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Properties of Physically Deposited Thin Aluminium Film Coatings: A Review

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Abstract

Aluminium thin films exhibit excellent coating properties suitable for optical, microelectronics, telecommunications and constructional/structural applications. Thin aluminium film deposition is mainly accomplished via physical or chemical methods at varying deposition conditions, parameters and substrates. This study focuses on thin aluminium films prepared using physical methods which have superior properties to chemical methods and are extensively researched in the published literature. The review discusses the properties of thin aluminium films and their complex interactions with process parameters. The properties of thin films depend on the deposition parameters which include substrate temperature, deposition rate, power, process pressure, substrate surface finish, and target temperature. Post-deposition treatment of the films and the type of substrate also influence the properties of thin films. This review therefore highlights the significance of optimising the deposition methods and identifies research gaps in the published studies. The work can be a primary resource for selection of essential process parameters during physical deposition aluminium films.

Keywords: aluminium, thin films, corrosion, electrical, optical, physical deposition, properties

1.0 Introduction

Pure aluminium (Al) films find application in the optical, microelectronics, telecommunications and construction/structural industries due to their excellent properties such as high conductance, low resistivity, high reflectance, better adhesion, resistance to oxidation and corrosion [1]. The naturally formed thin layer of oxide on pure aluminium film further imparts optical, thermal, electrical and chemical enhancing properties to the coating. Aluminium thin films continue to receive high industrial and research interest because, successful depositions have been achieved using a broad spectrum of substrates including mild steels, stainless steel, titanium, silver, silicon (100), Polyethylene Terephthalate (PET), polycarbonates, and glass [1, 2]. Thin aluminium film, the deposition parameters of which make tuning them for specific applications possible, is achieved through physical and chemical methods. The existing literature shows a significant preference for physical methods which mainly include thermal and vapour deposition. Physical deposition methods produce higher adhesion, lower substrate temperatures, and are environmentally cleaner [3]. The main drawback of chemical techniques is the use of toxic solvents such as hydrazine which is

environmentally unfriendly [4]. Furthermore, deposition of thinner and metastable films and control of stress states are possible using physical deposition methods [3]. Because of these advantages, there exists considerable volumes of research on physical deposition of thin aluminium films.

This paper reviews the properties of physically deposited thin aluminium films in relation to deposition parameters and conditions as reported in the literature. It provides a comprehensive resource for preliminary selection of parametric conditions for optimising the process of thin aluminium film preparation, and aims to highlight the significance of the different process parameters during the physical deposition of the films to gain new research insights for improved properties and industrial applications., This review counts among a few of its kind which specifically focus on the properties of thin aluminium film prepared by physical methods, and is therefore novel. The work references a wide spectrum of published journals on thin aluminium films prepared through physical deposition methods. The existing literature indicates that the preparation, properties and applications of aluminium coatings can be summarised according to Figure 1.

This review firstly examines the structural properties of thin films with an emphasis on microstructure, hillocks, texture and mechanical properties in section 2.1. In section 2.2, the corrosion properties essential for application requirements and conditions of thin aluminium films are reported. Electrical and optical properties are discussed in section 2.3 and 2.4 respectively. The identified literature gaps are summarised in section 3.0.

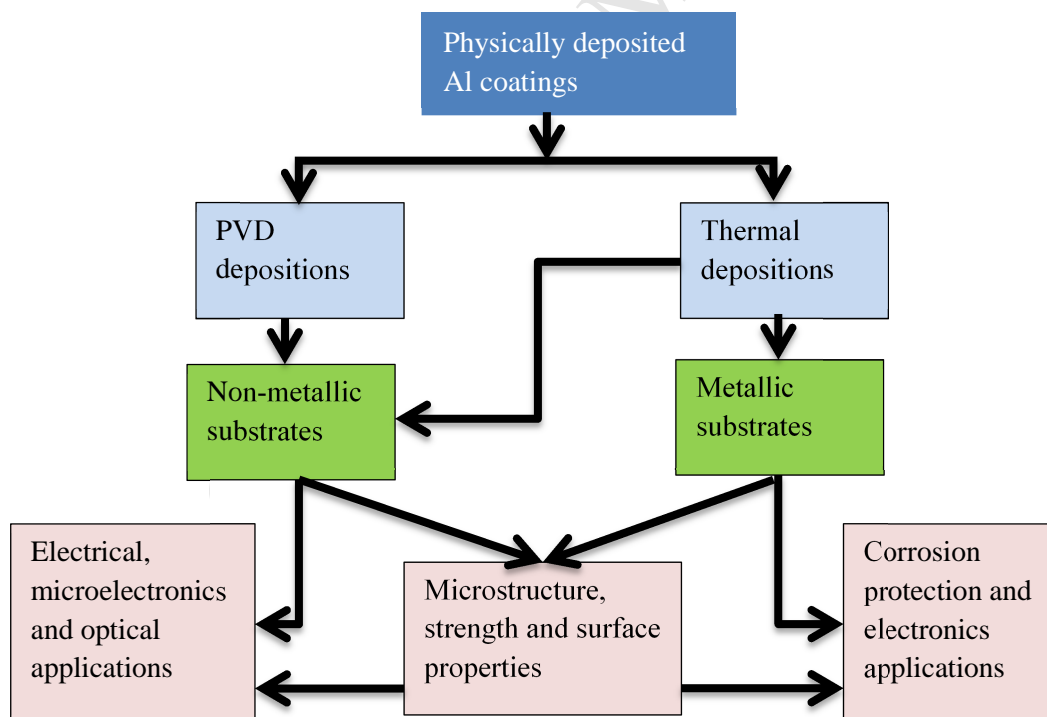


Figure 1. Summary of the information from the existing literature on physically deposited aluminium coatings

2.0 Properties of Aluminium thin film coatings

2.1 Structural and morphological properties

To understand and evaluate the suitability of thin aluminium films for different applications, their structural features need to be investigated, and there is a wealth of information available on the structural properties of thin aluminium films [1, 5, 6, 7, 8, 9]. The properties are characterised in relation to the mechanical and tribological features of the films. Figure 2 presents a summary of how the existing literature reports on the structural properties of physically deposited thin aluminium films.. The results also show that the tribological properties depend on the mechanical properties of the films. Experimental evidence is also available on the effects of the mechanical and tribological loading on the microstructure of these films. The review is therefore based on the structural properties of thin aluminium films as shown in Figure 2.

2.1.1. Microstructure and deposition conditions

A microstructural examination involves using optical, scanning and transmission electron microscopy (SEM and TEM), x-ray diffractions (XRD), and Raman spectroscopy among other techniques to study the various microstructural features of the thin films [10, 11]. Topographical studies of thin films involve an examination of the surface of the film with techniques such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) [12].

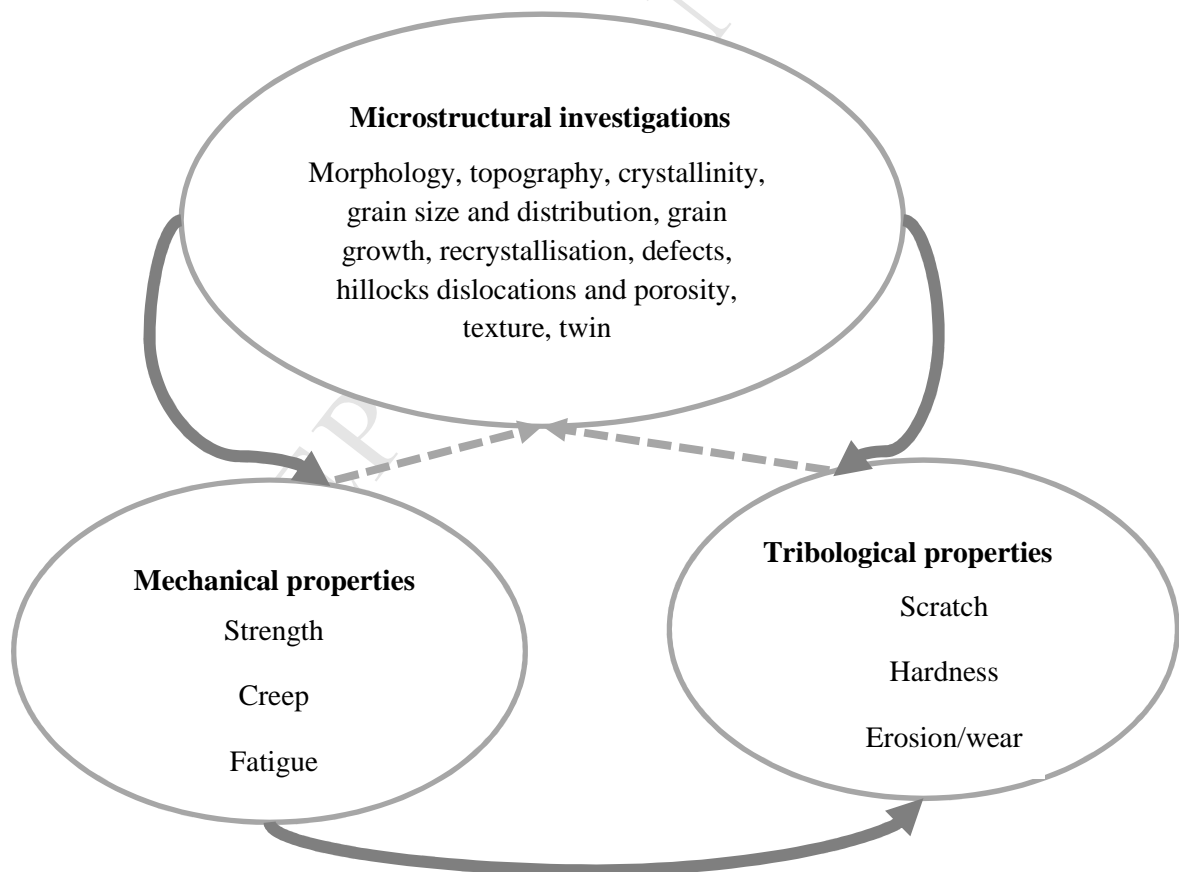


Figure 2. Structural properties and interrelationships of thin Al films as reported in the literature

Microstructural examination of thin aluminium films through SEM and TEM involves studying morphology, porosity, defects and structure types on the surface and across the

Al/substrate interface [13]. For instance, through SEM characterisations, Garbacz et al. [14] revealed that the surface of thin Al films deposited on a Ti6Al4V substrate through vacuum evaporation has higher porosity, more cracks and non-homogenous microstructure than those deposited through magnetron sputtering on the same substrate. Thickness measurement, phase identification, and percentage quantification of porosity across the interface of thin Al films have been investigated through SEM studies [2]. XRD, on the other hand, is used to study crystallinity/orientation [15], and texture and stresses [14, 16] on the surface of the deposited films. For instance, through XRD, the thermal stability of Al-Mo films prepared through sputtering was reported and shown that the level of crystallinity depends on the applied temperature [17].

The structure of thin Al films depends on deposition conditions [18, 19] such as rates of deposition [20, 21, 22, 23], aluminium alloy composition [24], substrate type [11], substrate temperature, substrate roughness [1, 25], applied external stress [26] and electrical current [27]. The structural properties of thin Al films have also been shown to depend on type of deposition technique [28], film thickness and annealing temperatures [29]. As such, several studies have reported microstructural properties for different conditions. Table 1 illustrates the microstructural properties of thin Al films deposited at different conditions and substrates.

Table 1 Microstructural properties of thin Al films deposited at different conditions and substrates

Ref.	Film/Substrate	Physical method	Conditions	Characterisation techniques	Conclusions
[6]	Al/Silicon (100)	Vacuum evaporation	Film thickness range: 0.06-3 μm Substrate-source distance: 120 mm	Grazing XRD; AFM	Increase in film thickness, main peak (111) dominates both parallel and perpendicular directions
[30, 31]	Al-4wt.%Cu/SiO ₂ /Si (100)	Rf Magnetron sputtering	Argon pressure: 5mTorr Target input power: 7kW Rf bias voltage: 0-200 V	Rutherford backscattering spectroscopy (RBS), TEM, EDX and XRD analysis	-RBS shows that Cu concentration increases with bias voltage -Increase in bias voltage increase the number of particles at the interface; particles width increases with bias voltage -XRD; predominant orientation was (111)
[32]	Al/Silicon	Magnetron sputtering	Bias voltage: 0-150 V	XRD	Preferred orientation (111)

[33]	Al-2.0at% Ta/Glass; Al-2.0at.%Nd/Glass	DC magnetron sputtering	Deposition rate: 2.5 nm/s ; Base pressure: 1.0×10^{-4} Annealing temperature: 100°C-500°C	AFM, XRD, TEM, SEM-EDX	-Lower hillock density for Al-2.0at%Nd film -Hillock density increased with annealing temperature for Al-2.0at% Ta; nearly constant for Nd-doped Al film -Rare change of microstructure of Al-2.0at.%Ta films on annealing -Surface stress decreased with annealing temperature
[34]	Al-Sn-N/Si (100); Al-Sn-N/SiO ₂	Rf Magnetron sputtering	Base pressure: 10^{-8} mbar; rf-bias -60V; substrate temperature 200°C; Target power: 0-50 W	X-ray photoelectron spectroscopy (XPS), XRD, SEM	-Increase in Sn content results in formation of glassy-like morphology of Al films -XRD and XPS shows a single-phase (wurtzite) solid solution present
[35]	Al-0.5wt.%Cu/Ti/Si (100)	Magnetron sputtering	Base pressure: 2×10^{-8} Torr Film thickness: 10-1.6 μm	AFM, cross-sectional TEM, XRD	-The effect of Ti underlayer on structure of Al-0.5wt.%Cu thin films -Ti reduce size of columnar grain size of AlCu -Ti enhance exact Al (111) texture development
[36]	Al/SiO ₂ /Si (100)	Electron beam evaporation	Vacuum: 6×10^{-5} Pa; Deposition rate: 9-12 nm/s; Ion energy: 870-1070eV; power density: 0.29-0.67 W/cm ²	SEM, TEM and XRD	-Grain size increases with film thickness -Grain growth rate: 0.07-0.16 $\mu\text{m/s}$ -Large grains are observed for very smooth morphologies; roughness

					decreased with average grain size
[37]	Al/SiO ₂	Magnetron sputtering	Varying film thickness; varying substrate temperatures	Grazing-incidence XRD, TEM and SEM	-Early stages of deposition showed inter-connected structures and randomly oriented grains -Above 100nm film thickness, (111) texture was observed -Growth hillocks observed at 295K substrate temperature; No hillocks at higher temperature -Grain size: 500 nm at 295K; at 675K, grain size was 4 μm
[38] [39]	Al/Si (100) and Al-xSc/Si(100)	DC Magnetron sputtering	Varying concentration of dopant (Sc) Vacuum pressure: 1.3x10 ⁻⁴ ; Argon pressure: 4x10 ⁻¹ Pa; Power: 110W Annealing: 200-500°C	XPS, XRD, TEM, SEM, AFM	-TEM grain size of film decreased with addition of Sc -Annealing temperature affects grain growth of pure Al films -Grain size in Sc-doped Al films does not change considerably with annealing temperature -Hillock formation reduces with addition of Sc dopant
[40]	Al/SiO ₂	Vacuum evaporation	Annealing temperature: 400-660°C At different annealing times; from 3s to several days	Optical microscopy (OM), SEM, EDX	-At low temperatures, there is formation of pores on thin film -Annealing leads to precipitation of silicon and forms Si-rich clusters
[11] [2]	Al/Low carbon steel	Thermal arc spray	Air pressure: 4-6 bars; no variable	SEM/EDX and XRD	Plate-like microstructures; pores/defects on

			parameters		film; high grade crystalline pure Al (111) was detected; EDX showed Al, Fe and O elements on the film
[14]	Al/Ti6Al4V	Vacuum evaporation (VE) and Magnetron sputtering (MS)	Constant process parameters; comparisons of deposition methods	SEM/EDX and XRD	-High porosity micro-cracks and defects in the VE samples -XRD texture analysis stresses reported
[41]	Al/STS 304	Thermal spray	Film thickness: 60-120 μm	SEM/EDX	-Plate-shaped structures observed for all thicknesses -EDX: Al, O and Cr -There was no relationship between thickness and structure

2.1.2. Hillock and defect formation

There are two important conclusions drawn from Table 1. Firstly, thin Al films deposited on metallic substrates contain defects/porosities and secondly, there is the formation of hillocks on Al films deposited on non-metallic substrates. Micro-cracks and porosity occur when Al films are deposited on substrates at room temperature, primarily through evaporation method. These defects are caused by the tensile stresses generated in the film during cooling and solidification [14, 42]. During rapid solidification of thermally sprayed Al films on steel substrates, a splash zone forms on the surface of the film [11]. Due to condensation and coalescence during the nucleation stage, there is usually a formation of a porous region at the interface. Based on extensive reports [11, 43, 14, 25, 2], the concept of porosity evolution in thin Al films can be represented as the illustration in Figure 3.

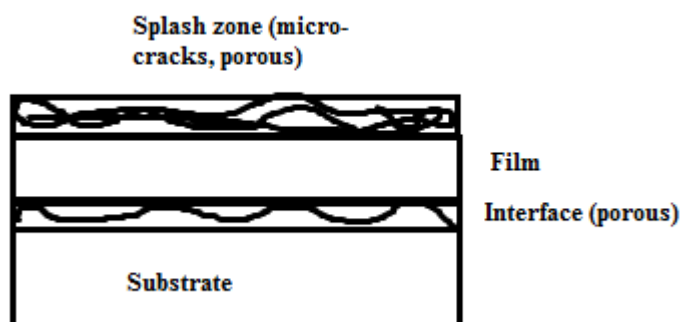


Figure 3. Development of porosity across the substrate-film section. At the top surface of the film, there is a thick film consisting of pores, cracks, oxides and other atmospheric impurities while at the interface there is a

high concentration of porosity. These porosities are due to condensation during nucleation, solidification and coalescence of the film during growth.

However, as reported by the study [25], optimisation of the deposition parameters [40], substrate preparation and conditioning and proper choice of deposition methods can reduce such defects and improve on the performance of the films. We note that more work is necessary to detail the evolution of porosity and microcracks specifically in thin Al films at different process parameters.

Microstructural imperfections and defects occur during physical deposition methods. These defects originate from substrate imperfections, deposition chamber impurities and during film growth [44]. The literature reports different types of defects in physically prepared thin films, the most common being nodular and trough defects. [45]. Such defects reduce the capability of the films to protect the substrate from corrosion [46]. Extensive literature is available on the defects in different films including Al_2O_3 and TiN [45, 47, 48]. Liang et al. [49] recently studied dislocations in thin Al films before and after electrical current stressing. The study reported low dislocation density before stressing and high dislocation density in the order of 10^{16} m^{-2} and lattice distortion upon current stressing. Such dislocations decrease the electrical conductivity of thin Al films [50, 51]. Defects and dislocations also affect the mechanical and tribological properties of thin films. However, it is noted that scanty research exists on the relationship between the dislocations and such properties. It is also noted that further work on detailed analysis, from a crystallographic perspective, on the mechanisms of formation of dislocations/defects in thin Al films is necessary.

Formation of hillocks or splats occurs either during the physical deposition process or the thermal treatment of thin Al films; the formation of hillocks is driven by the differences in thermal expansions between the film and substrate materials [51, 52, 53, 54]. Figure 4 gives a typical example of hillocks obtained from thin Al films deposited through rf magnetron sputtering on glass substrates [51]. The hillocks appear as extrusions and occur on the grain boundaries due to a microstructural mismatch of the substrate and the thin film [55, 56, 57, 58]. Several TEM studies showing that the hillocks are preferentially formed along the grain boundaries are available in the published literature [59, 60, 61, 62, 63], and that their formation depends on the microstructure, grain size and crystal orientation [64, 65].

The ability of thin Al films to form hillocks is a significant limitation to electrical applications and research emphasis on the control of these hillocks is therefore necessary. Extensive studies on the formation of the hillocks at different conditions such as annealing temperatures and deposition rates are have been conducted to minimise these formations [66, 67, 60, 68]. Since hillocks form preferentially along grain boundaries, their formation is affected by grain size and orientation [69]. Studies into the thermal behaviour of thin Al films have shown that the growth of hillocks increases with a rise in temperature [70]. Increase in annealing temperature increases the size of the hillocks in thin Al films [52, 53]. A study by Arai et al. [71] in which Al-Nd films were used for LCD applications reveal that the addition of 2 wt. % Nd to Al suppresses the formation of hillocks and whiskers in the films. Doping Al films with copper reduces electromigration and hence hillock formation [72], as does the addition of transition metals such as Fe, Co and Ni [73]. The effect of capping on the hillock

formation on Al/glass substrates by different materials such as Ti, Mo and SiO₂, was reported [74]. It was shown that the volume of hillocks for samples annealed for 400 minutes at 280°C, decreased with the thickness of the capping layers [74]. In a similar study, Kim et al. [75] evaluated the effect of thickness of the passivation layer (SiO₂) on the formation of hillocks and reported 250 nm as the optimal thickness to suppress their formation in thin Al films. A study [76] in which thin Al films were covered with sputter-deposited fine-grained polycrystalline pure Al shows that no hillocks are formed even after exposure to thermo-mechanical stresses.

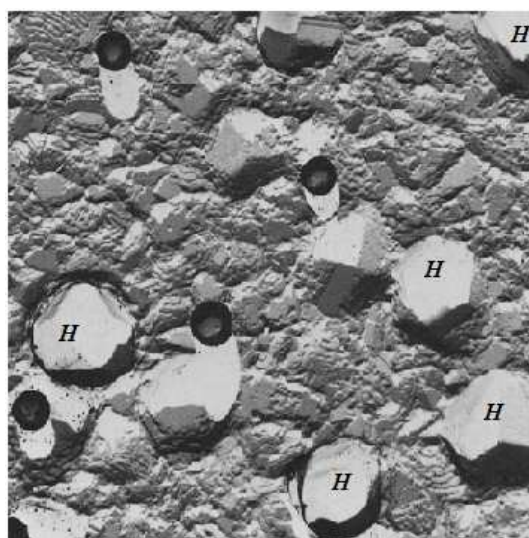


Figure 4. Hillocks (indicated as *H*) at the surface of a 30,000Å thick film deposited at a substrate temperature of 300°C at a rate of 2000Å per min (Adapted from D' Heurle 1970 [51])

Resnik et al. [77] investigated the effect of the target composition, thermal treatment and deposition temperature on the hillock formation of DC magnetron-sputtered Al films. They concluded that films deposited from Al-Si-Cu targets resulted in a lower density of hillocks compared with those sputtered from Al-Si targets. The study illustrated that hillock formation was strongly dependent on the deposition temperature rather than the annealing temperature. Smaller sizes of hillocks resulted when Al layers were sputtered on an Si substrate than when deposited on SiO₂ substrates. This observation was attributed to <111> texture in the SiO₂ substrate which is prone to hillock formation. The effect of diffusion-fatigue on the formation of hillocks on thin Al films, when exposed to thermal cycles, has been discussed by Ri and Saka [78]. Zaborowski and Dumania [56] reported on the kinetics of hillock growth and the distribution of thin Al films. Both reports show that stress relaxation in thin Al films occurs through the formation of hillocks, creep and adjustments in the microstructure. A study [79] which investigated the effect of annealing conditions on the formation of hillocks for Al films deposited through thermal evaporation on sapphire substrates, reported that hillocks form when annealing is carried out in the presence of oxygen/air.

Smith et al. [80] observed three phenomena on local stress relaxation of thin Al films formed on silicon substrates through electron beam evaporation and magnetron sputtering. At elevated temperatures, the compressive stresses of the films were relaxed through the formation of hillocks. The mechanism for hillock formation was also observed in *in situ*

SEM/TEM studies which showed that the tensional stresses on the films were relieved through the “collapsing” of singular Al grains [80]. Kylvner and Mattson [81] undertook a real-time observation of the initial formation of hillocks in Al films deposited through electron beam evaporation on silicon wafers at different heating rates, and reported that the density of hillocks increased rapidly with an increase in temperature, especially for higher heating rates. The effect of grain boundary migration on the formation of hillocks for unpassivated thin aluminium films under thermal cycles has also been reported; films which experience grain growth during thermal loading form more hillocks [82]. Similar results for Al-Cu and pure aluminium deposited on silicon wafers through electron beam evaporation were observed in another study [83].

From these findings, two significant paths of research are evident: (1) Hillock formation is driven by stress relaxation and depends on temperature, substrate type, and annealing conditions. However, information on the relationship between films’ grains (which play a significant role during stress relaxation) and hillock evolution is scarce which begs the question: What is the relationship between hillock growth and grain boundary energy in Al films? (2) The use of dopants and capping inhibits hillock formation, but the mechanisms involved reducing hillocks through capping and doping methods are not fully understood. What then are the criteria for choosing different dopants for thin Al films? Extensive data on the effect of a wide range of dopants is required to answer this question.

2.1.3. Formation of structures in film growth

The microstructure evolution during film growth of pure metallic films deposited through physical methods for different conditions is well explained with regards to the atom mobility described in the structure zone model (SZM) [12]. The SZM has three zones, namely zone I, transition zone T and zone II as illustrated by Petrov et al. [84] in Figure 5. Generally, at low substrate temperature, T_s (zone I), the adatom mobility is low, and the microstructure of thin films consists of fine fibre, porous or even amorphous texture; it contains small and significant equiaxed grains. In the transition zone T, there is a higher diffusion of adatoms which leads to the formation of a coarser structure. In this zone competitive grain growth and a preferred crystallographic orientation with respect to the film thickness are likely to occur [85, 86]. At a higher substrate temperature in zone II, there is bulk mobility of adatoms, grain growth and recrystallisation leading to a coarser/columnar structure. The structure zone model is an ideal illustration of microstructure evolution during film growth because it does not incorporate the effect of impurities and other process parameters. However, the growth mechanisms of thin Al films prepared through different physical methods can be explained by using a modified SZM. For instance, thin Al films deposited through high-vacuum evaporation at ambient temperature conditions exhibit coarse and columnar structures consisting of parallel grain boundaries usually oriented to the silicon wafer substrate [87]. Analogous to zone II of the structure zone model in Figure 5, the structures extend homogeneously through the whole film thickness.

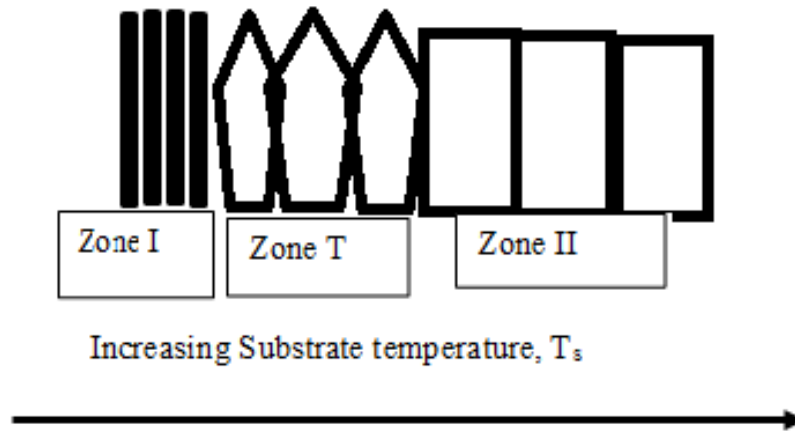


Figure 5. Structure zone model idealising the evolution of microstructure with the temperature of substrate for thin films of pure metals [84].

Based on the existing literature on the growth of thin Al films, the physical mechanism for the formation of structures at different zones of SZM can be described using the Stransky and Krastanov (S-K) model [86, 88, 89]. According to the S-K model, a layer-by-layer mode is responsible for nucleation and grain growth whereas the formation of discrete nuclei is responsible for film growth. Film formation occurs through nucleation, the growth of islands, blending of the islands, the growth of polycrystalline islands and the formation of a continuous structure, hence film thickness [86]. These mechanisms are influenced by the deposition conditions and determine the structures and texture of thin Al films. When thin Al films are deposited in high-vacuum (impurity-free) conditions, the structure formation is dominated by restructuring, according to S-K model, resulting in columnar microstructures as those described in zone II of SZM [87, 90, 91]. In impurity-free conditions, there is high grain boundary motion and grain growth because of minimum surface energy. These films have fine $\langle 111 \rangle$ texture and smooth surfaces [87]. The introduction of low quantities of impurities such as oxygen during the deposition process, affects the Al film growth by contaminating the grain boundaries and limiting their mobility. As such, the structures of zones II and T are characterised by smaller columnar grains and the evolution of $\langle 111 \rangle$ and $\langle 311 \rangle$ textures. The surfaces of the films in these zones are rougher and have a higher density of hillocks. At a very high concentration of oxygen impurities, the characteristics of zone I are observed. According to the S-K model, the oxide phase covers the $\{111\}$ crystal faces so that there is minimal nucleation, grain boundary motion and grain formation especially towards the surface of the thin films. There are no distinct crystal structures and texture observable in such cases. This evolution has also been reported for thin Al films co-sputtered with other elements, and on some non-metallic substrates [90, 91, 92]. Figure 6 illustrates the S-K model for thin Al films under the influence of different deposition conditions for the three SZM zones based on the reported literature. As different process parameters change, there is an evolution of other intermediate structures and textures.

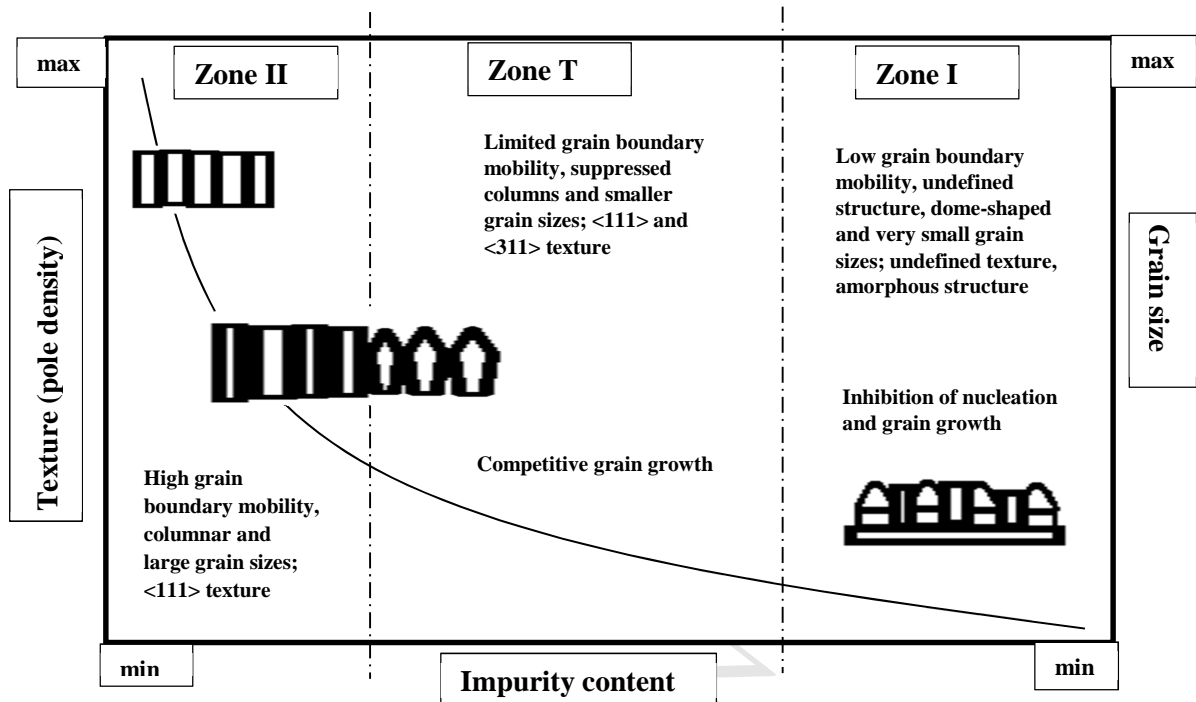


Figure 6. The microstructure evolution during physical deposition of thin Al films with respect to grain size and impurity content. The mobility of the adatoms and grain boundaries which leads to nucleation and grain growth according to the S-K model are functions of different deposition parameters such as impurity content, chamber pressure and substrate temperature.

2.1.4. Texture and texture effects

Texture influences electrical, elastic or mechanical, thermal, and magnetic properties of thin films [93, 94, 95]. For instance, the study on the effect of orientation of Al on electromigration behaviour reveals that $\langle 111 \rangle$ texture is the most ideal for electronic applications [94]. In a somewhat different study [96], the texture was shown to influence the transport properties of Mg_2Si thin films. It was also revealed to affect the optical performance of AlSi alloy thin films deposited on Si substrates through DC magnetron sputtering [97]. The texture is usually represented using pole plots of Kakuchi patterns from XRD and Electron Backscatter Diffraction (EBSD). This review into the existing literature on texture studies on thin Al films deposited through physical methods elicits two critical considerations, namely (1) the mechanism of texture formation and (2) the texture and process parameter relationships in physically deposited thin Al films.

The formation of texture in thin films depends on surface energy, grain boundary mobility, surface and lattice diffusivity [93]. These kinetic parameters control texture evolution from nucleation, grain growth and film thickening. Different authors agree that texture formation in thin films occurs during the coalescence of islands, thickening and the post-deposition annealing processes in thin films. Details of the texture formation which is largely driven by both surface and strain energy minimisations are well reported in the literature [93]. During the physical deposition of thin Al films, there is grain growth which decreases the total grain boundary energy. This decrease in surface and interface energies enhances the preferential

orientation of grain growth, hence texture development [94]. When FCC metals such as thin Al films are deposited on amorphous substrates, $\langle 111 \rangle$ textures develop because of surface and interface energy minimisation. The textural orientation for thin Al films in $\langle 001 \rangle$ and $\langle 011 \rangle$ on W/MgO is attributed to strain minimisation through lattice matching [98]. We observe that there is limited literature on surface and strain energy minimisation contributions to textural development in thin Al films.

Texture development depends on properties such as temperature, substrate, power and rate of deposition as may be inferred from Figure 6. To understand the effect of different parameters on texture development during Al film deposition, we ought to relate these parameters to the energy minimisations concept. Mostly, when Al films are deposited on a substrate, it results in the growth of close-packed planes perpendicular to the substrate surface. This growth reduces the surface, and interfacial energy of the substrate and texture development begins when the surface atoms have enough energy to move to the low energy regions. During physical deposition processes such as sputtering, there is a bombardment of low-energy ions [95]. This bombardment enhances the mobility of adatoms, increases nucleation, and decreases the surface energy and therefore texture development. Thus, any combination of parameters leading to increased low-energy ion bombardment enhances texture development in thin films. For instance, an increase in rf-bias power and a decrease in deposition pressure during sputtering has been reported to enhance preferential formation $\langle 111 \rangle$ Al texture thin films [95]. Very high pressure increases the energy of ion collisions thereby reducing the mobility of adatoms. The effects of deposition temperature, film thickness, co-deposition impurities and substrate conditions on texture formation have also been investigated [87, 99, 35] and their effects can be related to the energy minimisation. We note that texture evolution and its effects on mechanical properties under different preparation conditions of thin Al films is still not fully understood.

Topographical studies

Surface morphology studies through atomic force microscope (AFM) and scanning tunnelling microscope (STM) are used to report on the topography of the surface of thin films. AFM explicitly shows the morphology of thin films and the root mean square (RMS) or average (R_a) roughness of the films [100, 101]. The RMS value of roughness which corresponds to the standard deviation of the Z-heights in the AFM data, is determined by the formula in the following equation [101]:

$$R_{rms} = \sqrt{\frac{1}{N} \int_0^N \{Z(x)\}^2 dx} \quad \text{Equation 1}$$

where N is the number of points taken for the calculation of the surface roughness and Z , is the total area of scan within the x sampling length.

The surface roughness of thin Al films depends on several factors [102, 103, 104] - some of which are illustrated in Table 2.

Table 2. Factors influencing surface roughness for physically deposited thin Al films

Reference	Film/Substrate	Physical method	Factors reported	Findings
[6] [22]	Al/Si (100)	Vacuum evaporation & Magnetron sputtering	-Film thickness -Time (8 months)	-Surface roughness increases linearly with film thickness -Increase in roughness with film thickness is related by $R_{RMS} \propto h^{0.55}$ -Roughness decreases with time up to a constant value
[105]	Al/SiO ₂ /Si (100)	DC Magnetron sputtering	Deposition time	-Island size and height (roughness) increases with deposition time -Island density decreases with deposition type
[106]	AlCu/Ti and Al/Ti/TiN	Magnetron sputtering	-Substrate type -Deposition temperature	-Substrate type affects the nucleation and grain growth of the films; Ti substrates result in smooth AlCu films -Island density decreases with deposition time
[107]	AlCu/Glass	Thermal evaporation	Copper atomic concentration (concentration of the dopant)	-Increase in Cu concentrations decrease the R_{rms} roughness of AlCu films on glass
[108] [109]	Al/Si (100) & Al/Ti(100)	DC Magnetron sputtering	Deposition time	-The roughness increases with deposition time
[110]	99.9% Al/Si (100)	Vacuum evaporation	Effect of current on roughness	There is decrease in surface roughness with applied current
[111]	Al/Glass	Electron beam	Substrate temperature on roughness	Surface roughness increase with substrate temperature

Most of the roughness characterisations have been carried out using R_{rms} and R_a . However, these methods are limited in illustrating the lateral distribution of the roughness over the topographic images and therefore the information may not be sufficient. Besides, skewness and kurtosis are also used to describe the general distribution and shape profile of the surfaces of the films. Power spectral density (PSD) provides detailed information about surface roughness by using the frequency domain of the topographic images to describe the

spatial distribution of the wavelengths. The data from the PSD profiles is then fitted into different models to interpret the frequency results in respect of surface information. PSD method has been used in a few thin film studies [112, 113], but not to evaluate the effect of different deposition parameters on surface topography because very few data points are generated by this method. However, with the extended spatial length technique presented by [113], PSD can be used to study the roughness of thin films, and should be used in future studies including Al films.

2.1.5. Mechanical and tribological properties

Although thin Al films are mostly used for corrosion, electrical and optical applications, their mechanical and tribological properties are essential for the durability of the functional components. The most significant mechanical properties of thin films are strength, fatigue and creep. On the other hand, tribology is described by wear, hardness and adhesion strength [114, 115]. Both tribology and mechanical characterisations of thin Al films have been reported on at different conditions and parameters [116, 117, 118]. However, since these properties are dependent on the microstructural features described earlier, we only focus on the critical issues relevant to thin Al films with the aim of expanding research ideas.

Strength properties such as stiffness, hardness and modulus are easily measured through nanoindentation techniques whereas adhesion strength is measured through a scratch test. Fatigue, creep and wear in thin films are difficult to characterise because of the nature of the films. These properties cannot be measured using conventional standards for bulk materials. Consequently different researchers have embarked on using the scratch test method to study the fatigue and wear properties of thin films [119]. Attempts have also been made to develop fatigue and wear analysis models for hard coatings and bulk materials from scratch tests [120, 121]. We note that so far none of the scratch models has been applied in soft thin films such as Al. Based on scratch test mechanics and concepts in the existing models, researchers are using finite element techniques to model fatigue and wear properties of thin films [122, 123, 124, 125]. Creep is significant in thin Al films used in microelectronics applications operating at high temperatures. Because of its low melting point, Al is highly sensitive to creep and viscoelastic behaviour and is therefore anelastic [126, 127]. Creep theory in materials is detailed elsewhere [128]. During the operation of some microelectronic devices such as RF-MEMS, creep occurs at a low temperature-high stress regime. In this case creep deformation occurs through dislocation gliding. Creep control can be achieved by limiting the dislocation gliding through obstacles [129]. The creep deformation mechanism is described by biaxial stress, σ , Equation 2:

$$\sigma = -\frac{kT}{a} \ln \left[\exp \left(-\frac{a\sigma_0}{kT} \right) + \left(\frac{ac}{kT} \right) t \right] \text{Equation 2}$$

where

$$a = \frac{\Delta F}{\sqrt{3}\tau}$$

$$c = \frac{\dot{\gamma}_0}{2\sqrt{3}} \frac{E_f}{1 - \nu_f} \exp\left(\frac{-\Delta F}{kT}\right)$$

At time $t = 0$, biaxial stress is σ_0 , τ is the athermal flow stress, k is Boltzmann's constant, T is the absolute temperature, ΔF is the activation energy, $\dot{\gamma}_0$ is a quasi-constant for large stresses, E_f is the Young's modulus and ν_f is Poisson's ratio of the material.

In the equation 2 the two most important parameters in the creep of thin films are activation energy and athermal flow stress. Activation energy is the energy required by the dislocations to overcome barriers within the structure of the material. The higher the activation energy and flow stress, the higher the creep resistant in thin Al film. The nature of the precipitates in the microstructure of the Al alloy films can enhance these parameters. For instance, Al_{93.5}Cu_{4.4}Mg_{1.5}Mn_{0.6} thin film alloy consists of strong S-phase, coherent and highly dense precipitates. Such precipitates increase ΔF and τ , thereby hindering the movement of dislocations [129]. The creep resistant can also be enhanced by grain refinement enhanced by precipitation hardening. For instance, an increase in the Mg content in Al-Mg thin films was shown to reduce the grain size and increase the ΔF and τ and hence enhance resistance to viscoelastic relaxation and creep at both low and high temperatures [130]. The effect of the thickness of Al films on stress relaxation and creep was studied by Hyun et al. [131], who reported that creep resistance increased with the thickness of the film. This behaviour was attributed to dislocation locking, meaning that creep is highly dependent on deposition parameters such as deposition rate, temperature, time, power and substrate conditions. Studies relating these parameters (directly) to the creep behaviour of Al films are few, and since creep is a highly statistical property more research is necessary.

2.2 Corrosion properties

Extensive studies exist on corrosion tests of aluminium films deposited on various metal substrates through physical vapour and thermal spray techniques [2, 43, 15, 11, 42]. The general observation from these studies is that aluminium film coatings act as sacrificial corrosion protections on metal substrates [11], which means that due to the anodic nature of aluminium its corrosion products are deposited on the coating surface and substrate, thereby enhancing the corrosion resistance [2]. Studies have also shown that aluminium and aluminium-rich alloys provide effective cathodic protection to metals, especially steel, in atmospheres with very high chloride concentrations [132]. As such, aluminium coatings are useful corrosion protectors for steels in marine and industrial conditions [11]. Besides being cathodic protectors, aluminium and its alloys form an inert aluminium oxide film which acts as a barrier to corrosive media thereby providing corrosion protection in low chloride concentrations [42, 132]. According to the literature, there are three corrosion techniques used to evaluate the corrosion properties of aluminium film coatings deposited on metal substrates. They are: (1) electrochemical studies, (2) a salt spray chamber, and (3) low/ high-temperature oxidation [43, 15, 11]. A detailed review of the results obtained through each of these techniques by different researchers is presented below.

2.2.1 Electrochemical Studies

Electrochemical experiments have been used to evaluate the sacrificial protection of pure aluminium films to metal substrates using a standard three-electrode cell [2, 43, 11]. In this cell, the aluminium film acts as the working electrode (WE), the saturated calomel (SCE) as the reference electrode, and the platinum as the counter electrode (CE) [2, 11]. Figure 7 shows a schematic diagram of the three-electrode cell used in electrochemical experiments according to ASTM G5-94 standards.

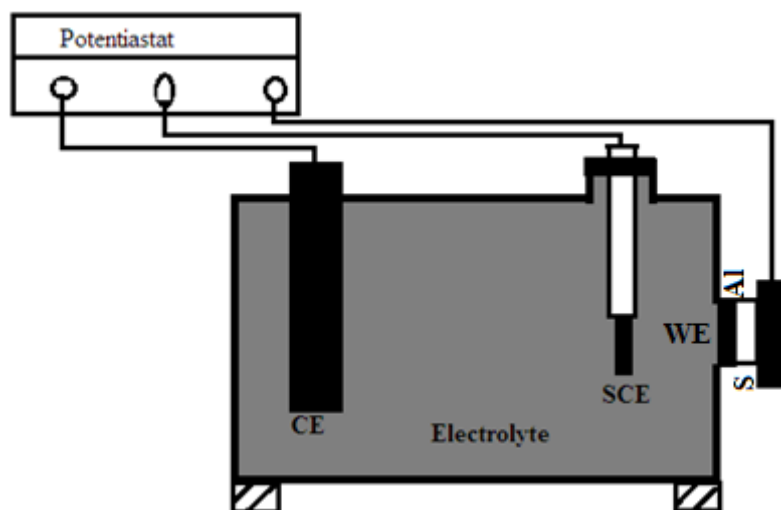


Figure 7. Schematic diagram of standard three-electrode cell for electrochemical corrosion studies [11]. The working electrode consists of aluminium film (Al) and the substrate (S) represented as dark and white backgrounds respectively.

In electrochemical studies the most important measurements are the potential of the WE versus the SCE plus the current densities from which Tafel polarisation plots are generated. Theories on the electrochemical cell, polarisation curves and corrosion rates are presented elsewhere [133]. A thin film coated substrate is said to have higher sacrificial corrosion resistance when its polarisation plot derived from the electrochemical measurements gives a higher absolute magnitude of potential and lower current density. For instance a study by Esfahani et al. [2], performed electrochemical measurements on 0.04C wt. % mild steel, arc-sprayed with 99% aluminium in 3.5% NaCl electrolyte. They revealed that the Tafel polarisation plot for the aluminium-coated steel gives a higher potential and lower current intensity compared to that of bare steel. A similar study on aluminium-dominant Al-Zn alloy coated mild steel reported the same results: lower current intensity and higher polarisation potential for the coated mild steel samples [134]. Lee et al. [11] reported similar results for 0.240C wt. % mild steel substrate arc sprayed with 99.95 wt. % commercially pure aluminium. In their study the bare and coated steel had corrosion densities of 15.22 and 12.95 $\mu\text{A}\cdot\text{cm}^{-2}$ respectively and potentials of -0.689 and -0.717 V respectively. In a related study, [43], the effect of hydrothermal sealing of thin Al films sprayed onto the Al-6061 substrate was studied through electrochemical measurements, and it was shown that the sealed samples have higher absolute potential and lower current density. These findings however, contradict the general principle that higher positive potential leads to lower corrosion rates. It is noted that bare steel has more positive potential than coated steel; a principle for sacrificial

corrosion protection. This observation indicates that aluminium coating corrodes in preference to the steel substrate, therefore providing sacrificial corrosion protection.

Another finding derived from Tafel polarisation plots reported in the literature is that aluminium-coated samples exhibit passive and trans-passive regions whereas bare metals such as steel, shows active regions [11]. The presence of active regions for bare steel is attributed to the pitting corrosion which takes place on the surface [2, 43] whereas the passive regions in the aluminium-coated samples are caused by a tendency in aluminium to form passive corrosion products with various media. For instance, if electrolysed in 3.5 wt. % NaCl at room temperature, aluminium-coated mild steel forms about 30% oxides [2], which can act as a sealant to porosity/defects [134] and as a passive layer alumina (Al_2O_3) which inhibits further corrosion of the aluminium-coated steel [43, 132]. Corrosion products consisting of passive films of hydroxide [$\text{Al}(\text{OH})_3$] and Al_2O_3 were reported during an electrochemical study of hydrothermally sealed aluminium coating sprayed on mild steel substrate; these passive films were the reason for large passive regions on the polarisation curves [43]. Similarly, when pure aluminium-coated stainless steel 304 was investigated under natural seawater, $\text{Al}(\text{OH})_3$ was reported as the primary corrosion product [135]. The corrosion products depend on the corrosive medium and the composition of the coating. For instance, when coated steels were exposed to an electrochemical process with *SAE J2334 solution* [11], which contained NaCl, CaCl_2 and NaHCO_3 , there was a formation of impervious and insoluble layers of dawsonite, gibbsite and bayerite which protect the substrate from pitting and from the formation of uniform corrosion. On the other hand, for a multi-component Al-Zn coating [134] in 3.5% NaCl electrolyte, complex corrosion products such as simonkolleite [$\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$], zinc aluminium hydroxaltes and aluminium chloride hydroxide hydrate [$\text{Al}_5\text{Cl}_3(\text{OH})_{12}\cdot 4\text{H}_2\text{O}$] are formed. These products act as self-sealant to the pores on the coating.

The corrosion rates (CR) and polarisation resistance (R_p), which further explain the corrosion resistance of films, have also been reported from Tafel polarisation plots [11, 134]. CR is usually calculated using Faraday's Law illustrated in Equation 3 below [136]:

$$CR \left(\frac{\mu\text{m}}{\text{year}} \right) = \frac{3.27 I_{corr} \cdot E \cdot W}{d} \quad \text{Equation 3}$$

where $E \cdot W$ is the equivalent weight in grams, d is the density of the metal and I_{corr} is the corrosion current density per square centimetres. On the other hand, the polarisation resistance (R_p) which measures the resistance of flow of electrons by the electrode, can be determined from the relationship in Equation 4 [133].

$$R_p = \frac{2.303 b_a b_c}{b_a + b_c} \left(\frac{1}{I_{corr}} \right) \quad \text{Equation 4}$$

where b_a and b_c are slopes on the anodic and cathodic Tafel slopes respectively determined from the polarisation curves within the Tafel region. I_{corr} can be computed through extrapolation of the Tafel region as indicated in the idealised polarisation plot in Figure 8.

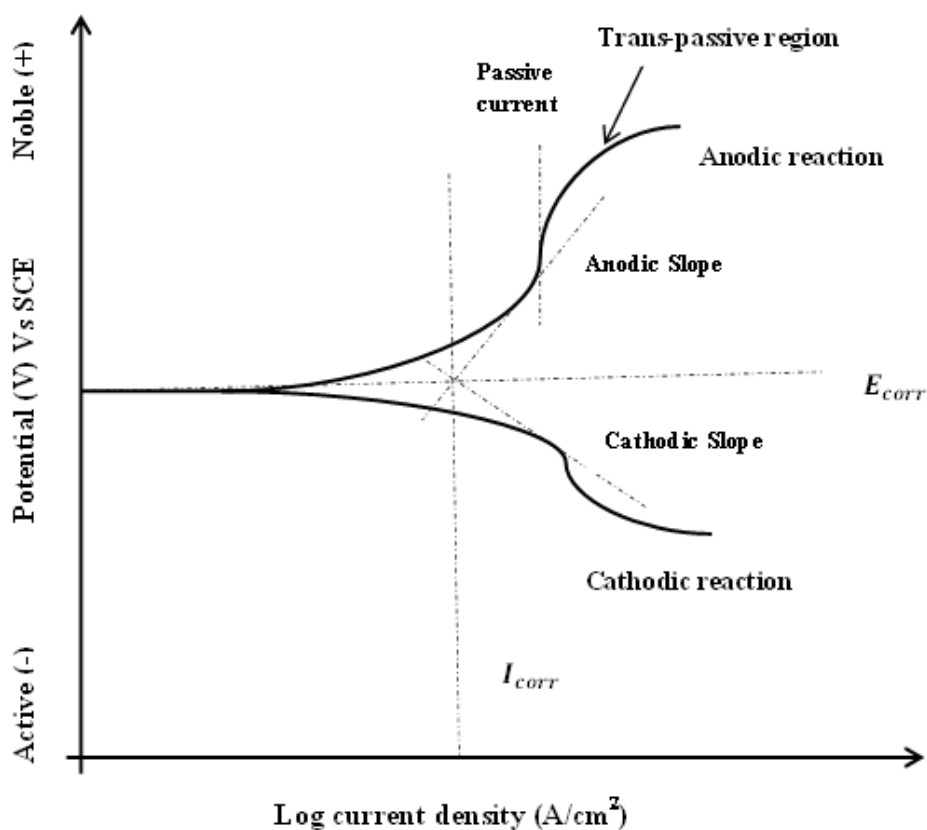


Figure 8. Idealised diagram for general cathodic and anodic polarisation plot for an electrochemical corrosion experiment [133]

Through this method, the corrosion rates for bare steel and Al-coated steels have been calculated. Reports show that Al-coated steel has lower CR compared to bare steel [134]. Similarly, the polarisation resistances for aluminium-coated steels are higher compared to those of bare steel. Thus, aluminium coating improves the corrosion resistance of metal substrates [11]. Similar results have been reported on aluminium films deposited on aluminium and magnesium substrates through a cold spray process [136]. Table 3 shows the key results reported in the literature on electrochemical studies of thin Al films.

Table 3 Key aspects of electrochemical corrosion studies of aluminium-coated metals

Reference / year	Substrate	Al-coating	Electrolyte	Electrochemical studies	Corrosion products	Key results
Lee et al. [11]/2016	Mild steel (0.24C wt.%)	Pure Al	SAE J2334 solution (contains: NaCl, CaCl ₂ and NaHCO ₃)	EIS, Open circuit potential (OCP), Polarisation curves	NaAlCO ₃ (OH) ₂ (Dawsonite), Gibbsite and Bayerite (Al(OH) ₃)	Corrosion rate (CR), polarisation resistance (R_p), Tafel plots, Nyquist and Bode plots
Jiang et al. [134]/2014	Q235 Mild steel	Al-rich-Zn-Si-RE alloy	3.5 wt.% NaCl	EIS, OCP, Polarisation curves	Simonkolleite (Zn ₅ (OH) ₈ Cl ₂ H ₂ O), Zinc	Corrosion rate (CR), polarisation

			solution		aluminium hydroxalclites, Aluminium chloride hydrate	resistance (R_p), Tafel plots, Nyquist and Bode plots
Esfahani et al. [2]/2012	0.05C wt. %	99% Commercial purity Al	3.5 wt.% NaCl	EIS, Polarisation curves	Al(OH) ₃ and Al ₂ O ₃	Nyquist and Bode plots, Corrosion rates, Tafel plots, Polarisation resistance (R_p)
Carboneras et al. [137]/2010	ZE41 Mg Alloy	99.5% pure Al and Al-rich Al/SiC alloy	3.5 wt.% NaCl	Polarisation curves	Mg(OH) ₂ /MgO .H ₂ O, Chloride products (on the interface) and Al ₂ O ₃ (On coating)	Tafel plots, Polarisation resistance (R_p)
Han et al. [41]/2009	Stainless steel 304	99.7% Al	Sea water	Open Circuit Potential (OCP), Polarisation curves	Not reported	Tafel plots, Polarisation resistance (R_p)
Hernandez et al. [138]/1995	Si(100)	Aluminium	3.5 wt.% NaCl	Polarisation curves and EIS	Al(OH) ₃ and Al ₂ O ₃	Nyquist and Bode plots, Corrosion rates, Tafel plots, Polarisation resistance (R_p) for different thicknesses of the Al films

As can be observed in the summary in Table 3, information on the effect of different deposition variables and film microstructure to corrosion is lacking. Frankel et al. [139] investigated the effects of the vacuum pressure of a sputtering system on the corrosion resistance of pure thin Al films. This study revealed that an increase in vacuum pressure (lower vacuum quality) increases the corrosion resistance of thin Al films. This increase in resistance has been attributed to the presence of oxygen and nitrogen elements in the microstructure of the Al films [140, 141]. These studies imply that the deposition parameters influence the composition and microstructure, hence the electrochemical properties of Al films. In slightly different studies, the microstructure and composition were shown to affect the corrosion properties of TiN_x [142, 143]. Grain size and distribution is another feature which has been shown to alter the corrosion properties of metals and alloys. Although there is no direct correlation between the two factors based on the nature of the environment, grain size plays an important role. For instance, in an active environment small grain sizes reduce

the corrosion resistance and vice versa for passive environments [144, 145]. However, a literature search shows that the relationship between grain size and corrosion behaviour of thin Al films has not yet been fully understood. Future studies should therefore focus on the effect of deposition parameters, microstructure, composition and grain size on the electrochemical properties of thin Al films.

2.2.2 Salt Spray Studies

Salt spray experiments are conducted according to the ASTM B117 standard in which the test samples are exposed to a high-pressure spray of NaCl solution for a known time at room temperature [146]. These tests are performed to simulate marine and high chloride operating atmospheres in coatings [15]. Several studies have reported on salt spray experiments with aluminium and aluminium-rich alloy films on different substrates [2, 13, 15, 42]. The general conclusions from these studies are that when aluminium-coated metals are exposed to NaCl solutions, impervious corrosion products are formed which eventually enhance the corrosion resistance of the aluminium coating [134]. These products depend on the chemical composition of the coating substrate, and concentration of the operating medium [132, 147].

When aluminium-coated metallic substrates are exposed to salt spray conditions at room temperature, the corrosive medium (or chloride solution) tends to flow through the pores, defects or channels on the surface and the substrate-coating interface to form oxides and chlorides. Esfahani et al. [2] conducted a salt spray experiment on arc-sprayed aluminium-coated mild steel in 3.5 wt. % NaCl at room temperature for up to 1500 hours. Electron discharge spectrometer (EDS) results on the surface of the Al coating revealed that 39% and 1% oxygen and chlorine-rich compounds were present. This high oxidation of the surface can be explained by the fact that as the exposure time increases, there is more deposition of the oxides within the surface pores. The oxides act as sealants to pores so that no more corrosive mediums can infiltrate the coating. When aluminium-rich (Al-Zn) alloy coated mild steel was exposed to 3.5 wt. % NaCl in a study [134], it was reported that the corrosive medium penetrated the coating through the lamellar structure to form a thick layer of corrosion products. After longer exposure times, the study [134] revealed that the whole Al-Zn coating was covered with corrosion products which filled the defects and porosity so that no further attacks by the NaCl medium was possible. It can therefore be deduced that the corrosion products formed during salt spray experiments (or in marine conditions) enhance self-sealing of the defects and porosity of aluminium films thereby inhibiting further corrosion of the material. This phenomenon has been widely reported in the literature and is attributable to the corrosion resistance of aluminium-coated metals [15, 42, 132, 148].

Besides enhancing self-sealing on aluminium films, the corrosion products formed also act as physical barriers to corrosion of the substrate. The corrosion products formed in salt spray conditions are impervious and enhance the passive nature of the aluminium coatings. Aluminium oxide (Al_2O_3) is a typical corrosion product formed when Al-coated samples are exposed to a saline environment because of the high oxidation behaviour of aluminium in such conditions. The oxide is passive and is hydroxylated on the surface [149]. Usually, the thickness of the oxide film ranges between 40 and 100Å; the oxide evolves into boehmite and bayerite with exposure time [150]. Other corrosion products formed include hydrates,

hydroxides and chlorides [2, 15]. Most studies on pure aluminium films exposed to 3 wt. % NaCl media have not reported on chloride products since they are usually present in low concentrations and the XRD method cannot detect them. In a study [2], the Al_2O_3 and $\text{Al}(\text{OH})_3$ were identified as corrosion products after 1500 hours of exposure of Al-coated mild steel in 3.5 wt. % NaCl. In a similar experiment Rodriguez et al. [42], revealed that when a flame and arc sprayed Al-coated ASTM-283 steel plate was exposed to 3.5 wt. % NaCl, $\text{Al}(\text{OH})_3$ and AlOOH are formed as corrosion products. However, chloride compounds have also been reported in higher concentrations of NaCl. In Al-coated low alloy steel exposed to 5 wt. % NaCl, the AlHO , Al_2O_3 and AlOCl were identified as corrosion products on the surface of the coating [15]. When immersed in 3.5 wt.% NaCl, Mg/Al alloys coated with pure aluminium form a $\text{Mg}(\text{OH})_2$ layer as the corrosion layer [13, 151]. These oxides and hydroxides are impervious and act as physical barriers to protect the substrate from corrosion attacks by the medium [152]. However in Al-coated Mg/Al alloys, formation of layers such as $\text{Mg}(\text{OH})_2$ at the interface results in the detachment of coatings after exposure in chloride conditions for extended periods [137, 153].

When Al-coated substrates are exposed to conditions of high chloride concentration such as a 5 wt.% NaCl medium, there is considerable 'chloride effect' on the coating surface [15, 13]. For instance, Al-coatings exposed to 5 wt. % NaCl salt spray chambers for one month revealed the presence of surface cavities [15]. These pits were attributed to the presence of chlorides observed on the surface. The chlorides cause local breakdown and form cavities. Due to the continued local breakdown and formation of cavities, it has been noted that more prolonged exposure of Al-coated steels to 5 wt. % NaCl may lead to more significant pits and eventual failure of the coating [15]. Similarly, the formation of cavities and eventual spalling of the coat layer was reported by [13] on Al/SiC coated magnesium alloys. When as-sprayed pure aluminium coated Mg/Al alloys are exposed to 3.5 wt.% NaCl, crevice corrosion occurs in the cavities of the aluminium coating [151, 153]. This crevice corrosion can also be attributed to the chloride effect. The breakdown of electric arc sprayed Al coatings on steels when exposed to 3.5 wt. % NaCl medium is attributed to the formation of oxides during the deposition process; these oxides (boehmite) are said to form weak points on the passive layer. The chlorides can attack the weak points in the corrosive environment leading to the breakdown of the coating [42, 151]. At a low chloride concentration atmosphere ($>100 \text{ mg Cl m}^{-2} \text{ day}^{-1}$), aluminium and aluminium-rich alloy coatings tend to be passive due to the inert aluminium oxide on its surface [132]. In such conditions the coatings do not afford cathodic protection to the substrates; the protection is caused by inert corrosion products (impervious layers) formed on the surface of the coatings. In the presence of very high chlorides, passive layers on aluminium films tend to become active and can react. In such conditions, the protection of the substrate is cathodic.

The behaviour of Al-coated samples can be understood by considering the corrosion mechanisms of bulk aluminium in chloride solutions. When aluminium is immersed in a chloride solution such as NaCl, three possible mechanisms are likely to occur, namely dissolution, solution filtration through the pores, or ion transport through defects [150]. In oxide dissolution there is adsorption of the chloride ions into the surface of the Al_2O_3 ,

resulting in dissolution of the passive aluminium oxide film [149]. This decomposition is enhanced by the formation of compound anionic ligands on the surface. It is argued that the negatively charged ligands of the oxide surface make the bonds of the hydroxylated weak and aluminium species are released into the aqueous solution [150] resulting in corrosion of the aluminium. Frankel et al. [154] have also recently explained the mechanism of localised corrosion in thin films and similar results have been reported.

Extensive studies exist on the characterisation of corrosion pitting in thin Al films in salt spray conditions [155, 156]. Proost et al. [157] reported on the morphology of corrosion pits in thin Al films sputtered on an SiO₂ substrate after immersion in chloride-containing electrolyte for 15 minutes. The study showed that the corrosion pits exhibit different morphologies for different substrate temperatures. It was shown that the cavities exhibit fractal-like patterns with a clear tendency towards circular growth. However, the density of the patterns was observed to increase with an increase in substrate temperature. Zhao et al. [158] used a light scattering technique to study the depth, area, surface fractal dimension, and density of pits in thin Al films deposited on *p*-type Si (100). The initiation of pitting in thin Al films in a chloride medium has been studied through AFM, TEM and SEM [159]. Balazs et al. [160] examined the morphology of pitting corrosion in thin Al films evaporated on glass substrates for different compositions of Cl⁻ and Fe³⁺ media; they found that at different compositions of the media, the pits formed have uniform fractal properties.

2.2.3 Oxidation and High-Temperature Corrosion Studies

Aluminium and Al-alloy films have excellent resistance to oxidation and high-temperature corrosion because of their tendency to form a protective Al₂O₃ coatings on their surfaces [161, 162, 163, 164, 165]. In oxidation studies, thin Al films are exposed to a high-temperature stream of air for a given time after which a thermo-gravimetric analysis is undertaken [166]. The corrosion of Al films to high-temperature sulphur-containing media has also been studied [165, 166]. These studies are essential since they evaluate and simulate the corrosion resistance of Al films for applications in petrochemical plants such as heat exchangers, coal-gasification plants, reaction vessels, and turbines.

The general finding from the oxidation studies conducted on thin Al films is that the oxidation rates and mechanisms depend on the temperature of oxidation. High-temperature oxidation on thermally sprayed Al films on 0.11%C steel has been reported [15]. The samples in question were exposed to temperatures up to 1000°C with airflow of 50-ml/min at a heating rate of 10°C/min. The study revealed that at high temperatures gradual oxidation occurs in the thin film, and after exposure to air Al₂O₃ and Fe₂O₃ dominate the coating [15]. Thomas [167] investigated the oxidation of Al films annealed in atmosphere at low and high temperatures, and reported that at low temperatures there was formation of amorphous Al₂O₃ and at high temperatures accelerated oxidation resulting in the formation of structurally ordered Al₂O₃. In some of the oldest studies Krueger and Pollack [168, 169] presented a model to explain low-temperature oxidation in thin Al films and reported formation of amorphous and highly porous films. Maciel et al. [170] observed that when thermally deposited Al film on tin oxide is annealed in air at 500°C, there is formation of tetragonal

Al₂O₃. Initial growth and oxidation of thin Al monolayers sputtered on Ag (111) and annealed up to 500°C has also been reported by Oughaddou et al. [171].

2.3 Electrical properties

As illustrated in Figure 1, thin Al coatings deposited by both PVD and thermal spray techniques find applications in electrical and microelectronics fields. In these applications pure aluminium films are deposited on non-metallic substrates such as silicon semiconductors [172], PET and polyimide (PI) for integrated circuits (IC) and solar cell applications. Specifically, pure aluminium thin films in IC circuits are used to interconnect various isolated components of a circuit on a single substrate. Their application in the electrical field is based on good adhesion to substrates such as silicon/silicon dioxide, and they have low resistivity ($\sim 3 \mu\Omega cm$) [51, 173, 174]. As such, pure aluminium films have been extensively deposited on non-metals and metals as IC interconnections, Ohmic contacts and transistors [51, 173, 175, 176]. When deposited through a vacuum evaporation method on poly methyl meta acrylic (PMMA) thin Al films were shown to provide excellent capacitive properties [177].

The deposition of aluminium on non-metallic substrates for semiconductor devices is associated with challenges such as reactions, electro-migration, corrosion and surface reconstruction [174]). Research emphasis has thus been on property-process investigations with the objective of optimising the electrical performance of thin films [51, 173, 175, 178]. The electrical behaviour of thin films are usually characterised by resistivity, resistivity ratio, sheet resistance and capacitance.

One of the oldest studies [51] investigated the effect of power and deposition rate on the resistivity and resistivity ratio for rf-magnetron sputtered thin aluminium films. It was shown that an increase in rf-power and deposition rate gradually lowers the resistivity to almost that of the bulk aluminium metal. Resistivity is a measure of the opposition to the flow of current by the film, while resistivity ratio is the ratio of room temperature resistivity to measured resistivity at a given temperature. Resistivities and resistance ratios were also investigated for magnetron sputtered Al films on silicon substrates at different deposition rates and thicknesses [175], and the results were comparable to those reported by **D'Heurle** [51]. Another significant finding in these two studies [51, 175] is that the resistivity of thin films deposited through magnetron sputtering was nearly equal to that of the bulk aluminium. The observation implies that this technique (magnetron sputtering) prepares films of high-purity compared to thermal evaporation methods.

Panta and Subedi [179] studied the effect of thickness of thin Al films deposited on a glass substrate using a PVD technique (vacuum evaporation) on electrical resistivity and sheet resistance. The study revealed that an increase in film thickness decreases the resistivity and sheet resistance and increases the electrical conductivity of the films. Zhong and Wang [180] earlier reported on the factors affecting the uniformity of thin Al films on large wafers deposited through PVD sputtering. They reported that target-substrate spacing and process pressure are the most significant parameters affecting aluminium film uniformity and the sheet resistance of films. The effect of deposition rate and film thickness on the resistivity of aluminium films evaporated on an unheated glass substrate has also been presented [181], and the study showed that as the deposition rate increases from 10 to 33 nm/min, the

resistivity decreases from 5×10^{-7} to $3 \times 10^{-8} \Omega m$. It further showed that an increase in film thickness decreases resistivity (although the relationship is nonlinear). Yu-Qing et al. [182] concluded that annealing, crystallinity and crystal size determine the resistivity of thin Al films deposited on a glass substrate through atomic laser deposition.

Al thin films are ideal for integration with flexible microelectronic circuits and sensors. Silva et al. [183] studied this effect by investigating the relationship between resistance and elongation of various textile and polymeric materials coated with thin Al films through magnetron sputtering. The study reported that materials with high stiffness, low elasticity and uniform coatings (such as flexible textiles with PVC coatings), have low variation in resistance to elongation. Similarly, various researchers have investigated the electrical behaviour of aluminium coated polyester fabrics for flexible solar cell applications [184, 185, 186] and reported that electrical properties, resistance, and conductivity vary with the elasticity of the substrates.

Faraj et al. [187] compared the electrical properties of thin Al films deposited on PET by DC magnetron sputtering and evaporation. They reported that samples prepared from DC sputtering have lower electrical resistivity than those developed through evaporation. Pakhuruddin et al. investigated the effect of annealing temperature on the sheet resistance of thin Al films deposited through evaporation on PET [188], and reported that the sheet resistance of Al-coated PET decreases linearly with an increase in annealing temperature. This finding was attributed to the grain growth which takes place with an increase in temperature. Grain growth lowers the density of the grain boundaries and therefore the number of electrons 'lost' within the grain boundaries reduces. This means that most of the electrons are involved in 'electricity transport', and there is a corresponding reduction in sheet resistance. In a current study, Faraji and Ibrahim [189] characterised the structural properties of Al films thermally evaporated on PET and polyimide (PI) substrates, and reported that both samples could be used as back contact layers in thin film silicon solar cells. The crack propagation and electrical behaviour of thin Al film sputtered on PET under stretching were reported by Gahtar et al. [190]. The study found that electrical resistance of thin Al films increases with straining regardless of film thickness.

The electrical properties of thin films of Al-doped ZnO are extensively discussed in the literature [191, 192, 193, 194]; specifically that electrical conductivity of undoped ZnO films is lower than that of Al-doped ZnO [191]. In studies by Ghamdi et al. [192] conducted on the properties of Al-doped ZnO thin films deposited on glass substrates through spin coating at different Al concentrations of the films, it was found that conductivity, mobility carriers and carrier concentration increased with increasing concentration of Al in the ZnO thin films. This indicates that pure aluminium-doped ZnO films have excellent semiconductor properties [195]. However, the addition of dopants to pure aluminium films has been shown to lower electrical resistance in the thin films [38].

Absent in the literature are direct comparisons between the two most used methods, namely sputtering and thermal spray. . Figure 9 shows a comparison of the resistivity values reported at different conditions, according to these two methods. Al films prepared through magnetron

sputtering have higher resistivity than those prepared through thermal methods. However, more direct comparative experiments conducted at similar conditions need to be undertaken to validate this observation and explain the reasons for this trend.

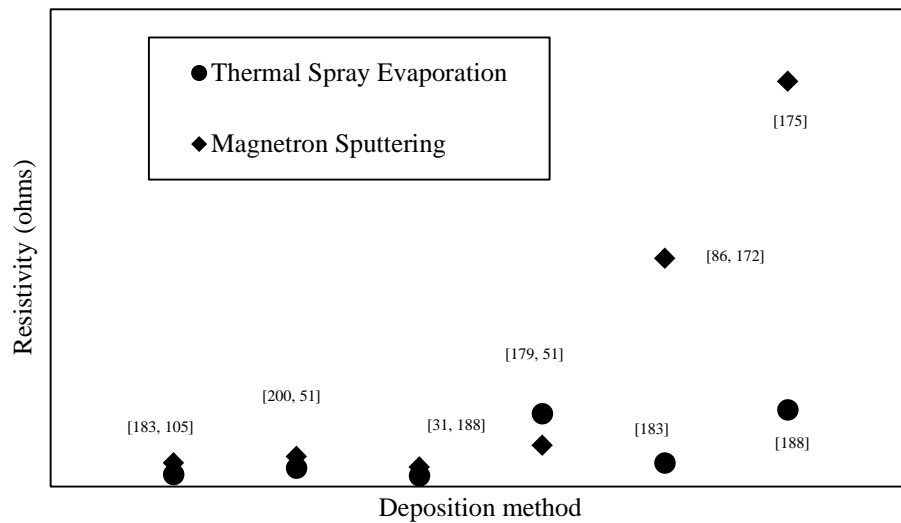


Figure 9. Comparison of resistivity values of thin Al films prepared by thermal spray evaporation and magnetron sputtering methods as reported in the literature

2.4 Optical properties

Optical reflectance, the ability to reflect light energy from a surface, is the most significant property of thin aluminium films. which have a high ability to collect sunlight energy by the use of solar concentrators [196]. **An extensive literature available on optical reflectance of thin Al films shows that the optical properties of the films are significantly influenced by the process parameters** [197, 198]. [197, 198]Table 4 summarises the conclusions of some of the most relevant studies on optical reflectance for physically deposited aluminium thin films over time.

Table 4. Factors influencing optical reflectance of aluminium thin films

Reference/year	Film/substrate	Process parameters/film properties-reflectance investigated	Deposition method	Conclusions
Muralidhar et al. [116]/2016	Al/Polycarbonate	Influence of power and argon gas flow on reflectance of films at different wavelengths	DC magnetron sputtering	There is no linear relationship between power and reflectance at a given gas flow rate. Highest reflectance of 96% reported at 2000W at all wavelengths
Lugolole and Obwoya [196]/2015	Al/Ceramics (clay)	Influence of film thickness on the optical reflectance of the film	Vacuum deposition	Reflectance increases with increase in film thickness. The maximum reflectance of 90% was achieved for the highest thickness of 750 nm.

Fekkai et al. [200]/2014	Al/Glass	Effect of annealing on reflectance of Al films	Vacuum evaporation	Reflectance increases from 93% to 95% when the films are annealed at 300°C
Jing [201]/2013	Al/Quartz	Effects of annealing air on the reflectance of Al films	Thermal evaporation	With the increase in annealing temperature at the constant wavelength (600 nm), there is a gradual decrease in optical reflectance. Reflectance increases with wavelength at a constant temperature.
Pakhuruddin et al. [188]/2012	Al/PET	Effects of annealing temperature on the reflectance of Al films	Thermal evaporation	Increase in annealing temperature at wide range of wavelengths decreases the reflectance of the films; at 80°C , the reflectance was about 73% , while at 200°C , the reflectance was about 70%
Lin et al. [39]/2011 Wöltgens et al. [202]/2009 and Barron et al. [203]/2007	Al-Ti/Glass and Al-Cr/Glass	Effects of addition of Sc, Ti, Cu and Cr into thin Al films reflectance; Effect of annealing on reflectance	DC magnetron sputtering	Doping with Ti or Cr decreases the reflectivity of thin Al films. Addition of Sc and Cu enhances reflectance of the films
Kim et al. [204]/2001	Al-1%Si/Ti/SiO ₂ /(100) Si	Effect of surface roughness on reflectivity; effect of time of exposure to reflectivity; effect of condition of the underlying SiO ₂ on reflectivity	DC magnetron sputtering	For wavelength of 365 nm , reflectivity decreases with increase in surface roughness. Reflectivity changes with time of exposure of the thin Al films (higher values of reflectivity were recorded after four (4) days)
Kylner and Mattsson [205]/1999	Al/Silicon and AlCu/Silicon wafers	Comparative study on reflectance of pure Al and Cu-doped Al films	Thermal evaporation	Over short wavelengths, 200-300 nm , Cu-doped films shows very high reflectance; at high wavelengths, above 500 nm , the reflectance of Cu-doped was nearly equal to that of pure Al films
Nahar and Devashrayee [206]/1985	Al-2%Si/Silicon wafers	Relationships among target voltage, surface roughness and reflectivity	Rf magnetron sputtering	Increase in target voltage increases surface roughness; at constant wavelength of 485 nm , reflectivity decreased with roughness of the films
Kamoshida et al. [207]/1985	AlSi and AlCu/Silicon wafers	Influence of film thickness, argon pressure and substrate temperature on reflectance	DC magnetron sputtering	Increase in film thickness decreases reflectivity; substrate temperature increases reflectivity; No predictable relationship between argon pressure and reflectivity

According to Table 4, film thickness, substrate temperature, annealing conditions, argon gas pressure (for sputtering processes), target voltage, surface roughness, process power and doping are among the main parameters which previous researchers have investigated in relation to the reflectance of thin aluminium films. The effects of sputtering gas composition and distance between target and substrate on the reflectance of the deposited films have also been reported [199]. However, one of the conspicuously missing concepts, which has a significant influence on thin Al films is oxygen partial pressure of the deposition process. Oxygen has been shown to influence the optical properties of alumina thin films, and therefore its effect on pure Al and alloy films should be investigated [208]. The studies summarised in Table 4 have not fully reported on the direct relationship between the microstructural features and optical properties of thin Al films. Future studies on these concepts are necessary for improvement and control of thin Al films for optical applications.

3.0 Conclusion

The characterisation of structural, corrosion, optical and electrical properties for physically deposited thin Al films is comprehensively presented in this review. The properties of thin films were found to depend on substrate conditions, process parameters, and post-processing treatments. As is evident, the existing literature contains rich studies on the properties of physically deposited Al and Al alloy films. However, four gaps for future studies have been identified:

- i. Understanding the oxidation behaviour of Al films at high temperatures is necessary for its potential applications in the petrochemical industry and turbine coatings. Research on the mechanisms of high-temperature oxidation related to thin Al films is limited.
- ii. The increasing demand for thin Al films in coating steel pipelines and heat exchangers makes it imperative that corrosion resulting from the flow of high-temperature fluids (petroleum and steam) is explored and understood. These high-temperature systems find applications in several inter- and multidisciplinary fields, and therefore provides an opportunity for diverse and specialised studies. It is clear from the literature review that the characteristics, mechanisms, parameters and conditions influencing corrosion of physically deposited thin Al films have not been extensively studied.
- iii. Very few comparative studies on physical deposition methods such as thermal spray and physical vapour deposition exist. Such comparisons are important for optimising the deposition methods and preparation processes of Al film. Although thermal spraying has received a lot of research interest and publications, studies on physical vapour deposition are limited. The areas requiring urgent attention include the optimisation of process parameters and conditions influencing the corrosion of thin Al films and corrosion protection of metallic substrates during physical vapour deposition.
- iv. Although the effect of various parameters on properties of thin Al films are reported, the relationship between the properties and conditions of applications are widely explored. Future studies should evaluate the effect of applied stress, current, and time

of exposure on the properties of thin Al films under varying conditions. The influence of fatigue, crack initiation and growth in thin films should also be studied. In the marine and automotive industries where aluminium coated steel is widely used in structural members, thin film exposure to cyclic stresses is critical to assess and comprehensively understand crack initiation and failure. Extensive research is still required in the quest for optimising design and process parameters.

Based on these gaps, this work will be useful in improving research into the properties of thin Al films prepared through physical methods while providing a knowledge base for expanding its applications in high-performance areas.

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