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Scripta Materialia 59 (2008) 297-300

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Nitrate ions as cathodic alkalization promoters for the electro-assisted deposition of sol-gel thin films

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> Received 20 October 2007; revised 17 March 2008; accepted 24 March 2008 Available online 1 April 2008

Nitrate was used as a promoter to prepare dodecyltrimethoxysilane thin films on aluminum substrates. With the addition of nitrate into silane sol-gel precursors, the electro-assisted formation of silane films was facilitated, as indicated by electrochemical impedance spectroscopy, scanning electron microscopy and secondary-ion mass spectroscopy, due to the promotion in cathodic alkalization. However, an extra-high concentration of nitrate would be harmful because of the salting-out effect in precursors and the soluble nitrate remaining in silane films.

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Keywords: Thin films; Sol-gel; Electro-assisted deposition; Nitrate; Aluminum

The sol-gel method has been widely applied in the preparation of various functional materials (e.g., catalysts [1], biomaterials [2], optical devices [3] and anti-corrosion materials [4]) due to its mild and controllable conditions. Recently, a new preparation technique, namely electro-assisted deposition, has been developed to facilitate the formation of sol-gel films on conductive substrates [5-9]. Mandler's group electrodeposited methyltrimethoxysilane (MTMS) onto indium-tin oxide (ITO) and gold electrodes, and were the first to propose the possible mechanism for sol-gel electro-assisted deposition [5]. They also extended this technique for the preparation of ZrO_2 and dye-doped TiO₂ films from sol-gel precursors [10,11]. It was considered that this novel technique could especially facilitate the sol-gel film formation on complex shape components and opened the possibility for the co-electrodeposition of sol-gel-derived functional composite materials [5,11]. In our previous works, several different silane films were successfully prepared on aluminum alloys by electro-assisted deposition for corrosion protection [12,13]. The influence of deposition potential on the physical structure and corrosion performance of the obtained films was also investigated. The critical cathodic potential (CCP) was observed for each of the above-mentioned silane systems. Films deposited at CCP exhibit the highest compactness and uniformity, and thus have the best barrier property. Now this technique has been intensively used in the preparation of sol-gel films for corrosion protection [9,14] and electrochemical sensor fabrication [15,16].

It was considered that the cathodic electro-assisted deposition technique facilitates sol-gel-derived film formation via producing OH^- ions that catalyze the condensation of sol near the cathode surface [5–8,12–14,16]. The main cathodic reaction occurring at the electrode surface is oxygen reduction when the deposition potential is not very negative [12,13]

$$1/2O_2 + H_2O + 2e \rightarrow 2OH^- \tag{1}$$

The interfacial pH is strongly limited by the concentration of dissolved oxygen in silane solutions. However, if the deposition potential shifts to become too negative, e.g., below CCP as stated in our previous works, intensive hydrogen evolution caused by the decomposition of water (reaction (2)) would occur, causing the obtained films to have a porous structure and poor protectiveness [8,12,13].

$$2H_2O + 2e \rightarrow 2OH^- + H_2 \uparrow$$
 (2)

Thus it can be seen that both oxygen and water are not ideal reactants for producing OH⁻ ions if the aim is to improve the compactness and the barrier property of sol-gel films deposited with electro-assistance in practical circumstances.

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As a consequence, if a higher interfacial pH of the cathodic region is needed, additional reduction processes to produce OH⁻ ions are necessary. In order to promote cathodic alkalization in inorganic aqueous solutions for the preparation of metal oxides (e.g., ZnO), nitrate ions have been added to the precursors. This is considered to be a promising way to increase the interfacial pH near the cathodes as it is a simple process and has a high efficiency of OH⁻ production [17,18]. For this reason, Nobial et al. [19] investigated the mechanism of nitrate reduction and showed that the interfacial pH near the cathode can be increased to 12.0 without hydrogen evolution due to water decomposition, which is far bigger than the maximum pH of 10.4 in the case of the reduction of only-dissolved oxygen under the condition of limiting diffusion. This suggests that the addition of nitrate ions could not only overcome the shortage of the limited concentration of dissolved oxygen in aqueous solutions, but could also avoid the harmful hydrogen evolution.

In this work, we added potassium nitrate (KNO₃) to silane sol–gel systems, to show its promotional role in the electro-assisted formation of silane films by effecting cathodic alkalization. To our knowledge, we are the first to investigate the influence of nitrate concentration on the growth kinetics and the barrier property of the obtained films. The results indicate that the right amount of KNO₃ could facilitate the electro-assisted deposition of silane films, making the films thicker and with better barrier performance. However, it was found that an extra-high concentration of nitrate would be detrimental to the process. Although some groups [5,8,15] have already tried using nitrate ions when electro-depositing silane films, they failed to fully understand the role of nitrate ions.

Pure aluminum rods (99.999%, 6.35 mm diameter, $S \approx 0.32 \text{ cm}^2$, Aldrich) were used as the metal substrates after pretreatment as described in our previous work [20].

Silane agent (Dodecyltrimethoxysilane (DTMS): CH₃(CH₂)₁₁Si(OCH₃)₃, 95% purity) was purchased from DaDi Chemical (Hangzhou, China) and used as received without further purification. The deposition solutions used here were prepared by mixing 75 vol.% ethanol and 5 vol.% silane monomer into 20 vol.% water. The pH of the solutions was adjusted to 4.5 using acetic acid. The obtained solutions were prehydrolyzed at 35 °C for 48 h. Different amounts of KNO₃ salt were then added, by controlling the concentration (0, 0.04, 0.16, 0.45 and 0.80 mol 1^{-1} , respectively), where the conductivity of these solutions was about 14, 200, 500, 1000 and 1450 µS cm⁻¹, respectively. The samples were prepared immediately after the KNO₃ salt was dissolved. The electro-assisted deposition of silane films was performed in a three-electrode compartment [20]. The dip-coated films were also prepared for comparison. The deposition was conducted for 200 s without any stirring, after which the samples were removed and blow-dried with nitrogen to remove any excess liquid, before a final curing at 100 °C for 30 min in an air atmosphere. The deposition current was also recorded during the electro-assisted deposition in silane solutions.

Electrochemical impedance spectroscopy (EIS) was employed to evaluate the barrier property of the silane-covered specimens. The testing electrolyte was a 3.5 wt.% NaCl aqueous solution prepared with DI water, and all the samples were immersed for 12 h before EIS measurements. A similar three-electrode compartment was used as stated above. The measurement was carried out at the open-circuit potential ($\sim -0.7 \text{ V/}$ SCE in the testing solution), and the frequency range was chosen from 200 kHz to 46 mHz, with an AC excitation amplitude of 10 mV. To show the positive role of NO₃⁻ ions on cathodic production of OH⁻ ions, the cathodic voltammetry was measured in silane-free solutions (75/20 (v/v) ethanol/water, pH 4.5) with the addition of KNO₃. For comparison, the ethanol/water solution with the addition of an inert supporting electrolyte, Na₂SO₄, was also prepared. All the electrochemical measurements were carried out at 25 °C on a VMP2 multi-channel potentiostat.

The surface morphology of silane films was observed on a SIRION field emission scanning electron microscopy (SEM) produced by FEI Co. Ltd. The depth profiles of the relevant atoms were measured on a Cameca IMS-6F secondary-ion mass spectroscopy (SIMS). A 12.49 kV O^{2+} ion beam with a beam current of ~600 nA was used to raster over a 250 × 250 μ m² area.

Figure 1 shows the cathodic voltammetric curves of pure aluminum electrodes in CH₃CH₂OH/H₂O/KNO₃ and $CH_3CH_2OH/H_2O/Na_2SO_4$ solutions (pH 4.5 and conductivity = 85 μ S cm⁻¹ for both) from -0.4 to -1.2 V/SCE. Two distinct regions are observed in both the two curves. In the Na₂SO₄ solution, the former region with cathodic potential up to -0.8 V/SCE is related to the oxygen reduction process, while the latter region corresponding to a sharp increase in current response should be associated with the water decomposition process, i.e., the hydrogen evolution reaction. However, in the KNO₃ solution, a higher current response is observed than in the Na₂SO₄ solution across the whole potential range, indicating the presence of some other cathodic reactions that may enhance the alkalization in the cathodic region. The offset potential for hydrogen evolution performs almost identically in the two solutions. Therefore, in order to avoid the hydrogen evolution that may deteriorate the films' barrier performance, the deposition potential for electro-assisted depositing of DTMS films was selected to be -0.8 V/SCE in this work, which was also the critical



Figure 1. Cathodic voltammetric curves of aluminum electrodes in $CH_3CH_2OH/H_2O/KNO_3$ (1) and $CH_3CH_2OH/H_2O/Na_2SO_4$ (2) solutions. Scanning rate = 0.05 V s⁻¹.

potential to obtain the films with the best anti-corrosion performance reported in our previous work [13].

EIS has been widely applied for evaluating the barrier property of thin films. In this work, the low-frequency impedance data (Z_{1f}) was considered as a parameter for quantitatively comparing the barrier performance of silane films [21]. Figure 2 displays the Z_{lf} values of electro-assistance deposited and dip-coated silane films as a function of nitrate concentration in sol-gel precursors. When the nitrate concentration is not very high $(\leq 0.45 \text{ mol } l^{-1})$, it is observed that the electro-assistance deposited films have higher $Z_{\rm lf}$ values than the dip-coated ones, indicating that the films formation was promoted by electro-assisted deposition. As the nitrate concentration in the deposition solution increases, the impedance values for the electro-assistance deposited films first increase and then decrease, reaching a maximum when the nitrate concentration is $0.16 \text{ mol } l^{-1}$, showing that the resistance of electro-assistance deposited DTMS films can be improved by adding proper amount of KNO₃ into the deposition solutions. However, for the silane films prepared in the 0.80 mol 1^{-1} nitrate-containing solution, the dip-coated film performs higher $Z_{\rm lf}$ value than the electro-assistance deposited one. This abnormal phenomenon suggests that nitrate ions have different roles in different nitrate concentration solutions. It is also found that, different from the electro-assistance deposited films, the resistance of dipcoated silane films does not obviously increase in line with the nitrate concentration in the preparation solutions. The benefit of the nitrate ions is seen mainly in the electro-assisted deposition case, indicating that nitrate ions participate in the electro-assisted deposition process.

Figure 3 displays the SEM images of DTMS films electro-assistance deposited from different nitrate concentration solutions. Without nitrate ions, the film electro-assistance deposited is uniform and smooth (Fig. 3a), as what we have observed in previous works [12,13]. When the nitrate concentration in silane solution increases to $0.16 \text{ mol } 1^{-1}$ by loading KNO₃, the silane film remains compact but tiny clusters can be seen on the surface (Fig. 3b) which are richer in Si than other areas of the film as detected by EDX. These clusters may be related to condensation products of silane agents, indicating that condensation reactions are facilitated on the aluminum surface. However, as detected by EDX, many crystals enriched with *K*, up to several microns in size, are observed in the film electro-assisted.



Figure 2. Z_{If} values of DTMS-covered Al electrodes in NaCl solution as a function of the nitrate concentration in silane precursors.



Figure 3. SEM images of electro-assistance deposited DTMS films prepared from silane solution with (a) 0, (b) 0.16 and (c) $0.80 \text{ mol } l^{-1} \text{ KNO}_3$.

tance deposited from the $0.80 \text{ mol } l^{-1}$ nitrate-containing solution. These crystals are presumably KNO₃ or its reduction products, which may easily suffer dissolution after being immersed in the corrosive solution. The incorporation of a pronounced amount of soluble components is, therefore, one of the reasons for the inferior barrier performance of silane films prepared from precursors containing a high concentration of nitrate ions.

The thickness of the silane films was roughly characterized by SIMS on DTMS films electro-assistance deposited in the silane solution without nitrate ions (denoted as "pure" film) and in the $0.16 \text{ mol } 1^{-1}$ nitratecontaining silane solution (denoted as " $0.16 \text{ mol } 1^{-1}$ nitrate" film), respectively (Fig. 4). It is observed that the time required for the complete removal of silicon element in "pure" film is 300 s, while the sputtering time required for " $0.16 \text{ mol } 1^{-1}$ nitrate" film (~650 s) is far longer. This indicates that electro-assistance deposited silane films can be thickened by the presence of nitrate in the preparation solutions.

It has been reported that nitrate ions could be reduced to nitrite, nitrogen or ammonia at the cathode [22,23]. However, the latter two products can only be



Figure 4. SIMS depth profiles of Si element obtained on aluminum covered with electro-assistance deposited DTMS film prepared from silane solution with 0 and $0.16 \text{ mol } l^{-1} \text{ KNO}_3$.

produced at very negative potentials (e.g. -2.9 V vs. Ag/AgCl) and can be ignored at the -0.8 V/SCE selected here. The promotion of nitrate ions in the current response is mainly attributed to the reduction of nitrate to nitrite [19]

$$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2OH^-$$
 (3)

The OH⁻ ions produced from the nitrate reduction process increase the local pH near the aluminum cathode. This additional cathodic reaction is inconsistent with the bigger current response in KNO₃ solution as compared with that in Na₂SO₄ solution, as shown in Figure 1, and also results in the increase in the electro-assisted deposition current of aluminum in silane precursors when adding KNO₃ (from 0.97 μ A in nitrate-free silane solution to 29 μ A in 0.16 mol l⁻¹ nitrate-containing silane solution). During the electro-assisted deposition of silane films, the cathodically generated OH⁻ ions could facilitate (catalyze) the film formation, thereby improving the film's barrier performance [12–14,16]. This is in good agreement with the experimental data shown in Figures 2 and 4.

However, the reduction of nitrate alone cannot explain the decrease in the electro-assistance deposited film's barrier performance when the nitrate concentration in silane solutions is higher than $0.16 \text{ mol } l^{-1}$, which was not observed in the silane-free solutions. The precise reason for this phenomenon is still not clear, but one possible explanation is associated with the "overcatalysis" of silane condensation in the solutions. It has been reported that the irreversible condensation of silane in the solution is strongly catalyzed by the high concentration of ions [24]. This condensation is not so widespread in dip-coated silane films, because the films are prepared immediately after the added KNO₃ is dissolved. However, with electro-assist depositing silane films, this condensation is catalyzed by both the unspecified ions and the cathodically produced OH⁻ ions. It is not so serious when the nitrate concentration is not very high ($\leq 0.16 \text{ mol } l^{-1}$), but in the case of high nitrate concentration ($\ge 0.16 \text{ mol } l^{-1}$) this harmful condensation of silane in the solution can be "overcatalyzed", leading to a decrease in active silanol concentration in the precursors and thereby deteriorating the silane film formation in the case of electro-assisted deposition. This might also be a reason for the abnormally low $Z_{\rm lf}$ value of the electro-assistance deposited film compared with that of the dip-coated film in extra-high nitrate concentration $(0.80 \text{ mol } 1^{-1})$ solutions. In addition, it is interesting that the deposition current starts to decrease when the nitrate concentration in silane solution increases beyond $0.16 \text{ mol } l^{-1}$, while the deposition current continues to increase as the nitrate concentration increases in the nitrate-containing silane-free solutions. This abnormal phenomenon may also result in the deterioration in film's barrier performance when the nitrate concentration in the silane solution is above $0.16 \text{ mol } l^{-1}$, although the reason for this is still being investigated.

In summary, the correct concentration of nitrate ions in DTMS sol-gel solutions could facilitate the electroassisted formation of silane films, while an extra-high concentration of nitrate ions would "overcatalyze" the harmful silane condensation in the solution during electro-assisted deposition, leading to a deterioration in the film's barrier performance. DTMS films prepared by electro-assisted deposition were observed to be clearly thickened by loading the correct amount of KNO₃ into the silane solution. Nitrate ions were considered to facilitate the electro-assisted deposition of DTMS films by producing OH^- ions near the cathode via reduction of the nitrate to nitrite ions. The detrimental effect of an excessive amount of nitrate ions on the formation kinetics and protectiveness of silane films indicates that one should be careful to choose the right concentration when using nitrate as the deposition promoter in electrochemically generated sol–gel system.

This work was supported by the National Natural Science Foundation of China (Nos. 50571090 and 50499336) and the Zhejiang Provincial Natural Science Foundation (No. Y404295).

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