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Short Communication

Effect of Deposition Potential on Preparation and Corrosion Resistance of SiO_2 Film on Copper

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The silanization of metal surface is a new and environmental anti-corrosion technology. SiO_2 film has been prepared on copper by an electrochemically-assisted deposition technology using tetraethoxysilane as a silane reagent in this research. The effect of deposition potential on structure and performance of SiO_2 film were also studied. The results indicate that SiO_2 is the main component of the deposited films. As the deposition potential changes from -1.0V to -1.5V, the value of SiO_2 content, film deposition rate and film thickness all increase first and then decrease. When the deposition potential is -1.4V, the deposition rate of SiO_2 film is the fastest ($1.13\times10^{-5}g\cdot cm^{-2}\cdot s^{-1}$) and this film is also the thickest (69.1 μm). Moreover, the prepared SiO_2 film has obvious barrier property and can improve the corrosion resistance of the Cu substrate.

Keywords: Electrochemically-assisted deposition, Silane, Sol-gel method, Corrosion resistance

1. INTRODUCTION

Silanization of metal surface is a new and environmental metal anti-corrosion technology [1,2], which avoids pollution caused by chromate passivation [3] and phosphate conversion [4], without containing other harmful heavy metal ions. This technology is easy to operate and has high production efficiency. However, the thickness of the silane film prepared by dipping, pulling or spin coating is only a few hundred nanometers, which limit its application in many fields [5-7]. Mandler's group [8] first proposed the use of electrochemically-assisted deposition technology to prepare silicon-based sol-gel films in 1999. It is based on the mechanism of local alkalinization. The experiment applies a cathodic potential to the working electrode. The active components in the solution obtain electrons to be reduced to OH^-, which promote the formation of films.

The electrodeposition of silane films has attracted extensive attention in recent years [9,10]. The researches mainly focus on the selection of silane systems, doped composite particles and deposition

conditions (electrolyte, water-ethanol ratio, pH value, reaction temperature) [11-14]. Mrad [15] has added sodium nitrate to the precursor solution and studied the effect of nitrate ion on the silane condensation reaction. Giordano [16] found that with the increase of TEOS concentration and the HCl/TEOS ratio, the thickness of film deposited on the stainless steel gradually increased. He also pointed out that the reaction temperature is an essential factor affecting the thickness. Sheffer [17] has studied the corrosion resistance of various silane films electrodeposited on the Al substrate. The results show that the film with phenyltrimethoxysilane (PTMS) as the precursor is the most hydrophobic and has excellent corrosion resistance.

However, the existing researches are mainly focused on silane protection for aluminum alloy and steel with electrochemically-assisted deposition technology [18-21]. It is necessary to broaden the applicability of silane protection on different metal materials. Copper is a kind of common metal material widely used in the fields of power, electronics, machinery and light industry [22, 23], but it is easy to be corroded in wet environment. There is little research on the protection of copper by silane film with electrochemically-assisted deposition technology [24]. It is significant to increase the research on the preparation and protection property of silane films on copper.

In this paper, tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) is selected as the silane reagent and electrochemically-assisted deposition technology is used to prepare silicon-based sol-gel films on the surface of copper. The effect of applied cathode potential on film structure, surface morphology, deposition rate, roughness and thickness is discussed, and then the corrosion resistance of SiO_2/Cu sample is finally be explored. From this research, a controlled preparation of silane films with better corrosion resistance on copper substrate can be achieved, which provide theoretical basis and technical support for future research on different silane protection systems.

2. EXPERIMENTAL

2.1 Pretreatment of substrate

Copper (purity≥99.90%) was selected as the substrate with the size of 40.0 mm×10.0 mm×0.1mm. The working area of the copper substrate was 10.0 mm×10.0 mm, and the rest was sealed with resin. After the work electrode has been grind to 1200#, it was soaked in 1M H_2SO_4 solution for 1.0 minute and rinsed with deionized water. Then it was soaked in 1M NaOH aqueous solution for 1.0 minute, rinsed with deionized water again, and finally dried with nitrogen.

2.2 Preparation of SiO_2 film

The electroplating liquid was a kind of sol-gel solution prepared by deionized water, and the specific experimental method was set according to the references [25-27]. The precursor solution was consisted by mixing 50.0 ml ethanol, 50.0 ml 0.2M KNO_3 aqueous solution, and 5.0 ml tetraethoxysilane (TEOS, 98%, Aladdin). Hydrochloric acid was selected to adjust the pH value of the precursor solution to 3.0±0.1. Before electrodeposition, the precursor solution was kept under stirring and pre-hydrolyzed at 25°C for 3h.

The electrodeposition of SiO_2 film was performed on electrochemical working station (PARSTAT®2273). A three-electrode cell was used in which a copper sheet was treated as the working electrode, a platinum foil (purity 99.99%, 20.0mm×20.0mm) as a counter electrode, and an Ag/AgCl electrode (in saturated KCl solution) as the reference electrode. SiO_2 films were deposited from the prepared plating solution by applying a cathode potential for the 300s. Specific deposition potential values and corresponding sample acronyms were listed in Table 1. After rinsing with deionized water, the samples were dried with nitrogen and stored in a vacuum dryer.

Table 1. Specific deposition potential values and corresponding sample acronyms

Potential applied to copper	Corresponding sample acronym
-1.0V	SiO_2/Cu1
-1.1V	SiO_2/Cu2
-1.2V	SiO_2/Cu3
-1.3V	SiO_2/Cu4
-1.4V	SiO_2/Cu5
-1.5V	SiO_2/Cu6

An electronic microbalance (accuracy of 0.1 mg, ME204) was used to record the deposition mass of SiO_2, and the deposition rate was calculated according to Eq. 1, where v is the deposition rate ($g\cdot cm^{-2}s^{-1}$); m is the deposition mass (g); s is the deposition area (cm^2); t is the deposition time (s).

$$v = \frac{m}{s \cdot t} \qquad (1)$$

2.3 Corrosion resistance analysis

The corrosion resistance of the prepared SiO_2/Cu samples was evaluated by potentiodynamic polarization measurements and electrochemical impedance spectroscopy (EIS) . The test was performed on electrochemical working station with the same three-electrode cell as the previous experiment shown in 2.2 section. The test environment was in 3.5 wt.% NaCl aqueous solution at 25°C. EIS was carried out at a range of 10mHz~100kHz with a 5mV perturbation signal at the corrosion potential. The test range of the potentiodynamic polarization curve was [E_{ocp}-300mV, E_{ocp}+300mV] with the scanning speed of 1.0m $V\cdot s^{-1}$. Duplicate experiments were conducted to ensure the reliability and reproducibility of the measurements.

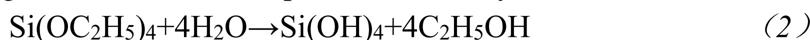
2.4 Morphology and structure analysis

X-ray diffraction (XPert Philips PW1830) was used to observe the phase structure of the prepared samples, where CuKα radiation was used as an incident beam (40kV, 150mA). Scanning electron microscopy (SEM, Hitachis-4800) was used to observe the surface morphology of prepared samples,

optical microscope (Smart zoom 5, Carl Zeiss) and step profiler (P-6, KLA-Tencor) were used to characterize the thickness and roughness of each sample.

3. RESULTS AND DISCUSSION

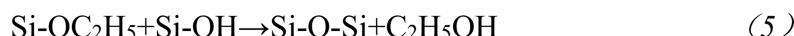
In the experiment, the silane reagent TEOS ($Si(OC_2H_5)_4$) is prone to hydrolysis in acidic solution and will generate silanols Si-OH (Eq. 2). The generated silanols and the metal with hydroxyl groups on the surface (Cu-OH) will undergo dehydration polycondensation on the substrate (Eq. 3). Polycondensation will also occur between the generated silanols (Eq. 4), forming a network structure attached to the substrate. Besides, a loss-of-alcohol polycondensation (Eq. 5) occurs between the TEOS and the generated silanols, which promotes the combination of silane and substrate. A series of hydrolysis and condensation reactions [28-30] will form a stable structure and adhere to the substrate. After drying and curing, a silicon oxide compound will finally be established.



$$Si(OC_2H_5)_4+4H_2O \rightarrow Si(OH)_4+4C_2H_5OH \quad (2)$$

$$Si\text{-}OH+Cu\text{-}OH \rightarrow Si\text{-}O\text{-}Cu+H_2O \quad (3)$$

$$Si\text{-}OH+Si\text{-}OH \rightarrow Si\text{-}O\text{-}Si+H_2O \quad (4)$$



$$Si\text{-}OC_2H_5+Si\text{-}OH \rightarrow Si\text{-}O\text{-}Si+C_2H_5OH \quad (5)$$

The preparation of the precursor solution usually chooses a slightly acidic environment that is prone to silane hydrolysis. However, it is not conducive to the subsequent polycondensation reaction, resulting in insufficient silane film formation power. By introducing electrochemically-assisted deposition technology, a specific cathodic potential is applied to the electrodes, some active substances in the solution such as H_2O, O_2 undergo electron reduction to generate OH^-, thereby increasing the basicity around the substrate. The polycondensation reaction further occurs and promotes the film formation of the silane. Electrochemical sol-gel technology can make the surface of the substrate locally conductive and achieve alkalization. The overall solution can still maintain a large acidic environment and has good stability.

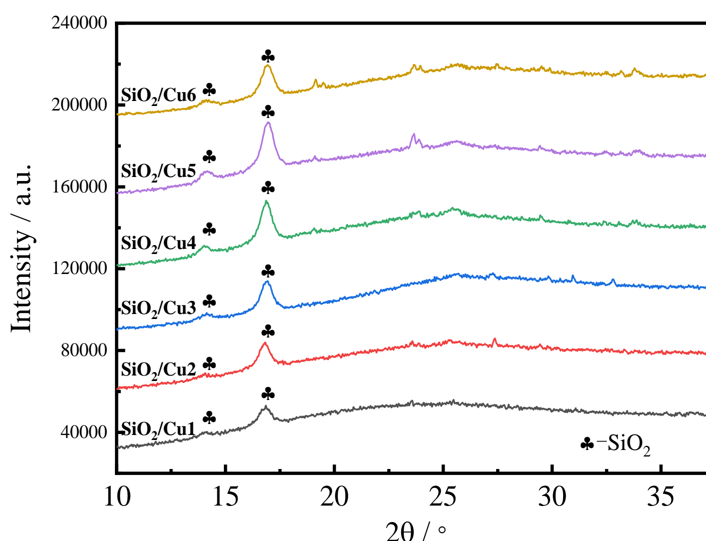


Figure 1. XRD of SiO_2/Cu samples prepared at different deposition potentials

Structural analysis of SiO_2 films deposited on Cu substrate at different deposition potentials was performed by XRD (Fig.1). The component of prepared film are mainly SiO_2 and the crystallographic orientations of SiO_2 are presented at $2\theta \approx 14.3°$ and $17.1°$. As the applied potential changes from -1.0V to -1.5V, the content of SiO_2 in films first increases and then decreases. When the deposition potential is -1.4V, the content of SiO_2 in film is the most, which is advantageous to improve the corrosion resistance of SiO_2/Cu sample [31].

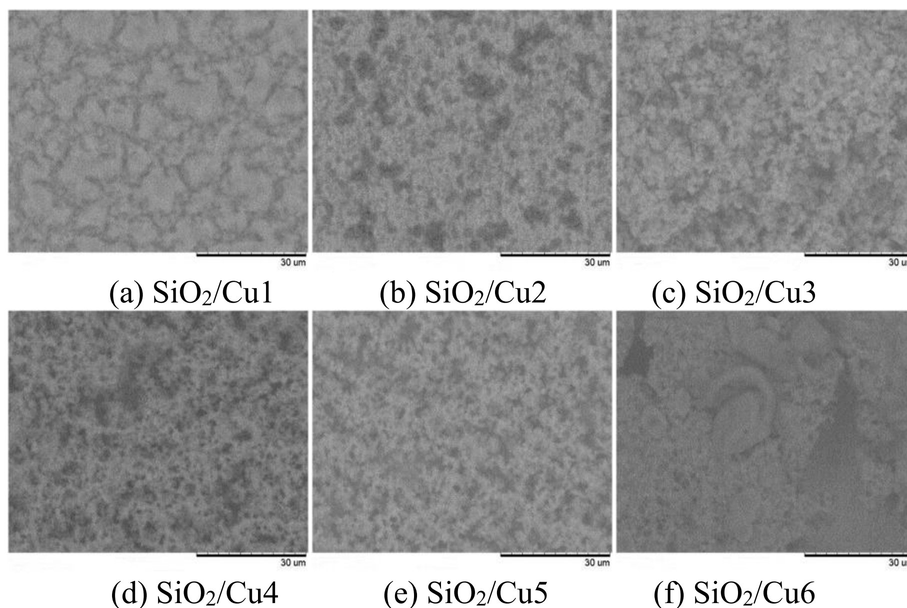


Figure 2. SEM images of SiO_2/Cu samples prepared at different deposition potentials

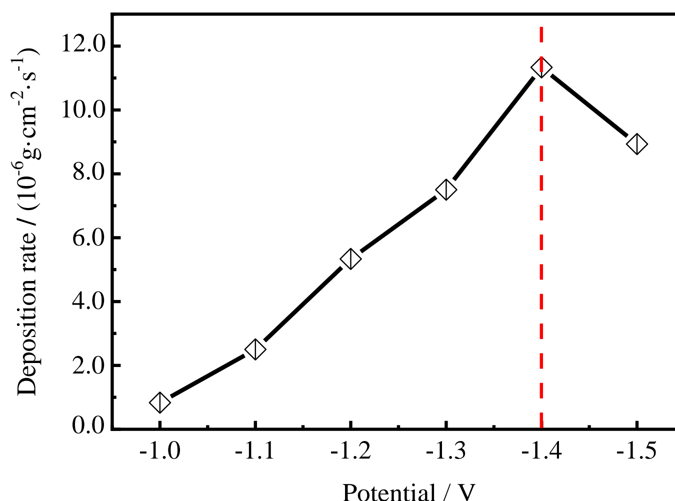


Figure 3. Deposition rate variation curve of SiO_2 films prepared on Cu substrate at different deposition potentials

Fig.2 shows the morphology of SiO_2/Cu samples prepared at different deposition potentials. When the deposition potential is -1.0V, massive agglomerates appeared on the substrate with some

cracks (Fig.2a); as the deposition potential increases, SiO_2 spherical particles gradually appear (Fig.2b) and increase (Fig.2c, 2d); when the deposition potential reaches to -1.4V, SiO_2 particles become more densely with compact and even film surface (Fig.2e); when the deposition potential is -1.5V, the film become partially uneven or even peeled (Fig.2f). This phenomenon can be deduced that excessive deposition potential will promote the hydrogen evolution reaction and restrain the formation of a uniform SiO_2 film during the deposition process [30, 31].

Fig.3 shows the deposition rate variation curve of SiO_2 films prepared on Cu substrate at different deposition potentials. With the change of the deposition potentials from -1.0V to -1.5V, the deposition rate of SiO_2 film on Cu substrate increases first and then decreases (shown in Fig.3); when the deposition potential is -1.4V, the deposition rate is the fastest, achieving to $1.13\times10^{-5}g\cdot cm^{-2}\cdot s^{-1}$. It shows that the increase of the deposition potential can promote the formation of SiO_2 film. This phenomenon can be explained that when more cathode potential is applied to the working electrode, more active components in the plating solution can get electrons and be reduced to OH^- [14, 15]. The increase of alkalinity in the area near the substrate promotes the formation of SiO_2 film. Nitrate added in the plating solution accepts electrons to be reduced to OH^- (Eq. 6), which also promotes alkalinization around the copper surface. When the applied deposition potential is -1.5V, the deposition rate is slightly reduced, which is related to the phenomenon (discussed in Fig.2) that partially film was uneven or even peeled off.

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \qquad (6)$$

Fig.4 and Fig.5 show the cross-sectional image, thickness and roughness of SiO_2 films prepared on Cu substrate at different deposition potentials. It can be known that as the deposition potential changes from -1.0V to -1.5V, the film grows uniformly with increased roughness, while the thickness of the film rises first and then decreases.

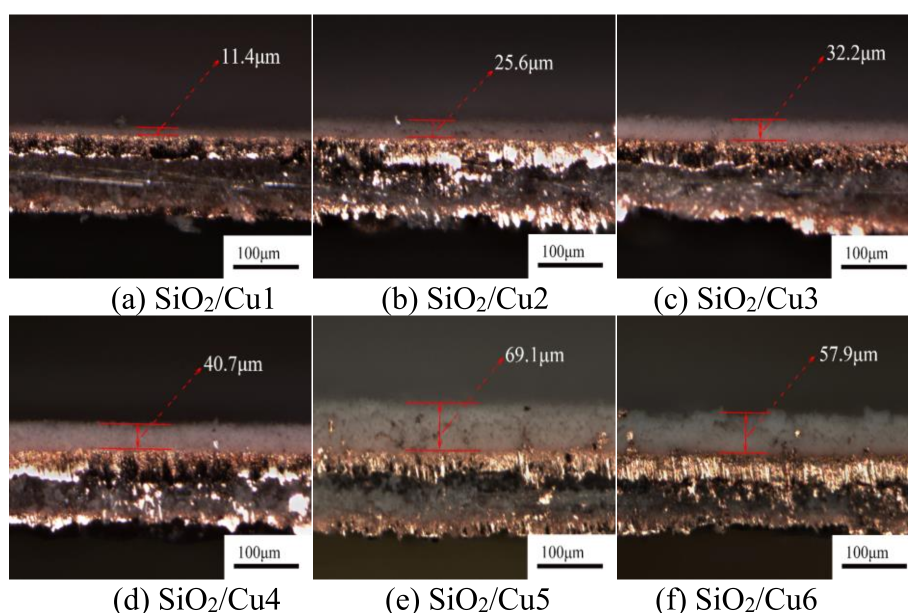


Figure 4. Cross-sectional images of SiO_2/Cu samples prepared at different deposition potentials

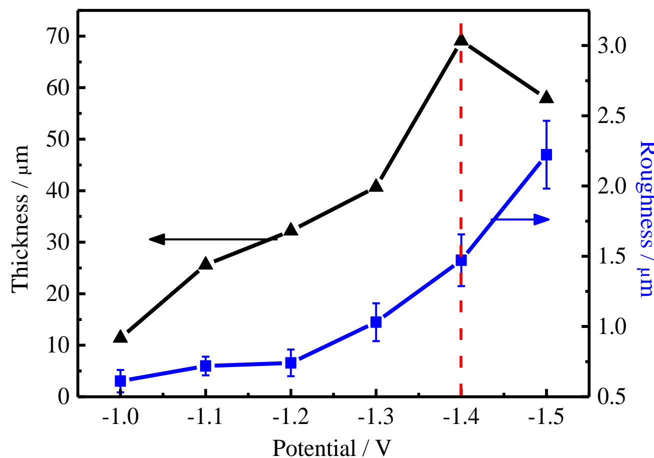


Figure 5. Thickness and roughness of SiO_2 films prepared on Cu substrate at different deposition potentials

When the deposition potential is -1.4V, the film is the thickest (69.1 μm). However, when the deposition potential is -1.5V, the thickness of SiO_2 film slightly reduces (57.9 μm) with uneven film surface (shown in Fig.4f). It can be deduced that the larger deposition potential may cause more severe hydrogen evolution on the reaction surface, which hinders the film formation. The results are consistent with the experimental conclusion from Fig. 2 and 3.

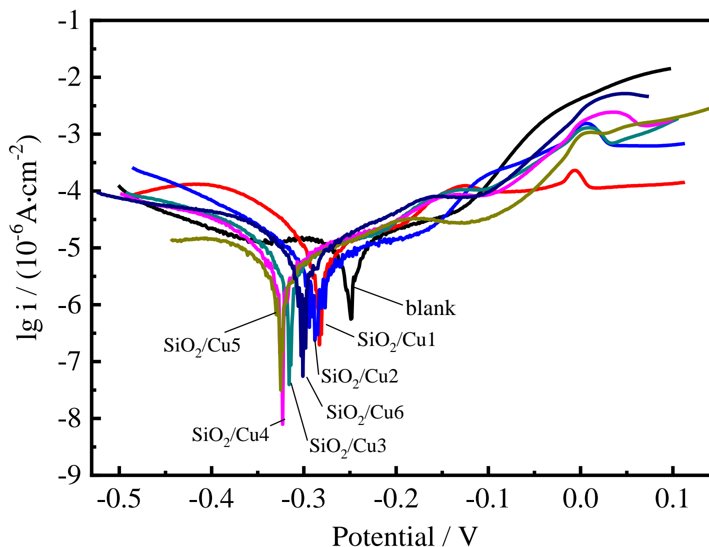


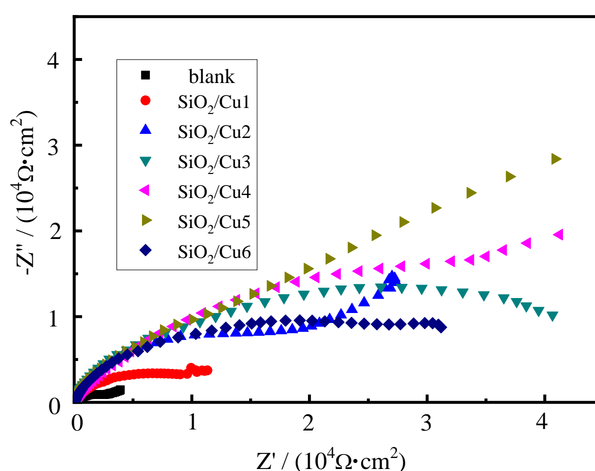
Figure 6. Potentiodynamic polarization curves of SiO_2/Cu samples prepared at different deposition potentials in 3.5wt.% NaCl aqueous solution

Fig.6 shows the potentiodynamic polarization curves of SiO_2/Cu samples prepared at different deposition potentials. Table 2 shows electrochemical corrosion data corresponding to potentiodynamic polarization curves. In this corrosion system, the electrochemical reaction process is controlled by the oxygen diffusion process. Compared with the Cu substrate without deposited SiO_2 film (blank, shown

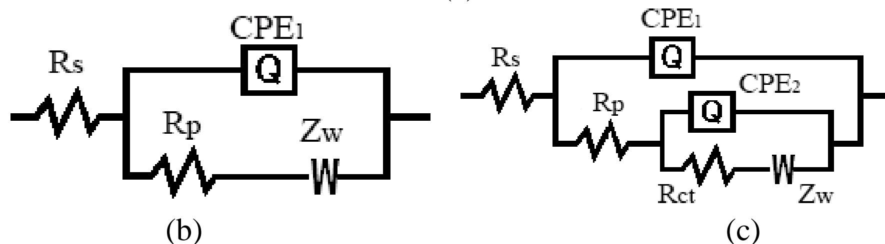
in Table 2), the corrosion current density of SiO_2/Cu samples are lower. As the deposition potential increases, the self-corrosion potential of the SiO_2/Cu sample has a negative shift, and the corrosion current density decreases first and then increases. When the deposition potential is -1.4V (SiO_2/Cu5 sample), the self-corrosion potential reaches to a maximum negative value (-0.325V), and the corrosion current density is the minimum value (6.021×10^{-6}A·cm^{-2}). However, when the deposition potential is -1.5V (SiO_2/Cu6 sample), the corrosion current density increase. This is consistent with the results obtained from the phase and morphology analysis.

Table 2. Electrochemical corrosion data corresponding to potentiodynamic polarization curves of SiO_2/Cu samples prepared at different deposition potentials in 3.5wt.% NaCl aqueous solution

Sample	E_{corr}/V	I_{corr}/(10^{-6}A·cm^{-2})
Cu	-0.249	22.560
SiO_2/Cu1	-0.283	18.290
SiO_2/Cu2	-0.288	9.005
SiO_2/Cu3	-0.316	8.611
SiO_2/Cu4	-0.323	7.440
SiO_2/Cu5	-0.325	6.021
SiO_2/Cu6	-0.301	9.003



(a)



(b) (c)

Figure 7. Nyquist plots and equivalent circuits for SiO_2/Cu samples in 3.5wt.% NaCl aqueous solution: (a)Nyquist plots; (b) and (c) are equivalent circuits (R_s: solution resistance; R_{ct}: charge transfer resistance; R_p: SiO_2 film resistance; CPE_1: SiO_2 film capacitance; CPE_2: the double layer capacitance; Z_w: Warburg impedance)

Table 3. Values of the elements in the equivalent circuit of SiO_2/Cu samples in 3.5wt.% NaCl aqueous solution

Sample	R_s/ ($\Omega\cdot cm^2$)	CPE_1/ ($\mu F\cdot cm^2$)	n_1	R_{ct}/ ($\Omega\cdot cm^2$)	CPE_2/ ($\mu F\cdot cm^2$)	n_2	R_p/ ($\Omega\cdot cm^2$)	Zw/ ($S\cdot sec^{0.5}\cdot cm^{-2}$)
blank	9.48	14.67	0.807	2703	--	--	--	184.0
SiO_2/Cu1	10.43	13.59	0.778	3146	29.16	0.548	6980	764.9
SiO_2/Cu2	10.10	13.05	0.897	3428	10.75	0.715	9441	146.3
SiO_2/Cu3	10.28	13.81	0.931	3685	28.41	0.778	36160	137.5
SiO_2/Cu4	10.97	13.01	0.931	4022	29.11	0.812	40860	207.6
SiO_2/Cu5	10.78	13.67	0.946	3835	23.77	0.874	71130	364.4
SiO_2/Cu6	10.26	13.18	0.850	3606	20.45	0.396	42650	394.5

Fig.7 shows the Nyquist plots and equivalent circuits of SiO_2/Cu samples in 3.5wt.% NaCl aqueous solution and the values of fitting elements were listed in Table 3. The formation of the electrochemical double layer, the dissolution of the film in the corrosive environment, and the adsorption and deposition of the corrosion products on the sample all affect the corrosion process [32]. With the increase of the deposition potential, the film resistance R_p in the solution increases first and then decreases. It can be deduced that the corrosion rate ($1/R_p$) decreases first and then increases. The SiO_2 film prepared on the copper surface at -1.4V potential has the highest resistance and the smallest corrosion current density. This conclusion is consistent with the results obtained by the polarization curve measurement. Compare with previous studies[33], SiO_2/Cu samples with better corrosion resistance can be prepared using electrochemically-assisted deposition technology.

4. CONCLUSIONS

In this paper, tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$) is selected as the silane reagent and electrochemically-assisted deposition technology is used to prepare silicon-based sol-gel films on the surface of copper. The results are drawn as following:

(1)The structure and morphology analysis of prepared films show that component of film is mainly SiO_2. As the deposition potential changes from -1.0V to -1.5V, the content of SiO_2 in films first increases and then decreases. When the deposition potential is -1.4V, the content of SiO_2 in film is the most and the film surface become denser and more compact.

(2) With the change of the deposition potentials from -1.0V to -1.5V, the film roughness of SiO_2/Cu samples increases; while the deposition rate and thickness of SiO_2 film on Cu substrate increases first and then decreases. When the deposition potential is -1.4V, the deposition rate of SiO_2 film is the fastest ($1.13\times10^{-5} g\cdot cm^{-2}\cdot s^{-1}$) and this film is also the thickest (69.1 μm).

(3) The corrosion resistance of SiO_2/Cu samples were test by potentiodynamic polarization curves and electrochemical impedance spectroscopy. In this corrosion system, the electrochemical reaction process is controlled by the oxygen diffusion process. Compared with the Cu substrate without deposited SiO_2 film, the corrosion current density of SiO_2/Cu samples are lower. The SiO_2 film prepared on the copper

surface at -1.4V potential (SiO_2/Cu5 sample) has the highest corrosion resistance and the smallest corrosion current density.

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