Corrosion Evolution of AZ31 Mg Alloy with a Nano Crystallized Film

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Abstract. A comprehensive investigation of nano crystallized GaN film synthesized on AZ31 magnesium alloy substrate using atomic layer deposition (ALD) is presented in this paper. The microstructure and mechanical analysis indicate the nano crystallized film is homogeneous, well adhesive to Mg alloy substrate. The corrosion experimental results demonstrate that the nanometer crystallized film turns Mg alloy corrosion process from longitudinal/non-uniform horizontal/uniform corrosion, which is deduced from the facts that a great but less fluctuations in surface potential mapping, a smaller $\Delta E_{\text{corr}}$ and a more uniform corroded morphology. A higher $E_{\text{corr}}$, a smaller $i_{\text{corr}}$ and a higher $Z$ also mean the film can yield a prominent amelioration in the Mg alloy corrosion resistance. The work proposes that a uniform coverage even in a nano magnitude and crystallized form could make corrosion more uniform and later.

Keywords. Mg alloy; nano crystallized film; corrosion resistance; ALD; GaN.

1. Introduction
Magnesium alloys as light structural metal material are charming for manufacturing industry, especially in transportation, electronics, aerospace field where a lighter engineering system are key to reduce energy consumption. However, Mg alloys is plagued with the poor corrosion resistance due to the active chemical properties compared to other engineering metal, such as steel and aluminum alloys [1-4]. Over the past decades, nanometer amorphous film is very common as passive layer in the areas as microelectronics, optics and solar cells devices [5-7], which would impart remarkable resistance to general corrosion. The protective characteristics of nanometer amorphous passive films have been reported by many researchers [8]. B. Díaz et al. deposited 50nm thickness oxide layers on stainless steel and low alloy substrates reducing the corrosion rates by 3 orders of magnitude [9] Mirhashemihaghighi, Światowska, Mauric, Seyeux, Klein, Salmi, Ritala and Marcus (2016) obtained 10nm alumina coatings on copper, which increased $Z$ module by 2 orders of magnitude [8]. Leppäniemi, Sippola, Broas, Aromaa, Lipsanen and Koskinen (2017) demonstrated that multi-layer nano films could decrease the high-speed steel’s $i_{\text{corr}}$ by approximately 2 orders of magnitude [10]. Zhang et al. has recently unmasked the working way and the breakdown of the nano amorphous passive film [11]. The nano amorphous film could be used as corrosion resistant layer should it still work when the nano film is in crystalline form? Generally, amorphous film is weakly bonded to Mg alloy substrate for
mismatching in thermal expansion coefficient or lattice [12]. Would crystalline film overcome it?

In this paper, the nano crystallized GaN film was deposited on AZ31 Mg alloy to establish the nano crystallized film influence on corrosion performance. In order to get high fabrication quality, the film is prepared by atomic layer deposition (ALD) [10], which is applicable for fabricating ultra-thin film. The microstructure and composition of film were firstly characterized, then the corrosion performance was evaluated by scanning Kelvin probe (SKP), neutral salt spray test (NSS) and electrochemical characterization. Finally, the corrosion evolution mechanism of AZ31 alloy nanocrystalline film was discussed.

2. Experimental

2.1. Film Preparation
AZ31 Mg alloy sheet (3.04 wt% Al, 0.84 wt% Zn, 0.3 wt% Mn, 0.014 wt% Si, 0.002 wt% Fe, 0.0049 wt% Ca, 0.0012 wt% Cu, Mg balance) was used as substrate and cut into 25×25×0.5 mm³. Prior to the deposition, the substrate was firstly grounded by silicon carbide abrasive papers from P120 to P2000, then polished by diamond abrasive papers with 0.05μm, and finally rinsed with isopropyl alcohol in an ultrasonic bath. The substrate was named as S0.

ALD GaN film was deposited by the gas source as Triethylhydrazine (Ga(C2H5)3) and Nitrogen (N2). Argon (Ar) act as carrier gas and purge gas at flow rate of 20 Sccm. The working pressure is 30Pa. A typical ALD cycle consisted of a certain cycle at 400°C (each cycle in the sequence as Ga(C2H5)3, 0.02s → Ar purge, 60s → N2, 0.02s → Ar purge, 60s). The growth rate is 0.2Å/cycl and thus the thickness of the GaN film can be accurately controlled by the number of deposition cycles. The substrate with the GaN film was then named as SF.

2.2. Film Characterization
Grazing incidence X-ray diffraction (GIXRD, 40kV and 40mA, Cu-Kα radiation) was used to examine the constitution of phase. X-ray reflectance (XRR) characterize the thickness of the film by measuring the simultaneously deposited GaN film but on a glass substrate.

The surface morphology of the sample was analyzed by optical microscopy (OM, BX51M), scanning electron microscopy (SEM, FEI Quanta 200F) and energy dispersive spectrometer (EDS, Oxford X-maxn, <130kV).

X-ray photoelectron spectroscopy (XPS, ESCALAB250XI) with an X-ray source as a monochromatic Al-Kα (1486.6eV) was used to analyze chemical bonding and C 1s (284.6eV) of adventitious carbon contamination was used to calibrate binding energies.

Nano-indentation tester (Fischerscope, HM2000) was used to evaluate the mechanical properties and using the secondary electron images to analyze the load scratch and film wrinkle.

2.3. Corrosion Behavior
(1) Neutral salt Spray test was performed following the standard method ASTM B-117. The test was conducted in salt atmosphere laboratory with 3.5 wt% NaCl spray at 35±2°C for 48h. The samples were dried with N2 and then observed under SEM/EDS.

(2) Scanning Kelvin probe (SKP) function of electrochemical scanning system (with Ø 250 μm tungsten probe) was used to map the surface potential of the samples.

(3) Electrochemical workstation (CHI650D) was used to perform the reverse potentiodynamic polarization (RPDP), potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) tests and all tests were conducted in 3.5 wt% NaCl solution with 1cm² exposed area of samples [13]. Zview software was then used to analysis EIS plots to get the equivalent electrical circuits.

Reliability for corrosion behavior testing was verified by more than three copies.
3. Results

3.1. Film Characterization

Figure 1 presents the surface morphology, phase constitution and film thickness of the samples. $S0$ (figure 1a) is inhomogeneous in the surface with a large amount of defects (scratches and pinholes) and $SF$ (figure 1b) is similar to $S0$. According to figure 1c, $\alpha$-Mg is the main phase in $S0$, while the main phases of $SF$ are $\alpha$-Mg and GaN (the characteristic diffraction angles of hexagonal GaN are similar to $\alpha$-Mg. Planes as (101), (103), (110), (112), (201), (202) have been enhanced after ALD process. By the equation $d \approx \frac{\lambda}{2} \sqrt{\theta_{c}^{2} - \theta_{m}^{2} - \theta_{m+1}^{2}}$ ($\lambda$, $\theta_c$, $\theta_m$, $\theta_{m+1}$ are the wavelength of X-ray, the critical angle of total reflection, and the constructive interference diffraction peaks of incident angle respectively) [14, 15]. The film thickness is figured out as 18.46 ± 0.01nm (figure 1d).

![Figure 1](image_url)

Figure 1. (a)-(b) Optical microscopies, (c) GIXRD patterns, and (d) XRR plots for samples.

The morphology and composition of surface are shown in details by SEM along with EDS (as shown in figure 2). The morphology has not changed much with the big inclusion protruding particles and scratches can be seen in both samples (figures 2a-2b). But the surface has been well covered by a dense GaN film (the insets in figure 2b), figures 2c-2d show the EDS mappings for $S0$ and $SF$ respectively (The four highest content elements have been shown). With regard to $S0$ (elements as Mg, Al, Zn, Mn are the top ones in element contents), elements as Ga, N are added for $SF$ with Ga/N atomic ratio -1.03 (Table 1). Furthermore, elements as Ga and N are distributed uniformly on the surface (figure 2d), which indicates GaN film covers the surface homogeneously.
XPS is performed to determine the chemical composition. **S0** XPS survey consists of the BEs of Mg 2p, O 1s and Al 2p (49.8eV, 532.0eV, 73.9eV, figure 3b). O 1s high-resolution XPS spectrum consists of two peaks located at 534.6eV and 532.1eV, ascribed to O-O (from absorbed O₂) and O-Me (from metal oxide) [16]. Al 2p spectrum can be deconvoluted into two peaks, the former one should be assigned to Al-O while the latter one should be assigned to the metallic Al [17, 18]. **SF** XPS survey consists of the BEs of Mg 2p, O 1s, Al 2p, Gd 3d, N 1s (49.8eV, 532.0eV, 73.9eV, 397.3eV, 18.1eV, figure 3a). O 1s spectrum still consists of two peaks, but the latter peak (for metal oxide) intensity decreased. Al 2p spectrum has only one peak belonging to the metallic Al. N 1s spectrum has a binding energy (BE) peak originate from the N-Ga bonding [19]. Ga 2p spectrum can be deconvoluted into two peaks located at 19.7eV and 17.8eV, related to Ga-N and elemental gallium respectively [18, 20].

The mechanical properties of the samples are shown in figure 4 by Nano-indentation method. There is no any zigzag fluctuation and disconnection in **SF** curve illustrates that GaN film is smooth and no-cracking during loading process (figure 4a). So the film is well adhesive to the AZ31 substrate. **SF** was also treated for T4 (400°C for 12h) and T5 (180°C for 12h) separately. Using SEM to determine the load for the appearance of film wrinkles and serve as an indirect measurement of adhesion (figure 4a) [21]. Shown in inserts of figure 4a, the morphologies of **SF, SF-T4, SF-T5** exhibit rarely wrinkles. It is due to the film and Mg alloy substrate have similar lattice parameters (shown in XRD analysis), and also have similar thermal expansion coefficient (AZ31 Mg alloy [22]: 25.1x10⁻⁶ K⁻¹; GaN [23]: 3.17–5.59x10⁻⁶ K⁻¹). Even though they have been treated at different temperatures, they all show good adhesion between the substrate and film.

**Table 1.** Element content analysis for samples.

| Samples/ at% | Mg  | Al  | Ga  | N   | O   |
|--------------|-----|-----|-----|-----|-----|
| S0           | 94.9| 3.63| 0   | 0   | 0   |
| SF           | 47.34| 1.81| 41.71| 8.12| 0.30|

![Figure 2](image1.png)

**Figure 2.** (a)-(b) Second electronic images and (c)-(d) EDS mappings for samples.

![Figure 3](image2.png)

**Figure 3.** XPS survey and high resolution XPS spectra of N 1s, Ga 3d, O 1s, Al 2p for samples.
Young’s modulus and stiffness were get from Load-displacement curves (According to equation (1) [24] $S = \frac{dP}{dh} = \beta h \sqrt{A}$ and equation (2) [24]: $\frac{1}{E_I} = \frac{1-v^2}{E} + \frac{1-v_I^2}{E_I}$, where $A$ is the contact area, $E$, $v$ are the reduced modulus, Young’s modulus and poisson’s ratio respectively. $E_I$, $v_I$ and $\beta$ are shape constants according to the indenter $j$ and Hardness (according to equation (3) [25]: $H = \frac{P_{\text{Max}}}{A}$, $P_{\text{Max}}$ and $A$ present maximum load and contact area respectively, equation (4) [25]: $A_e = 24.5h_c^2 + 1449.029h_c$, the corresponding depth $h_c$ is obtained from equation (5) [25]: $h_c = h - \frac{P}{S}$, $S$ is a constant related to the indentation geometry.) are shown in figure 4b. GaN film could improve all mechanical properties except the stiffness, just as Reference [26] reported.

![Figure 4](image_url)

**Figure 4.** Morphology of nano-indentation load scratches and load-displacement curves (a) and corresponding data (b) of Nano-indentation method for samples.

Based on film characterization (Section 3.1), it is known that nano crystallized GaN film cover the surface with excellent uniformity and surface elements distribution becomes more uniform. Hardness and Young’s modulus of AZ31 substrate with GaN film increase and there is also good adhesion between film and substrate.

3.2. Corrosion Behavior

3.2.1. Neutral Salt Spray Test (NSS). As shown in figures 5a-5b, the corrosion morphology of S0 is rough, revealing many pits and cracks spread the whole surface (marked by red circle). For SF, the corrosion morphology still has cracks but without the pits (figures 5c-5d). Figures 5b-5d show the EDS mappings for S0 and SF after salt spray test respectively. With regard to S0 (elements as Mg, O, Na, Cl, Al are the top five in element contents), elements as Ga take the place of Al to the new among top five for SF. Figure 6 presents the phase composition of samples after NSS by GIXRD. The corroded products of S0 mainly consists of Mg(OH)$_2$, MgAl$_2$O$_4$ (figure 6). Those of SF are Mg(OH)$_2$, MgAl$_2$O$_4$, Ga$_2$O$_3$ (figure 6b). It is can be seen that GaN film adds new corroded product as Ga$_2$O$_3$ and make the corroded morphology more uniform (for example, there is no pits).
3.2.2. Scanning Kelvin Probe (SKP). Figure 7 presents surface potential mapping by SKP. It can provide information on corrosion trends (the higher the potential, the harder the surface is to corrode) and can also predict whether uniform corrosion occurs [27]. Comparing SF (figure 7c) with S0 (figure 7a), the surface potential increases from -(3020–2290) mV to -(1580-1260)mV (means a decrease in corrosion tendency), and potential fluctuation drops from ±730 mV to ±320 V (indicates a more uniform corrosion mode). Furthermore, equipotential lines in S0 are parallel, this is due to the fact that shallow scratches on the surface are parallel and which caused by polishing in a certain direction (Section 2.1). For SF, equipotential lines are circle around certain points, which inducing by the inclusion bulge in the surface. It is known to all, surface roughness would influence potential fluctuation [28]. Although, GaN film can’t eliminate, it weaken the surface roughness effect (such as shallow scratches).

After exposing for 2 hours in the atmosphere (figures 7b, 7d), the surface potential values for S0 are -(1480-1330)mV, and -(1240-949)mV for SF. It could be noted that a rising in surface potential and a drop in potential fluctuation for both samples. A higher surface potential also means decrease in the corrosion tendency, and a less potential fluctuation means more uniform corrosion mode. Moreover, no parallel equipotential lines in S0 after the exposure, for corrosion products such as oxides or hydroxides cover the surface. It can be deduced that the chemical composition may weaken roughness influence on surface potential.
3.2.3. Reverse Potentiodynamic Polarization (RPDP). Reverse polarization curve can be used to predict the corrosion developing direction in a longitudinal direction (such as pitting corrosion) or in a horizontal direction (plane corrosion, a uniform corrosion). The smaller potential difference ($\Delta E_{rev,c}$) is, the more likely the plane corrosion takes place [12]. For $S0$, $\Delta E_{rev,c}$ is 0.122V (the former corrosion potential is -1.457V and reverse corrosion potential is -1.579V), in figure 8. For $SF$, $\Delta E_{rev,c}$ is 0.021V (the former one is -1.349V and the reverse one is -1.370V). $\Delta E_{rev,c}$ of $S0$ is larger than that of $SF$. So $SF$ would have a more uniform corrosion than $S0$.

![Figure 7](image1.png)

**Figure 7.** Potential mapping as (a), (c) received and (b), (d) exposed for 2 hours in the atmosphere for samples.

![Figure 8](image2.png)

**Figure 8.** Reverse polarization profiles for samples.
3.2.4. Potentiodynamic Polarization (PDP). Figure 9 presents the polarization curves and the corrosion parameters are summarized in Table 2. Compared SF with S0, $E_{corr}$ (corrosion potential) shifts positively (-1.62→-1.38V), implying that GaN film could delay the corrosion beginning. Furthermore, the decreasing of $i_{corr}$ (current density, 61.71 → 2.97μA/cm²), higher $R_p$ (polarization resistance, 15.79→28.64 kΩ/cm²) and a lower corrosion rate (1.41→0.07 mm/y, by using the Tafel extrapolation method [29, 30] as the equation: 
\[
\text{corrosion rate} = \frac{A \times I_{corr}}{n \times F \times \rho} \times 87600
\]
, in which $M$ is the molar mass of the metal (24.3 g/mol for Mg), $i_{corr}$ is the current density, $n$ is the number of electrons exchanged in the corrosion reaction, $F$ is the Faraday constant (26.801A·h) and $\rho$ is the density of Mg as 1.74 g/cm³), which imply a lower corrosion rate once the corrosion begins. It can be deduced that nano crystallized GaN film can block the Mg alloy surface and delay the penetration of Cl⁻ and H₂O molecule, which results in $E_{corr}$ increasing, $i_{corr}$ decreasing and corrosion rate dropping.

| Samples | $E_{corr}$(V/SCE) | $i_{corr}$(μA/cm²) | $\beta_a$(mV/dec) | $\beta_c$(mV/dec) | $R_p$(KΩ/cm²) | Corrosion rate(mm/y) |
|---------|-------------------|---------------------|-------------------|-------------------|----------------|----------------------|
| S0      | -1.62±0.05        | 61.71±0.07          | 328.60±0.3        | 117.00±0.1        | 15.79±0.01     | 1.41                 |
| SF      | -1.38±0.02        | 2.97±0.03           | 408.80±0.3        | 87.20±0.2         | 28.64±0.01     | 0.07                 |

![Figure 9. Potentiodynamic polarization profiles for samples.](image)

3.2.5. Electrochemical Impedance Spectroscopy (EIS). EIS profile of S0 is characterized by a capacitive + inductive loop, coherent to previous reports (figure 10a) [31, 32]. A similar loop for SF is also observed, indicating a similar corrosion mechanism. Compared SF with S0, the diameter of the curves increases slightly, which means a higher capacity value (C). Furthermore, a bigger intercept with X axis indicates a bigger resistance value ($R$). Both would lead to an increase in impedance during the corrosion process [33].

![Figure 10. (a) EIS profiles and (b) equivalent circuits for samples.](image)
Table 3. Equivalent circuit data by fitting EIS profiles for samples.

| Samples | $R_s$ (Ω·cm$^2$) | $R_{ct}$ (Ω·cm$^2$) | $CPE$ (Ω·cm$^2$) | $n$ | $R_L$ (Ω·cm$^2$) | $L$ (H·cm$^2$) |
|---------|-----------------|-------------------|-----------------|-----|-----------------|---------------|
| $S0$    | 1.80            | 118.20            | 7.55×10$^{-5}$  | 0.91| 41.40           | 98.60         |
| $SF$    | 21.29           | 119.20            | 7.56×10$^{-5}$  | 0.95| 121.07          | 97.65         |

Equivalent circuit fitting can make a clearer understanding of EIS profile. The circuit data obtained by fitting EIS profiles are listed in Table 3. $R_s$ and $R_{ct}$ are the resistance of the solution and charge transfer resistance respectively. $L$ and $R_L$ denote the corrosion behavior at low frequencies during the dissolution of the Mg alloy. $CPE$ represents the constant phase elements, defined by admittance $Y$ and power index number $n$ through the formula $Y_{CPE} = Y_0(j\omega)^n$ ($0 < n \leq 1$). When $n=1$, the circuit element reflects pure capacitance properties [28, 30]. The equivalent circuits for the samples are in the same mode as $R_s$ (CPE $R_{ct}$ ($R_L$)). Comparing $SF$ equivalent circuit parameters value with $S0$, the $R_{ct}$ value and CPE value ($n$ value is almost same) are similar, while $R_s$ became larger. It indicates an increase in resistance during the corrosion process. Furthermore, the larger $R_s$ but with similar $L$, which means the corroded production is harder to dissolution, which would result in pitting corrosion tendency decreases. All these indicated that the sample has an increase in impedance during the corrosion process with the GaN film.

4. Discussion

The corrosion mechanism is schematic represented in figure 11. Chloride ions tend to be adsorbed at certain distinct defects which are non-uniformly distributed would make the pitting corrosion happens during corrosion [34]. As shown in figure 11 a1 and figure 11 b1, when exposed to Cl$^-$ containing media, for $S0$, Cl$^-$ is concentrated in uneven areas such as scratches and second-phase particles protruding, while for $SF$, the distribution of Cl$^-$ is more uniform due to the covering of GaN film. Pitting corrosion would be more likely to occur around the defects (such as scratches and precipitates) for $S0$. However, the uniform GaN film covers the defects of substrate completely (such as scratches and pinholes), which leads to the corrosion medium distribute homogeneously, Figure 11 a2 and figure 11 b2. Additionally, the uniform film can work as a protective barrier to prevent erosion from medium solution. So, the GaN film can effectively blocks penetration of corrosion medium and makes corrode uniform. Under the action of corrosive medium, the surface film is gradually consumed, and some area of magnesium alloy matrix is exposed and eroded, figure 11 a3 and figure 11 b3. However, the distribution of corrosion products is more uniform comparing $SF$ with $S0$. From the perspective of electrochemistry, the galvanic couple corrosion appear to be less seriously [35].
5. Conclusions
Nano crystallized GaN film was deposited on AZ31 magnesium alloy successfully by ALD in this paper. The microstructure and composition of film were characterized, then the corrosion performance was evaluated by SKP, NSS and electrochemical characterization. Following conclusions could be gotten:

(1) A nano crystallized GaN film with a thickness of 18.46 ± 0.01nm can be obtained by ALD, and this film exhibits a well-adhesive and homogeneous coverage on AZ31 Mg alloy surface.

(2) The film induce a horizontal/uniform corroded mode to Mg alloy in the beginning, by a higher and less fluctuation surface potential (-3020~2290)mV → -1580~1260)mV, by SKP), ΔE_{rev corr} is smaller (0.122V→0.021V, by RPDP).

(3) The film can maintain corrosion resistance, as no corroded pits and cracks in surface by NSS, a higher E_{corr} value (-1.62V→-1.38V) and a smaller i_{corr} value (61.71μA/cm²→2.97μA/cm², by PDP) and homologous EIS profiles/ equivalent circuits but a higher impedance resistance comparing with the S0.

The nano crystallized GaN film is well-adhesive to Mg alloy. The film not only makes a uniform coverage to delay the beginning of corrosion, but also makes a more uniform corrosion mode and a slower corrosion rate. It suggests a new strategy for corrosion resistance coating designs.

Acknowledgments
National Key Research and Development Program (Nos. 2021YFB3501001 and 2021YFB3501004), National Natural Science Foundation of China (Nos. 51671101 and 52061028), Natural Science Foundation of Jiangxi Province (Nos. 20212BAB204049), Key Research and Development Program of Jiangxi Province (No. GJJ150010), Postgraduate Innovation Special Fund of Jiangxi Province (No. YC-2021-S124), Nanchang University Innovation and Scientific Research Training Project Fund (NO. S202110403044).

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