

Article

Enhanced Corrosion Resistance of SUS304 Stainless Steel via Atomic Layer Deposited $\text{Al}_2\text{O}_3/\text{ZrO}_2$ Nanolaminates

Jae-Hyun Kim ¹, Ameer Farithkhan ^{1,2}, Myung-Jin Jung ¹ and Se-Hun Kwon ^{1,2,3,*} 

¹ School of Materials Science and Engineering, Pusan National University, Busan 46241, Republic of Korea; wogusmaple@pusan.ac.kr (J.-H.K.); farithkhanameer@gmail.com (A.F.); wjdaudwls6@pusan.ac.kr (M.-J.J.)

² The Institute of Materials Technology, Pusan National University, Busan 46241, Republic of Korea

³ National Core Research Center for Hybrid Materials Solution, Pusan National University, Busan 46241, Republic of Korea

* Correspondence: sehun@pusan.ac.kr

Abstract

Atomic layer deposition (ALD) was employed to fabricate single-layer Al_2O_3 , single-layer ZrO_2 , and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate coatings on SUS304 to enhance corrosion protection in chloride-containing environments. All coatings were deposited at 250 °C using optimized self-limiting ALD processes, and the total film thickness was controlled at approximately 54 nm for a fair comparison. Structural characterization revealed that Al_2O_3 films remained amorphous, whereas ZrO_2 films exhibited a thickness-dependent transition from amorphous to crystalline phases. In the nanolaminate structures, thinner ZrO_2 sublayers (<9 nm) retained amorphous or locally nanocrystalline characteristics, while thicker ZrO_2 sublayers (15 nm) developed polycrystalline features with increased grain boundary density. Electrochemical corrosion tests conducted in 3.5 wt% NaCl solution demonstrated that the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate coatings exhibited significantly lower corrosion current densities and delayed pitting corrosion compared to single-layer coatings. Among all samples, the [Al_2O_3 (15 nm)/ ZrO_2 (3 nm)] × 3 nanolaminate showed the best corrosion resistance, with the lowest corrosion current density ($I_{\text{corr}} = 6.20 \text{ nA/cm}^2$) and the highest protective efficiency (98.34%). These results highlight the critical role of nanolaminate architecture and sublayer crystallinity in suppressing ionic diffusion and provide an effective strategy for designing ultrathin, high-performance corrosion barrier coatings for stainless steel.

Keywords: atomic layer deposition; $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolamination coating; corrosion resistance



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1. Introduction

Stainless steel, especially SUS304, is widely used in various industrial fields such as machinery, electronics, and construction parts manufacturing due to its excellent corrosion resistance derived from the formation of a chromium oxide-based passive film on the surface [1]. However, mechanical and thermal processing, such as rolling or polishing, can locally damage this passive film, creating micro-defects that serve as initiation sites for localized corrosion, particularly in chloride-rich environments such as seawater [2–4]. Although complete prevention of corrosion is impractical, developing effective surface coating strategies to slow down corrosion progression is essential for improving the durability and lifetime of metallic components. Oxide-based protective coatings such as Al_2O_3 , TiO_2 , SiO_2 , and ZrO_2 have been widely studied for their chemical stability and barrier properties [5–8]. Conventional physical vapor deposition (PVD) techniques, including

magnetron sputtering and pulsed laser deposition, have been employed to synthesize such coatings; however, these methods rely on a line-of-sight deposition mechanism, making it difficult to achieve conformal, defect-free passivation films. Moreover, PVD-deposited films often exhibit columnar grain structures, and these grain boundaries can act as fast diffusion pathways for corrosive ions, thereby compromising the protective function of the coating [9,10]. To overcome these limitations, atomic layer deposition (ALD) has emerged as a promising technique for forming highly conformal, pinhole-free thin films through self-limiting surface reactions by sequentially exposing the substrate surface to precursor and reactant gases. ALD offers precise thickness control at the nanometer scale, excellent step coverage on complex surface geometries, and scalability for large-area substrates, making it particularly suitable for synthesizing protective coatings in industrial sectors such as marine construction [11]. ALD corrosion-protective coatings can achieve enhanced corrosion resistance not only through single-layer barrier films but also by forming nanolaminate structures composed of alternately stacked different materials. In particular, ALD nanolaminate structures increase the tortuosity of ion diffusion pathways and suppress crack propagation throughout the coating, resulting in improved long-term corrosion resistance compared with single-layer films [12,13]. However, most previous studies have primarily focused on variations in the number of stacking layers in nanolaminate coatings at a fixed total thickness, changes in the total film thickness, or the general effects of introducing nanolaminate structures [10,12,13]. Therefore, a more in-depth understanding of the role of each individual layer is required for the rational design of ALD nanolaminate corrosion-protective coatings.

In this study, single-layer Al_2O_3 , ZrO_2 , and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate coatings were deposited on SUS304 stainless steel substrates using ALD to improve corrosion resistance in saline environments. Amorphous Al_2O_3 acts as a dense chemical barrier that effectively blocks the penetration of corrosive ions. Meanwhile, ZrO_2 is thermodynamically compatible with Al_2O_3 , forming no compounds between the two oxides according to the phase diagram, thereby ensuring excellent interfacial stability and structural integrity of the laminated structure [14]. By alternately stacking these layers, a nanoscale lamination structure was fabricated to enhance protection performance. In particular, by maintaining an identical total film thickness and a fixed number of laminate repetitions while selectively varying only the thickness of individual Al_2O_3 and ZrO_2 sublayers, this study aims to elucidate how thickness-dependent crystallization behavior within the internal sublayers influences ion diffusion pathways and, ultimately, corrosion resistance. This approach provides a differentiated and mechanistic understanding of structure–property relationships in nanolaminate corrosion barrier coatings.

2. Materials and Methods

2.1. Preparation of Single-Layer Al_2O_3 , Single-Layer ZrO_2 , and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ Nanolaminate Films

Prior to film deposition, SUS304 stainless steel (5 cm × 5 cm) and single-crystalline (100) Si wafer (6-inch) substrates were ultrasonically cleaned with acetone ($\text{C}_3\text{H}_6\text{O}$) and ethanol ($\text{C}_2\text{H}_5\text{OH}$). Single-layer Al_2O_3 , Single-layer ZrO_2 , and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate films were deposited using a thermal ALD (LUCIDA D100, NCD Co., Ltd., Daejeon, Republic of Korea) at 250 °C. An ALD growth temperature of 250 °C was selected within the overlapping ALD windows of trimethylaluminum (TMA, iChems Co., Ltd., Hwaseong-si, Gyeonggi-do, Republic of Korea) (50–300 °C) [15] and tetrakis(ethylmethylamido)zirconium (TEMAZr, iChems Co., Ltd., Hwaseong-si, Gyeonggi-do, Republic of Korea) (150–250 °C) [16] for the preparation of ALD- $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate films. At first, TMA was used for Al_2O_3 deposition, as the Al precursors and H_2O served as the reactant. For stable supply, TMA and H_2O were maintained at 10 °C. One ALD cycle of Al_2O_3 consisted of a 0.3 s

TMA pulse, a 15 s N₂ purge, a 0.3 s H₂O pulse, and another 15 s N₂ purge. And for ZrO₂ deposition, TEMA_{Zr} was employed as the Zr precursor and H₂O as the reactant. During the ALD-ZrO₂ process, TEMA_{Zr} was heated to 70 °C to maintain sufficient vapor pressure. The ALD sequence for ZrO₂ consisted of a 2 s TEMA_{Zr} pulse, a 30 s N₂ purge, a 1 s H₂O pulse and a 30 s N₂ purge.

To fabricate the films with a laminated structure, Al₂O₃ and ZrO₂ layers were alternately deposited in situ within the same ALD chamber. Three types of nanolaminate samples with different Al₂O₃/ZrO₂ thickness ratios were prepared. Each laminated sample consisted of three repeated Al₂O₃/ZrO₂ bilayers, and for comparison, single-layer Al₂O₃ and ZrO₂ coatings were also deposited. The laminated films were designed as [Al₂O₃ (3 nm)/ZrO₂ (15 nm)] × 3, [Al₂O₃ (9 nm)/ZrO₂ (9 nm)] × 3, and [Al₂O₃ (15 nm)/ZrO₂ (3 nm)] × 3 structures. To ensure a fair comparison, the total film thickness for all samples was controlled to approximately 54 nm, and the schematic of the intended film structure is shown in Figure 1.

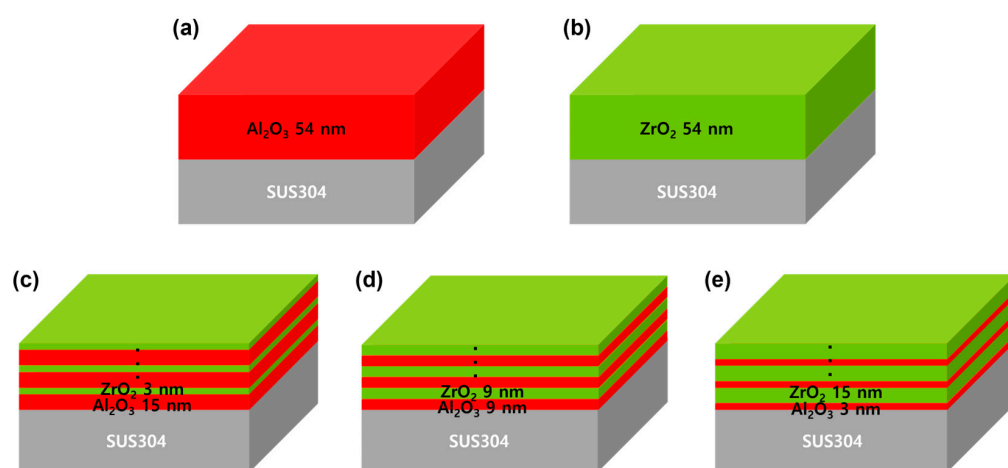


Figure 1. Schematic illustration of the cross-sectional structure of SUS304 coated with (a) single-layer Al₂O₃, (b) single-layer ZrO₂, (c) [Al₂O₃ (15 nm)/ZrO₂ (3 nm)] × 3, (d) [Al₂O₃ (9 nm)/ZrO₂ (9 nm)] × 3, and (e) [Al₂O₃ (3 nm)/ZrO₂ (15 nm)] × 3 nanolaminate films.

2.2. Characterization of Thin Films

An ellipsometer (α -SE, J. A. Woollam Co., Inc., Lincoln, NE, USA) operating at a wavelength of 632.5 nm was used to measure the thicknesses of the deposited thin films. The overall crystalline structure of the films was examined using X-ray diffraction (XRD, Ultima IV, Rigaku Co., Akishima-shi, Tokyo, Japan) with Cu-K α_1 radiation in the 2 θ range of 20 to 80° with a scan step of 0.02°. The detailed cross-sectional micrograph and energy-dispersive X-ray spectroscopy (EDS) of the films were obtained using high-resolution transmission electron microscopy (HRTEM, Talos F200X, Thermo Fisher Scientific, Waltham, MA, USA) after focused ion beam (FIB, Scios 2, Thermo Fisher Scientific, Waltham, MA, USA) sample preparation. For FIB sample preparation, a protective Pt layer was deposited on the ALD-coated SUS304 stainless substrate. Also, crystallographic information was extracted from the HRTEM images using fast Fourier transform (FFT) analysis. The top-view morphology of the films was observed using field-emission scanning electron microscopy (FE-SEM, JSM-7000F, JEOL Ltd., Akishima-shi, Tokyo, Japan).

2.3. Electrochemical Characterization of Thin Films

Electrochemical properties of samples were measured with VersaSTAT4 electrochemical analyzer (AMETEK Scientific Instruments, Berwyn, PA, USA). Electrochemical properties for corrosion, including potentiodynamic and potentiostatic polarization were eval-

uated with three electrode cell system, consisting of prepared samples with an area of 0.7 cm^2 as the working electrode, Ag/AgCl electrode with a standard potential of $E^0(\text{Ag}/\text{AgCl}) = 0.21 \text{ V}$ vs. standard hydrogen electrode (SHE) at 25°C as reference electrode, and a stainless steel rod was used as the counter electrode. The electrolyte conditions were conducted in a 3.5 wt% NaCl aqueous solution, and the solution temperature was maintained at 30°C during the experiment. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were extracted from the potentiodynamic polarization curves using the Tafel extrapolation method.

3. Results and Discussion

First, the self-limiting surface reactions in the ALD process were ensured by optimizing the pulse durations for each precursor and reactant at a growth temperature of 250°C (Figure 2). All experiments were performed using films deposited on 6-inch Si wafers, and the film thicknesses were measured using spectroscopic ellipsometry. Figure 2a shows the growth rate of Al_2O_3 films as a function of TMA precursor pulse time. The TMA pulse duration was increased from 0.3 s to 0.5 s, while the purge and reactant pulse times were set to 15 s (N_2 purge) and 0.5 s (H_2O injection), respectively, to ensure sufficient surface reactions. When the TMA pulse time exceeded 0.3 s, the growth rate of Al_2O_3 thin films was saturated at 0.11 nm/cycle, indicating that the self-limiting adsorption reaction of TMA was stabilized beyond 0.3 s. Similarly, the effect of the H_2O reactant pulse time was examined, as shown in Figure 2b. The purge time was fixed at 15 s, and the TMA pulse duration was set to 0.3 s, as determined from Figure 2a. When the H_2O pulse exceeded 0.3 s, the growth rate of Al_2O_3 thin films was also saturated at 0.11 nm/cycle, indicating that the ligand exchange reaction between the chemisorbed TMA and H_2O was completed beyond 0.3 s. Thus, the saturated growth rate of Al_2O_3 thin film was confirmed to be 0.11 nm/cycle at 250°C . Under these conditions, the refractive index of Al_2O_3 was measured to be 1.65. Next, the optimization of the ALD- ZrO_2 process was confirmed, as shown in Figure 2c,d. Figure 2c shows the variation in the growth rate of ZrO_2 films as a function of the TEMAZr precursor pulse time. The purge and reactant pulse times were set to 30 s (N_2 purge) and 2 s (H_2O injection), respectively, to allow sufficient surface reactions. When the TEMAZr pulse time exceeded 2 s, the growth rate of ZrO_2 films was saturated at $\sim 0.08 \text{ nm/cycle}$, confirming that the self-limiting adsorption of TEMAZr was achieved beyond this duration. Figure 2d shows the variation in the growth rate of ZrO_2 films as a function of H_2O reactant pulse time. The purge time was fixed at 30 s, and the TEMAZr pulse time was set to 2 s based on the optimized condition shown in Figure 2c. The saturated growth rate of $\sim 0.08 \text{ nm/cycle}$ was obtained when the H_2O pulse exceeded 1 s. Thus, the saturated growth rate of ZrO_2 film was confirmed to be 0.08 nm/cycle at 250°C , with a corresponding refractive index of 2.13. Thus, the self-limiting reactions in the ALD- Al_2O_3 and ALD- ZrO_2 were clearly confirmed. In addition, both ALD- Al_2O_3 and ALD- ZrO_2 films exhibited high thickness uniformity ($\sim 95\%$) on 6-inch Si wafers under these optimized ALD conditions. After then, single-layer Al_2O_3 , single-layer ZrO_2 , and three types of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate films with different thickness ratios ($[\text{Al}_2\text{O}_3 (3 \text{ nm})/\text{ZrO}_2 (15 \text{ nm})] \times 3$, $[\text{Al}_2\text{O}_3 (9 \text{ nm})/\text{ZrO}_2 (9 \text{ nm})] \times 3$, and $[\text{Al}_2\text{O}_3 (15 \text{ nm})/\text{ZrO}_2 (3 \text{ nm})] \times 3$) were prepared based on the optimized ALD processes for Al_2O_3 and ZrO_2 . To enable a fair comparison by eliminating the influence of film thickness on corrosion behavior, the total thickness of all films was maintained at approximately 54 nm. Considering the confirmed growth rates of ALD- Al_2O_3 and ALD- ZrO_2 , the thicknesses of the individual Al_2O_3 and ZrO_2 layers constituting the laminated films were controlled by independently adjusting the number of ALD- Al_2O_3 and ALD- ZrO_2 cycles, respectively.

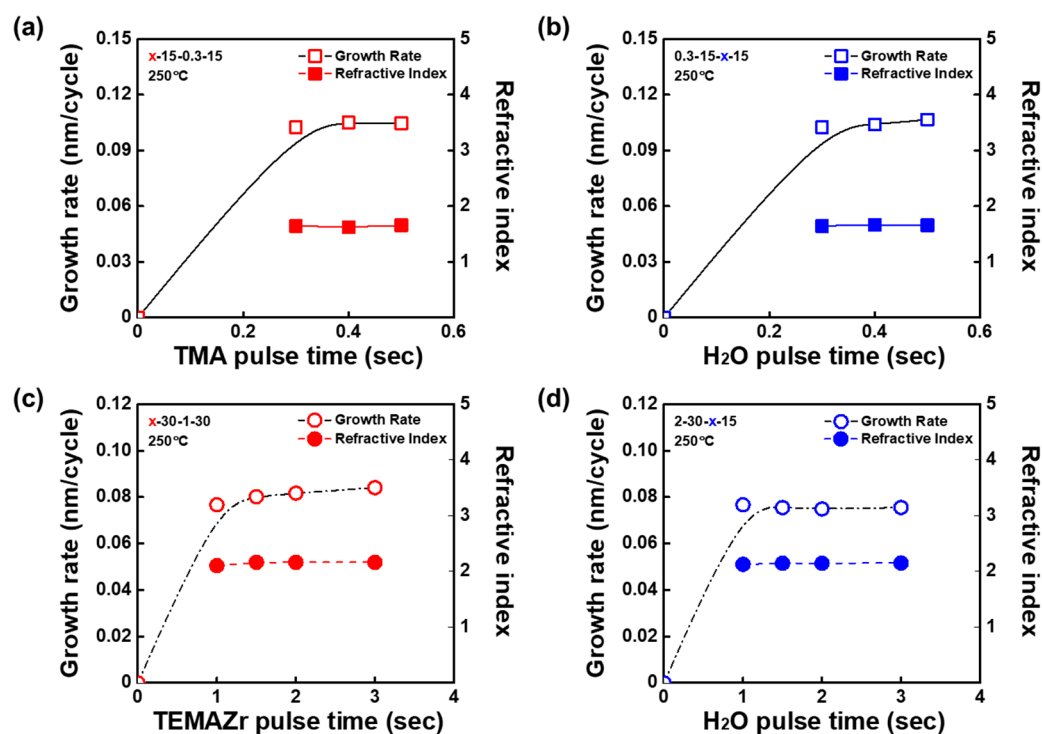


Figure 2. Growth rate and refractive index of ALD-Al₂O₃ on Si substrate as a function of (a) TMA pulse time and (b) H₂O pulse time. And, growth rate and refractive index of ALD-ZrO₂ films on Si substrate as a function of (c) TMAZr pulse time and (d) H₂O pulse time. The growth temperature for both ALD-Al₂O₃ and ZrO₂ was fixed at a temperature of 250 °C.

To investigate the crystallinity of the films deposited on SUS304, XRD analysis was performed in the 2θ range of 20° – 80° using a fixed incidence angle of $\theta = 1^\circ$. The obtained XRD patterns are shown in Figure 3. Diffraction peaks originating from the SUS304 substrate appeared at $2\theta = 43.58^\circ$, 50.79° , and 74.69° , corresponding to the (111), (200), and (220) planes of austenitic stainless steel, respectively, in good agreement with the reference Joint Committee on Powder Diffraction Standards (JCPDS) card (No. 33-0397). The single-layer Al₂O₃ film deposited on SUS304 exhibited a typical amorphous structure, with no distinct diffraction peaks attributable to Al₂O₃. In contrast, the single-layer ZrO₂ film-coated SUS304 exhibited clear diffraction peaks in addition to those from the substrate, observed at $2\theta = 30.27^\circ$, 34.81° , 35.26° , 50.37° , and 60.21° . These peaks correspond to the (011), (002), (110), (112), and (121) planes of tetragonal ZrO₂ (JCPDS card No. 50-1089), respectively. For the nanolaminate film-coated samples, distinct crystallization behaviors were observed for some samples depending on the individual ZrO₂ layer thicknesses (3, 9, and 15 nm) within the laminated structure. In the [Al₂O₃ (15 nm)/ZrO₂ (3 nm)] $\times$ 3 nanolaminate film-coated sample, the microstructure remained amorphous without any detectable diffraction peaks, indicating that both the 3 nm-thick ZrO₂ layers as well as the 15 nm-thick Al₂O₃ layers exhibited amorphous structures. Similarly, in the [Al₂O₃ (9 nm)/ZrO₂ (9 nm)] $\times$ 3 nanolaminate film-coated sample, no distinct diffraction peaks were observed, indicating that both the ZrO₂ and the Al₂O₃ layers remained amorphous. However, in the Al₂O₃ [(3 nm)/ZrO₂ (15 nm)] $\times$ 3 nanolaminate film-coated sample, the XRD pattern exhibited clear diffraction peaks similar to those of the single-layer ZrO₂ film. A prominent peak appeared at $2\theta = 30.27^\circ$, accompanied by several additional weaker peaks corresponding to the planes of tetragonal ZrO₂. These results suggest that when the individual ZrO₂ layer thickness reaches 15 nm, the film exceeds the critical thickness required for crystallization.

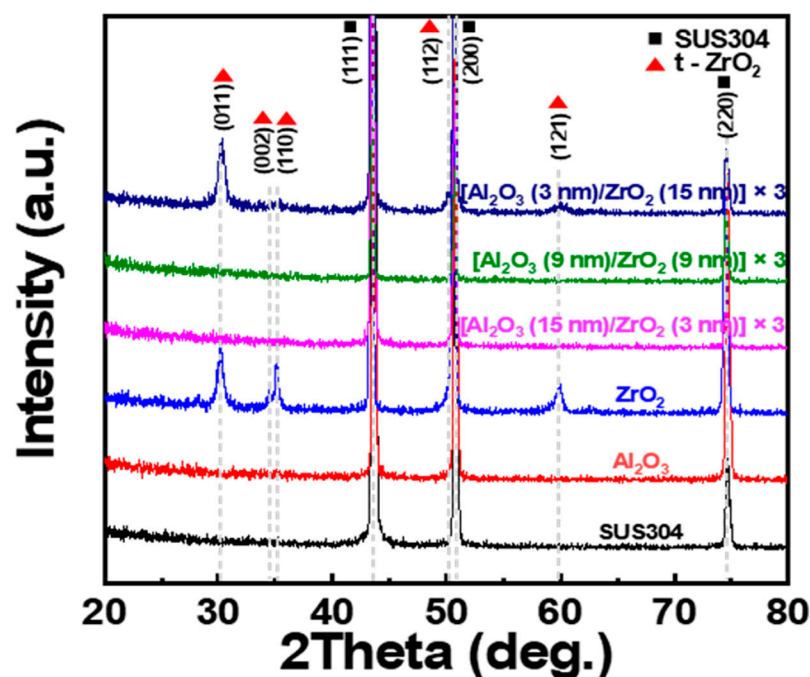


Figure 3. Grazing incidence XRD patterns of the bare SUS304, single-layer Al_2O_3 and ZrO_2 coated, and $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate film-coated SUS304 samples.

To clearly reveal the detailed microstructure, the cross-sectional microstructure and elemental distribution of the thin films were examined using HRTEM. Figure 4 shows the cross-sectional HRTEM images of the films along with their corresponding FFT patterns and EDS elemental mapping results. Figure 4a presents the cross-sectional image of the $[\text{Al}_2\text{O}_3 (15 \text{ nm})/\text{ZrO}_2 (3 \text{ nm})] \times 3$ nanolaminate film. The results show that an Al_2O_3 layer with a thickness of $\sim 15.3 \text{ nm}$ and a ZrO_2 layer with a thickness of $\sim 3.2 \text{ nm}$ were uniformly deposited, forming a well-defined laminated structure. In the corresponding FFT image (Figure 4a'), a diffused halo pattern indicates a typical amorphous structure. The corresponding EDS elemental mapping obtained from the same $[\text{Al}_2\text{O}_3 (15 \text{ nm})/\text{ZrO}_2 (3 \text{ nm})] \times 3$ nanolaminate film is shown in Figure 4a''. Clear spatial distributions of Al, Zr, O, Fe, and Cr were observed, confirming that the Al_2O_3 and ZrO_2 layers remained distinctly separated without the formation of interfacial compounds, which can be attributed to their high thermodynamic stability. These results indicate the successful formation of a stable nanolaminate structure. A similar uniform and well-defined nanolaminate structure was observed for the $[\text{Al}_2\text{O}_3 (9 \text{ nm})/\text{ZrO}_2 (9 \text{ nm})] \times 3$ nanolaminate film, as shown in Figure 4b–b''. From the enlarged view of the laminate film and the corresponding local structure analysis based on FFT patterns (Figure 4b'), the $[\text{Al}_2\text{O}_3 (9 \text{ nm})/\text{ZrO}_2 (9 \text{ nm})] \times 3$ nanolaminate film exhibited partially formed fringe patterns in certain local regions, suggesting the presence of limited nanocrystalline domains. The corresponding FFT image also shows a few spot patterns at the same lattice spacing, although these features were not detected in the XRD analysis (Figure 3). Notably, the EDS mapping shown in Figure 4b'' indicates the presence of surface defects on the stainless-steel substrate, such as Cr-rich precipitates. However, after deposition of the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate film, these surface defects were completely passivated. This demonstrates that ALD-deposited nanolaminate coatings can grow uniformly even on substrates with surface irregularities, thereby forming a highly conformal and protective passivation layer.

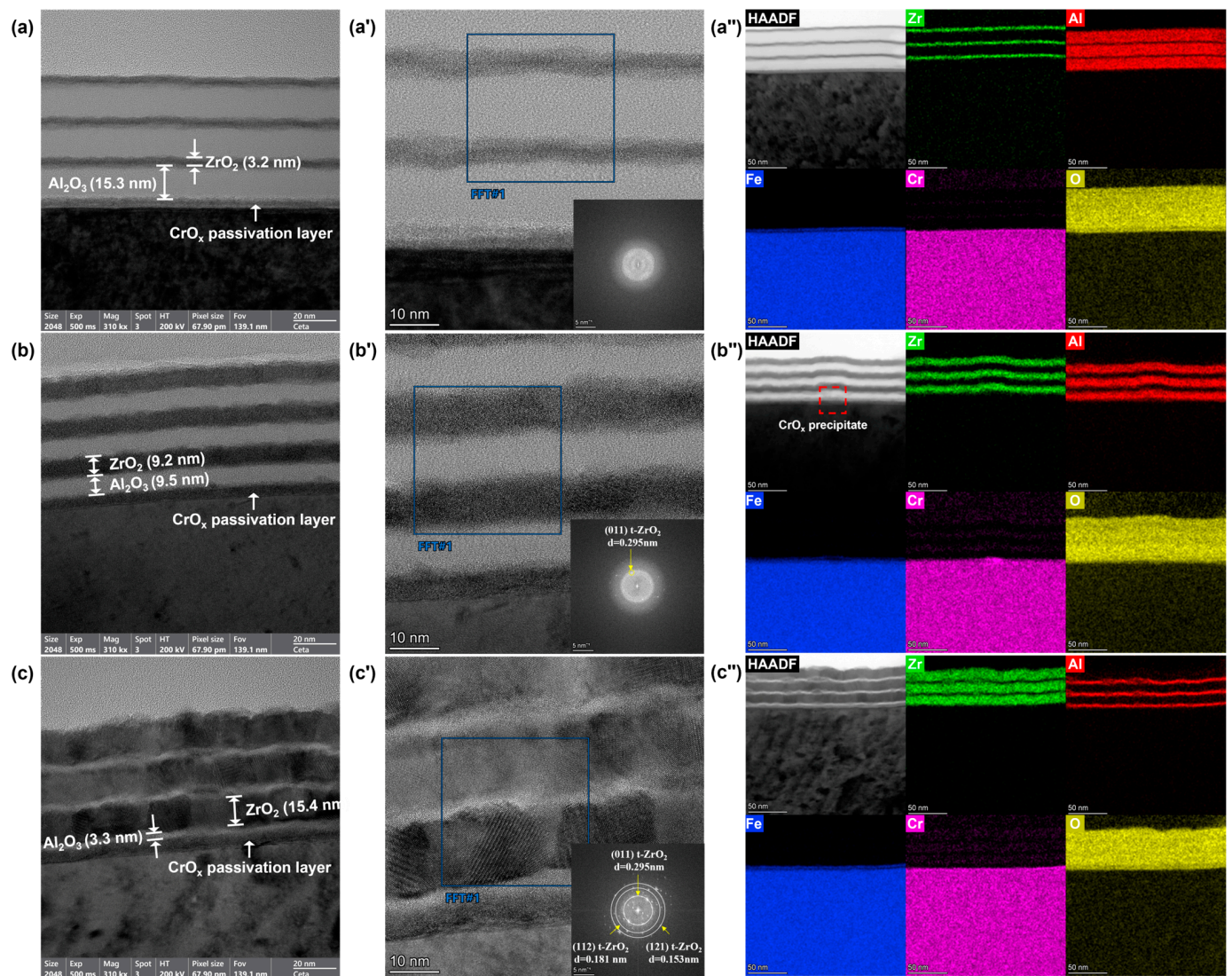


Figure 4. Cross-sectional HRTEM images, along with the corresponding FFT patterns and EDS elemental mappings of (a–a'') Al_2O_3 (15 nm)/ ZrO_2 (3 nm) $\times 3$, (b–b'') Al_2O_3 (9 nm)/ ZrO_2 (9 nm) $\times 3$, and (c–c'') Al_2O_3 (3 nm)/ ZrO_2 (15 nm) $\times 3$ nanolaminate films on SUS304 substrate.

Figure 4c–c'' presents the cross-sectional HRTEM image, along with the corresponding FFT patterns and EDS elemental mappings, of the $[\text{Al}_2\text{O}_3$ (3 nm)/ ZrO_2 (15 nm)] $\times 3$ nanolaminate film, in which alternating layers of approximately 3.3 nm Al_2O_3 and 15.4 nm ZrO_2 were clearly observed. The HRTEM and EDS mapping results also indicate that the Al_2O_3 / ZrO_2 nanolaminate films were successfully deposited according to the designed layer architecture. However, in contrast to the films of $[\text{Al}_2\text{O}_3$ (15 nm)/ ZrO_2 (3 nm)] $\times 3$ and $[\text{Al}_2\text{O}_3$ (9 nm)/ ZrO_2 (9 nm)] $\times 3$ nanolaminate films, the 15 nm-thick ZrO_2 layer clearly exhibited multiple fringe patterns indicating a polycrystalline ZrO_2 microstructure. In the corresponding FFT image (Figure 4c'), multiple diffraction spots associated with these spacings were distributed in continuous ring patterns, indicating the presence of numerous nanocrystallites with random orientations. These findings are consistent with the diffraction peaks observed in the XRD results of Figure 3, confirming that thicker ZrO_2 layers tend to crystallize and evolve into polycrystalline structures. From these observations, it is evident that as the ZrO_2 layer thickness increases ($> \sim 9$ nm), localized crystallization occurs within the film, leading to the development of polycrystalline structures. In contrast, the thinner ZrO_2 layer (~ 3 nm) maintains an amorphous structure, forming a dense and defect-free interface. A similar thickness-dependent crystallization behavior was observed in ALD-

ZrO₂ using TEMAZr and O₃, where a transition from an amorphous to a crystalline phase occurred at a critical thickness of approximately 6–8 nm [17]. These structural observations provide a basis for the subsequent electrochemical corrosion evaluation, in which the influence of crystallinity-dependent ionic diffusion pathways on the corrosion behavior of the nanolaminate films will be further examined.

To evaluate the corrosion behavior of the ALD films, potentiodynamic and potentiostatic polarization tests were conducted on the prepared samples. Figure 5a shows the potentiodynamic polarization test result of bare SUS304, single-layer Al₂O₃ and ZrO₂ coated, and three types of nanolaminate film-coated SUS304. The extracted electrochemical parameters E_{corr} , I_{corr} , and protective efficiency (PE) were calculated using the Tafel equation and summarized in Table 1. The protective efficiency was calculated using the following equation:

$$\text{Protective Efficiency (PE)} = \left(1 - \frac{I_{corr, coated}}{I_{corr, bare}}\right) \times 100 \quad (1)$$

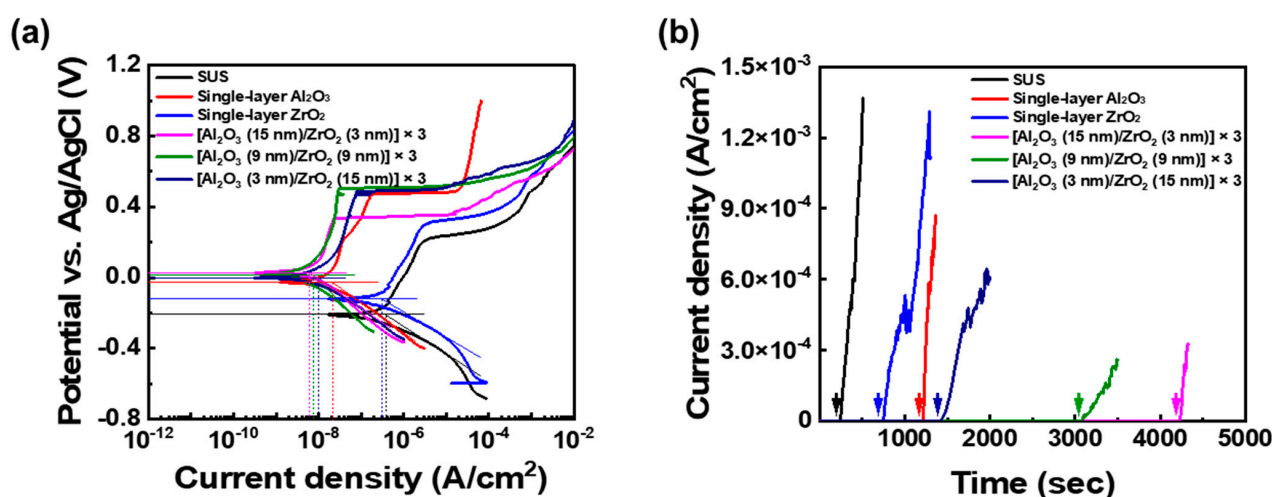


Figure 5. (a) Potentiodynamic polarization curves and (b) Potentiostatic polarization curves of the bare SUS304, single-layer Al₂O₃ and ZrO₂ film-coated SUS304, and three types of Al₂O₃/ZrO₂ nanolaminate film-coated SUS304 samples. The arrows in Figure 5b indicate the onset of pitting.

Table 1. Extracted electrochemical parameters, including corrosion potential (E_{corr}), corrosion current density (I_{corr}), and protective efficiency (PE).

Samples	SUS304	Single Layer Al ₂ O ₃	Single Layer ZrO ₂	[Al ₂ O ₃ (15 nm)/ZrO ₂ (3 nm)] × 3	[Al ₂ O ₃ (9 nm)/ZrO ₂ (9 nm)] × 3	[Al ₂ O ₃ (3 nm)/ZrO ₂ (15 nm)] × 3
E_{corr} (mV)	−208.98	−120.91	−26.64	26.98	15.69	−2.37
I_{corr} (nA/cm ²)	373.86	21.14	307.64	6.20	7.62	10.09
PE (%)	0	94.32	17.71	98.34	97.96	97.30

The results showed a general increase in E_{corr} and decrease in I_{corr} for all coated samples compared to the bare SUS304 substrate. The bare stainless steel exhibited an E_{corr} of −208.98 mV and an I_{corr} of 373.86 nA/cm², whereas the coated samples showed more positive E_{corr} values and significantly lower I_{corr} values. For instance, the single-layer Al₂O₃ and ZrO₂ film-coated samples showed E_{corr} values of −120.91 mV and −26.64 mV, and I_{corr} values of 21.14 nA/cm² and 307.64 nA/cm², respectively. The nanolaminate structures exhibited a greater reduction in I_{corr} than single-layer Al₂O₃ or ZrO₂ films. Among the three types of nanolaminate film-coated samples, the [Al₂O₃ (15 nm)/ZrO₂ (3 nm)] × 3

nanolaminate film exhibited the most positive E_{corr} values (26.98 mV) and the lowest I_{corr} (6.20 nA/cm²), indicating the best corrosion resistance properties. This enhanced performance is attributed to the amorphous structure of both Al₂O₃ and ZrO₂ layers, which effectively block the pathways of ion diffusion and delay corrosion initiation.

Next, potentiostatic polarization tests were conducted to investigate the long-term stability of the bare SUS304 substrate, single-layer Al₂O₃ and ZrO₂ film, and three types of Al₂O₃/ZrO₂ nanolaminate films. Figure 5b shows the results of potentiostatic polarization tests conducted at a constant applied potential of 0.4 V vs. Ag/AgCl. This method evaluates the initiation of pitting corrosion by monitoring changes in current density over time under constant potential conditions. For the bare SUS304 sample, a rapid increase in current density was observed after approximately 200 s, indicating that pitting corrosion occurred at a very early stage. Similar behavior was observed for the single-layer ZrO₂ and Al₂O₃ coatings, though the onset of pitting varied depending on the film type. In particular, the single-layer ZrO₂ film exhibited pitting after about 700 s, which is attributed to the grain boundaries present in its polycrystalline structure acting as diffusion pathways for external ions, allowing rapid penetration and corrosion initiation. In contrast, the single-layer Al₂O₃ film exhibited pitting only after approximately 1200 s, as its dense amorphous structure effectively blocked ion diffusion. Meanwhile, all nanolaminate coatings maintained relatively stable current densities over an extended polarization period. The onset times of pitting corrosion were delayed to approximately 1400 s for the [Al₂O₃ (3 nm)/ZrO₂ (15 nm)] × 3, 3100 s for the [Al₂O₃ (9 nm)/ZrO₂ (9 nm)] × 3, and 4200 s for the [Al₂O₃ (15 nm)/ZrO₂ (3 nm)] × 3 nanolaminate films, respectively. This progressive delay can be interpreted as a consequence of microstructural evolution induced by changes in the crystallinity of the ZrO₂ layer with increasing thickness, which affects ion diffusion pathways and, consequently, the overall protective performance of the coating. After potentiostatic tests, the changes in the surface of the samples were observed as shown in Figure 6. The uncoated SUS304 exhibited severe pitting corrosion, with pit diameters of up to ~50 µm (Figure 6a). In contrast, the pit size of the coated samples varied depending on the film structure and composition. As shown in Figure 6b,c, the single-layer film-coated samples effectively suppressed the progression of pitting corrosion, with pit diameters limited to around 10 µm. Furthermore, in the nanolaminate film-coated samples (Figure 6d–f), only fine pits smaller than 1 µm were observed, indicating that both the initiation and progression rates of pitting corrosion were significantly inhibited.

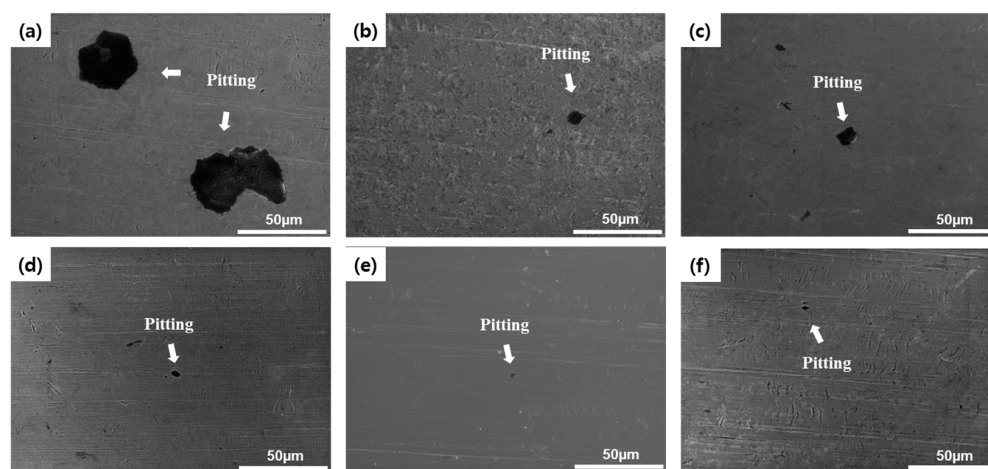


Figure 6. Top-view SEM images of (a) bare SUS304 substrate, (b) single-layer Al₂O₃-coated SUS304, (c) single-layer ZrO₂-coated SUS304, (d) [Al₂O₃ (3 nm)/ZrO₂ (15 nm)] × 3 nanolaminate film-coated SUS304, (e) [Al₂O₃ (9 nm)/ZrO₂ (9 nm)] × 3 nanolaminate film-coated SUS304, and (f) [Al₂O₃ (15 nm)/ZrO₂ (3 nm)] × 3 nanolaminate film-coated SUS304.

4. Conclusions

In this study, a corrosion-protection strategy was proposed by employing oxide nanolaminated films deposited via ALD on SUS304 substrates. Single-layer Al_2O_3 and ZrO_2 films, as well as three types of $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate films with varying sublayer thicknesses, were fabricated and systematically investigated in terms of their structural and electrochemical properties. These protective films were formed into well-defined lamination structures through the optimized ALD process. Compared with the single-layer films, the nanolaminate coatings demonstrated superior corrosion resistance, which is attributed to the synergistic effect of more complex ion diffusion pathways and the intrinsic chemical stability of both Al_2O_3 and ZrO_2 . In particular, the ZrO_2 layers exhibited a transition from amorphous to crystalline structure as the sublayer thickness increased from 3 nm to 15 nm, introducing more grain boundaries within the $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminated coatings. Notably, in the $[\text{Al}_2\text{O}_3 (15 \text{ nm})/\text{ZrO}_2 (3 \text{ nm})] \times 3$ sample, the grain-boundary-free growth of both layers effectively delayed the penetration of aggressive chloride ions, thereby further enhancing the corrosion resistance of the SUS304 substrate.

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Abbreviations

The following abbreviations are used in this manuscript:

ALD	Atomic layer deposition
PVD	Physical vapor deposition
TMA	Trimethylaluminum
TEMAZr	Tetrakis(ethylmethyamido)zirconium
EDS	Energy-dispersive X-ray spectroscopy
HRTEM	High-resolution transmission electron microscopy
FIB	Focused ion beam
FFT	Fast Fourier transform
XRD	X-ray diffraction
FE-SEM	Field-emission scanning electron microscopy
EIS	Electrochemical impedance spectroscopy
JCPDS	Joint Committee on Powder Diffraction Standards
PE	Protective efficiency
SHE	Standard hydrogen electrode

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