International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

Preparation of Mg_xZn_{1-x}O Resistive Switching Film by Sol-gel Method and its Corrosion Behavior in 3.5 wt% NaCl solution

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Received: 2 October 2020 / Accepted: 4 December 2020 / Published: 31 December 2020

 $Mg_xZn_{1-x}O$ resistive switching films with different Mg content were prepared on SS 304 stainless steel by the sol-gel method. The morphology, structure and composition of the films were analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy and XPS techniques. The semiconductor type and corrosion resistance of Mg_xZn_{1-x}O films were studied by Mott-Schottky curve, polarization curve and electrochemical impedance spectroscopy (EIS) methods. The prepared $Mg_xZn_{1-x}O$ resistive switching films are composed of fine equiaxed grains, with the grain size and lattice constant of the films decreasing on increasing the Mg content. The $Mg_xZn_{1-x}O$ films are belonged to *n*-type materials and the oxygen vacancy concentration in the films is enhanced with the Mg content. The $Mg_xZn_{1-x}O$ resistive switching films in 3.5% NaCl solution exhibit a lower corrosion current density and a higher polarization resistance than that of SS304 stainless steel, and the corrosion resistance is decreased on enhancing the content of the Mg element. During the immersion process, the O₂ molecules dissolve in the solution could be absorbed on the film and react with the oxygen vacancies, thus, the concentration of oxygen vacancy in the film is reduced and the corrosion resistance of film is subsequently improved. After immersion test, the concentration of the oxygen vacancy in the film could be restored again by the application of the positive voltage on the corroded films.

Keywords: Resistive switching film; $Mg_xZn_{1-x}O$; Mg content; corrosion resistance; oxygen vacancy

1. INTRODUCTION

Steel is the most extensively used material due to its superior mechanical properties, relatively low cost and machinability, which is widely applied in various industrial fields such as petrochemical, construction and transportation. Nevertheless, the bare steel is generally prone to corrosion in the presence of chlorides and other aggressive species in the service environments, which leads to a lingering, detrimental impact on the integrity of steel as well as significant financial losses [1, 2]. Globally, it was estimated that the annual cost of corrosion damage and corrosion prevention strategies is more than 4 trillion US dollars [3]. At the same time, it has been estimated that about 15%-35% of the corrosion cost could be controlled by applying appropriate corrosion protection strategies [4]. In the past few decades, there have been many technologies to prevent the corrosion of steel, including surface coating technology, electrochemical protection, and addition of corrosion inhibitors [5-7].

Surface coating technology, providing a physical barrier between the substrate and corrosive medium, is a simple and effective method for enhancing the corrosion resistance of steel. A large range of coating have been used for protecting steels in various environments and can be divided into metallic coating, organic coating and ceramic coating [8-11]. Among these coatings, the ceramic coatings are commonly used in the industry owning to their strong resistance against corrosion, oxidation and wear in some extreme conditions [12]. However, the majority of these coatings could only provide mechanical isolation and protection for the substrates, and the corrosive medium can also penetrate to the steels/coating interface through cracks and pores on the coatings. So it is necessary to develop new kind of ceramic coating with lower cost, high stability and long service time.

Zinc oxide (ZnO), as a non-toxic and low-cheap ceramic material, has received significant research attention due to its optimal thermal and chemical durability. Meanwhile, ZnO film can also be applied in the corrosion protection of steel [13-15]. Furthermore, the doping ZnO film with the selective elements is also an effective strategy to improve the corrosion resistance. For example, Nidoped ZnO film coated on low carbon steel exhibits a better corrosion resistance than ZnO film [16]. ZnO nanorod arrays doped with cobalt by using the simple aqueous solution method exhibit enhanced photocathodic protection performance with the increasing of cobalt concentration [17]. In addition, ZnO based films also exhibit superior resistance switching behaviors. For example, Co-doped ZnO has a higher stability of memory device and a lower setting voltage due to the existence of oxygen vacancies [18]. Mn-doped ZnO memory devices have a better bipolar resistive switching behavior than that of undoped ZnO devices [19]. The widely accepted switching mechanisms for the doped ZnO depends on the redox reaction of the oxygen vacancies in the film and O₂ molecules in the environment to control the formation and rupture of conducting filaments dominated by oxygen vacancies in the film [20]. Based on the above mechanism, this resistance switching films can be potentially used as corrosion protection films by the formation of oxygen vacancies and diffusion of oxygen from corrosive environment.

In this study, the $Mg_xZn_{1-x}O$ resistive switching films with different Mg content were prepared on SS 304 stainless steel by using the sol-gel and spinning method. The surface morphology, composition and structure $Mg_xZn_{1-x}O$ films were investigated by scanning electron microscopy (SEM), atomic force microscope (AFM), energy-dispersive X-ray spectrum (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy (XPS) techniques, and the electrical resistivity of the films was measured by four-point probe apparatus. The semiconductor properties and corrosion behavior of films were characterized by Mott-Schottky curves, immersion test, potentiodynamic polarization curves and electrochemical impedance spectroscopy. And finally the resistance switching and protection mechanism of $Mg_xZn_{1-x}O$ resistive switching films were proposed and discussed.

2. EXPERIMENTAL

2.1 Materials

Zinc acetate dihydrate $[Zn(CH_3COO)_2 \cdot 2H_2O]$, magnesium acetate tetrahydrate $[Mg(CH_3COO)_2 \cdot 4H_2O]$ and monoethanolamine $[C_2H_7NO]$ were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. 2-methoxyethanol $[CH_3OCH_2CH_2OH, 99.5\%$ purity] and NaCl were got from Chemart Chemical Technology Co., Ltd. SS304 stainless steel (0.08 wt.%C, 18.00 wt.%Cr, 9.00 wt.%Ni, 2.00 wt.%Mn, 1.00 wt.%Si, 0.045 wt.%P, 0.03 wt.%S and Fe balance) was applied as the film substrate. Before the film preparation, SS304 stainless steel (15mm×15mm×3mm) were polished by using 400, 1000, 1500, 2000-drit sandpapers, and then polished by 1 µm diamond paste. After that the specimens above were cleaned ultrasonically in ethanol, rinsed with deionized water and dried with a cold air blaster.

2.2 Preparation

The preparation of $Mg_xZn_{1-x}O$ film with different Mg content is prepared as followed. Firstly 11.853 g, 10.536 g and 9.219 g Zn(CH₃COO)₂·2H₂O were dissolved into 100 ml 2-methoxyethanol respectively, and then 1.287g, 2.574g and 3.860g Mg(CH₃COO)₂·4H₂O were added in turn to the above solution as dopant to achieve different contents (10%, 20%, and 30%). The total concentration of metal ions in the solution was kept at 0.6 mol/L. And then the above solutions were stirred at room temperature by a magnetic stirrer to get homogeneous suspensions. 3.6mL monoethanolamine was added into the above three suspension solutions as stabilizing agent. The obtained solutions were gradually become transparent, and the transparent sol solutions were obtained by stirring for 12 h at room temperature. The sol solution was then dropped on the stainless steel surface, and the pre-coated film was obtained by spin coating method at 2000 rpm for 20 s. After dried at 150°C for 10 min, the above preparation processes were repeated with twelve times, and then the gel films were prepared. Finally, the gel films were sintered at 450°C for 1 h in a furnace under the atmosphere of nitrogen with a heating rate of 1°C/min, and then the Mg_xZn_{1-x}O films with different Mg content were obtained.

For comparison with the $Mg_xZn_{1-x}O$ film, ZnO film was also prepared. Firstly 13.170 g $Zn(CH_3COO)_2 \cdot 2H_2O$ was dissolved into 100 ml 2-methoxyethanol, and a homogeneous suspension solution was obtained by stirring at room temperature. And then 3.6mL monoethanolamine was added into the above solution, and the transparent sol solution was got by stirring for 12 h at room temperature. Finally, the ZnO film was synthesized after drying at 150°C for 10 min and sintering at 450°C for 1 h.

2.3 Characterization

The surface morphology of the $Mg_xZn_{1-x}O$ films was observed by scanning electron microscopy (Hitachi S-4800, Japan) and atomic force microscopy (Agilent AFM5500, USA). The elemental composition and valence of the $Mg_xZn_{1-x}O$ films were determined by energy dispersive spectroscopy (EDS, X-MAX20, England) at 15 kV accelerating voltage and X-ray photoelectron spectroscopy (XPS, ESCALAB-250Xi, Thermo Scientific, USA), and C 1s peak at 284.8 eV was set as the reference to correct the shifts.

The crystalline structure of the Mg_xZn_{1-x}O films was measured by using glancing angle X-ray diffractometer (GAXRD, D8 advanced, Bruker, Germany) with Cu- α radiation (λ = 1.54 Å) and incidence angle of 1° at a scan speed of 2°/min in the 2 θ range of 20-80°. FT-IR spectrum of the Mg_xZn_{1-x}O films was analyzed by using FTIR-850 spectrophotometer in the wavenumber region of 4000-400 cm⁻¹ with potassium bromide tablet.

The electrical resistivity of the $Mg_xZn_{1-x}O$ films before and after immersion test in 3.5wt % NaCl solution was measured by using four-point probe method (ST2253, China), in which WC probes with the diameter of 0.5 mm and a probe spacing of 1mm were applied. The electrical resistivity value of the $Mg_xZn_{1-x}O$ films was obtained by the average of three positions in the film.

2.4 Electrochemical test

The electrochemical performance including Mott-schottky curves, polarization curves, and electrochemical impedance spectroscopy of the $Mg_xZn_{1-x}O$ films was investigated by Autolab 302 N electrochemical workstation in 3.5 wt% NaCl solution at room temperature. A conventional three-electrode system was used in which Ag/AgCl electrode (saturated KCl) as reference electrode (RE), platinum plate as a counter electrode (CE) and the $Mg_xZn_{1-x}O$ films with the exposed area of 1 cm² as working electrode (WE).

The Mott-Schottky curves of the $Mg_xZn_{1-x}O$ film was measured in the potential range of -0.8V to 0.8V (vs. Ag/AgCl) at the fixed frequency of 1000 Hz. The semiconductor behavior of the $Mg_xZn_{1-x}O$ films was analyzed by the following M-S equation [21]:

$$\frac{1}{C^2} = \left(\frac{2}{q\varepsilon\varepsilon_0 N_{\rm D}}\right) \left(E - E_{\rm FB} - \frac{kT}{q}\right) \tag{1}$$

Where *C* is the space charge capacitance, *q* is the electron charge (1.602×10^{-19} C), ε is the dielectric constant of the films ($10.0 \text{ F} \cdot \text{cm}^{-1}$ [24]), ε_0 is the vacuum permittivity ($8.854 \times 10^{-14} \text{ F} \cdot \text{cm}^{-1}$), N_D is the carrier concentration for a donor, *E* is the applied electrode potential, E_{FB} is the flat-potential, *k* is the Boltzmann's constant (1.38×10^{-23} J/K), and *T* is the absolute temperature. The carrier concentration N_D in the film could be calculated as following equation [21]:

$$N_{\rm D} = \left(\frac{2}{q\varepsilon\varepsilon_0}\right) \left[\frac{\mathrm{d}\left(\frac{1}{C^2}\right)}{\mathrm{d}V}\right]^{-1} \tag{2}$$

The potentiodynamic polarization curves of the Mg_xZn_{1-x}O films was measured at a scan rate of 0.1mV/s in the potential range of -300 mV and 300 mV (vs.Ag/AgCl). The protection efficiency of the Mg_xZn_{1-x}O films in 3.5wt % NaCl solution was calculated by the following equation:

$$\eta_1 = \frac{I_0 - I_{\text{coor}}}{I_0} \tag{3}$$

Where η_1 is the protection efficiency of the Mg_xZn_{1-x}O resistive switching films; I_0 is the corrosion current density of SS 304 stainless steel in 3.5wt % NaCl solution; I_{corr} is the corrosion current density of the Mg_xZn_{1-x}O resistive switching films in 3.5wt % NaCl solution.

Electrochemical impedance spectroscopy (EIS) of the $Mg_xZn_{1-x}O$ films were carried out at OCP in the frequency ranging from 100 kHz to 10 mHz under AC signal with an amplitude of 10 mV. After measurements, the EIS spectrum of film was fitted by ZSimpWin software under the given equivalent circuit.

2.5 Resistive switching test

In order to explore the resistance switching behavior, the $Mg_xZn_{1-x}O$ films was immersed in 3.5wt % NaCl solution for 4 hours, and the EIS spectrum of film under the immersion time of 0.5 and 4 hours was measured. After that, the $Mg_xZn_{1-x}O$ film was transferred to deionized water and polarized by a positive bias voltage of +0.4 V for 10 minutes, and then the EIS spectrum of polarized films (labelled as I-0.5h and I-4h) was measured again in 3.5wt % NaCl solution under the immersion time of 0.5 and 4 hours. The above immersion and polarization process were repeated three times, and the EIS spectrum of polarized films (labelled as II-0.5h, II-4h, III-0.5h and III-4 h respectively) was also measured under the immersion time of 0.5 and 4 hours.

3. RESULTS

3.1. Surface morphology

Fig.1 shows the surface morphology of the $Mg_xZn_{1-x}O$ films with different Mg content. It can be observed that the $Mg_xZn_{1-x}O$ films exhibit a smooth and compact surface with homogeneous particles, and the size of particle is decreased on enhancing the Mg content from 10% to 30% (Fig.1b, Fig.1d and Fig.1f).

Fig.2 displays the composition and EDS mapping of the $Mg_xZn_{1-x}O$ resistive switching films. There are Mg, O, Zn, Fe, Cr, Ni, O elements existed in the film, in which Mg, O and Zn elements distributed uniformly on the surface are belonged to the $Mg_xZn_{1-x}O$ films and Fe, Cr, Ni, O elements are attributed from the substrate of stainless steel. With the increasing of Mg content, the atomic content of Mg element in the $Mg_xZn_{1-x}O$ films is enhanced gradually from 1.53%, 2.05% to 2.91% (Fig.2c, Fig.2f and Fig.2i), whereas the atomic content of Zn is reduced from 14.00%, 11.42% to 10.31%. All these results mean that the $Mg_xZn_{1-x}O$ films with different Mg content was successfully prepared on stainless steel.



Figure 1. Surface morphology of the $Mg_xZn_{1-x}O$ resistive switching films with different Mg content at lower and higher magnification.





Figure 2. EDS mapping of Mg, O, and Zn elements in the $Mg_xZn_{1-x}O$ films with different Mg content.

3.2 Grain size and roughness

The three-dimensional (3D) and two-dimensional (2D) AFM topographic morphology of the $Mg_xZn_{1-x}O$ films is shown in Fig.3, and the calculated grain size and mean surface roughness of the $Mg_xZn_{1-x}O$ films are shown in Table 1. It can be observed that the $Mg_xZn_{1-x}O$ films exhibit a uniform columnar structure and smooth morphology. With the increasing of Mg content, the grain size of the $Mg_xZn_{1-x}O$ films is reduced from 7.15 nm, 4.18nm to 2.96 nm, and the mean surface roughness is varied from 5.63 nm, 3.28nm to 2.37 nm. These results are in accordance with the surface morphology in Fig.1





Figure 3. 3D and 2D AFM images of the $Mg_xZn_{1-x}O$ resistive switching films with different Mg content.

Table 1. Grain size and mean roughness calculated from AFM image of the Mg_xZn_{1-x}O films

Sample	Grain Size (nm)	Roughness (nm)
Mg _{0.1} Zn _{0.9} O	7.15	5.63
Mg _{0.2} Zn _{0.8} O	4.18	3.28
Mg _{0.3} Zn _{0.7} O	2.96	2.37

3.3 Phase structure

Fig.4 is the XRD pattern of SS304 steel substrate, the ZnO film and the Mg_xZn_{1-x}O films. In the XRD spectrum of SS304 steel, the diffraction peaks at 43.49°, 50.67° and 74.54° are corresponded to (111), (200) and (220) planes of austenitic γ phase of steel substrate, and the diffraction peak at 44.35° is belonged to (110) plane of ferrite α phase of steel substrate [22]. For the ZnO film, the diffraction peaks at 43.49°, 50.67°, and 74.54° belong to γ phase of steel substrate, and the peak at 44.35° is

assigned to ferrite phase of steel substrate. Three characteristic peaks at 31.65° , 34.24° , and 36.08° are identified as (100), (002) and (101) crystallographic planes of ZnO hexagonal structure (JCPDS No.36-1451). After calculation, the lattice constants *a* and *c* of ZnO hexagonal structure are 0.3260 nm and 0.5233 nm respectively.

In the XRD pattern of Mg_{0.1}Zn_{0.9}O film, apart from the diffraction peaks of γ phase and ferrite phase from steel substrate, the diffraction peaks are located at 31.69°, 34.49°, and 36.18°, which belong to (100), (002), and (101) planes of ZnO structure, and the calculated lattice constants *a* and *c* are decreased to 0.3258 nm and 0.5206 nm. In the case of Mg_{0.2}Zn_{0.8}O, the diffraction peaks of (100), (002), and (101) crystallographic planes of ZnO hexagonal structure are appeared at 31.96°, 34.45° and 36.39°, and the calculated lattice constants *a* and *c* are 0.3249 nm and 0.5203 nm respectively. Finally, in the Mg_{0.3}Zn_{0.7}O film, the diffraction peaks of (100), (002), and (101) crystallographic planes of ZnO hexagonal structure are shifted to 32.05°, 35.23°, and 36.95°, and the calculated lattice constants *a* and *c* are reduced to 0.3235 nm and 0.5193 nm. From these experimental results, the lattice constants of ZnO hexagonal structure are observed to decrease on increasing Mg content in the Mg_xZn_{1-x}O film [23].



Figure 4. XRD pattern of SS 304 substrate, the ZnO film and the Mg_xZn_{1-x}O films with different Mg content

3.4 FT-IR analysis

FT-IR spectrum of the $Mg_xZn_{1-x}O$ films with different Mg content is shown in Fig.5. In the FT-IR spectrum of the $Mg_{0.1}Zn_{0.9}O$ film, the broad peak around 3430 cm⁻¹ is attributed to the stretching vibration of O-H group [24], and the absorption peak at 1602 cm⁻¹ is corresponded to N-H bending vibration of amide groups which belonged to monoethanolamine [25]. Meanwhile the absorption peak at 1239 cm⁻¹ is corresponded to the stretching vibration of Mg-O [26]. The salient peak at 453 cm⁻¹ is related the stretching vibration of Zn-O group, and the feeble peak at 528 cm⁻¹ is attributed to the vibration of Zn-Mg-O group [27]. In the spectrum of the $Mg_{0.2}Zn_{0.8}O$ and $Mg_{0.3}Zn_{0.7}O$ films, the absorption peaks at 3430 cm⁻¹, 1602 cm⁻¹, and 528 cm⁻¹ are all in agreement with the spectrum of the $Mg_{0.1}Zn_{0.9}O$ film, but the absorption peak of Zn-O stretching vibration is shifted to 455 cm⁻¹ and 456 cm⁻¹ respectively, which indicating the successful substitution of Zn²⁺ ion by Mg^{2+} ion in the ZnO crystal lattice [28].



Figure 5. FT-IR spectrum of the Mg_xZn_{1-x}O films with different Mg content

3.5 XPS spectrum

Fig.6 is the XPS survey spectrum and high-resolution elemental spectrum of the Mg_xZn_{1-x}O films. In the survey spectrum, there are Zn, Mg and O elements observed in the film (Fig.6a), which is consistent with the EDS spectrum in Fig.2. In O 1s spectrum, there are two peaks at binding energy values 530.1 eV, 531.6 eV (Fig.6b), in which the peak at 530.1 eV (O_L) is attributed to O²⁻ ions surrounded by Zn²⁺ ions in ZnO lattice [29], and the peak at 531.6 eV (O_V) belongs to the oxygen vacancies [30]. And then the content of the oxygen vacancy in the Mg_xZn_{1-x}O film was calculated and listed in Table 2. It can be observed that the content of the oxygen vacancy is increased from 37.39% (*x*=0.1), 39.65% (*x*=0.2) to 42.67% (*x*=0.3) with the increasing of Mg content, which means that the more increases Mg content, the more promotes the formation of the oxygen vacancy in the Mg_xZn_{1-x}O film.





Figure 6. XPS spectrum of the Mg_xZn_{1-x}O films with different Mg content, (a) survey spectrum; (b) O 1s region; (c) Zn 2p region; (d) Mg 1s region

In Zn 2p spectrum (Fig.6c), there are two symmetric peaks at 1021.4 eV and 1044.5 eV, which are corresponded to Zn 2 $p_{3/2}$ and Zn 2 $p_{1/2}$ of Zn-O bond in the film respectively [31]. In Mg 1s spectrum (Fig. 6d), there is only one peak at 1303.8 eV, which is attributed to the Mg-O bond, suggesting that the Mg element is entirely incorporated into the ZnO lattice [32].

Sampla	Binding Energy	Valance state of	Relative percentage	
Sample	(eV)	oxygen	(%)	
Ma. 7n. O	530.1	OL	62.61	
WIg0.1ZI10.90	531.6	O_V	37.39	
M_{α} 7_{μ} O	530.1	O_L	60.35	
WIG0.2ZII0.8O	531.6	Ov	39.65	
Ma7n0	530.1	OL	57.33	
WI <u>g</u> 0.3ZII0.7U	531.6	O_V	42.67	

Table 2. Binding energy and valance state of oxygen from O 1s spectrum

3.6 Electrical resistivity

The electrical resistivity of the Mg_xZn_{1-x}O films with various Mg content is shown in Fig.7. The electrical resistivity of the Mg_{0.1}Zn_{0.9}O film possesses is 3.03 k Ω /cm. With the increase of Mg content, the electrical resistivity of the Mg_xZn_{1-x}O film is reduced to 2.61 and 2.42 k Ω /cm respectively. This reduction of electrical resistivity could be caused by the increase of the oxygen vacancy and carrier density in the Mg_xZn_{1-x}O film [33].



Figure 7. Electrical resistivity of the $Mg_xZn_{1-x}O$ films with different Mg content

3.7 Motte-Schottky behavior

Fig.8 shows the Mott-Schottky curve of 304 stainless steel substrate, the ZnO film and the $Mg_xZn_{1-x}O$ films in 3.5wt % NaCl solution at 10 kHz. In the potential range of -0.4 V to 0.4 V, there is a positive slope for steel substrate, the ZnO film, and the $Mg_xZn_{1-x}O$ films, which suggests that the passive film of 304 stainless steel, the ZnO film, and the $Mg_xZn_{1-x}O$ films are noted to be in *n*-type semiconductor, and the carrier ions should be oxygen vacancy. These results are in accordance with XPS spectrum in Fig.6b and Table 2.



Figure 8. Motte-Schottky curve of 304 steel substrate, the ZnO film and the Mg_xZn_{1-x}O films in 3.5wt % NaCl solution at 10 kHz

Sample	Slope (cm ⁴ ·F ⁻² ·V ⁻¹)	$N_{\rm D}~({\rm cm}^{-3})$	$E_{\mathrm{FB}}\left(\mathrm{V} ight)$
SS 304	2.19×10^{9}	6.43×10 ²¹	-0.49
ZnO	2.31×10^{10}	6.11×10^{20}	-0.14
$Mg_{0.1}Zn_{0.9}O$	8.18×10^{9}	1.99×10^{21}	-0.25
$Mg_{0.2}Zn_{0.8}O$	7.69×10^{9}	2.12×10^{21}	-0.30
Mg _{0.3} Zn _{0.7} O	3.99×10^{9}	4.08×10^{21}	-0.53

Table 3. Flat band potential (E_{FB}) and carrier density (N_D) for the Mg_xZn_{1-x}O film with different Mg content

After calculation, the carrier density and flat-band potential of 304 stainless steel substrate, the ZnO film and the $Mg_xZn_{1-x}O$ film are listed in Table 3. The passive film of 304 stainless steel has a higher carrier density of 6.43×10^{21} cm⁻³, which is caused by the abundant oxygen vacancies in the passive film on the substrate [34]. Whereas the ZnO film has a lower carrier density of 6.11×10^{20} cm⁻³, and a higher flat-band potential of -0.14V. With the increasing of Mg content, the carrier density of the $Mg_xZn_{1-x}O$ films is increased from 1.99×10^{21} cm⁻³ to 2.12×10^{21} cm⁻³ and 4.08×10^{21} cm⁻³, which is caused by the formation of the oxygen vacancies and the metal interstitials in the $Mg_xZn_{1-x}O$ films [35]. Meanwhile the flat-band potential of the $Mg_xZn_{1-x}O$ films is decreased from -0.25 V to -0.30 V and -0.53 V. As the flat-band potential is related the work function of electron (electron transfer capability) in the film [36], the $Mg_{0.1}Zn_{0.9}O$ film with lower carrier density and higher flat-band potential should have a higher electrical resistivity and corrosion resistance. This conclusion will be proved in following section of 3.8 and 3.9.

3.8 Polarization curve

Fig.9 shows the polarization curve of SS 304 steel substrate and the Mg_xZn_{1-x}O films in 3.5wt % NaCl solution, the fitted corrosion potential (E_{coor}), corrosion current density (I_{corr}) and protection efficiency η_1 are exhibited in Table 4.



Figure 9. Polarization curve of SS 304 steel substrate and the Mg_xZn_{1-x}O films in 3.5wt % NaCl solution

Sample	$E_{\rm corr}~({ m mV})$	$I_{\rm corr}$ (A/cm ²)	η_1 (%)
SS304	-190	1.38×10 ⁻⁷	-
Mg _{0.1} Zn _{0.9} O	-43	9.58×10 ⁻⁹	93.06
Mg _{0.2} Zn _{0.8} O	-57	1.34×10 ⁻⁸	90.29
Mg _{0.3} Zn _{0.7} O	-71	1.74×10 ⁻⁸	87.39

Table 4. Corrosion potential, current density and protection efficiency of the Mg_xZn_{1-x}O film in 3.5wt % NaCl solution by polarization curve

The corrosion potential and corrosion current density of the SS 304 steel substrate are -190 mV and 1.38×10^{-7} A/cm², respectively. After the formation of the Mg_xZn_{1-x}O films on steel substrate, the corrosion potential is increased to -43 mV, -57 mV and -71 mV respectively. Meanwhile the corrosion current densities of the Mg_xZn_{1-x}O films are decreased to 9.58×10^{-9} A/cm², 1.34×10^{-8} A/cm² and 1.74×10^{-8} A/cm² respectively and thus the prepared the Mg_xZn_{1-x}O films have a protection efficiency of 93.06%, 90.29% and 87.39%. But the corrosion resistance of the Mg_xZn_{1-x}O films is reduced with the increasing of Mg content, which is agreed with the Motte-Schottky behavior in Fig.8 and Table 3.

3.9 EIS spectrum

Fig.10 shows the EIS spectrum of SS 304 substrate and the Mg_xZn_{1-x}O resistive switching films in 3.5wt % NaCl solution. In the EIS spectrum SS 304 substrate, there is only one capacitance arc with the impedance modulus of $5.52 \times 10^5 \ \Omega \cdot \text{cm}^2$ at 0.01Hz (Fig.10a). After the formation of the Mg_xZn_{1-x}O film on the steel substrate, there are two capacitance arcs observed, in which the capacitance arc at higher frequency is result from the resistance and the capacitance of the Mg_xZn_{1-x}O films and the capacitance arc at lower frequency is caused by the charge transfer resistance and double layer capacitance of the steel substrate [37]. Meanwhile, there are a slope of -1 and a phase angle of almost -90° in middle frequency range of Bode plots (Fig.10b, Fig.10c), which implies that the Mg_xZn_{1-x}O films are in an obvious capacitive behavior with a higher corrosion resistance [38, 39].



Figure 10. EIS spectrum of SS304 steel substrate and the Mg_xZn_{1-x}O films in 3.5wt % NaCl solution, (a) Nyquist plot; (b) and (c) Bode plots

The impedance modulus of the $Mg_xZn_{1-x}O$ film at 0.01Hz is 1.92×10^6 ($Mg_{0.1}Zn_{0.9}O$ film), 1.86×10^6 ($Mg_{0.2}Zn_{0.8}O$ film) and $1.85 \times 10^6 \Omega \cdot cm^2$ ($Mg_{0.3}Zn_{0.7}O$ film) respectively (Fig.10b), which is higher than that of SS 304 steel substrate. This result is also proved that the $Mg_xZn_{1-x}O$ films have a higher corrosion resistance and the corrosion resistance of the $Mg_xZn_{1-x}O$ film is slightly decreased on enhancing the Mg content, which is in consistence with the polarization curve results in the Fig.9 and Table 4.

Based on the above analysis, the equivalent circuits in Fig.11 were used to fit the EIS spectrum in Fig.10. In the equivalent circuit, R_s is the solution resistance, R_{ct} and Q_{dl} are the charge transfer resistance and double layer capacitance of steel substrate, R_f and Q_f represent the resistance and capacitance of the Mg_xZn_{1-x}O films.

After calculation, the fitted electrochemical parameters are listed in Table 5. It can be seen that SS 304 steel substrate has a lower corrosion resistance in 3.5wt % NaCl solution $(1.17 \times 10^5 \Omega \cdot \text{cm}^2)$. After the formation of the Mg_xZn_{1-x}O films on steel substrate, a higher corrosion resistance of $3.34 \times 10^7 \sim 4.30 \times 10^{14} \Omega \cdot \text{cm}^2$ is obtained, in which the Mg_{0.1}Zn_{0.9}O film has the highest charge transfer resistance $(4.30 \times 10^{14} \Omega \cdot \text{cm}^2)$ and the Mg_{0.3}Zn_{0.7}O film has the lowest charge transfer resistance $(3.34 \times 10^7 \Omega \cdot \text{cm}^2)$.



Figure 11. Equivalent electrical circuit used for EIS spectrum, (a) SS304 steel; (b) the Mg_xZn_{1-x}O films

Table 5. Fitting eletrochemical parameters for EIS spectrum of SS304 steel substrate and the Mg_xZn_1 . _xO films in 3.5wt % NaCl solution

Sample	$R_{\rm s}$ ($\Omega \cdot {\rm cm}^2$)	$Q_{\rm f}$ ($\mu {\rm F} \cdot {\rm cm}^2$)	$n_{ m f}$	$R_{ m f}$ ($\Omega \cdot m cm^2$)	$Q_{ m dl}$ ($\mu m F \cdot cm^2$)	$n_{ m dl}$	$R_{\rm ct}$ ($\Omega \cdot {\rm cm}^2$)
SS304	3.91	-	-	-	1.34×10^{-4}	0.90	1.17×10^{5}
$Mg_{0.1}Zn_{0.9}O$	7.14	3.35×10 ⁻⁵	0.93	72.73	2.37×10 ⁻⁵	0.98	4.30×10^{14}
$Mg_{0.2}Zn_{0.8}O$	9.82	3.22×10 ⁻⁵	0.90	66.07	2.14×10 ⁻⁵	0.90	1.07×10^{13}
Mg _{0.3} Zn _{0.7} O	8.54	2.88×10^{-5}	0.92	16.99	2.58×10 ⁻⁵	0.91	3.34×10^{7}

3.10 Immersion behavior

During the immersion process in 3.5wt % NaCl solution, EIS spectrum of the Mg_{0.1}Zn_{0.9}O film under different immersion time is shown in Fig.12. In the EIS spectrum of spectrum the Mg_{0.1}Zn_{0.9}O film, there are two capacitance arcs observed in Nyquist plot (Fig.12a), and a slope of -1 and a phase angle of almost -90° in the middle frequency range of Bode plots (Fig.12b, Fig.12c), which implies that the Mg_xZn_{1-x}O film is still in a higher corrosion resistance during the corrosion process.

By using the equivalent circuit in Fig. 10b, the fitted electrochemical parameters of the Mg_{0.1}Zn_{0.9}O film under different immersion time are listed in Table 6. It can be observed that the charge transfer resistance of the Mg_{0.1}Zn_{0.9}O film is firstly increased and then decreased with the immersion time in 3.5wt % NaCl solution, and the highest resistance R_{ct} (5.99×10⁵ $\Omega \cdot cm^2$) is located in the immersion time of 9 hours. These experimental results could be related the decrease of the oxygen vacancy in the Mg_{0.1}Zn_{0.9}O film in the initial immersion process and the penetration of oxygen ions from the Mg_{0.1}Zn_{0.9}O film to the steel substrate after the immersion time longer than 9 hours, which will be discussed in the following discussion section.



Figure 12. EIS spectrum of the Mg_{0.1}Zn_{0.9}O film in 3.5wt % NaCl solution under different immersion time, (a) Nyquist plot; (b)-(c) Bode plots

Table 6. Fitting eletrochemical parameters of the Mg_{0.1}Zn_{0.9}O film in 3.5wt % NaCl solution under different immersion time

Immersion	Rs	$Q_{ m f}$	14 .	$R_{ m f}$	$Q_{ m dl}$	10	$R_{\rm ct}$
time (h)	$(\Omega \cdot cm^2)$	$(F \cdot cm^2)$	$n_{\rm f}$	$(\Omega \cdot cm^2)$	$(F \cdot cm^2)$	$n_{\rm dl}$	$(\Omega \cdot cm^2)$
0.5	7.15	3.37×10 ⁻⁵	0.94	33.19	2.86×10 ⁻⁵	0.94	1.28×10^{14}
2	7.08	3.28×10 ⁻⁵	0.94	38.61	2.86×10 ⁻⁵	0.94	5.39×10^{14}
4	6.75	3.10×10 ⁻⁵	0.93	44.68	2.50×10 ⁻⁵	0.94	5.58×10^{15}
9	7.56	3.01×10 ⁻⁵	0.92	82.37	1.95×10^{-5}	0.94	5.99×10^{15}
12	7.25	2.97×10 ⁻⁵	0.92	97.05	1.77×10 ⁻⁶	0.94	1.21×10^{15}
24	7.79	2.70×10 ⁻⁵	0.91	64.08	8.80×10^{-6}	0.93	1.06×10^{15}
36	7.60	1.72×10^{-5}	0.92	40.27	4.92×10 ⁻⁵	0.90	2.12×10^{7}
48	6.84	1.57×10 ⁻⁵	0.94	57.27	3.82×10 ⁻⁶	0.93	5.75×10^{6}

After immersion test in 3.5wt % NaCl solution, the electrical resistivity of the Mg_{0.1}Zn_{0.9}O film under different immersion time is shown in Fig.13. During the initial immersion process, the electrical resistivity of the Mg_{0.1}Zn_{0.9}O film is increased from 3.03 kΩ/cm to 3.17 kΩ/cm. But with the immersion time increasing to 12 hours, the electrical resistivity is decreased to 2.45 kΩ/cm, which is less than that under the immersion time of 0.5 hour and 4.0 hours, which is in accordance with the charge transfer resistance R_{ct} in Table 6.



Figure 13. Electrical resistivity of the Mg_{0.1}Zn_{0.9}O film after immersion in 3.5wt % NaCl solution

3.11 Resistance switching behavior

During the immersion and polarization process, EIS spectrum of the $Mg_{0.1}Zn_{0.9}O$ film in 3.5wt % NaCl solution is shown in Fig.14. In the EIS spectrum of the $Mg_{0.1}Zn_{0.9}O$ film, there are still two capacitance arcs observed in Nyquist plot (Fig.13a), and a slope of -1 and a phase angle of almost -90° in the middle frequency range of Bode plots (Fig.13b, Fig.13c), which implies that the $Mg_{0.1}Zn_{0.9}O$ film has a higher corrosion resistance during the immersion and polarization process.

By using the equivalent circuit in Fig. 10b, the fitted electrochemical parameters of the $Mg_{0.1}Zn_{0.9}O$ film during the immersion and polarization process are listed in Table 7. It can be seen that the $Mg_{0.1}Zn_{0.9}O$ film possesses a lower charge transfer resistance of $9.96 \times 10^{14} \,\Omega \cdot \mathrm{cm}^2$ in the initial immersion of 0.5 hour. With the immersion time prolonged to 4.0 hours, the charge transfer resistance of film increases to $7.65 \times 10^{15} \,\Omega \cdot \mathrm{cm}^2$. After polarized at 0.4 V for 10 minutes, the charge transfer resistance of the above immersed film is reduced to $2.26 \times 10^{13} \,\Omega \cdot \mathrm{cm}^2$. With the further immersion for 4.0 hours, the charge transfer resistance of the polarized film increases again to $6.36 \times 10^{15} \,\Omega \cdot \mathrm{cm}^2$. With the proceeding of polarization and immersion process in the second and third time, the charge transfer resistance of $4.75 \times 10^{15} \,\Omega \cdot \mathrm{cm}^2$. All these results show that the $Mg_{0.1}Zn_{0.9}O$ film exhibits a better reversible resistance switching behavior and could be applied for the protection film with adjustable corrosion resistance.



Figure 14. EIS spectrum of the Mg_{0.1}Zn_{0.9}O film in 3.5wt % NaCl solution during the immersion and polarization process, (a) Nyquist plot; (b)-(c) Bode plots

Table 7. Fitting eletrochemical parameters of the Mg_{0.1}Zn_{0.9}O film in 3.5wt % NaCl solution during the immersion and polarization process

Sample	$R_{\rm s}$	$Q_{ m f}$	14 .	$R_{ m f}$	$Q_{ m dl}$	10 11	$R_{\rm ct}$
Sample	$(\Omega \cdot cm^2)$	$(F \cdot cm^2)$	$n_{\rm f}$	$(\Omega \cdot cm^2)$	$(F \cdot cm^2)$	$n_{\rm dl}$	$(\Omega \cdot cm^2)$
0.5 h	7.18	4.39×10 ⁻⁵	0.90	61.75	2.01×10 ⁻⁵	0.90	9.96×10 ¹⁴
4 h	7.30	4.01×10 ⁻⁵	0.90	58.66	1.73×10 ⁻⁵	0.89	7.65×10^{15}
I-0.5h	6.93	3.22×10 ⁻⁵	0.89	25.72	1.47×10^{-5}	0.87	2.26×10^{13}
I-4 h	7.06	3.61×10 ⁻⁵	0.89	63.16	1.38×10 ⁻⁵	0.88	6.36×10 ¹⁵
II-0.5h	8.18	3.19×10 ⁻⁵	0.88	47.32	8.28×10 ⁻⁶	0.87	2.34×10^{13}
II-4 h	6.74	3.63×10 ⁻⁵	0.89	86.28	1.34×10 ⁻⁵	0.88	4.75×10^{15}
III-0.5h	6.30	2.82×10 ⁻⁵	0.89	26.57	1.23×10 ⁻⁵	0.87	3.32×10^{13}
III-4 h	6.37	3.13×10 ⁻⁵	0.89	60.99	1.15×10 ⁻⁶	0.88	4.87×10^{15}

Fig.15 shows the Mott-Schottky curve of the $Mg_{0.1}Zn_{0.9}O$ film during the immersion and polarization process. It can be seen that during the immersion and polarization process the $Mg_{0.1}Zn_{0.9}O$ film has a positive slope, which indicating that the $Mg_{0.1}Zn_{0.9}O$ film is noted to be *n*-type semiconductor.

The calculated carrier density of the $Mg_{0.1}Zn_{0.9}O$ film during the immersion and polarization process is listed in Table 8. The carrier density of the $Mg_{0.1}Zn_{0.9}O$ film is 1.73×10^{21} cm⁻³ in the initial immersion time of 0.5 hour. With the immersion time increased to 4 hours, the carrier density of film

decreases to 1.31×10^{21} cm⁻³. After polarized at 0.4 V for 10 minutes, the carrier density increases to 2.31×10^{21} cm⁻³. With the further immersion to 4 hours, the carrier density of film decreases again to 1.97×10^{21} cm⁻³. These results prove that the carrier density of film could be adjusted by the immersion and polarization process.



Figure 15. Motte-Schottky plots of the Mg_{0.1}Zn_{0.9}O film in 3.5wt % NaCl solution at 10 kHz during the immersion and polarization process

Table 8. Carrier density (N_D) for the Mg_{0.1}Zn_{0.9}O film during the immersion and polarization process

Sample	Slope (cm ⁴ ·F ⁻² ·V ⁻¹)	$N_{\rm D}({\rm cm}^{-3})$
0.5 h	2.19×10^{9}	1.73×10^{21}
4 h	1.08×10^{10}	1.31×10^{21}
I-0.5h	8.18×10^{9}	2.31×10^{21}
I-4 h	7.17×10^{9}	1.97×10^{21}

4. DISCUSSION

From the above experimental results, it can be found that the $Mg_xZn_{1-x}O$ films not only own a higher corrosion resistance, but also exhibit a resistance switching behavior in 3.5wt % NaCl solution. In order to reveal the influence of Mg content on the corrosion resistance of the $Mg_xZn_{1-x}O$ film, the relationship between the crystal structure and the resistance switching mechanism is proposed and discussed.

4.1 Effect of Mg content

From Fig.4 it can be known that ZnO has a hexagonal structure with the lattice constants *a* and *c* of 0.3260 nm and 0.5233 nm respectively. With the introduction of the Mg element in the ZnO film, $Mg_xZn_{1-x}O$ film is still in the hexagonal structure with the substitution of Zn site in the lattice by Mg

ions due to the same charger state (+2) and the similar ion radius of Mg²⁺ (0.057nm) and Zn²⁺ (0.060nm). Meanwhile the lattice constants *a* and *c* of the Mg_xZn_{1-x}O film decrease with the increasing of Mg content because the radius of Mg²⁺ ions (0.057nm) is less than that of Zn²⁺ ions (0.060nm) (Fig.4).

But as the electronegativity difference between Mg^{2+} (1.35) and Zn^{2+} (1.65) ions and the additional hybridization between Mg-*s* and Zn-*s*, *p* orbitals [40], the Mg_xZn_{1-x}O film has a distorted structure and a higher nucleation growth rate and thus has a finer microstructure (Fig.1, Fig.3) [41]. Meanwhile with the increasing of Mg content the defect formation energy of film could be reduced [40], and thus the Mg_xZn_{1-x}O film has a larger oxygen vacancy concentration (carrier density) than that of the ZnO film (Fig.8, Table 2 and Table 3).

4.2 Resistive switching characteristic and protection mechanism

As the above structural characteristics, the properties of the $Mg_xZn_{1-x}O$ film such as electrical resistivity, corrosion resistance and resistance switching behavior are highly depended on the oxygen vacancy concentration. From Table 2 and Table 3 it can be concluded that the $Mg_xZn_{1-x}O$ film has a larger oxygen concentration (carrier density) with the increasing of Mg content (Fig.16a). Thus the $Mg_xZn_{1-x}O$ film has a lower electrical resistivity (Fig.7), lower charge transfer resistance (Table 5) and higher corrosion current density (Fig.9) with the increasing of Mg content based on the conductive filaments theory in resistance switching film [42-45].

During the immersion in 3.5%NaCl solution, the O₂ molecules dissolve in the solution could be absorbed on the film surface to form chemisorbed $O_{2(ad)}^{r}$, and the oxygen vacancies in the film act as the electron acceptors [46]. After the redox reaction between $O_{2(ad)}^{r}$ and oxygen vacancies, the concentration of the oxygen vacancies in the film is reduced, and the conductive filaments in the film are broken down (Fig.16b). Consequently, the corrosion resistance of the Mg_xZn_{1-x}O film is enhanced for the immersion durations up to 9 hours (Fig.9 and Table 6). But with further prolongation of the immersion duration, the absorbed O₂ molecules continually react with the oxygen vacancies and diffuse to the steel substrate (Fig.16c), and thus the corrosion resistance of the Mg_xZn_{1-x}O film is decreased after immersion for more than 12 hours (Fig.9 and Table 6).

In order to avoid the reduction of corrosion resistance with the prolongation of immersion duration, a positive voltage is applied on the Mg_xZn_{1-x}O film. The oxygen atoms in the film can escape under the electrical field owing to the reaction between $O_{2(ad)}^{-}$ and the oxygen vacancies, the concentration of the oxygen vacancy in the film raises again (Table 8, Fig.16d), and the Mg_xZn_{1-x}O film switches to a lower corrosion resistance state (Table 7). During the immersion and polarization process, the Mg_xZn_{1-x}O film can transform between the low and high corrosion resistance states due to the disappearance and regeneration of the oxygen vacancies in the film (Table 8, Fig.16b, Fig.16d and Fig.16e). Moreover, the Mg_xZn_{1-x}O film exhibits a superior reversible resistance switching behavior, thus, can be applied as the protection film owing to the adjustable corrosion resistance.



● Cl⁻ ∘ Oxygen Vacancy • Oxygen Ion • Oxygen Ion Migration → Oxygen Escape

Figure 16. Schematic diagram of resistance switching and protection mechanism of the Mg_xZn_{1-x}O film, (a) Initial state of the Mg_xZn_{1-x}O film in NaCl solution, (b) Immersion in NaCl solution for 4 hours, (c) Immersion in NaCl solution for 24 hours, (d) Oxygen ions escape from the film under a positive voltage and regeneration of oxygen vacancy, (e) Immersion in NaCl solution again for 4 hours

5. CONCLUSION

(1) The $Mg_xZn_{1-x}O$ resistive switching films were successfully synthesized by using sol-gel and spinning method on SS 304 stainless steel. The prepared $Mg_xZn_{1-x}O$ films have fine equiaxed grains and the grain size and lattice constant of films are decreased with the increasing of Mg content.

(2) The $Mg_xZn_{1-x}O$ films are belonged to *n*-type materials and the oxygen vacancy concentration of film is enhanced with the Mg content.

(3) The $Mg_xZn_{1-x}O$ resistive switching films possess a lower corrosion current density and a higher polarization resistance in 3.5% NaCl solution as compared to SS304 stainless steel, and the corrosion resistance of films decreases on increasing the Mg content.

(4) The $Mg_xZn_{1-x}O$ films demonstrate a superior reversible resistance switching behavior and can be applied as the protection films with adjustable corrosion resistance. After immersion test, the concentration of the oxygen vacancy in the film can be restored again by the application of the positive voltage on the corroded films.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (No. 51771133).

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