of different metallic oxide layers for use in corrosion inhibition of metals and alloys such as stainless steel [21–27], aluminum [28], aluminum alloy [29], Mg alloy [30], silver [31, 32] and copper [33–38]. In particular, for corrosion protection of copper in hot water [38] and for thermal oxidation protection of copper molds for patterned optical components [35]. ALD alumina films were used owing to high dielectric property, good adhesion to many surfaces, amorphous structure and mechanical property of Al₂O₃ [24, 25].

ALD performed under controlled conditions and pre-treated substrate surfaces provide pinhole-free and conformal films with nanometer thicknesses [26, 27]. However, it is a very slow and expensive process and it
must be economically viable when used for a certain application. In particular use of ALD for corrosion inhibition of metals and other materials (e.g., Cu, Mg, stainless steel, Al and etc) is reported by many researchers [26, 28, 39] due to adverse effects of corrosion damages in terms of economic aspects including repair and maintenance costs, loss of materials, damage to equipment, a decrease in efficiency, and loss of useful or productive life. In addition, corrosion causes social damages, such as safety impacts (cause of fire, explosions, release of toxic products), health impacts (personal injuries, pollution due to contamination of toxic products), the depletion of resources, etc [40]. Hence, protection against these damages should be reason why different techniques though time consuming and somewhat costly are used for different applications.

Considering that physical vapor deposition methods fail in fabrication of conformal coatings on substrates with complex shape, hence researchers have considered ALD technology as a promising method for coatings while it also has the advantage of producing films with low residual stress and is a self-limiting process too. ALD is a periodic process in a reactor in which two precursors are entered the chamber with an inert gas in between as a purging gas. By adjusting ALD parameters, reaction reaches saturation state and condition for the layer self-limiting growth is obtained. This self-limiting growth provides the condition for the growth of uniform and conformal formation of ALD metal oxide layer on large scale surfaces with a controlled thickness. Generally, the deposition rate in ALD technique as mentioned above is very low, therefore it is usually used for deposition of thin layers of the order of a few nano-meters [41, 42], although some industrial examples report on application of the ALD films of hundreds of nm and even µm in thickness [43, 44].

Mirhashemihaghighi et al [33] in their study on the influence of interfacial native oxide on the corrosion protection of copper coated with ALD alumina reported that dissolution of this native oxide using H3PO4 before ALD alumina coating (pre-treatment of the substrate surface) enhances the sealing property of the coating, hence improves the corrosion resistance of the substrate (i.e., copper) exposed through channel defects. They found that the surface covered by the freshly re-grown native oxide exposes less Cu(0)/Cu(I) sites, hence is less active for the cathodic oxygen reduction than the surface covered by an aged native oxide, which decreases the corrosion current by about one order of magnitude. Their Electrochemical Impedance Spectroscopy (EIS) analysis demonstrated a substantially lower porosity in the bulk of ALD Al2O3 to that of the interface between coating and the substrate, from which they concluded that the interfacial trenching is the major mechanism in reducing the corrosion inhibition. They suggested that the growth of a fresh interfacial oxide on the pre-treated substrate surface reduces the interfacial trenching.

Fusco et al [39] carried out a detailed and thorough investigation of corrosion of copper in 0.1 M NaCl using ALD Al2O3 and ALD TiO2 nanolaminate coatings with specific application of copper in radio frequency (RF) devices (i.e., traveling-wave tubes and crossed-field amplifiers). These devices typically contain fluid-cooled copper collectors and/or copper cooling channels [45, 46]. They used pre-treated and copper surfaces to reduce the surface native oxide as that reported by Mirhashemihaghighi et al [33]. Their impedance spectroscopy analysis for ALD Al2O3 coated samples showed increases in polarization resistance over uncoated copper, up to 12 MΩ cm².

During the last decade there have been many works published on the ALD and its application while numerous review articles have also become available each of which devoted to a different application of ALD. In 2011, Marin et al [44] published a detailed review and the state-of-the-art as well as research/industrial perspectives on ALD covering the history of the field until 2011, the main ALD techniques, considering their main advantages and drawbacks, ALD applications, and the most useful and used instruments for the analysis and characterization of ALD as well as discussion on some results with emphasis on corrosion protection of different metallic alloys of common industrial interest.

Ponraj et al [47] gave a review on ALD deposition and application of oxides in memristor: the non volatile memories design with the ability to retain data and memory states even in power-off condition.

In 2014 Johnson et al [48] published their review paper concentrating on ALD applications, including Cu(In, Ga)Se2 solar cell devices, high-k transistors, and solid oxide fuel cells to show the variety of technologies that are impacted by ALD, the range of materials that ALD can deposit from metal oxides such as Zn1–xSnxOy, ZrO2, Y2O3, to noble metals such as Pt.

Tripathi and Karpinnen [49] in their review paper published in 2017 refer to the increased search for high quality new p-type compound semiconductor thin films using ALD technique. They have given the state of the art of the research including ALD processes developed for fabrication of p-type (transparent) conducting materials as well as optical properties obtained for such coatings.


In this work, Al2O3 layer with 62 nm thickness is deposited on copper substrate at 473 K using ALD method by Trimethylaluminium (Al(CH3)3) (TMA) and water as precursors. Corrosion inhibition property of Cu coated by Al2O3 was studied in 3.5% (0.6 M) NaCl solution using electrochemical impedance spectroscopy (EIS) and electrochemical polarization methods. Surface morphology of the samples was obtained by atomic force microscopy.
microscope (AFM) and scanning electron microscope (SEM) analyses, while the crystallographic structure and chemical composition of the samples were analyzed using x-ray diffraction (XRD) and energy dispersive spectroscopy (EDS).

The validity of the results obtained from the EIS measurements was confirmed by Kramers-Kronig transformation (KKT), before trying to fit any theoretical model to the experimental data. KKT are a number of integral transformations between real and imaginary elements of complex transformation function. These transformations are obtained by considering the four following conditions: linearity, causality, stability and finiteness. Therefore, in this study we used the KKT to verify/investigate the validity of our impedance data. Results are compared with the available data in the literature [33, 34, 39] with a detailed discussion on the parameters affecting corrosion inhibition of Cu in NaCl solution using ALD method.

2. Experimental details

Commercial copper of 1 mm thickness were used in the form of square samples (20 × 20 mm²). The composition of Cu used in this work was obtained using x-ray fluorescence (XRF) method (Spectro Xepos) and is given in table 1. In order to remove defects and contaminations which can affect the proper layer formation on the surface of Cu [23, 51], they were abraded with successively finer grades of emery paper: 2000 and 4000. Then they were cleaned using an ultrasonic bath with heated detergent solution, acetone then ethanol, respectively and finally they were mounted on the substrate holder and positioned in the atomic layer deposition (ALD).

Deposition of Al₂O₃ was carried out at 473 K using TFS 200 ALD reactor Beneq, Finland. Trimethylaluminium (Al₂(CH₃)₃) (TMA) with 97% purity (Sigma-Aldrich, USA) and water were used as Al and oxygen precursors. The ALD-Al₂O₃ growth happens during periodic exposures to TMA and H₂O. Two chemical reactions may occur on the surface during the ALD-Al₂O₃ processes as [33]:

\[
\text{AlOH}^* + \text{Al(CH₃)}₃ \rightarrow \text{AlOAl(CH₃)}₂^* + \text{CH}_4
\]

\[
\text{AlCH}_₃ + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + \text{CH}_4
\]

where the asterisks denote the surface species. Dillon et al [52] confirmed that these two surface chemical reactions involve ligand exchange. In reaction (1), ligands of CH₃ from TMA exchange with ligands of OH⁺ on the surface. In reaction (2), ligands of OH from H₂O exchange with CH₃⁺ on the surface.

A deposition rate of 0.11 nm/cycle was obtained from deposition of Al₂O₃ on Si wafer substrate using different numbers of cycles. The growth of alumina on Cu substrate could be slightly different. In order to obtain a better idea of the thickness of the film formed on Cu substrate after 600 cycles FESEM images were obtained from the cracks made on the surface of the sample by bending it. Figure 1 shows a typical FESEM image taken from such sample which shows a thickness of about 62 nm.

Crystallographic structure of the produced samples was obtained using a STOE model STADI MP Diffractometer (Cu Kα), Germany with a step size of 0.02° and count time of 1.0 s per step, while the surface physical morphology/nanostructure and roughness was obtained by means of AFM (Nt-mdt scanning probe microscope, BL022, Russia; with low stress silicon nitride tip of less than 200 Å radius and tip opening of 18°) analysis. The surface roughness and average grain size of the samples were obtained from the two dimensional (2D) AFM images using WSXM and JMicr0Vision Codes, respectively. Surface physical morphology of the

| Table 1. Chemical composition of Cu used in this work. |
|-----------------|------|-----|------|-----|-----|-----|-----|
| Element         | Ta   | P   | Zn   | Ca  | Si  | Cl  | Cu  |
| (wt%)           | 1.45 | 0.52| 0.22 | 0.11| 0.04| 0.01| Bal.|

![Figure 1. FESEM image of a crack on the surface of ALD Al₂O₃ coating on Cu substrate showing the thickness of the coating.](image)
samples before polarization test was obtained by means of scanning electron microscope (Zeiss Ultra 55) analysis. Several samples (at least four samples) were used in all analysis to guarantee reproducibility of the results by checking the data at different stages of the work (different analyses; XRD, AFM, electrochemical impedance spectroscopy (EIS) and polarization).

EIS was performed using a potentiostat coupled to PC (Ivium, De Zaale 11, 5612 AJ Eindhoven, Netherlands) with reference to the open circuit potential (OCP) and in the frequency range of 100 KHz to 0.01 Hz with a voltage amplitude of 0.01 V. In order to carry out this analysis only an area of 1 cm² was exposed to the 3.5% (0.6 M) NaCl corroding medium. An Ag/AgCl (saturated KCl) (+0.197 V versus standard hydrogen electrode potential) electrode was used as a reference electrode and a platinum electrode used as auxiliary one while the test sample was mounted in an inert fixture (polyamide) acted as the working electrode. This allowed an electrical contact to be supplied to the sample, without being influenced by undesirable effects on the working electrode. Before starting the EIS test, the samples were immersed in the solution and the OCP measurement was carried out until it became stable and remained stable for at least 30 min.

The polarization potential was applied via a copper wire contacted to the back side of the sample in the inert fixture (polyamide) acted as the working electrode, while similar setup as EIS measurement was employed. For cathodic scan, the initial potential was fixed at a slightly more positive potential (about 10 mV) than Ecorr and then scanned towards more negative values at the rate of 1 mVs⁻¹. The anodic branches were obtained similarly by scanning towards more positive potentials. All measurements were performed at 298 K and the reproducibility of the results was confirmed by carrying out measurements on several samples (at least 4 samples) and the data presented are the mean of these measurements. All of the potentials presented in this work are as a function of Ag/AgCl electrode.

3. Results and discussions

3.1. XRD results

In figure 2 the XRD pattern of uncoated Cu shows four peaks at diffraction angles of 43.32, 50.42, 74.11, and 89.9 degrees that belong to Cu(111), Cu(200), Cu(220) and Cu(311) according to the JCPDS card number: 01-085-1326. The XRD pattern of Al₂O₃/Cu sample in addition to four peaks belonging to Cu shows two extra peaks at 35.94° and 37.00° with very low intensities. According to the literature, these small peaks cannot be related to the crystallization of Al₂O₃. However, copper oxide of Cu₈O₇(202) and Cu₂O(111) phases with 100% intensities according to the JCPDS card Nos: (00-003-0879 and 00-034-1354) show diffraction peaks at 35.89° and 37.01°. The formation of these diffraction lines with very low intensities could be due to air formed native oxide at the interface of coating and the substrate or spurious growth of thermal oxide on the surface of Cu substrate [28, 34]. The latter can continue to form while the substrate surface is exposed to water vapor until it is completely covered with alumina film or during the time lapse until the reactor reaches thermal stability before the coating process starts [28, 34]. The formation of substrate oxide at the interface between ALD coating and the substrate is consistent with the data reported for alumina and other oxides on stainless steel and low alloy steel substrates [23–25, 53–56].
3.2. AFM and SEM results

In Figure 3 the two dimensional (2D) and three dimensional (3D) AFM images of both uncoated Cu and Al₂O₃/Cu samples are given. It can be observed that the uncoated Cu surface consists of small grains, hence numerous grain boundaries, and some grooves which can be due to polishing process of the sample. The AFM image of the Al₂O₃/Cu sample shows larger grains and one may also suggest that the grooves seen in the uncoated Cu are disappeared as result of Al₂O₃ grains formation on the Cu substrate. The average surface roughness ($R_{\text{ave}}$), root mean square surface roughness ($R_{\text{rms}}$) of both samples and percentage of surface void fraction as well as grain sizes obtained from the AFM images of Al₂O₃/Cu sample using ImicroVision and WSXM codes are given in Table 2. The increase of surface roughness and grain size in the Al₂O₃/Cu sample could be due to the formation of Al₂O₃ grains (50 to 60 nm in size) on the peaks/heights of the surface and possible nucleation delay on the smooth areas of the substrate surface. Increase of surface roughness for ALD TiO₂ coating on Cu substrate is also reported by [57] that is related to island nucleation on the Cu surface leading to increase of surface roughness [38].

The SEM images of both samples are given in Figure 4. The grooves produced as result of polishing process are clearly observable on the surface of the uncoated Cu (figure 4(a)), while they are almost disappeared when the sample was coated with Al₂O₃ (figure 4(b)) which can be the result of Al₂O₃ coating as pointed out above.

In addition, it should also be mentioned that some pinholes can be observed on the surface of ALD Al₂O₃ coated sample. These pinholes (defects) may have resulted from the rough substrate surface, presence of contaminant species or nucleation during initial cycles of ALD [51, 58]. Other researchers [52, 59] have related them to the residual hydrogen from an incomplete chemical reaction in the ALD process.

Results of energy dispersive electron spectroscopy (EDS) of Al₂O₃/Cu sample before corrosion test is given in Figure 5, in which presence of O and Al confirms the formation of Al₂O₃.

3.3. EIS analysis

EIS measurements were carried out for both uncoated Cu and Al₂O₃/Cu samples as they were exposed to 3.5% (0.6 M) NaCl solution and an applied sinusoidal voltage. When Cu substrate is exposed to electrolyte environment, an oxide layer will form on the surface [60–62], hence in this case the equivalent circuit consists of

![Figure 3. 2D and 3D AFM images of: (a) uncoated Cu, (b) Al₂O₃/Cu samples.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{\text{rms}}$ (nm)</th>
<th>$R_{\text{ave}}$ (nm)</th>
<th>$D$ (nm)</th>
<th>Surface porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.05</td>
<td>3.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃/Cu</td>
<td>23.91</td>
<td>19.20</td>
<td>56</td>
<td>33.48</td>
</tr>
</tbody>
</table>

Table 2. Surface roughness, average grain sizes and surface porosity obtained from AFM images for uncoated Cu and Al₂O₃/Cu samples.
two time constants (figure 6(a)). In this circuit $R_1$ and $CPE_2$ indicate the dielectric properties of the surface oxide layer. Corrosion of Cu substrate happens via small pores of the oxide layer and because Cu corrodes quickly, the products of interaction of electrolyte and surface atoms/ions of Cu may block these pores and reduce penetration of elements of interaction (e.g., $\text{Cl}^-$ and $\text{O}_2$) and reaction products ($\text{CuCl}^{2-}$) at active sites [63–67]. In this case corrosion not only controlled by mass transition but also controlled by mass diffusion process. This diffusion process is modeled by diffusion impedance $W$. $R_2$ and $CPE_2$ are charge transfer resistance and capacitance of double layer that are attributed to the fine (very small) pores at the substrate/electrolyte interface. In this model the constant phase element ($CPE$) substitutes the ideal capacitor. $CPE$ impedance is given as:

---

**Figure 4.** SEM images of: (a) uncoated Cu, (b) $\text{Al}_2\text{O}_3$/Cu samples.

**Figure 5.** EDS spectra of the $\text{Al}_2\text{O}_3$/Cu sample.

**Figure 6.** Electrical equivalent circuits of: (a) uncoated Cu and, (b) $\text{Al}_2\text{O}_3$/Cu samples.
Where, CPE and \( n \) are adjustable parameters that can be obtained from non-linear fitting process. The value of \( n \) is between 0 and 1. The deviation from ideal capacitive behavior is related to inhomogeneity of the surface \([68]\), surface roughness \([69, 70]\), inequality in current or potential distributions due to electrode geometry \([71, 72]\), porosity and non-uniform conductivity of layers on the surface \([73]\). In case of a rough surface the real surface which becomes exposed to the electrolyte solution is larger than the geometrically defined surface, hence \( n \) varies from unity. However, for a smooth surface \( n \) is usually equal to unity. If \( n = 0.5 \) it would be better to use a Warburg impedance instead of \( \text{CPE} \). Many researchers have also reported of Warburg impedance for Cu corrosion in different media \([74–76]\).

Usually this type of coated system is simulated by an equivalent circuit consisting of two time constants which is shown in figure 6(b). \( R_1 \) and \( \text{CPE}_1 \) elements that are parallel to each other in this circuit are pore resistance and coating capacitance which are related to the dielectric property of the coating. \( R_2 \) and \( \text{CPE}_2 \) are charge transfer resistance and capacitance of double layer. Results of EIS measurement for uncoated Cu and \( \text{Al}_2\text{O}_3/\text{Cu} \) samples are given in figure 7. Nyquist plot is given in figure 7(a), while in figures 7(b) and (c) Bode and Phase diagrams are presented, respectively. The inset shows the same plot with an expanded scale to allow a clearer observation of the points at high frequencies. Two time constants can be observed in these diagrams which are consistent with the suggested equivalent circuit. Phase diagram in high frequency region provides information about capacitance of the layer/coating. As it can be deduced from the phase diagram of \( \text{Al}_2\text{O}_3/\text{Cu} \) sample (figure 7(c)) increase of phase angle in high frequency range and also high value of \( n \) in table 3 for this sample indicate that capacitor behavior of this sample is increased/enhanced. The impedance in low frequencies is related to the resistance of the layer/coating. In figure 7(c) it can be seen that the resistance for the \( \text{Al}_2\text{O}_3/\text{Cu} \) sample is higher than that for the uncoated Cu sample.

\( \text{Al}_2\text{O}_3 \) coated on Cu substrate has a high electrical insulating property; hence anodic oxidation on the surface of the coating rarely happens. Instead, in the pores of the coating where the electrolyte is directly in contact with the Cu surface usually anodic reaction occurs. Different parameters obtained from fitting of EIS data using the equivalent circuit are given in table 3. The polarization resistance \( R_p \) is defined as:

\[
Z_{\text{CPE}} = \frac{1}{(\text{CPE}) (j\omega)^n}
\]
And corrosion inhibition enhancement factor is defined as:

\[
\eta = \frac{R_{\text{p, film}} - R_{\text{p}}}{R_{\text{p, film}}} \times 100
\]

(4)

Where \(R_p\) and \(R_{\text{p, film}}\) are polarization resistances of uncoated Cu and Al\(_2\)O\(_3\) coated Cu, respectively. In table 3 the value of \(\eta\) obtained from the data of measurement is 97.48% which shows a high enhancement in the corrosion inhibition of Cu by Al\(_2\)O\(_3\) coating.

3.4. Kramers-Kronig transformation

Impedance method is usually used in different electrochemical systems to study corrosion system features. Prior to start analyzing and simulating the experimental results it is necessary to determine the correctness of impedance data. Kramers and Kronig introduced a general mathematical technique to confirm the correctness of impedance data which was further developed by Bode and includes four fundamental conditions for the correctness of calculated impedance during impedance measurements [77–79];

(1) Linearity: A system is linear if its response to the sum of excitants is equal to sum of the response of the system to each of the excitants. Electrochemical systems are usually nonlinear and the related impedance is determined by linearize equations over a small range. For a linear system response is independent of amplitude.

(2) Causality: response of the system must be determined perfectly/completely by considering the applied potential disturbance and should only depend on the input values.

(3) Stability: stability of a system is determined by its response to the inputs of the system. A stable system remains stable unless it becomes excited by an external source and returns to its stable state if the external source is removed.

(4) Finiteness: real and imaginary elements of impedance must have finite values within the frequency range of \(0<\omega<\infty\)

Kramers-Kronig equations facilitates calculation of the real and imaginary elements of the impedance by considering the above mentioned four conditions. In Kramers-Kronig transformation, for calculation of real and imaginary elements of experimental electrochemical impedance the following equations (equations (6) and (7)) are used [80]:

\[
\text{Re}(\omega) = \text{Re}(\infty) + \left(\frac{2}{\pi}\right) \int_0^{\infty} \frac{x \text{Im}(x) - \omega \text{Im}(\omega)}{x^2 - \omega^2} \, dx
\]

(6)

\[
\text{Im}(\omega) = \left(\frac{2\omega}{\pi}\right) \int_0^{\infty} \frac{\text{Re}(x) - \text{Re}(\omega)}{x^2 - \omega^2} \, dx
\]

(7)

The percentage of error is calculated by:

\[
AE(\%) = \frac{100}{N} \times \sum |Z_{\text{ex, max}}(\omega) - Z_{\text{KKT}}(\omega)|
\]

(8)

Where \(N\) is the number of real/imaginary pairs and \(Z_{\text{ex, max}}\) is the one with the maximum value among \(Z_{\text{ex}}\).

In figure 8 results of experimental measurements for the real and imaginary elements of impedance obtained for both uncoated Cu and Al\(_2\)O\(_3\)/Cu samples and those achieved through Kramers-Kronig calculations are given. Values of \(AE\%)\) are also given in table 4. It can be seen that there is a good agreement between experimental values and those obtained using Kramers-Kronig transformation. Hence, the EIS results are validated by this transformation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(R_s) ((\Omega\cm²))</th>
<th>(CPE_1) ((\Omega^{-1}\cm^{-1})) (n_1)</th>
<th>(R_1) ((\Omega\cm²))</th>
<th>(CPE_2) ((\Omega^{-1}\cm^{-1})) (n_2)</th>
<th>(R_2) ((\Omega\cm²))</th>
<th>(W) ((\Omega^{-1}\cm^{-1})) (n)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>57.84</td>
<td>9.8 \times 10^{-3}</td>
<td>0.65</td>
<td>84.6</td>
<td>3 \times 10^{-4}</td>
<td>0.59</td>
<td>2492</td>
</tr>
<tr>
<td>Al(_2)O(_3)/Cu</td>
<td>86.51</td>
<td>1.81 \times 10^{-6}</td>
<td>0.89</td>
<td>40 744</td>
<td>9.19 \times 10^{-6}</td>
<td>0.72</td>
<td>61 850</td>
</tr>
</tbody>
</table>

Table 3. Electrochemical parameters of uncoated Cu and Al\(_2\)O\(_3\)/Cu subjected to corrosion test in 3.5% NaCl solution, obtained from the simulation procedure using the Zview program.
3.5 Electrochemical polarization

The cathodic and anodic branches of polarization curves for both uncoated Cu and Al2O3/Cu are shown in figures 9(a) and (b), respectively. It is expected that the Stern-Geary equation be applied to these curves near open circuit potential (OCP). Stern-Geary equation assumes that both cathodic and anodic processes are purely additives and obey the Tafel rule \[ I = I_{corr} \exp \left( \frac{2.3(E - E_{corr})}{b_a} \right) - \exp \left( \frac{2.3(E - E_{corr})}{b_a} \right) \]

where, \( I_{corr} \) (A/cm\(^2\)) is the corrosion current density and \( b_a \) and \( b_c \) are Tafel constants.

\( I_{corr}, E_{corr}, b_a \) and \( b_c \) are determined using the non-linear least squares fitting procedure to the cathodic or anodic branches of polarization curves. In all cases the correlation factor \( R^2 \) was greater than 0.99 which confirms the acceptable fitting results. Results of this investigation for the cathodic branch of the polarization curves obtained from uncoated Cu and Al2O3/Cu are given in figures 10(a) and (b), respectively. In this calculation, the process used in the literature [82–84] was used; the potential domain is limited to 10 mV towards more anodic direction and 50 mV towards more cathodic direction with respect to the corrosion potential. A good agreement between the experimental data and fitting parameters (table 5) are obtained. In order to carrying out this investigation for the anodic branch of the polarization curve, the potential domain was limited 10 mV towards more cathodic direction and 50 mV towards anodic direction with respect to the corrosion potential. It should be mentioned that the corrosion current is a combination of the cathodic and anodic currents.

Table 5. The percentage of error (AE%) calculated from Kramers-Kronig transformations for experimental data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( Z' )</th>
<th>( Z'' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.19</td>
<td>0.53</td>
</tr>
<tr>
<td>Al2O3/Cu</td>
<td>0.67</td>
<td>1.79</td>
</tr>
</tbody>
</table>
Considering that Al$_2$O$_3$ is a dielectric insulator and does not have electrochemical activity; hence polarization curves obtained from the uncoated Cu and Al$_2$O$_3$/Cu only show the activity of the Cu substrate and similar polarization curves are obtained for both of these samples. Therefore, it can be concluded that the corrosion mechanism is the same for both of these samples, but with reduced corrosion current for the Al$_2$O$_3$/Cu. The obtained corrosion current for the latter sample should be due to remaining/residual electrochemical activity of Cu substrate as result of penetration of corroding medium through defects of different forms (e.g., residual pinholes and/or channel defects connecting the substrate to the electrolyte through the coating and possibly preferentially located at internodular sites of the coating [34]) in the Al$_2$O$_3$ coating.

The kinetic and solution mechanism of Cu in chloride medium are explained by the following reactions [85]:

$$\text{Cu} \rightarrow \text{Cu}^+ + \text{Cl}^-$$ (10)
Anodic dissolution of Cu is controlled through two mechanisms: (a) electrode dissolution of metal and (b) penetration of CuCl$_2^-$ to corroding medium. Cathodic corrosion reaction of Cu is the result of oxygen reduction in air and can be described by:

\[
\text{Cu}^++\text{Cl}^-\rightleftharpoons\text{CuCl}_{\text{ads}} \quad (11)
\]

\[
\text{CuCl}_{\text{ads}} + \text{Cl}^- \rightarrow \text{CuCl}_2^- \quad (12)
\]

The corrosion potential obtained for the Al$_2$O$_3$ coated Cu sample is negatively shifted relative to the corrosion potential of uncoated Cu. This indicates that Al$_2$O$_3$ coating has hindered the cathodic reaction. It can be deduced that this coating by partially blocking the surface of metal caused a delay in the reaction of oxygen reduction and has acted like a barrier against transition of O$_2$ to cathodic locations/areas on the Cu surface. This Al$_2$O$_3$ coating may also stop/block the partial anodic reaction which leads to reduction of corrosion current density of Al$_2$O$_3$ coated Cu relative to uncoated Cu.

Corrosion inhibition efficiency/yield (PE\%) may be estimated for cathodic and anodic branches using cathodic and anodic currents as discussed above using [86]:

\[
\text{PE}(\%) = \frac{I_{\text{corr}}^0 - I_{\text{corr}}^c}{I_{\text{corr}}^0} \times 100 \quad (14)
\]

where, $I_{\text{corr}}^0$ is corrosion current density (cathodic or anodic) of Cu and $I_{\text{corr}}^c$ is the corrosion current density (cathodic or anodic) of coated sample. The quantitative values obtained from this equation (93.95\% and 69.02\%) for cathodic and anodic branches, respectively (table 5) agree well with the EIS result for ($\eta$).

The polarization resistance, $R_p$, can also be determined from the slope of the $E$-$I$ curve in the range of $\pm 10$ mV about the corrosion potential [28]. The value of $R_p$ obtained for Al$_2$O$_3$/Cu was about two and half times greater than that for uncoated Cu (table 5). Comparison of $R_p$ resulted from this analysis with that obtained from EIS procedure (table 3), shows that the value obtained from EIS is about 15 times higher than that obtained from polarization. This difference can be related to the type of current which is applied (AC or DC).

The porosity of Al$_2$O$_3$ layer on the Cu substrate can be obtained from comparison of corrosion results ($R_p$) for uncoated Cu and Al$_2$O$_3$/Cu [87]:

\[
P = \left( \frac{R_{p0}}{R_p} \right) \times 10^\left( \frac{\Delta E_{\text{corr}}}{b_p} \right) \quad (15)
\]

where, $R_{p0}$ and $R_p$ are polarization resistances of the uncoated Cu and Al$_2$O$_3$/Cu, respectively. $\Delta E_{\text{corr}}$ is the corrosion potential difference between uncoated Cu and Al$_2$O$_3$/Cu and $b_p$ is the Tafel slope of the anodic branch of uncoated Cu. A value of 20\% was obtained for the Al$_2$O$_3$/Cu.

The EIS and polarization results of this work in terms of corrosion inhibition enhancement factor ($\eta$) and corrosion inhibition efficiency/yield (PE\%) are compared with the results reported by Mirhashemihaghighi et al [33, 34] and those of Fusco et al [39] in table 6, using equations (5) and (14), respectively. Results of the present work are as good as [33] and [34], for both $\eta$ and PE\%, while they are better than those of Fusco et al [39] in most cases. It is worthwhile to mention that those references mentioned in table 6 who used the process of removing (pre-treatment) the native oxide from the surface of Cu substrate (i.e., the substrates were electropolished in H$_3$PO$_4$) before ALD Al$_2$O$_3$ deposition reported that this process generally improves the corrosion current by an order of magnitude. We did not use this process in our work and the surface of the substrate should have been covered with native oxide as there was a long time lapse between cleaning the substrates and performing the ALD coating. In addition, Mirhashemihaghighi et al [33, 34] used copper with 99.99\% purity and Fusco et al [39] used copper with 99.9% purity, while we carried out our investigation on a copper with a composition given in table 1 (purity of $\sim$97.65\%). Presence of elements given in table 1 may affect the corrosion resistance when compared with pure Cu as used by [33, 34, 39], although it should be considered that their wt\% in the body of the substrate is very low. It can be seen that Fusco et al [39] results are not comparable with the rest of the results in table 6, despite pre-treating and deoxygenation (see foot note of table 6) procedures they carried out in their investigation. The deposition rate is almost the same for all the works mentioned in table 6. Hence this parameter can not be the cause of differences observed. In addition, the deposition temperature for Mirhashemihaghighi et al [33, 34] and Fusco et al [39] are the same while the latter group reported that increase of temperature from 150 °C to 250 °C although enhances the film quality, but it is counterproductive for long-term corrosion protection. Considering that concentration of NaCl solution in Fusco et al [39] work was much lower than the rest of works reported in table 6, one may come to a conclusion that the lower values of $\eta$ and PE\% in their work may be related to the high surface roughness of their sample: micro-scale compared to nano-scale (table 6).
Table 6. Comparison of results of this work with those published in the literature.

<table>
<thead>
<tr>
<th>References and substrate</th>
<th>Film thickness (nm)</th>
<th>Deposition rate (nm/Cycle)</th>
<th>NaCl concentration</th>
<th>Deposition temperature (°C)</th>
<th>η (%)</th>
<th>PE (%)</th>
<th>R rms (nm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare Cu</td>
<td>62</td>
<td>0.11</td>
<td>0.6 M</td>
<td>200</td>
<td>97.48</td>
<td>93.95</td>
<td>23.91</td>
<td>NPT</td>
</tr>
<tr>
<td>Coated Cu</td>
<td>50</td>
<td>0.10</td>
<td>0.5 M</td>
<td>250</td>
<td>99.6</td>
<td>99.71</td>
<td>2–8 nm</td>
<td>PT</td>
</tr>
<tr>
<td>Bare Cu</td>
<td>20</td>
<td>0.10</td>
<td>0.5 M</td>
<td>250</td>
<td>99.80</td>
<td>99.87</td>
<td>Not reported</td>
<td>NPT</td>
</tr>
<tr>
<td>Coated Cu</td>
<td>20</td>
<td>0.10</td>
<td>0.5 M</td>
<td>250</td>
<td>99.78</td>
<td>99.89</td>
<td>Not reported</td>
<td>PT</td>
</tr>
<tr>
<td>Bare Cu</td>
<td>50</td>
<td>0.125</td>
<td>0.1 M</td>
<td>150 and 250</td>
<td>97.94</td>
<td>88.14</td>
<td>0.1–0.3 μm</td>
<td>PT and Deoxygenated</td>
</tr>
<tr>
<td>Coated Cu</td>
<td>50</td>
<td>50</td>
<td>0.1 M</td>
<td>150 and 250</td>
<td>71.29</td>
<td>71.61</td>
<td>0.1–0.3 μm</td>
<td>PT and Oxygenated</td>
</tr>
</tbody>
</table>

PT: Pre-treated.
NPT: Non pre-treated.
Deoxygenated: for experiments where deoxygenation was performed, nitrogen was bubbled through the electrolyte for at least 15 min prior to and continuously during testing. The nitrogen was passed through a gas washing bottle of 0.1 M NaCl to pre-saturate the dry gas before its introduction into the test cell [39].
Oxygenated: refers to cases in which no nitrogen purging of the electrolyte was performed [39].
4. Conclusion

Al₂O₃ with 60 nm thickness at 473 K was coated on Cu substrate by atomic layer deposition technique. The corrosion resistance of the produced samples in 3.5% (0.6 M) NaCl solution was proved a high degree of enhancement: corrosion inhibition enhancement factor of $\eta = 97.48\%$ was obtained from EIS measurements and electrical equivalent circuit simulation, and corrosion inhibition efficiency/yield ($\text{PE} = 93\%$) was obtained from cathodic branch of polarization curve. The SEM and the AFM analyses provided information about the morphology and surface roughness as well as grain sizes of the alumina on the samples. Kramers–Kronig transformations validated the EIS results. Stern–Geary relation was used to fit the polarization curves near the open circuit potential leading to corrosion parameters. It was observed that the corrosion potential for the coated Cu sample is lower than uncoated Cu. This shows the alumina coating has acted as a barrier for the cathodic reaction. Comparison of the data obtained in this work with the results published by researchers [33, 34, 39] showed good agreement. Inconsistencies with the results reported by [39] are related to the surface roughness of the samples used by [39].

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