Highly reflective metallic thin films for high brightness LEDs

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NANYANG
TECHNOLOGICAL
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**HIGHLY REFLECTIVE METALLIC THIN FILMS FOR HIGH
BRIGHTNESS LEDs**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

HIGHLY REFLECTIVE METALLIC THIN FILMS FOR HIGH BRIGHTNESS LEDs

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

25/7/2017

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Date

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Abstract

Improving light extraction efficiency is vital for ensuring the performance of high brightness light emitting diodes (LEDs). One of the improvement methods is to electrodeposit highly reflective silver thin films on the leadframe surfaces. Due to stricter rules and regulations, less toxic electrolytes have become more favorable in the plating industries. To date, comprehensive study on the key factors for developing highly reflective Ag films has not been widely explored. This thesis aims not only to develop low cyanide or cyanide-free electrolytes via a detailed understanding of the electrochemical science, but also to build up quantitative correlation between microstructure and reflectance of Ag films.

Firstly, the literature which are relevant to the scope of this thesis are reviewed thoroughly. The recent findings, solutions and current research gap are also highlighted. Despite the increasing environmental pressure as well as health concern on the applications of cyanide, less toxic (low cyanide or cyanide free) silver plating solutions are not widely accepted in leadframe industries due to their poor light reflection performance and solution stability. Therefore, a comprehensive relationship between the microstructure of silver film and its reflectance has to be established. This review has found that more works are needed to improve the silver film reflectivity using less toxic plating solutions.

The first effort starts from the Ag electroplating using a lower concentration cyanide solution ($< 10\text{g/L KCN}$). The electrochemical behaviors of KAg(CN)_2 , KCN , KNO_3 electrolytes and the plating solutions pH were investigated using cyclic voltammetry for the first time. Besides that, suitable working conditions for high speed, low cyanide silver electrodeposition were also proposed. Moreover, Ag thin films were also electroplated under different current densities and their light reflection performance was determined via the reflectance measurement. The structural characteristics of these Ag films were also studied so as to correlate their influence on the films reflectance.

Subsequently, a comprehensive study that correlates the effects of crystal orientation on the reflectance of silver is carried out for the first time. This can be achieved by using single

crystal Ag with different crystal orientation but with controllable surface roughness. 2D (R_a) and 3D (S_{dr}) roughness parameters were used to characterize the surface texture of single crystal silver. It is found that surface roughness plays a more critical role in determining the reflectance while the crystal (100), (110) and (111) orientations have negligible effect on the silver reflectance. Moreover, correlations in predicting the silver reflectance by employing either 2D or 3D roughness parameters as the input variables have also been proposed. Lastly, polycrystalline silvers were used to verify the accuracy of these equations. It is observed that S_{dr} is a better roughness indicator in predicting the reflectance of polycrystalline silver when compared to R_a .

In addition, in order to advance into developing non-cyanide system based on the aforementioned studies, the electrochemical behaviors and the effects of $AgNO_3$, DMH, KOH, KNO_3 , K_2HPO_4 electrolytes and solutions pH on the Ag electrodeposition and dissolution were first investigated by using cyclic voltammetry. Moreover, suitable working conditions for non-cyanide silver electrodeposition were also proposed. The surface and material characteristics of Ag films deposited by non-cyanide solution were also compared with those deposited by low and high cyanide solutions as well as physical vapour deposited silver.

Lastly, the research findings and goals that have been achieved are summarized. Key achievements include the development of low cyanide electroplating chemistry for high speed and highly reflective silver plating, DMH-based non-cyanide electroplating chemistry for highly reflective silver plating and statistical correlations between microstructure and reflectance of silver. This chapter also discusses the implications and limitation of this study and future opportunities such as improving the chemistry, process and performance of non-cyanide silver electroplating chemistry.

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Abbreviations

AC	Alternate Current
AFM	Atomic Force Microscopy
ASD	Ampere per Square Decimetre
A.U.	Arbitrary Unit
BEI	Backscatter Electron Image
BSE	Backscattered Electron
CD	Current Density
CV	Cyclic Voltammetry
DC	Direct Current
DMH	5,5-dimethylhydantoin
DoE	Design of Experiment
EDS/EDX	Energy Dispersive X-ray Spectroscopy
HB LED	High Brightness LED
HDTV	High-Definition TV
IHP	Inner Helmholtz Plane
JCPDS	Joint Committee on Powder Diffraction Standards
LCVD	Laser Chemical Vapour Deposition
LED	Light Emitting Diode
LPVD	Laser Physical Vapour Deposition
OHP	Outer Helmholtz Plane
PVD	Physical Vapour Deposition
R	Reflectance
RGB	Red, Green and Blue
SEI	Secondary Electron Images
SEM	Scanning Electron Microscopy
STM	Scanning Tunneling Microscopy
WOLED	White Organic LED
XPS	X-ray Photoelectron Spectroscopy

XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

Chapter 1

Introduction

Improving light extraction efficiency is vital for ensuring the performance of high brightness light emitting diodes (LEDs). One of the improvement methods is to electrodeposit a highly reflective silver thin film on the leadframe surfaces. Due to stricter rules and regulations, low cyanide or cyanide-free electrolytes become more favorable in plating industry, and a detailed understanding of the electrochemical science is essential for developing the less toxic electrolytes. On the other hand, the quantitative correlation of microstructure and reflectance of Ag films has not been explored. This chapter highlights the motivation, objectives and scope of this research.

1.1 Hypothesis/Problem Statement

Recently, the applications of light emitting diodes (LEDs) as an alternative light source have been increasing rapidly, especially, high brightness LEDs (HB LEDs) have been widely used in many applications. In particular, high light extraction efficiency is one of the critical factors for ensuring the performance of HB LEDs, attempts to improve the light extraction efficiencies are vital for pushing the brightness of LED to a higher level. One of the methods is to reduce the light scattering and enhance light output from leadframes towards the top component by depositing a highly reflective silver thin film on the leadframes surfaces. For decades, the high cyanide silver electrolytes are commonly used to deposit the reflective Ag films on the leadframes. Nevertheless, due to stricter rules and regulations, low cyanide or non-cyanide electrolytes become more favorable in plating industry, a detailed understanding of the electrochemical science is essential for developing the less toxic electrolytes. Besides that, the qualitative relationship between microstructure and brightness of metals have been reported few decades ago, the quantitative correlation of microstructure and reflectance of Ag films have not been explored.

1.2 Objectives and Scope

The main objectives targeted in the study of highly reflective metallic thin films are as follows:

1. To develop low cyanide silver plating formulations for high speed and mirror bright silver electroplating via understanding the electrochemical process of basic electrolytes of silver plating solutions and the role of cyanide in enhancing the reflectance of Ag thin films.
2. To understand the effect of surface morphology, crystal structure, film texture and chemical composition on the optical properties of the plated films.
3. To build up a statistical model to simulate the above correlations for demonstrating the influences of material design, process selection, and surface characteristics on optical properties.

4. Based on the generated understandings, new cyanide-free silver plating formulation and process are developed.

The scope of this research work was confined by three main components, i.e. low cyanide electrolyte, correlation of microstructure and reflectance, non-cyanide electrolyte.

A reflective silver thin film is coated on the leadframe surfaces. The roles of silver film are to enhance the solderability, heat dissipation as well as to reduce the light scattering so that the reflected light output can be further improved [1]. Pure silver metal is known to have high reflectivity of 95 % in the visible light wavelength region and its excellent reflective characteristics can help to improve the LED luminous efficiency [2, 3]. However the reflectivity of the current products in the market is typically below 80%, therefore there is a large room for improving the reflectance of silver thin film coated on leadframes in order to enhance the LED performance. In practical terms, increasing the reflectance of deposited silver to more than 85 % will open more opportunities to improve the light extraction efficiency which in turn enhance the LED performance.

To date, electroplating is the most commonly used method for depositing silver thin films on leadframes in LED industries because electroplating process is relatively inexpensive, efficient, suitable for different geometric shapes and sizes, and does not require advanced equipment and facilities. However, the silver plating baths always contain toxic potassium argentocyanide [$\text{KAg}(\text{CN})_2$] and potassium cyanide salts because of the high bath stability and consistent, high quality of silver deposits obtained from these cyanide baths. From environmental point of view, it will be highly desirable to develop low cyanide or even cyanide-free plating solutions. In this thesis, the low cyanide electroplating chemistry is first developed to obtain the highly reflective Ag films. Furthermore, the cyanide-free electroplating chemistry as an aggressive aim is attempted as well. Cyclic voltammetry is a powerful tool to study the electrochemical behaviors in the electrolytes, in this study, cyclic voltammetric technique is used to understand the electrochemical behaviors and individual and joint effects so as to serve as a guideline to screen the chemical candidates and optimize the operating parameters, and help the formulation development.

This work also aims to establish a comprehensive relationship between the microstructure of silver thin film and its reflectance as well as to propose a statistical model, the study can be achieved by using single crystal Ag with different crystal orientation but with controllable surface roughness. Attention will be paid to the individual impact of the film crystal orientation and surface topological factors, as well as their joint effect.

1.3 Dissertation Overview

The thesis address the highly reflective silver thin films for high brightness LEDs. This thesis contains seven chapters. The first highlights the motivation of this research, research objectives and scopes. Chapter 2 covers the review on LED, optical properties of metals and electroplating processes, and also analyzes the knowledge gaps in the literature. Chapter 3 explains the Ag deposition and material characterization techniques used to deposit the Ag films and study the properties and electrochemical behaviors of basic electrolytes. Chapter 4 investigates the electrochemical behaviors and effects of basic electrolytes and solution pH in low cyanide system by using cyclic voltammetric technique, this chapter also studies the structural characteristics of deposited Ag films so as to initially correlate their influence on the films reflectance. Chapter 5 quantitatively correlate the crystal orientation and surface roughness to reflectance by using single crystal Ag with different crystal orientation but with controllable surface roughness, and also establishes the statistical model of the correlation. Chapter 6 studies the electrochemical behaviors and effects of basic electrolytes and solution pH in DMH-based non-cyanide system by cyclic voltammetry, this chapter also makes comparisons on the surface and material characteristics of Ag films deposited by non-cyanide, low and high cyanide solutions as well as physical vapour deposited Ag films. Chapter 7 summarize the findings, limitations and implications of entire research. The current research goal and opportunities for future work have also been discussed.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Developing low cyanide, high speed and bright Ag plating formulation and process
2. Developing non-cyanide and bright Ag plating formulation and process
3. Studying the electrochemical behaviors and understanding the effects of basic electrolytes and solution pH in low cyanide system and DMH-based non-cyanide system respectively by using cyclic voltammetric technique.
4. Correlating the crystal orientation and surface roughness to reflectance by using single crystal Ag with different crystal orientation but with controllable surface roughness

Chapter 2

Literature Review

This chapter reviews the literature that are relevant to the scope of this thesis: highly reflective metallic thin films for high brightness LEDs. It covers the introduction of LED and LED leadframe, fundamentals of optical properties of metals, factors affecting metal reflectivity, fundamentals of electroplating, laser assisted surface modification, physical vapour deposition, enhancement of reflectance by different measures and thesis in context to knowledge gaps. This review highlights the recent findings, solutions and current research gap. Despite the increasing environmental pressure as well as health concern on the applications of cyanide, less toxic (low cyanide or cyanide free) silver plating solutions are not widely accepted in leadframe industries due to the poor light reflection performance and solution stability, a comprehensive relationship between the microstructure of silver thin film and its reflectance is not established. This review has revealed that works on improving the silver film reflectivity, as well as which plating solutions are less toxic to the environment and widely accepted by plating industries, are still insufficient and the available studies have many limitations.

2.1 Introduction of LED and LED Leadframe

Light Emitting Diodes (LEDs) are p-n junctions that are designed to produce light via electroluminescence [4]. Since the discovery of the first p-n junction in the 1940s, and the first visible red LED was invented in 1962 by Holonyak and Bevacqua [5], LEDs have been rapidly developed and widely utilized for over 70 years, especially in traffic signals, exit signs, imaging displays, automotive signaling, and decorative applications, etc. Nowadays, the term “LED” is universally referred to devices that emit visible light with a very narrow spectral band (400 - 800nm) [6, 7]. There are many different types of light-emitting materials which produce three primary colors, i.e. red, green, and blue (RGB) lights. With these emitters, white light can be generated with either a red-green-blue array or blue-yellow combination; several colors can also be accomplished by blending different colors together (Figure 2.1).

Figure 2.1 The primary three colors - RGB (Red, Green, Blue) and colors mixing chart [8].

In order to assess the prospects of the lighting technologies, multidimensional parameters should be analyzed [7]. Figure 2.2 illustrates the most critical parameters, including lighting efficiency, emission color, driving convenience, manufacturing cost,

environmental concerns and lifetime, and briefly compares the key performance parameters among the available lighting technologies, such as incandescent and fluorescent lamps, inorganic LEDs as well as WOLEDs (white organic LED), etc.

Figure 2.2 The plot shows the comparison of the key performance parameters among incandescent and fluorescent lamps, inorganic LEDs as well as WOLEDs (white organic LED). The data represents commercially available light sources [7].

The basic structure of a LED consists of a light emitting chip, a leadframe where the chip is placed, and the encapsulation epoxy (Figure 2.3). Being one of the key components of LED packaging, the leadframe must have excellent optical, electrical, thermal, mechanical properties [1].

Figure 2.3 Schematic representation of LED structure.

Different approaches have been proposed or applied to enhance the light extraction from LEDs, which A.I. Zhmakin [9] has grouped into two main categories. First, enhancing the light intensity by controlling the flow of the light emitted from the active region through the modification of the chips shapes, reflectors or surface morphologies. Second, modifying the spontaneous emission (microcavity effect or photonic crystals or surface plasmons).

HB LEDs could be realized by using a more reflective metal deposited on the leadframe (Figure 2.4). Among the metallic reflectors, silver is commonly used for HB LEDs [1, 10, 11]. Silver is the best known metallic reflector at visible wavelengths as its excellent reflective characteristics can help to improve the LED luminous efficiency [2, 3]; furthermore, silver possesses excellent electrical conductivity and thermal conductivity [12-16].

Figure 2.4 LED leadframe deposited with silver [17].

The total internal reflection by silver reflectors is the main factor for light extraction efficiency [9]. Currently, at the visible wavelengths, the reflectance of plated silver thin films can only achieve less than 80% of the incident light in the LED industry. However, theoretically, this value is much lower than the maximum achievable reflectance of 95%. Hence, development on improving the reflectance of silver films is very critical for pushing the brightness of LED to higher level.

2.2 Fundamentals of Optical Properties of Metals

The optical properties refer to the responses of materials under the exposure of electromagnetic radiation, especially in the visible light region [18]. When light travels from medium A to medium B, certain wavelengths of the light may be transmitted through the medium B while certain wavelengths of light will be absorbed or reflected at the interface between the medium A and B. In general, the total intensity (I_o) of the incident light to the surface of the irradiated solid medium must equal the sum of the intensities of the transmitted (I_T), absorbed (I_A), and reflected (I_R) light.

$$I_o = I_T + I_A + I_R \quad (2.1)$$

An alternative form of the above equation is

$$T + A + R = 1 \quad (2.2)$$

where T is the transmissivity (I_T/I_o), A is the absorptivity (I_A/I_o) and R is the reflectivity (I_R/I_o). The sum of transmitted, absorbed and reflected light must equal to unity [1, 18-21]. Depending on the radiation wavelengths, the T , A , and R of a medium are different. Figure 2.5 depicts the variation in the transmitted, absorbed and reflected light over the visible light region for a green glass.

Figure 2.5 The fractions of light transmitted, absorbed, and reflected through a green glass depends on the radiation wavelengths [18].

Metals appear to be opaque over the visible light region because the incident light is either absorbed or reflected. When the incident radiation has frequencies within the visible light region, electrons get excited into the unoccupied energy levels, i.e. above the Fermi energy level as depicted in Figure 2.6a. According to Planck's quantum theory, the incident radiation that is absorbed by the electron is $\Delta E = h\gamma$. Metals have continuous available unoccupied energy levels that allow electron transitions from occupied to unoccupied levels when metals absorb all frequencies of visible light. Metals can be viewed visually because of the reflected light which appears when most of the absorbed radiation is reemitted in the form of visible light equivalent to the absorbed wavelengths [18]. Therefore, metals are not only opaque but also highly reflective. Figure 2.6b shows the transition of electron after radiation. Most metals have reflectivity between 90 and 95 %.

Figure 2.6 (a) Schematic diagram of an electron of metal gets excited into a higher and unoccupied energy level after photon absorption. The difference in the energy of the electron before and after excitation is equal to the energy of the photon absorbed. (b) When the electron relaxes back to its stable state, a photon is emitted (redrawn from [18]).

If a metal is highly reflective over the visible light region, the metal appears to be silvery bright under the exposure of white light. Silver is one of the metals that exhibits this reflective behavior [18, 22-24]. As a result, silver thin film has been widely used as high-performance light reflectors in LED and various optical applications [25].

2.3 Factors Affecting Metal Reflectivity

The amount of light reflected off the metal specularly determines the brightness of the metal or its reflecting power [26]. In optics, there is a difference between the terms “reflectivity” and “reflectance”. The reflectivity is used for describing the properties of a pure material or element while reflectance refers to the properties of a particular sample of that material or a particular surface [27]. The reflectivity of silver is about 95 % and is therefore the limiting value of reflectance [28]. Therefore, instead of reflectivity, reflectance is more suitable to refer to the optical properties of deposited silver in this study.

Reflectance of a metal surface in air can be determined by using Eq. (2.3):

$$R\% = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \times 100 \quad (2.3)$$

where reflectance depends on the refraction index (n) and the extinction coefficient (k) of the metal [29].

1) Type of metal and its thickness

Different types of metals give rise to different reflectivity because their n and k values are different. Besides that, depending on the radiation wavelength, even the n and k values of same metal will also change accordingly.

As metals appear to be opaque when exposed to all electromagnetic radiation from the low frequency region to the middle of ultraviolet radiation, the perceived colour of the metal indicates the type of wavelength that is not absorbed or reflected. Metals which are highly reflective over the entire visible range appear to be bright and silvery, e.g. aluminum and silver. For these metals, the composition of the photons absorbed from the incident beam and the composition of the photons emitted from the reflected beam are approximately the same in terms of frequency and number. On the other hand, the colours of copper and gold are reddish orange and yellow respectively, because certain high energy photons are emitted beyond the visible light region [18].

In addition, the reflectance of a silver sample is affected by the sample thickness. Ultrathin layers of silver are transmissive before being reflective [30, 31]. Metal films with thickness $> 10 - 15$ nm are considered as thick films and hence are opaque to visible light [32]. When the thickness of the silver sample is increased, their reflectance will also increase [33, 34].

2) Grain size

Although a small grain size is a crucial condition for brightness and reflectivity, not all fine grained deposits are bright [35]. For example, fine grained deposits which have surface crevices are not bright. It has been reported that the brightness of a deposit depends on the degree to which its surface structural components are in the same plane [36]. In addition to the grain size, brightness is also determined by other factors such as lattice orientation, the degree of the preferred orientation and the codeposition of additives.

3) Crystal lattice orientation

A bright or reflective surface is said to have a certain crystal lattice orientation in which the light reflecting plane lies parallel to the material surface [36]. Silver deposited from silver cyanide complexes always have a basic orientation along $\langle 111 \rangle$ axis. When different complexing agents are used, the preferred orientation of the crystallite can be changed to other axes [37]. The degree of preferred orientation is one of the factors which can affect the surface roughness. Although the relationship between surface roughness and reflectance is found to be proportional, no direct correlation between brightness and preferred orientation has been reported [36].

4) Roughness / surface morphology

Perfectly smooth surfaces allow specular (mirror-like) reflection which obey law of reflection i.e. the angle of incident beam is equal to the angle of reflected beam (Figure 2.7a) whereas rough surfaces causes diffuse reflection as the incident beams are reflected in various directions (Figure 2.7b). Hence, a very smooth surface always appears glossy and mirror-like because the reflected light is concentrated around the specular angle. When the surface roughness increases, reflected light becomes more diffusive so the surface looks

matt or dull [38, 39]. As a consequence, the reflectance of a deposit can also be used to predict its surface roughness [40].

Figure 2.7 Schematic diagram of (a) mirror (specular) reflectance (b) rough surface diffuse reflectance.

5) Wavelength

As discussed in section 2.2, depending on the radiation wavelength, metals respond differently, i.e. their reflectivity varies with the wavelength of incident light [18, 25, 41]. Even though silver has high reflectivity over the visible light region, its reflectivity decreases significantly under the exposure of short optical wavelength radiation, particularly those below 500 nm. This is because in this blue light region, the refractive index of silver is increased slightly which in turn affect the silver reflectivity.

2.4 Fundamentals of Electroplating

The process of depositing a coating in which a desirable form can be obtained via electrolysis is called electroplating [42]. Figure 2.8 is a schematic diagram of electroplating process, the metal ions are reduced by gaining electrons and deposited on the cathode surface (workpiece) to form a metallic coating layer. Its primary objective is to modify the characteristics of the surface of a cathode so as to improve its appearance and to obtain desired properties [42-44].

Figure 2.8 Schematic diagram of electroplating process (redrawn from [45]).

Such electrochemical reactions are governed by Faraday's first law of electrolysis which states that the mass (m) of a substance altered at the electrode during the electrolytic process is directly proportional to the amount of electricity transferred at that electrode. The amount of electricity refers to the amount of electrical charge which is determined in coulomb [43, 46].

$$m = \left(\frac{Q}{F} \right) \left(\frac{M}{z} \right) \quad (2.4)$$

where m is the mass in grams of the substance liberated at the electrode; Q is the total electric charge passed through the substance; F is the Faraday's constant ($\approx 96485 \text{ C mol}^{-1}$); M is the molar mass of the substance; z is the valency of ions of the substance, i.e., the number of electrons transferred per ion.

In the scenario of constant current electrolysis, Eq. 2.4 can be rewrite to

$$m = \left(\frac{It}{F} \right) \left(\frac{M}{z} \right) \quad (2.5)$$

as $Q = It$, where I is applied constant current; t is the total time of the electrolytic process.

Figure 2.9 The scheme of double layer model and electrical potential profile across the double layer formed at the electrode-electrolyte interface (redrawn from [46]).

Figure 2.10 Schematic diagram of the double layer formed at the electrode-electrolyte interface (redrawn from [47]).

In practical electroplating processes, the chemical reaction around the electrode area occurs in a more complicated way than that shown in Figure 2.8. Helmholtz suggested the first

double layer model representing the charged metal surface contacting with an electrolyte in 1879. Based on this model, Gouy and Chapman extended the distance from the electrode surface and proposed the involvement of the diffuse layer. Stern model, appeared in the year 1924, suggested that the electrode - electrolyte interface should include both Helmholtz layers and diffuse layer of Gouy and Chapman [46, 47].

A classic double layer model is presented in Figure 2.9 and Figure 2.10, assuming that the metal electrode is charged negatively. The double layer comprised of two Helmholtz planes, i.e., IHP (inner Helmholtz plane) and OHP (outer Helmholtz plane) and the electrostatic forces of compact layer (IHP + OHP) are very strong. The diffuse layer is developed outside the OHP. The change in the electrical potential across the double layer is depicted in Figure 2.9 [46-48].

The electroplating process is as follows [46]:

- 1) Mass transfer: Under the influence of applied potential, diffusion as well as convection, the hydrated metal ions in the electrolyte will migrate towards the cathode surface.
- 2) Electron transfer: The hydrated metal ions will then enter into the diffuse layer and subsequently into the double layer where they become dehydrated.
- 3) Next, the dehydrated ions are reduced to neutral atoms and adsorbed on the electrode surface.
- 4) Ultimately, the adsorbed atoms nucleate and grow over the electrode surface.

Figure 2.11 shows the general pathway and reactions at electrode surface. Overall, the deposition rate is governed by the rates of the processes including (1) Mass transfer of reactant/product to and away from the electrode interface; (2) Electron transfer at the electrode-electrolyte interface; (3) Proceeding or following chemical reactions; (4) Electrode surface processes (adsorption, or desorption, or electroplating). The deposition rate-determining step is the slowest process [46].

Figure 2.11 General pathway and reactions at electrode surface (redrawn from [46]).

Basically, an electroplating solution (bath) is composed of the metal ions (salt) to be deposited, complexing agent for metal ions, conducting substances, bath stabilizer, pH buffer, additives such as brighteners, leveller and wetter, and anode activator / suppressor, etc [43]. Surprisingly, the amount of additives required is small in plating bath, but their functions are remarkable in terms of changing the properties of the metallic deposit on the cathode. The primary effects of additives include altering the polarization of the cathode, changing the deposit properties and the orientation of crystals, as well as reinforcing the synergism with other additives and extending the current density range, etc [35]. A large variety of additives can be chosen according to their functions and behaviors in the solutions as well as the specific application purposes [49].

2.4.1 Conventional Silver Electroplating Processes

Since 1840 when the first silver electroplating bath was patented, the conventional alkaline electrolyte, i.e. potassium argentocyanide $[\text{KAg}(\text{CN})_2]$ with excess free cyanide¹ has still remained as one of the most commonly used silver plating solutions in the electroplating

¹ Free cyanide refers to the cyanide (added as KCN) that is present in excess to that required to form the silver complexes e.g. $[\text{Ag}(\text{CN})_2]^-$, $[\text{Ag}(\text{CN})_3]^{2-}$ and $[\text{Ag}(\text{CN})_4]^{3-}$.

industries to date due to the ease of operation and silver salt replenishment, high bath stability and consistent, high quality of silver deposits obtained from these baths.

Recently, less toxic chemicals have become more favourable in metal plating processes due to stricter rules and regulations as well as high cost of wastewater treatment. Over the years, compounds such as thiocyanate, nitrate, thiourea, iodide, thiosulphate, pyrophosphate, sulfamate, succinimide and more have been suggested as alternatives to replace cyanides in silver plating solutions [23, 50, 51]. In spite of the less toxicity of these cyanide-free silver plating solutions, most of these electrolytes have limited practical applications in commercial manufacturing processes for several reasons, such as giving rise to Ag deposits with yellow tint, low reflectance, poor adhesion on nickel substrate, bath instability and sensitivity to metallic contamination [37, 52, 53].

Depending on the plating purpose, the bath composition, types of anodes, temperature, pH and current density may differ tremendously. For example, the silver plating solutions could contain as low as 3.5 – 5 g/L (for silver strike) to as high as 35 – 120 g/L (for high speed plating) silver content. In high speed selective plating, insoluble anode (platinised titanium mesh or platinum wire) is commonly used instead of the soluble silver anode.

2.4.2 Role of Cyanide in Silver Electroplating

Cyanide-free silver plating formulations have been available for decades and some even claimed to be able to produce bright silver deposits [54-57]. Despite the increasing environmental pressure as well as health concern on the applications of cyanide in commercial electroplating process, there are several reasons for the manufacturers to stay with cyanide in silver plating until today.

First, besides acting as a conducting salt, free cyanide is also a very good complexing agent which does not only complex silver ions but also other metallic impurities that inevitably present in the plating solution. Ag is usually plated on Cu or Ni-plated Cu substrates. Electrochemically, Ag ($E^\circ = + 0.799 \text{ V vs. NHE}$) is a noble metal when compared to Cu ($E^\circ = + 0.34 \text{ V vs. NHE}$) and Ni ($E^\circ = - 0.257 \text{ V vs. NHE}$) [58]. When Cu or Ni-plated Cu

substrates are immersed into a solution containing Ag ions, a displacement reaction will occur between the substrate surface and plating solution, causing the Cu and Ni to dissolve into the plating solution while Ag is precipitated out of the solution. Normally, Ag will be deposited as a non-adherent spongy deposit while Cu and Ni ions from the substrate will contaminate the plating solution. When free cyanide ions are present in the plating solution, CN^- ions complex with Ag^+ ion to form $\text{Ag}(\text{CN})_2^-$ complex ($E^\circ = -0.31 \text{ V vs. NHE}$) [59]. Cu or Ni becomes more noble than $\text{Ag}(\text{CN})_2^-$ complex so the displacement reaction will not occur between the substrate surface and plating solution. Furthermore, since free cyanide will complex with these metallic impurities, consistent quality of Ag deposit can be achieved even if these impurities have built up over time.

Second, cyanide-containing silver plating solution produces white and bright silver deposit which is always the requirements of end users. Silver cyanide complexes increase the cathode polarization and promote the growth of fine grained deposit [45]. When free cyanide complexes with silver ions, the equilibrium potential is shifted to more negative because the activity of free Ag ions is reduced. Since silver cyanide complexes are less noble than free Ag ions, silver cyanide complexes are more difficult to be reduced electrochemically, hence slowing down the rate of electrodeposition. This helps to contribute to fine-grained deposit by affecting the crystal growth. On the other hand, the presence of free cyanide also helps to promote the dissolution of silver anode when silver anode is utilized as the main source of Ag in some plating process.

Furthermore, cyanide solutions also offer good throwing power. Throwing power indicates the degree of metal thickness distribution over a substrate surface contour [60]. Solutions with high throwing power are favorable in plating process because they ensure uniform deposit on plated parts, especially on those with complex geometries as well as uneven current distribution.

On the other hand, cyanide-free silver plating solutions often make use of the weak chelating agent which only forms weak complexes with the metallic impurities. As a result, poor silver deposits are always formed in aging cyanide-free silver plating solutions as these metallic impurities are co-deposited with silver.

The weak silver complex formed in cyanide-free silver plating solutions have also increased the activity of free Ag ions which instead facilitate the displacement reactions between substrate and silver ions, releasing more metallic impurities into the plating solutions. Moreover, the huge potential difference between free Ag ions and Ni has also caused the Ag plating on Ni difficult, resulting in Ag films with poor adhesion on Ni.

On the other hand, the abilities of free cyanide to complex with metallic impurities have helped to maintain high bath stability over several months and ensure consistent coatings qualities. In short, it is the excellent complexing properties of cyanide which can be hardly substituted by non-cyanide compounds, refrain the wide implementation of cyanide-free silver plating solutions in plating industries.

Recent development on bright cyanide-free silver plating formulations for industrial use has been proposed and so far satisfactory plating results have only been reported on copper substrate [61-64]. In addition, the authors only determine the brightness of the plated Ag film qualitatively as only visual studies were performed. The adhesion issues of Ag films on Ni surface still remained unresolved in employing cyanide-free silver plating solutions, indicating much more work is needed towards the development of cyanide-free silver plating.

2.5 Laser Assisted Surface Modification

Laser - an acronym originated from “Light Amplification by Stimulated Emission of Radiation”. Laser devices emit light energy in large quantities and in controlled form. Basic laser device consists of two mirrors which are positioned parallel to one another to form a chamber in which the light will oscillate back and forth between the mirrors and a medium in which the light oscillations can be amplified by the mechanism of stimulated emission, Figure 2.12. The stimulated emission is a process by which an excited electron drops to its lower energy level when it interacts with an incoming photon of particular frequency. The transition of the excited electron from a higher to a lower energy level creates an additional photon identical to the photon of the incident wave in terms of its frequency, phase,

polarization and direction. Hence, by a series of stimulated emission, the incident photon can create light amplification, Figure 2.13.

Figure 2.12 Basic construction of a laser cavity.

Figure 2.13 Schematic diagram of stimulated emission.

As laser beam is an electromagnetic radiation which only penetrates the first few atomic layers of metals and the laser beam can be positioned precisely on the materials surfaces, laser has been widely used as a cost-effective tool for modifying or improving the surface and physical properties of materials. When a specific area of metal surface is radiated by laser beam, its temperature begins to increase as thermal energy from the laser beam is conducted into the metal. The structural properties such as crystal orientation of the metal begin to change when its critical transformation or transition temperature has been reached. After removing the laser beam from the metal surface, quenching from the bulk of the

metal has induced a cooling effect as they are only barely heated by this rapid heating process.

Although laser surface treatments have been mainly applied for improving the resistance to corrosion or wear initially, laser processing has extended its applications to surface heating (for phase transformation annealing or hardening), surface melting (for homogenization and refinement of microstructure, etc), laser induced plating by LPVD (Laser Physical Vapour Deposition) and LCVD (Laser Chemical Vapour Deposition), surface marking, surface roughening, etc [65]. This technique could be potentially useful for modifying the surface topology of silver deposits for the current project.

2.6 Physical Vapour Deposition (PVD)

PVD is a vacuum deposition process whereby the vapours of desired material, usually metals, is deposited on the substrate by condensation (Figure 2.14). The metals deposited are usually few nanometers to several micrometers thick. Three fundamental steps are always employed for depositing the metal on substrate despite there are several methods for vaporizing the desired material, including thermal evaporation, sputtering, pulse-laser, electron beam and more. First, the desired metal is vaporized from its source in high temperature vacuum or in the presence of gaseous plasma. Second, the metal vapours are transported to the substrate surface. Third, vapours condense on the substrate surface to form a thin film.

Figure 2.14 Scheme of Physical Vapour Deposition (PVD).

PVD is very useful in the fabrication of microelectronic devices, interconnects, optical and conductive coatings, surface modification etc [66]. PVD is also an environmental friendly deposition technique as toxic chemical solutions are not necessary in this process. Compared to electroplating, metal of very high purity can be deposited because impurities are less likely to co-deposit with the metal coatings during PVD process. On the other hand, the compositions of the deposited film can also be modified via the reaction with reactive gas such as oxygen [67].

Nonetheless, PVD requires advanced equipment and facility. PVD is also not very suitable for depositing materials with complex geometries. As a result, silver spot electroplating process is still commonly implemented by manufacturers for mass production of leadframes for LEDs. In the current work, PVD deposited Ag films are going to be used mainly to understand the effect of surface morphology and crystalline factors on the reflectance.

2.7 Enhancement of Reflectance by Different Measures

From section 2.3, it can be said that the structure and morphology of a metal determine its optical properties. Several treatments or additives which can modify or alter the growth and the morphology of the metallic deposits can thus be employed in order to enhance their reflectance.

1) Substrate surface conditions

Besides the surface morphology of the deposited metal, the substrate surface conditions are also critical in determining the quality and the reflectance of the metallic deposits. This is because the substrate surface morphologies and properties affect the growth of the deposits, which in turn affects the reflectance of the plated films [68]. In addition, during electroplating, the current density is not distributed homogeneously on the substrates with irregularly geometric shape. Hence, the metallic deposits always have non-uniform thickness on a non-even surface. Processes which give rise to smoother and more uniform surfaces help to enhance reflectance.

2) Pretreatment

Pretreatment process depends on the type of substrates and particular application requirements. Typical pretreatment processes include alkaline cleaning, microetching, metallic strike / undercoat, and activation. In general, these pretreatment steps are taken to improve the surface morphology of the substrate prior to plating process, which in turn can improve the quality and the reflectance of deposited metal.

Mechanical pretreatment such as polishing, roughening, abrading and grinding can also be utilized to alter the surface morphology of a substrate as well, but their effects are limited [35, 43].

3) Additives

Most plating baths contain one or more organic or inorganic additives that have specific functions in changing the properties of metallic deposits. These additives can be categorized as brightener, leveller, and wetter etc, depending on their functions in the plating process. They are usually added with a concentration range of about 10^{-4} - 10^{-2} M. Sometimes, these additives can also be incorporated in the deposited layer.

It is known that smoother or homogeneous surface can enhance reflectance. In this case, the levelling effect of certain additives can be used to improve the homogeneity of the deposited metal. These kind of additives are called levellers, which help to reduce the surface roughness of metals by preferentially adsorb on protrusions due to locally different current densities between recess areas and protrusions [35]. In this way, they inhibit or slow down the crystal growth at these areas while allow thicker deposits to form in small recesses where larger current densities are focused [42, 43, 69].

Other than leveling, some additives have brightening effect which changes the light reflectance from the deposited metals. The use of brighteners helps to produce fine grained deposits which have certain oriented crystal structure. The crystal size is typically much smaller than the visible light wavelength, i.e. < 400 nm [35, 70].

Despite the amount of the additives or dopants added into the plating baths is relatively small, they have significant impacts on microstructure, grain size and preferred lattice orientation, so as to change the reflectance of the metallic deposit.

Table 2.1 Composition of different electrolytes (concentrations in g l⁻¹) [37].

Reagent	Electrolyte							
	1	2	3	4	5	6	7	8
AgNO ₃	25	30	30	25	—	25	25	—
AgCl	—	—	—	—	20	—	—	—
Ag ₂ SO ₄	—	—	—	—	—	—	—	25
K ₄ Fe(CN) ₆ · 3H ₂ O	70	57	—	—	—	—	—	—
K ₂ CO ₃	30	—	—	8	—	—	—	—
KCN	—	23	23	45	—	—	—	—
KSCN	150	150	150	—	—	—	—	—
KNaC ₄ H ₄ O ₆ · 4H ₂ O	60	60	60	—	—	—	—	—
Na ₂ SO ₃ · 5H ₂ O	—	—	—	—	70	—	—	—
NaHSO ₃	—	—	—	—	10	—	—	—
Na ₂ SO ₄	—	—	—	—	20	—	—	—
EDTA sodium salt	—	—	—	—	—	200	—	—
NH ₄ NO ₃	—	—	—	—	—	40	—	—
NH ₄ OH	—	—	—	—	—	(pH 10)	—	—
NH ₄ SCN	—	—	—	—	—	—	250	—
H ₃ BO ₃	—	—	—	—	—	—	20	—
KI	—	—	—	—	—	—	—	250

Table 2.2 Characteristics of deposits versus different electrolytes with varying current density [37].

Electrolyte	$A\ dm^{-2}$	Texture
1	0.1–0.25	$\langle 111 \rangle + \langle 511 \rangle + \langle 311 \rangle$
	0.5	$\langle 111 \rangle + \langle 511 \rangle$
	0.75–1.0	random orientation
2	0.1–0.75	$\langle 111 \rangle + \langle 511 \rangle + \langle 311 \rangle$
	1.0	$\langle 111 \rangle + \langle 511 \rangle$
	1.5	random orientation
3	0.1–0.5	$\langle 111 \rangle + \langle 511 \rangle + \langle 311 \rangle$
	0.75	$\langle 111 \rangle + \langle 511 \rangle$
	1.0	$\langle 111 \rangle + \langle 511 \rangle$ poor perfection
	1.5	random orientation
4	0.1–0.25	$\langle 111 \rangle + \langle 511 \rangle + \langle 311 \rangle$
	0.5–0.75	$\langle 111 \rangle + \langle 511 \rangle$
	1.0–1.25	random orientation
5	0.1–0.25	$\langle 111 \rangle + \langle 511 \rangle$
	0.5	$\langle 110 \rangle$
6	0.1	$\langle 311 \rangle + \langle 755 \rangle$
	0.25	$\langle 100 \rangle$
	0.5	$\langle 110 \rangle$
7	0.1–0.75	random orientation
8	0.1–0.5	$\langle 211 \rangle + \langle 522 \rangle + \langle 2211 \rangle$
	0.75–1.0	$\langle 100 \rangle + \langle 221 \rangle$

4) Bath composition

In conjunction with the effect of additives, the complexing agent of a metal ion also controls the structural characteristics of the metallic deposits. Previous studies by other research groups have showed that the grain growth and the crystal lattice orientation depend on the complexing agents of silver ions [37, 71, 72]. Structural analysis reported by Kristev and Nikolova have found that the texture of silver was mainly along $\langle 111 \rangle$ axis and some included $\langle 311 \rangle$ when silver was electrodeposited from cyanide baths as well as non-cyanide bath (Table 2.1 and Table 2.2). Besides that, in non-cyanide baths, other orientations such as $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 211 \rangle$ were normally developed instead.

The reflectance of a metal surface can also be enhanced if the number of crystal lattice orientation which is parallel to the light reflecting plane is developed relatively larger than other orientation on the surface of metallic deposits [36].

5) Electroplating parameters / conditions

Other than the additives and bath composition, several attempts such as optimizing the electroplating parameters and conditions are also effective in controlling the grain growth, crystal size, lattice orientation and surface morphology of the deposited metals [53, 60, 73]. Generally, smooth and fine grained deposits are vital for improving the light reflection.

a) Temperature

The crystal size and the composition of the deposit can be altered by changing the temperature [74]. In general, increasing the bath temperature always causes an increase in the crystal size by enhancing the solubility, which in turns increases the transport number of the reacting species as well as the conductivity of the solution. This helps to make the replenishment of the double layer to proceed relatively faster and sufficiently.

b) Current density

On the other hand, increasing the current density decreases the crystal size of the deposit. When the current density is increased, the rate of nucleation will be increased which in

turns decreases the size of crystals [75]. Although increasing the current density helps to form fine grained deposit, once the current density used approaching the limiting current density, the chances of forming spongy and burnt deposits are increased as well because side reactions such as hydrogen evolution may happen in parallel with the electroplating process.

c) pH

pH must always be maintained and optimized during the deposition process because pH can affect the equilibrium between different complexes in the solutions. The shift in equilibrium will change the composition of the deposits as well as the grain size [74]. Besides that, the hydrogen evolution potential, the adsorption of additives and the removal of complexing agents from the metal prior to plating are also influenced by the pH of the solutions.

d) Agitation

Strong agitation facilitates the replenishment of metal ions at the cathode by reducing the thickness of diffusion layer. Moreover, strong agitation also reduces the gas bubbles formation which can lower the pits formation on the surface of deposits. This will help to improve the homogeneity of the metallic deposits [76].

6) Influence of metal thickness

In contrast to thin films which are transmissive to light, thick metal films are opaque to visible light and hence they are more reflective. Even though the reflectivity can also be enhanced by increasing the thickness of a metal with smooth surface, in the fabrication of leadframes for LEDs, the thickness of silver film is only about 2 – 2.5 μm . As a result, development focuses on controlling the crystal growth of silver deposit might allow further increase in the reflectance.

7) Laser surface treatment

By scanning a metal surface with a laser beam, the metal surface temperature begins to rise as thermal energy is conducted into the metal. The crystal structure of a metal can begin to realign when its critical transition temperature has been reached. Hence, laser treatment might be used to produce well-defined and controllable crystal lattice orientation which favors high surface reflection.

2.8 Thesis in Context to Knowledge Gaps

It is known that cyanide-free silver plating formulations could not produce Ag deposits with shiny appearance although several research groups have claimed to have developed bright silver deposits from cyanide-free silver plating formulations [61-64]. Nonetheless, their studies do not involve quantitative measurement on the optical properties (i.e reflectance) of the Ag films. The limited brightness of Ag films deposited from cyanide-free silver plating solutions might also be one of the reasons why cyanide-free silver plating solutions are not widely accepted in leadframes industries as the light reflection performance of Ag films is very critical in the LEDs applications.

The relationship between the microstructure and brightness of electroplated nickel has been reported few decades ago [36]. This study has shown the effect of grain size, crystal texture and surface morphology of nickel surface on its light reflecting capability or brightness.

On the other hand, the structural criteria for a metal surface to show mirror-brightness is previously characterized by Nikolic et al. via their scanning tunneling microscopy (STM) as well as atomic force microscopy (AFM) studies [26, 77, 78]. First, mirror-brightness is governed by flat and mutually parallel parts of the metal surface which exhibit smoothness at the atomic level. Second, mirror-brightness surfaces should have the distances of about several atomic diameters between the adjacent flat parts of the surface. Although their work has focused on the surface structural characteristics on the reflection of mirror silver on glass, the thickness of their silver coatings is not clearly specified and the relationship between the crystal growth or orientation of silver and its reflection is not examined [77].

Therefore, this work aims to establish a comprehensive relationship between the microstructure of silver thin film and its reflectance as well as to propose a statistical model of this correlation. Four coating prototypes using different deposition methods will be used for the investigation: (1) Ag films electroplated from low cyanide silver plating formulation; (2) PVD deposited highly reflective Ag thin films; (3) Ag films electroplated from conventional high cyanide silver plating formulation; (4) Ag films electroplated from cyanide free silver plating formulation. The PVD deposited Ag will be used a benchmark to compare with the Ag films deposited from electroplating process. Attention will be paid to the individual impact of the film crystal orientation and surface topological factors, as well as their joint effect.

Chapter 3

Experimental Methodology

This chapter describes the experimental methods for material characterization, Ag film deposition and physical property tests executed in Chapter 4, 5 and 6. The techniques and theories used for the characterization of the Ag thin films by atomic force microscopy (AFM), scanning electron microscopy (SEM), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and x-ray fluorescence (XRF), the electrochemical studies on the electrolytes by cyclic voltammetry as well as the physical properties (reflectance, hardness and resistivity) of the Ag thin films are discussed. The experimental details of customized spot plating machine and physical vapour deposition used for deposition of Ag films are also highlighted in this chapter.

3.1 Material Characterization

3.1.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is one of the most frequently used microscopy technique for studying specimen at nanoscale because this technique requires very minimum sample preparation. Besides that, either conductive or non-conductive specimen can be studied by AFM. AFM does not only provide various information on surface measurement, three-dimensional (3D) topography of the specimen can also be generated at atomic resolution with nano down to angstrom scale resolution height information.

In AFM, a cantilever with a very sharp tip is used to probe a specimen surface. When the cantilever tip approaches a surface, an attractive force between the surface and tip will cause the cantilever to deflect towards the specimen surface. However, when the cantilever tip is brought even closer to the surface, to the extent that the tip touches the specimen surface, a repulsive force overwhelms the attractive force and this will cause the cantilever to deflect away from the surface.

The degree of cantilever deflection towards or away from the specimen surface will then be detected by a laser beam deflection system (Figure 3.1). A photo-sensitive and position sensitive detector collects the reflected laser beam signal from the back of the reflective AFM lever where direction of the signal is dependent on the cantilever deflection. In this way, the peak and valley feature of a surface can be captured by the cantilever tip and the 3D topography of that surface feature can be generated [79].

Figure 3.1 AFM cantilever tip and laser beam deflection system (redrawn from [79]).

The surface roughness of samples in this work was measured using atomic force microscope (AFM, DI-3100, Digital Instruments).

3.1.2 Scanning Electron Microscopy

High magnification images with good depth of field can be obtained by Scanning Electron Microscope (SEM). In comparison to traditional optical microscope, a high resolution SEM can magnify closely spaced compound down to few Angstroms. The elemental composition of a specimen can also be determined when SEM is used in conjunction with energy dispersive X-ray (EDX). Nowadays, SEM is commonly used in fields including medicine, geology, life science, metallurgy and etc.

High resolution and high magnification images of a specimen can be obtained by SEM because images are magnified by electrons instead of light as used in an optical microscope. SEM consists of an electron gun, anode, magnetic lens, apertures, detector and display (Figure 3.2a). Electron gun produces a beam of electron which travels through several electromagnetic fields, condenser lenses and an objective lens. Typically, field emission (FE) electron gun is preferred for probing the surface because they provide high beam brightness which gives rise to higher resolution.

Condenser lenses and objective lens focus the electron beam before they hit the specimen. After that, backscattered electrons, secondary electrons and X-rays will be emitted from the specimen when the electron beam hits the specimen (Figure 3.2b). Detector collects the signals from these emitted electrons and convert them to image.

When highly energetic electron beams strike the atoms of the specimen, inelastic and elastic collision occur. Backscattered electrons are emitted from elastic collision while secondary electrons are emitted from inelastic collision.

Backscattered electrons give rise to the compositional contrast of an SEM image, i.e. it gives the information about the elemental composition in a specimen by varying the grey colours or levels in an SEM image. On the other hand, secondary electrons give rise to the

topographic contrast of an SEM image by mapping the geometric features of a specimen surface.

Figure 3.2 (a) Schematic of SEM components (b) Backscattered electrons, secondary electrons and x-ray (redrawn from [80]).

Detector converts electrons to images via the aid of a scintillator. Scintillator converts electrons to photons and these photons are amplified in a photomultiplier tube. The output from the photomultiplier is then further amplified for image display.

In all the experiments in this thesis, surface morphology of plated surface was observed under scanning electron microscope (SEM, JSM-6360A, JEOL).

3.1.3 X-Ray Diffraction

The crystal structure of a compound can be determined by using X-ray diffraction (XRD). XRD is a powerful tool which can be used to differentiate various phases of a crystalline compound with same composition. Besides that, the grain size, crystal lattice parameters, chemical composition and lateral structure of a compound can also be estimated by XRD.

When two parallel light waves with same wavelength travel in the same direction, they can be either in phase or out of phase. When the phase difference between two light waves is $n\lambda$ where n is an integer, constructive interference occurs (Figure 3.3) [81]. However, when

the phase difference is $n\lambda/2$, destructive interference occurs. These wave interference characteristic is employed in XRD determination and is described by Bragg's Law (Eq. 3.1).

$$n\lambda = 2d\sin\theta \quad (3.1)$$

Figure 3.3 Geometry for interference of a wave scattered from two planes (redrawn from [81]).

The angle of incidence of two parallel light waves is θ and the interplanar spacing, d describes the difference in path length for the light waves scattered from top plane and from bottom plane. The difference in path lengths for incident and scattered light waves is $2d\sin\theta$. Strong diffraction or constructive wave interference occurs when the difference in path length is $2d\sin\theta = \lambda$.

According to Bragg's Law and wavelength of incident light, the spacing between atomic planes of a compound can be determined when constructive interference occurs at specific incident angle. Crystal structure of a compound can be deduced from the diffraction patterns.

The chemical composition of a compound can also be deduced based on the crystal plane indices (hkl) at certain incident angle θ as many literature data has determined and published by International Center for Diffraction Data (ICDD).

XRD system consists of X-ray source, slits, sample stage, counter and detector. X-ray is the light wave used to determine the crystal structure of a compound. X-ray is produced from the collision between electrons and metal target (copper or molybdenum). When

highly energetic electrons collide with the metal target, an inner shell electron is excited to a higher energy state. The vacancy of this electron will be filled by an outer shell electron. Figure 3.4 depicts the formation of characteristic X-ray. When outer shell electrons from L and M fill the vacancies left by inner shell electrons from K, characteristic K_{α} and K_{β} X-radiation are formed. Typical CuK_{α} and MoK_{α} wavelengths are $1.5418 \text{ \AA}$ and $0.7107 \text{ \AA}$ respectively.

Figure 3.4 Schematic illustration the formation of characteristic K_{α} and K_{β} X radiation.

X-Ray diffraction (XRD, D8 Bruker Advance) with Cu K_{α} radiation is used to determine the crystal structures of plated silver and physical vapour deposited silver while Thin Film XRD (XRD-6000, Shimadzu) with Cu K_{α} radiation was used to confirm the single crystal structures.

3.1.4 X-Ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) is a powerful tool for not only identifying elemental composition of a specimen but also the chemical state of the elements. In addition, the relative elemental composition can be determined as well as the images or maps of the distribution of the elements and their chemical states can be generated in XPS. XPS is also especially useful when depth profile analysis is required.

The primary source of radiation in XPS is X-rays. Typically, the X-ray radiation used in most commercial XPS equipment is either Mg K_{α} (1253.6 eV) or Al K_{α} (1486.6 eV). When a specimen is radiated by X-ray with certain photon energy $h\nu$, an inner shell electron is ejected, resulting in a phenomenon called photoemission (Figure 3.5). The kinetic energy

(E_K) of the ejected electron is then analyzed by the electron spectrometer. The kinetic energy (E_K) is not dependent on the types of sample but it is dependent on the photo energy of X-ray ($h\nu$). The binding energy (E_B) of the electron, which is an intrinsic property of an element and its chemical state can then be determined by Eq. 3.2, where W refers to the work function of X-ray photoelectron spectrometer [82].

$$E_B = h\nu - E_K - W \quad (3.2)$$

Figure 3.5 Schematic diagram of the photoemission when a specimen is radiated by X-ray (redrawn from [82]).

The compositional profile of the silver films was investigated by X-ray photoelectron spectroscopy (Thermo Scientific, ESCALab 250Xi). The samples were scanned by Al K α (1486.6 eV) radiation.

3.1.5 Cyclic Voltammetry

Cyclic voltammetry is one of the most commonly used electroanalytical techniques for studying the electrochemical reactions of electroactive species. Cyclic voltammetry is widely used in electrochemistry because this technique can be used to determine the redox potentials of the electroactive species in a system. Besides that, it can be used to obtain valuable kinetic information about the electrochemical reactions occur at the electrodes [83].

Cyclic voltammetry is carried out by an electroanalytical system which consist of a potentiostat, electrochemical cell, current-to-voltage converter and a data acquisition system. The electroactive species or electrolytes are put inside an electrochemical cell which consists of a working electrode, counter electrode and a reference electrode (Figure 3.6).

Figure 3.6 An electrochemical cell consists of a working electrode, counter electrode and a reference electrode.

The working electrode potential is always measured against a reference electrode in order to ensure that constant potential has been applied. The counter electrode minimizes the potential drop in reference electrode by allowing the current to pass through it.

In cyclic voltammetry, potentiostat constantly changes the applied potential at working electrode versus the time in cyclical manner (Figure 3.7). The resulting current response is then shown in the cyclic voltammogram (Figure 3.8). Electrochemical reactions at the working electrode involves electron transfer, for example Ox/Red system as shown in Eq. 3.3. This reaction is affected by the electrode potential.

Figure 3.7 The applied potential at working electrode is constantly changed versus the time in cyclical manner.

Figure 3.8 Typical cyclic voltammogram.

Reversible reactions are governed by Nernst equation (Eq. 3.4) where E^0 is the standard redox potential for the couple reaction involves the oxidized (Ox) and reduced (Red) species, R is the molar gas constant ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), n is the number of electron transferred, F is the Faraday constant (96485 C/mol) while C is the concentration of the oxidized and reduced species [84].

$$E_{cell} = E^0 + \left(\frac{RT}{nF}\right) \ln\left(\frac{C_{Ox}}{C_{Red}}\right) \quad (3.4)$$

The rate of an electrochemical reaction is governed by several factors:

- 1) Mass transfer from the bulk solution to the electrode surface.
- 2) Rate of electrode transfer at the electrode surface.
- 3) Chemical reactions preceding or following the electron transfer.
- 4) Surface reaction such as adsorption or desorption.

The step that controls the rate of an electrochemical reaction is known as rate-determining step.

In this thesis the electrochemical studies of silver electrodeposition and dissolution were performed in a conventional three electrode cell using a computerized potentiostat (797 VA Computrace, Metrohm) at room temperature. Polished platinum rotating disk (Metrohm, A = 0.0314 cm²) was used as the working electrode. During the experiments, a Ag/AgCl (3 M KCl) reference electrode was mounted in an electrolyte vessel filled with 1 M KNO₃ solution and used as a double junction reference electrode. All potential referred to this electrode. A platinum rod which represented the insoluble anode in industrial practice was employed as the counter electrode. All the silver electrodeposition and dissolution processes were studied at angular speed (ω) of 1200 rpm. The cyclic voltammetry scan rate was 50 mVs⁻¹. Before each measurement, the electrode was cleaned in deionized water, followed by 50% HNO₃ solution and 10% KOH solution as well as rinsed with deionized water. After that, the electrode was sonicated in deionized water for 5 min before use.

3.1.6 X-Ray Fluorescence

X-ray fluorescence (XRF) is a powerful and non-destructive analytical method which does not only measure the thickness but also determine the elemental composition of a material. XRF is used in a broad range of applications as the samples can be liquids, solids or powders [85, 86].

Typically, XRF method requires no or simple sample preparation. Moreover, it gives fast qualitative and quantitative results, normally within seconds or minutes.

In XRF, a material is radiated by primary X-radiation. Electron from the inner electron shells is ejected and vacant energy level is left behind. Electron from outer shell then fall into the inner shell, emitting a fluorescence radiation with energy equivalent to the energy difference between the outer and inner electron shells (Figure 3.9). This fluorescence radiation is a characteristic of a particular element and can be detected by a detector.

Figure 3.9 X-ray fluorescence radiation is a characteristic of a particular element (redrawn from [85]).

During the thickness determination of a coated material, both coating layer and substrate give out fluorescence radiation. However, the coating layer diminishes the radiation arises from the substrate. The types and thickness of a coating determine the degree of its effect on the fluorescence radiation from the substrate. In this way, a correlation can be determined between the fluorescence radiation emitted from the coating and its thickness.

In the experiments reported in this thesis, the nickel and Ag thickness was measured by fluorescent x-ray coating thickness measurement gauge (Seiko SFT 9300).

3.2 Ag Film Deposition

3.2.1 Spot Plating Machine

Customized spot plating machine shown in Figure 3.10, was utilized for high speed silver spot plating. The substrate used was brass panel (Kocour) and the silver spot film ($A = 0.785 \text{ cm}^2$) was dc jet-electroplated on the substrate by following the process flow in Figure 4.1. In order to prevent Cu from diffusing into the Ag film, a layer of Ni is always plated before the Ag plating. The Ni thin film thickness was controlled within $0.55 - 0.75 \text{ }\mu\text{m}$ in the current work.

The silver plating bath was made up by 120 g/L $\text{KAg}(\text{CN})_2$, 6g/L KCN, 4.25 mL/L Heliofab Ag-920 B1, 15.6 mL/L Heliofab Ag-920 B2, 500 mL/L Heliofab Ag-920 C where Heliofab Ag-920 B1, B2 and C were the proprietary additives. The bath was kept at $57 \text{ }^\circ\text{C}$ and the flow rate was about $3.4 - 3.5 \text{ L/min}$ while the current densities (CD) used for silver plating were $5 - 100 \text{ ASD (Amps/dm}^2\text{)}$. The plating time was varied so that the thickness of silver spot film was maintained around $2 - 2.5 \text{ }\mu\text{m}$ for each current density used.

Figure 3.10 Spot plating machine (a) front view (b) side view.

Filter pump system removes foreign particles and by-products, circulates and agitate the chemical solution, supplies high pressure jet spray onto the substrate for plating. Rectifier

supplies direct current (DC) for electrodeposition. Temperature controller maintains temperature within the desired range.

3.2.2 Physical Vapour Deposition

PVD is a vacuum deposition process whereby the vapours of desired material, usually metal is deposited on the substrate by condensation (Figure 2.14). The metals deposited are usually few nanometers to several micrometers thick. Three fundamental steps are always employed for depositing the metal on substrate despite there are several methods for vaporizing the desired material, including thermal evaporation, sputtering, pulse-laser, electron beam and more. First, the desired metal is vaporized from its source in high temperature vacuum or in the presence of gaseous plasma. Second, the metal vapour is transported to the substrate surface. Third, vapours condense on the substrate surface to form a thin film.

PVD is very useful in the fabrication of microelectronic devices, interconnects, optical and conductive coatings, surface modification etc. PVD is also an environmental friendly deposition technique as toxic chemical solutions are not necessary in this process. Compared to electroplating, metal of very high purity can be deposited because impurities are less likely to co-deposit with the metal coatings during PVD process. On the other hand, the compositions of the deposited film can also be modified via the reaction with reactive gas such as oxygen.

Nonetheless, PVD requires advanced equipment and facility. PVD is also not very suitable for depositing materials with complex geometries. As a result, silver spot electroplating process is still commonly implemented by manufacturers for mass production of leadframes for LEDs. In the current work, PVD deposited Ag films are going to be used mainly to understand the effect of surface morphology and crystalline factors on the reflectance.

Physical vapour deposited silver films were prepared using UDP 550 - 4, TCL. Similar to the electrodeposition, a layer of Ni (0.55 – 0.75 μ m) was electrodeposited on the brass

panels following the same procedures. Next, middle frequency hydrogen plasma etching was used to remove native oxides so as to leave a clean and chemically balanced Ni surface. The etching time is 30 min at 8.0×10^{-4} torr. After that, alternate current (AC) sputtering was used to deposit the Ag films. The chamber was kept at 1.7×10^{-3} torr and the working conditions were 50 Hz, 60 V and 0.2 A. The thickness of each Ag film was controlled around 2.0 – 2.5 μm .

3.3 Physical Properties

3.3.1 Reflectance

When light travels from medium A to medium B, certain wavelengths of the light may be transmitted through the medium B while certain wavelengths of light will be absorbed or reflected at the interface between the medium A and B. In general, the total intensity (I_o) of the incident light to the surface of the irradiated solid medium must equal the sum of the intensities of the transmitted (I_T), absorbed (I_A), and reflected (I_R) light (Eq. 2.1), or, the sum of transmitted, absorbed and reflected light must equal to unity (Eq. 2.2).

There are two types of reflected light, one is resulted from the specular reflection and another one is resulted from diffuse reflection. Specular reflection is also known as mirror reflection, whereby all incident light is reflected at same angles from the normal incidence in accordance with law of reflection. On the other hand, diffuse reflection occurs when the reflected lights reflect in an unpredictable manner from the normal incidence.

Reflectance measurements [87, 88]

By definition, reflectance is the ratio of reflected light intensity over incident light intensity. It is measured by spectroscopic reflectometer (Raditech) at a light incidence angle of 0° . Silicon-based wafer was used as the reference and the intensity change of light reflected from the surface of Ag/Ni/brass samples were measured as a function of wavelength ($\lambda = 300 \text{ nm} - 1000 \text{ nm}$) at normal incidence as shown in Figure 3.11. The total reflectance was collected and analyzed. Reflectance readings were only taken at $\lambda = 450 \text{ nm}$ (blue light)

and 550 nm (yellow-green light) because these two wavelengths were more critical in the LED application.

Figure 3.11 Spectroscopic reflectometer measures total reflectance while incidence angle is 0° .

3.3.2 Hardness

Hardness describes the ability of a material to resist permanent deformation when an external compressive force is applied. Generally, hardness test is performed by penetrating an indenter probe into a surface under a specific load for certain dwell time. The hardness is then determined by the size and depth of the indentation (Figure 3.12). The types of sample will affect the contact depth (h_c) to be different from the displacement depth (h) because the surrounding parts will become elastically deflected during the indentation.

There are several hardness test methods, for example, Microhardness test, Vickers Hardness test, Knoop hardness test, Brinell hardness test, Moh's hardness test, Rockwell hardness test, etc.

The microhardness test is usually used for small and thin specimens or films and it is performed with loads equal to or less than 10 N or 1 KG. Typically, the indenters used in microhardness test are similar to the Vickers indenter (Figure 3.13 a) or the Knoop indenter (Figure 3.13 b). Precision microscopes with a magnification of about X500 are used to determine the indentations of the probe [89, 90].

Figure 3.12 The types of sample will affect the contact depth (h_c) to be different from the displacement depth (h).

Figure 3.13 (a) Vickers indenter (b) Knoop indenter.

The hardness of the Ag films electrodeposited by low cyanide and high cyanide solutions were measured by Micro Hardness Tester (Shimadzu HVM-2) with a 50 g load.

3.3.3 Resistivity

Four point probe is one of the most commonly used and convenient tool for the measurement of resistivity of a conductive object [91-93]. The tool is consisted of four spring loaded probes assembled in a straight line with equal spacing between the adjacent probes (Figure 3.14).

When a constant current is applied between two probes and the potential drop V between these two probes will be measured by a high impedance voltmeter. In this way, the resistance (R) of a conductive object can be determined by ohms law. In addition, at constant temperature, the resistance (R) of a conductive object is directly proportional to its length (L) while inversely proportional to its cross sectional area (A) as illustrated in Eq. 3.5 [2].

$$R = \rho \frac{L}{A} \quad (3.5)$$

where ρ is the resistivity in Ohmmeter (Ωm) of that specific conductive object.

In the experiments reported in this thesis, a four-point probe (CMT-SR2000N, AIT) was used to measure the resistivity of the Ag samples electrodeposited by low CN and high CN solutions.

Figure 3.14 The arrangements of four probes that measure voltage (V) and supply current (A) to the surface of the crystal.

Chapter 4

Processing and Characterization - *Cyclic Voltammetric Study of High Speed Silver Electrodeposition and Dissolution in Low Cyanide Solutions

The electrochemical processes in silver solutions with significantly much lesser amount of free cyanide (<10 g/L) than the conventional silver solutions were explored by cyclic voltammetry for the first time. The electrochemical behavior of $KAg(CN)_2$, KCN, KNO_3 electrolytes and solution pH were firstly studied. After that, suitable operating conditions for high speed, low cyanide silver electrodeposition were also proposed based on their effects on silver electrodeposition rate. Besides that, Ag thin films were also electroplated under different current densities and their light reflection performance was determined via the reflectance measurement. Lastly, the structural characteristics of these Ag films were also studied so as to correlate their influence on the films reflectance.

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4.1 Introduction

Silver coatings electrodeposited using cyanide-based solutions have existed for more than one century. Cyanide has played an important role in the silver electrodeposition processes. However due to stricter rules and regulations, as well as high cost of wastewater treatment, less toxic chemicals have become more favorable in most metal plating processes. Over the years, compounds such as ammonia [94, 95], uracil [61], HEDTA [96], 2-hydroxypyridine [97, 98], hydantoin [99], 5,5-dimethylhydantoin [100, 101], and more have been suggested as alternatives to replace cyanides in silver plating baths. In spite of the benefits for using low toxicity cyanide-free silver plating baths, most of these electrolytes have limited practical applications in commercial manufacturing process for reasons such as relatively higher cost, low bath stability, high sensitivity to temperature and metallic contamination, low deposit quality and brightness, and poor adhesion on substrates [61, 102-105].

Hence, the conventional alkaline electrolyte i.e. silver cyanide complex $[KAg(CN)_2]$ with excess free cyanide (i.e., NaCN or KCN salt in excess of that required to form silver cyanide complexes) remains one of the most commonly used systems in the electroplating industries to date. Besides being a conducting salt, cyanide is also an excellent complexing agent which does not only complex Ag ions but also other metallic impurities (especially copper and nickel ions) that are inevitably present in the plating solutions due to the displacement reaction between the substrate and solution ions. Impurities build up over time as Cu or Ni dissolves into the plating solution while Ag precipitates out of the solution. The free cyanide in the solutions will complex with these metallic impurities, thereby ensuring high bath stability and longer bath life. In this way, consistent high quality of Ag deposit can be obtained.

Furthermore, with the aid of suitable additives such as brighteners and levelers, cyanide-based silver solutions also improve the roughness and inhomogeneity of coatings because of their good throwing power, thus producing consistently high quality of white or bright deposits [45, 106]. High throwing power is very critical for giving rise to uniform deposit

on parts with complex geometries because of the uneven current distribution on these parts during electrodeposition.

On the other hand, weak chelating agents are normally used in cyanide-free silver plating solutions. In aging bath, they only form weak complexes with the metallic impurities so most of these impurities are co-deposited with silver, causing poor silver deposits. Besides that, weak silver complexes also facilitates the displacement reactions between substrate and silver ions because of the increased activity of free Ag ions in cyanide-free silver plating solutions. This in turn releases more metallic impurities into the solutions.

As a consequence, manufacturers still tend to stay with cyanide-based solutions due to their high bath stability, ease of operation and consistently high quality of silver coatings. Implementing cyanide-free plating solutions in manufacturing industries remains a great challenge [101].

Electrodeposited silver has been playing important roles in decorative applications and electronics industries for decades. In response to the high demands in advanced electronics products, good quality silver plating at high speed has become a critical step in the manufacturing process. Moreover, new applications in electronics and semiconductor industries have also encouraged the development of new silver chemistries for high speed selective plating, such as mirror bright silver spot plating on leadframes.

Similar to conventional alkaline silver electrolytes, high speed silver plating solutions usually have high potassium cyanide content (45 – 100 g/L) and are not suitable for selective or spot plating [107]. In high speed silver spot plating on leadframes, the leadframes are plated with silver to give a bondable area on the lead finger to allow second bond to form subsequently. This area must be slightly larger than the size of second bond. Insoluble anodes such as platinised titanium mesh or platinum wire are commonly used as only the tip of lead finger is plated for bonding [108]. Oxidation and polymerization of cyanide [109] at these insoluble anodes have caused rapid degradation of the high cyanide silver plating solutions.

Hence, it would be desirable if the negative effect of cyanide be minimized while at the same time the high quality of silver coatings could be maintained consistently. Besides that, because of the low cyanide content, the accumulation of carbonates could be slowed down. As a consequence, the low cyanide silver bath life could also be extended.

In this work, the silver electrochemical processes in solutions consists of a much lower amount of free cyanide (< 10 g/L KCN) than the conventional alkaline silver electrolytes were first explored by using cyclic voltammetric technique. The electrochemical behaviors and effects of the basic electrolytes (silver salt, potassium cyanide and conducting salt) and solution pH on the electrodeposition and dissolution processes were also investigated. In addition, the optimum working conditions for high speed silver electrodeposition in low cyanide system were also proposed. The characteristics such as morphologies, brightness, conductivity and hardness of Ag films electrodeposited by low cyanide system were also studied.

4.2 Experimental Methods

4.2.1 Chemicals and Plating Conditions

Chemicals used were Potassium silver (I) cyanide ($\text{KAg}(\text{CN})_2$), Potassium nitrate (KNO_3), Potassium cyanide (KCN), Nitric acid (HNO_3), Potassium hydroxide (KOH). All solutions were prepared with deionized water. pH of the solution was adjusted by using either 1 % HNO_3 or 1 % KOH solutions.

Brass hull cell panel was used as a substrate for silver electrodeposition. All the pretreatment, Ni as well as Ag electrodeposition chemicals used are proprietary products provided by MacDermid Enthone. Before deposition, the brass was cleaned in the Enprep 110 EC, Enprep 220 EC and Actane 345. After that, the brass was electrodeposited with a layer of nickel ($2 - 3 \mu\text{m}$) by using Heliofab Ni-370. Next, a thin layer of Ag was electrodeposited on the Ni/Brass panel by using two types of silver solutions, i.e. low cyanide silver solution or conventional high cyanide silver solution. The low cyanide silver solution was made up of 120 g/L $\text{KAg}(\text{CN})_2$, 6 g/L KCN, 120 g/L KNO_3 , 5 mL/L XRD

Ag-7000 B1 and 16 mL/L XRD Ag-7000 B2, while the high cyanide silver solution was consisted of 100 g/L $\text{KAg}(\text{CN})_2$, 150 g/L KCN, 6 g/L KOH, 20 g/L K_2CO_3 , 5 mL/L Heliofab Ag-900 C & T and 3 mL/L Heliofab Ag-900 H. The electrodeposition conditions followed the optimum parameters as recommended in the XRD Ag-7000 and Heliofab Ag-900 technical datasheets. The pH of the freshly prepared silver solutions were adjusted to about pH 10 - 12 for both low and conventional high cyanide solutions.

The current densities used for the electrodeposition are 0.6 A/cm^2 for low cyanide system and 0.03 A/cm^2 for conventional high cyanide system. The deposition time of the two systems was adjusted so that the Ag films had a similar thickness at $2.0 - 2.5 \text{ }\mu\text{m}$.

4.2.2 Cyclic Voltammetric Analysis

The electrochemical studies of silver electrodeposition and dissolution were performed in a conventional three electrode cell using a computerized potentiostat (797 VA Computrace, Metrohm) at room temperature. Polished platinum rotating disk (Metrohm, $A = 0.0314 \text{ cm}^2$) was used as the working electrode. During the experiments, a Ag/AgCl (3 M KCl) reference electrode was mounted in an electrolyte vessel filled with 1 M KNO_3 solution and used as a double junction reference electrode. All potential referred to this electrode. A platinum rod which represented the insoluble anode in industrial practice was employed as the counter electrode. All the silver electrodeposition and dissolution processes were studied at angular speed (ω) of 1200 rpm. The cyclic voltammetry scan rate was 50 mVs^{-1} . Before each measurement, the electrode was cleaned in deionized water, followed by 50% HNO_3 solution and 10% KOH solution as well as rinsed with deionized water. After that, the electrode was sonicated in deionized water for 5 min before use.

4.2.3 High Speed Silver Spot Plating

Customized spot plating machine shown in Figure 3.10, was utilized for high speed silver spot plating. The substrate used was brass panel (Kocour) and the silver spot film ($A = 0.785 \text{ cm}^2$) was dc jet-electroplated on the substrate by following the process flow in Figure 4.1. In order to prevent Cu from diffusing into the Ag film, a layer of Ni is always plated

before the Ag plating. The Ni thin film thickness was controlled within $0.55 - 0.75 \mu\text{m}$ in the current work.

Figure 4.1 Process flow and operating conditions of Ni and Ag plating on brass.

The silver plating bath was made up by 120 g/L KAg(CN)₂, 6g/L KCN, 4.25 mL/L Heliofab Ag-920 B1, 15.6 mL/L Heliofab Ag-920 B2, 500 mL/L Heliofab Ag-920 C where Heliofab Ag-920 B1, B2 and C were the proprietary additives. The bath was kept at 57 °C and the flow rate was about 3.4 – 3.5 L/min while the current densities (CD) used for silver plating were 5 – 100 ASD (Amps/dm²). The plating time was varied so that the thickness of silver spot film was maintained around 2 – 2.5 μm for each current density used. The thickness of Ag film was measured by fluorescent x-ray coating thickness measurement gauge (Seiko SFT 9300). 20 samples were plated under same operating conditions and used for measuring the average reflectance unless specified.

4.2.4 Reflectance Measurements

Reflectance is measured by spectroscopic reflectometer (Raditech) at a light incidence angle of 0° . Silicon-based wafer was used as the reference and the intensity change of light reflected from the surface of Ag/Ni/brass samples were measured as a function of wavelength ($\lambda = 300 \text{ nm} - 1000 \text{ nm}$) at normal incidence as shown in Figure 3.11. The total reflectance was collected and analyzed with respect to the reference. Reflectance readings were only taken at $\lambda = 450 \text{ nm}$ (blue light) and 550 nm (yellow-green light) because these two wavelengths were more critical in the LED application. The reflectance of five locations on each Ag surface was taken and the average reflectance of 20 samples plated under same current density was then determined.

4.2.5 Thin Film Characterization

In order to correlate the relationship between the surface structural characteristics of plated Ag films and their optical properties, Ag thin films with different determined reflectance of 20%, 50%, 70%, 80%, 90% and 95% were plated by using different current densities. The surface morphology and purity of the Ag/Ni/brass samples were observed and measured with SEM/EDS (JSM - 6360A, JEOL) while their surface roughness were measured by using AFM (DI - 3100, Digital Instruments). Furthermore, X-ray diffraction analysis was also conducted for characterizing the crystal orientation of plated Ag films. XRD Thin Film (XRD - 6000, Shimadzu) with Cu K_α radiation (40kV, 30 mA) was used. The samples were scanned continuously at $2^\circ 2\theta \text{ min}^{-1}$. A four-point probe (CMT-SR2000N, AIT) was used to measure the resistivity of the Ag samples. The hardness of the Ag layer was measured by Micro Hardness Tester (Shimadzu HMV-2) with a 50 g load.

4.3 Results and Discussion

4.3.1 Cyclic Voltammetry of Ag/Ag⁺ at Rotating Disk Platinum Electrode

The voltammetric studies of KAg(CN)_2 , KNO_3 , KCN electrolytes and solutions pH were performed over the platinum rotating disk electrode in order to analyze the different redox processes and to determine the suitable working potential range for silver electrodeposition.

Rotating disk electrode was used in the experiments because it gave an agitation to the solution which could reduce the thickness and prevent the impoverishment of diffusion layer lying between the bulk solution and the working electrode surface, thereby ensuring uniform deposition.

Figure 4.2a shows the redox reactions of 120 g/L $\text{KAg}(\text{CN})_2$ in the absence or presence of KNO_3 and KCN . During the 1st scan cycle of 120 g/L $\text{KAg}(\text{CN})_2$, it is observed that a drastic increase in the cathodic current appears at ~ -0.41 V (Figure 4.2a, peak C1) and an anodic reaction occurs at ~ -2 mV (Figure 4.2a, peak A1), corresponding to the silver electrodeposition and silver film dissolution respectively. An additional cathodic peak C2 become pronounced around -50 mV during the 2nd scan cycle (Figure 4.2b). This may be due to the incomplete silver dissolution during the first anodic scan, giving rise to the presence of oxidized and non-dissolved silver film on the platinum surface from the beginning of next scan [110].

In contrast to the onset potential of silver electrodeposition at 1st scan cycle, the reduction of silver ions starts at a more positive potential from the 2nd scan cycle onwards, which is at ~ -280 mV. As platinum working electrode (which is different from the deposited metal) is employed, the initiation of nucleation normally consumes more energy to produce the first nucleus [111]. Besides that, the presence of non-dissolved silver film on the electrode may also facilitate the nucleation and growth processes during the 2nd scan cycle.

The addition of supporting electrolyte KNO_3 into 120 g/L $\text{KAg}(\text{CN})_2$ solution has significantly lowered the cathodic current density of silver reduction as a steady-state limiting current is achieved when compared to that occurs in the $\text{KAg}(\text{CN})_2$ solution without supporting electrolyte. This is because the migration effect of silver ions is minimized in the presence of supporting electrolyte.

It is clear that in the presence of KCN , the onset potential of silver electrodeposition is shifted to more negative values (Figure 4.2a peak C3) while the silver dissolution wave (peak A2) becomes broader and the anodic current density reaches plateau before it drops abruptly. When the vertex potential of cathodic scan is raised to more negative values, the

amount of silver deposited is enhanced as depicted by the increase in the dissolution wave areas in Figure 4.2c. The cyclic voltammogram also shows a characteristic hysteresis which appears after potential sweep reversal. This is the characteristic of metal nucleation or growth on working electrode [112]. In addition, steady-state limiting current of silver electrodeposition is achieved around -0.83 V and the proton reduction or hydrogen evolution is noticed to occur beyond ~ -0.86 V. Any deposition carried out beyond these negative potentials might produce silver film with pitting and adhesion defects [105, 113]. As a result, the silver electrodeposition process will only be examined in the range more positive to -0.8 V in this study.

Assuming that only $\text{Ag}(\text{CN})_2^-$ complexes exist in the solutions and all silver atoms come from this complex, the charge transfer of silver electrodeposition in Figure 4.2a, peak C1 and C3 can be described by Eq. 4.1. The difference in the free cyanide concentration in the solution has induced the change in the onset potential of electrodeposition. On the contrary, the dissolution of Ag (peak A2) can also be represented by the reverse reaction of Eq. 4.1.

However, several chemical steps such as the dissociation of cyanide ions, reduction of silver ions and removal of cyanide ions from the electrode/electrolyte interface may take place simultaneously as well. Another situation that involves the partial or complete dissociation of $\text{Ag}(\text{CN})_2^-$ anion is shown in Eq. 4.2 – 4.5 [114]. The cathodic peak C2 shown in Figure 4.2b corresponds to Eq. 4.5 where the reduction of non-dissolved Ag film occurs.

Figure 4.2 Cyclic voltammograms of (a) silver electrodeposition and silver dissolution in the absence and presence of KNO_3 and KCN ; (b) 120 g/L $\text{KAg}(\text{CN})_2$ only; (c) the influence of cathodic vertex potential in 120 g/L $\text{KAg}(\text{CN})_2$, 6 g/L KCN and 120 g/L KNO_3 solutions. Arrows show the potential sweep direction. Initial potential = + 0.6 V. Sweep rate: 50 mVs^{-1} . C1, C2 and C3 denote the cathodic peaks while A1 and A2 correspond to the anodic peaks.

In fact, the silver electrodeposition process in cyanide system involves more complicated mechanisms because of the formation of more than one silver complex i.e. AgCN , $\text{Ag}(\text{CN})_2^-$, $\text{Ag}(\text{CN})_3^{2-}$, $\text{Ag}(\text{CN})_4^{3-}$, which equilibrium concentration and the predominant species that take part in the charge transfer process rely on the cyanide concentration in the solutions [115]. When the free cyanide is insufficient, the dissolution of Ag (Figure 4.2b, peak A1) may proceed in the reverse direction of Eq. 4.5.

4.3.2 The Effect of $\text{KAg}(\text{CN})_2$ Concentration on the Electrodeposition of Ag

Figure 4.3a shows the effect of $\text{KAg}(\text{CN})_2$ concentration on the silver electrodeposition as well as silver dissolution. When the amount of $\text{KAg}(\text{CN})_2$ is increased from 60 to 200 g/L in the solutions containing 6 g/L KCN, the onset potentials of silver electrodeposition are shifted towards more positive values (Figure 4.3b). In other words, as the source of silver increases, the cathodic polarization is lowered. When the amount of KCN remains constant, increasing $\text{KAg}(\text{CN})_2$ concentration will increase the number of silver cyanide complex ions as well as the silver cations in the solution, thus lowering the cyanide coordination number of silver complex, enabling the deposition to proceed more easily.

Moreover, higher $\text{KAg}(\text{CN})_2$ concentration enables higher current densities as well as larger amount of silver deposited, resulting in higher electrodeposition rate (Figure 4.3c). This also implies that large amount of silver salt is critical for high speed silver plating. Deposition rate is determined by Eq. 4.6:

$$\text{Deposition rate} = \frac{QM_{\text{Ag}}}{F\rho_{\text{Ag}}At} \times 10^4 \text{ (}\mu\text{m/min)} \quad (4.6)$$

where Q (C) is the charge involved in the silver dissolution; M_{Ag} (= 107.8682 g/mol) is the molar mass of silver; F (= 96485.3365 C/mol) is the Faraday Constant; ρ_{Ag} (= 10.49 g/cm³) is the density of silver; A (= 0.0314 cm²) is the Pt electrode area; t (min) is the deposition time during the cathodic sweep.

Figure 4.3 (a) Cyclic voltammograms of silver electrodeposition and silver dissolution in the solutions consisted of 6 g/L KCN, 120 g/L KNO_3 and 60 – 200 g/L KAg(CN)_2 . Inset: The current response of second anodic peak increases with increasing KAg(CN)_2 concentration during the anodic scan. (b) The effect of KAg(CN)_2 concentration on the onset potential of silver electrodeposition. (c) The influence of KAg(CN)_2 concentration on the electrodeposition rate in the sweeping potential range from + 0.6 V till – 0.7 V.

It is observed that one main silver dissolution wave and one shoulder peak appear during the anodic scan (Figure 4.3a). At low cyanide (6 g/L KCN) and high KAg(CN)_2 (>120 g/L) concentration, the dissolution waves of silver cover a broad potential range and achieve a steady-state limiting current. This may be due to the rate limiting steps which are involved in the cyanidation of dissolved silver.

On the other hand, the splitting of the dissolution wave can be due to the formation of different silver complex in the solutions. Increase in the KAg(CN)_2 concentration has also raised the anodic peak current at ~ -31 mV (Figure 4.3a inset). This shoulder peak is attributed to the formation of AgCN as the concentration of free cyanide available in the solution is insufficient to form soluble silver complex. This is even more noticeable when the amount of deposited Ag increased with increasing KAg(CN)_2 concentration while the free cyanide concentration remains constant.

4.3.3 The Effect of KCN Concentration on the Electrodeposition of Ag

It has been shown in Figure 4.2 that in the presence of KCN, both silver electrodeposition and silver film dissolution reactions are clearly shifted towards more negative potentials. Depending on the cyanide concentration in the solution, the coordination number of silver cyanide complexes and the predominant complex ions will change accordingly following Eq. (4.7 – 4.10) [116]. The species that are involved in the charge transfer process not only rely on the cyanide concentration, but also on the operating conditions. Previous studies [117, 118] had reported that it was the AgCN that is involved in the charge transfer when free cyanide $[\text{CN}^-]$ was in the concentration range of less than 0.1 M (2.6 g/L), whereas Ag(CN)_2^- complex took part in the charge transfer step when $[\text{CN}^-] > 0.2$ M (5.2 g/L). At high cyanide concentration, $[\text{CN}^-] > 0.9$ M (23.4 g/L), Ag(CN)_3^{2-} complex was suggested to be the species that are involved in the charge transfer process. On the other hand, the impedance study by Baltrunas [119] had showed that Ag(CN)_2^- complex is always involved in the direct charge transfer step regardless the cyanide concentration and the composition of the solutions.

Generally, due to the strong complex-forming effect between the cyanide ions and silver ions, the cyanide ions will shift the equilibrium potential to more negative values and increase the activation polarization by reducing the activity as well as the concentration of the free Ag^+ ions [45]. As a result, in contrast to the effect of increasing the $\text{KAg}(\text{CN})_2$ concentration, the higher the KCN concentration, the more negative the potential required to deposit silver coating on platinum electrode (Figure 4.4). The difference in the onset potential of silver electrodeposition between the solutions containing 6 g/L KCN and 0 g/L KCN was about - 0.38 V. Unlike cyanide-free silver electrolytes, cyanide-based silver electrolytes with the addition of suitable brighteners always produce white and bright silver deposits. This is because the increase in the cathodic polarization has helped promoting the growth of fine-grained deposits [45]. Moreover, silver cyanide complexes help to minimize the effects of metallic contaminants on the deposit quality. Metallic contaminants are accumulated because of the displacement reaction between Cu or Ni-plated substrates and Ag ions. Fine-grained deposit is the one of the requirements for giving rise to highly reflective Ag thin films.

From the kinetic point of view, the electrodeposition process involves multiple processes [120], i.e. mass transfer, electron transfer, Ag ion reduction and Ag nucleation on the cathode surface. The deposition rate is governed by the slowest rate of these processes. Slow and controllable deposition rate is critical for obtaining fine-grained deposits. The formation of silver cyanide complex slows down the mass transfer process in the bulk solution because silver cyanide complex ions ($\text{Ag}(\text{CN})_2^-$) are bigger than Ag ions (Ag^+) in terms of molecular size. Hence, the movement of $\text{Ag}(\text{CN})_2^-$ in the bulk solution is slower than that of Ag^+ . In addition, $\text{Ag}(\text{CN})_2^-$ carries negative charge while Ag^+ carries positive

charge, the mass transfer of $\text{Ag}(\text{CN})_2^-$ to the cathode direction in the bulk solution under the applied potential will be slowed down due to repulsive effect.

High level of free cyanide is necessary in order to maintain consistent and high quality of silver coatings in industrial practice. However, in the case of high speed selective plating where insoluble anodes are commonly employed, the silver plating solution should contain only as much free cyanide as necessary so that the formation of insoluble AgCN [121] at the anodes, which will impede the current flow, can be avoided.

According to Figure 4.4, less than about 45 g/L KCN in a solution consisted of 120g/L $\text{KAg}(\text{CN})_2$ and 120 g/L KNO_3 will ensure that the potential required to initiate the silver electrodeposition will not occur in parallel with the hydrogen evolution reaction. Since it is critical that only very low and necessary amount of KCN should be used in developing the new silver plating chemistry, 4 – 8 g/L KCN in the low cyanide region (< 10 g/L) is found suitable under existing given $\text{KAg}(\text{CN})_2$ and KNO_3 concentrations because slightly drop or increase in the KCN concentration will not significantly affect the polarization of the working electrode and thereby the plating solutions will be easier to control during operation.

Figure 4.4 The effect of KCN concentration on the onset potential of silver electrodeposition. The silver plating solution is consisted of 120 g/L $\text{KAg}(\text{CN})_2$, 120 g/L KNO_3 and 0 – 160 g/L KCN. Inset: The onset potential of silver electrodeposition in the range of 0 – 10 g/L KCN.

4.3.4 The Effect of KNO_3 Concentration on the Electrodeposition of Ag

As mentioned previously, addition of supporting electrolyte KNO_3 into the solution containing 120 g/L $\text{KAg}(\text{CN})_2$ has lowered the cathodic current density significantly. The same behavior is also observed in the solution consisted of 120g/L $\text{KAg}(\text{CN})_2$ and 6g/L KCN in Figure 4.5a. The higher the KNO_3 concentration, the lower the cathodic current density and as a consequence lesser silver is deposited on Pt electrode. The decrease in the dissolution peak areas with increasing KNO_3 concentration has also suggested that KNO_3 can be used to adjust the rate of electrodeposition process at constant applied potential, as shown in Figure 4.5b.

Figure 4.5 (a) Cyclic voltammograms of silver electrodeposition and silver film dissolution in the silver plating solution consisted of 120 g/L $\text{KAg}(\text{CN})_2$, 6 g/L KCN and 0–180 g/L KNO_3 . (b) The effect of 0–180 g/L KNO_3 on the deposition rate by sweeping the potential from + 0.6 V to – 0.7 V.

The cathodic current density in the absence or at a low concentration of KNO_3 , is obviously larger than that at higher concentration because the migration of the Ag^+ towards the working electrode during the cathodic scan has enhanced the faradaic current. At high concentration of KNO_3 , K^+ migration replaces that of Ag^+ and thus the observed faradaic current is mainly contributed by the diffusion current [122]. In this way, KNO_3 can improve the conductivity of the solution and it can also be used to control the deposition rate if required during application.

On the other hand, unlike $\text{KAg}(\text{CN})_2$ and KCN , KNO_3 does not alter the onset potential of electrodeposition process significantly. Moreover, in contrast with the influence of KNO_3 on the current density of silver electrodeposition, increasing $\text{KAg}(\text{CN})_2$ concentration has the opposite effect in which the current density increases with increasing silver ion concentration at constant potential. In other words, adding more KNO_3 salt may help to reduce the operating current density required for silver electrodeposition at high silver concentration. Normally, the high current density approaching the diffusion limiting current is not recommended in industrial practice because of the inverse effects due to the depletion of silver ions in the double layer and the high possibility of causing hydrogen evolution, leading to rough and poor deposit [123].

4.3.5 The Effect of Bath pH on the Electrodeposition of Ag

Silver cyanide complexes are known to be unstable at very low pH because of the formation of insoluble AgCN . This has imposed that the silver cyanide solution must be maintained in alkaline condition. Figure 4.6a and b show that increasing pH of the silver electrodeposition solution from pH 8.1 to pH 10 has shifted the onset of electrodeposition potential of silver to more negative direction and then remains constant in the range of pH 10 – 12. pH less than 9.0 has greater impact on the onset of silver electrodeposition potential. Maintaining appropriate pH range is essential to ensure the stability and solubility of silver cyanide complexes in the solution, which influence the deposition process and in turn affect the deposition quality.

On the other hand, the silver dissolution starts at around -0.65 V, there is one main dissolution peak, followed by a shoulder peak. At $\text{pH} > 9$, silver dissolution is dominated by the main peak around -0.35 V while the shoulder peak is much smaller. On the other hand, the shoulder peaks around 1.0 mV are considerably large when the solution pH is lower than pH 9.0. These peaks are positioned at the same potential with the oxidation peak of $\text{KAg}(\text{CN})_2$ solution as depicted in Figure 4.2b. This suggested that at $\text{pH} < 9$, the presence of $[\text{Ag}(\text{CN})_2]^-$ is very pronounced at the platinum electrode.

Figure 4.6 (a) Cyclic voltammograms shows the silver electrodeposition and silver film dissolution in the solutions consisted of 120 g/L $\text{KAg}(\text{CN})_2$, 6 g/L KCN and 120 g/L KNO_3 at pH 8 – 12. (b) The effect of pH of the silver solutions on the onset potential of electrodeposition of silver ion on Pt electrode surface.

Incomplete dissolution of silver at pH 8.1 was observed when the anodic scan was swept until + 0.6 V. The unusually long dissolution process in solution at pH 8.1 suggests that the deposited silver is coarse and not homogeneous enough to fully cover the platinum electrode surface as the oxidation peak of $[\text{Ag}(\text{CN})_2]^-$ ion is also observed. As a consequence, the optimum pH for the silver electrodeposition solution should be kept at $\text{pH} > 9.5$ or favorably pH 10 – 12 as their onset potential of silver electrodeposition remains quite constant and hence easier to control during the deposition process.

4.3.6 Effect of KCN on the Anodic Dissolution of Deposited Ag

The rate of anodic dissolution of metals strongly rely on the solution composition, particularly the type of anion and concentration [124]. For silver, its dissolution process involves free cyanide ions and depends on the cyanide concentration in the solution. The role of free cyanide in the dissolution of deposited silver can be described by Eq. 4.11 even though the dissolution process also involves the diffusion of free cyanide ions towards the silver surface, adsorption of cyanide ions, formation of chemical bond with silver atom, as well as charge transfer [125, 126].

The dissolution of deposited silver in cyanide containing solutions:

When increasing the cathodic vertex potential to more negative values, the silver dissolution waves in the solution containing 6g/L KCN seem to have reached the steady-state limiting current and cover a broad range of potential (Figure 4.2c). Whereas in the solution containing 40 g/L KCN, the silver dissolution peaks are sharper and the peak currents have also increased accordingly (Figure 4.7). This has indicated that the silver dissolution process is consisted of a limiting step and the reaction rate depends on the amount of free cyanide ions. It was reported that the dissolution of silver was limited by a stage of cyanide ions diffusion towards the electrode surface [107, 127]. As larger amount of free cyanide is available in high KCN containing solutions, the dissolution of deposited Ag is facilitated by the diffusion of free cyanide ions.

Figure 4.7 The current responses of dissolutions of silver to different cathodic vertex potentials in the solution containing high potassium cyanide electrolyte. Electrolyte: 40g/L KCN, 120g/L KAg(CN)₂ and 120g/L KNO₃. Initial potential: + 0.6V.

Figure 4.3a has also shown that regardless of the amount of silver ions in the 6 g/L KCN solutions, the dissolution behavior is similar to those observed in low free cyanide containing solutions. The dissolution waves cover a very broad range of potential which increases with increasing KAg(CN)₂ concentration. The anodic current densities of silver remain plateau before they drop rapidly. This also implies that increasing the KAg(CN)₂ concentration does not help to increase the amount of free cyanide ions.

4.3.7 Reflectance of Plated Ag Thin Film

The silver spot plating bath consists of 120 g/L KAg(CN)₂, 6 g/L KCN, 4.25 mL/L Heliofab Ag-920 B1, 15.6 mL/L Heliofab Ag-920 B2, 500 mL/L Heliofab Ag-920 C. All silver films ($A = 0.785\text{cm}^2$) are electroplated on Ni-plated brass substrates at 57°C. The plated Ag films are then used for reflectance measurements, surface morphology, surface roughness and XRD analysis.

The reflectance of five locations on each Ag surface is taken and the average reflectance ($\lambda = 450\text{ nm}$ and 550 nm) of 20 samples electroplated under same current density is then determined. In Figure 4.8a, the reflectance of Ag film on Ni-plated brass substrate

gradually increases with increasing current density from 5 – 70 ASD and then drops slightly from 80 – 100 ASD. This may suggest that 60 – 70 ASD is the optimum current density under the existing working conditions.

Figure 4.8 (a) The reflectance at $\lambda = 450 \text{ nm}$ and 550 nm of Ag thin film electroplated on Ni-plated brass substrates at 5 – 100 ASD in a silver plating bath. The reflectance is determined by averaging the reflectance of 20 samples each current density. (b) The plot shows the plating speed vs. current density. The plating time is varied so that the Ag film thickness is maintained 2 – 2.5 μm .

Under the exposure of short visible radiation, i.e. below 500 nm region, the reflectance of Ag film decreases because the refractive index (n) of silver is increases slightly which in turn affects its reflectance in this blue light region [25]. Hence, it can be seen from Figure 4.8a that the reflectance at $\lambda = 550$ nm is always considerably higher than that at $\lambda = 450$ nm.

Figure 4.8b shows the plating speed of Ag thin film vs. current density. The plating time is varied so that the Ag film thickness is maintained 2 – 2.5 μm and the plating speed is determined by

$$\text{Plating speed} = \frac{\text{thickness}_{\text{Ag}}}{\text{time}} (\mu\text{m}/\text{min}) \quad (6)$$

4.3.8 Characterization of the Plated Ag Thin Films

1) Surface morphology and surface roughness of plated Ag thin films

Figure 4.9 Scanning electron micrographs of Ag films plated on Ni-plated brass substrate at different current densities and their resulting reflectance (R), (a) 5 ASD; R = 20% (b) 10 ASD; R = 50% (c) 15 ASD; R = 70% (d) 20 ASD; R = 80% (e) 30 ASD; R = 90% (f) SEM/EDS of electroplated Ag films shows 100 ± 0.18 % Ag in mass.

Figure 4.10 (a) The 3D AFM images of Ag films plated at different current densities on Ni-plated brass substrates and their respective roughness, R_a and reflectance, R values (i) 5 ASD; $R_a = 56.4 \text{ nm}$; $R = 20\%$ (ii) 10 ASD; $R_a = 52.2 \text{ nm}$; $R = 50\%$ (iii) 15 ASD; $R_a = 47.7 \text{ nm}$; $R = 70\%$ (iv) 20 ASD; $R_a = 24.6 \text{ nm}$; $R = 80\%$ (v) 30 ASD; $R_a = 16.6 \text{ nm}$; $R = 90\%$ and (vi) 60 ASD; $R_a = 11.1 \text{ nm}$; $R = 95\%$; (b) The correlation of current density on the surface roughness and reflectance of plated Ag films.

The effect of current density on the reflectance has suggested that the surface properties of Ag films plated at < 30 ASD may be very different from those plated at ≥ 30 ASD. Hence, surface characterization techniques such as SEM and AFM are used to analyze the surface morphology as well as the roughness of Ag films.

The SEM images (Figure 4.9a – e) show marked differences in the morphology among Ag films with different plating conditions. When the current densities increase from 5 to 30 ASD, the surface morphologies of Ag films evolve from rough to smooth. Isolated crystals of variable sizes are clearly observed in Ag film plated at 20 ASD while fine-grained surface is observed in Ag film plated at 30 ASD. Since the Ag films plated in the range of 30 to 100 ASD have reflectance around 90 – 95%, this may indicate that these current densities have helped to develop fine grained Ag on Ni-plated brass substrates. The SEM/EDS shows about 100 ± 0.18 % Ag in mass within all electroplated Ag films (Figure 4.9f).

The 3D AFM images and surface roughness analysis in Figure 4.10a have further confirmed that the operating current density used for high speed Ag spot plating has played a role in affecting the crystal growth and grain structure of Ag which in turn resulting in different reflectance. Figure 4.10b showed the relationship between the current density and the surface roughness as well as the reflectance of Ag films. When the cathode current density has increased from 5 to 30 ASD, the surface roughness of Ag films is reduced as fine grains are developed, causing the reflectance of Ag films increases with increasing current density.

Both SEM and AFM surface analysis of Ag films are consistent with report by Nikolic et al. that the brightness of metallic thin films is determined by the flatness and smoothness of their surfaces at atomic level [26, 27]. Since the surface analysis has shown that plating conditions will affect the crystal growth, thus, it is also vital to study the crystal orientation of Ag and their effect on reflectance.

2) X-ray diffraction analysis of plated Ag thin films

The XRD patterns of Ag films electroplated on Ni-plated brass substrate are shown in Figure 4.11. It is clear that all Ag films are polycrystalline and exhibited (111), (200), (220) and (311) peaks. These four peaks are in consistent with the published XRD diffraction result of Ag (purity > 99.999%).⁹⁶ No other impurities peak is observed, showing high purity of the electroplated Ag films.

Figure 4.12 shows the intensities ratio of (200) to (111), (220) to (111) and (311) to (111) of standard Ag powder (JCPDS, File no. 04-0783) and electroplated Ag films. The result has showed that most of the Ag films ($R = 50 - 95\%$) have preferred orientation in (111) plane, as their relative intensities of (200), (220) and (311) planes to (111) plane are significantly lower than those of standard Ag powder. This is consistent with the structural analysis conducted by Kristev and Nikolova who specify that silver deposited from silver cyanide complexes always have a basic orientation along the [111] axis. However, the $I_{(200)} / I_{(111)}$ and $I_{(311)} / I_{(111)}$ of Ag films with $R = 20\%$ are larger than that of Ag standard 0.5969 vs 0.4 and 0.3337 vs 0.26 respectively, indicating (200) and (311) preferred orientations are developed within this film. The surface roughness, preferred orientation and reflectance of Ag films electroplated under different plating conditions are summarized in Table 4.1. The intensity of (111) preferred orientation is particularly high at Ag film with $R = 95\%$, indicating high crystallinity is formed within this film [128]. This may also suggest high intensity of (111) plane and high crystallinity within the Ag films help to contribute to the high reflectance.

From Table 4.1, it is also noticed that the Ag films electroplated at 5 and 10 ASD have similar surface roughness (56 – 52 nm) while their preferred orientations are completely different. The change in preferred orientation from (200), (311) to mainly (111) has enhanced the reflectance of Ag films, from $R = 20\%$ to 50% . Therefore, this may suggest that the crystal orientation can have also played a role in affecting the light reflection performance of these two Ag films as their reflectance values are significantly different while their roughness difference is negligible small.

Nonetheless, the effect of surface roughness and crystal preferred orientation cannot be distinguished from one another as the preferred orientation can in fact affect the surface

roughness. This is because the crystallite orientation on the surface will determine the extent of the grains protrudes outwards during growth. Investigation of the preferred orientation of Ag films has suggested that high surface roughness observed in Ag film with very low reflectance value (20%) may be due to the effect of crystal growth along the preferred [200] and [311] axes.

In the meantime, the Ag films electroplated at 10 – 60 ASD have similar preferred orientation but huge difference in the surface roughness. Hence, the joint effect of film crystal orientation and surface topological factors must have played a part in affecting the light reflection performance of Ag films. Further detailed analysis on the crystallite size or grain size may be helpful to understand the correlation of crystal structure to the reflectance in depth.

Figure 4.11 XRD patterns of Ag films with different measured surface roughness (R_a) and reflectance (R) values, electroplated on Ni-plated brass substrates. The y axes of all panels are presented in same scale.

Figure 4.12 The relative intensities of (200), (220) and (311) planes to (111) plane for Ag powder and plated Ag films on Ni-plated brass. *Standard Ag powder intensity result (File no. 04-0783) recorded in the database of Joint committee on Powder Diffraction Standards (JCPDS) is used as reference.

Table 4.1 Summary of surface roughness, texture and reflectance of Ag thin films electroplated on Ni-plated brass substrates under different plating conditions. *Standard Ag powder intensity result (File no. 04-0783) recorded in the database of JCPDS is used as the reference for determining the preferred orientation of plated Ag films.

Sample	Plating condition	Surface roughness	Texture				Reflectance
	CD, ASD	R _a , nm	I ₍₂₀₀₎ /I ₍₁₁₁₎	I ₍₂₂₀₎ /I ₍₁₁₁₎	I ₍₃₁₁₎ /I ₍₁₁₁₎	Preferred orientation	R, %
Ag powder*	-	-	0.4000	0.2500	0.2600	-	-
Ag film	5	56.4	0.5969	0.1999	0.3337	(200), (311)	20
	10	52.2	0.3156	0.1713	0.1564	(111)	50
	15	47.7	0.3292	0.1732	0.1565	(111)	70
	20	24.6	0.3178	0.1727	0.1625	(111)	80
	30	16.6	0.1983	0.2592	0.1579	(111)	90
	60	11.1	0.1479	0.1668	0.1034	(111)	95

3) Hardness and resistivity of plated Ag thin films

The Ag films have the hardness in the range of about 100 – 120 Hv_{0.05}. On the other hand, the resistivity of Ag films is found to be $0.50 \pm 0.02 \mu\Omega\cdot\text{cm}$. Both hardness and resistivity of the Ag films are comparable to those electrodeposited by conventional high cyanide system.

4.4 Conclusion

The study shows the electrochemical behaviors of KAg(CN)₂, KCN, KNO₃ electrolytes and solutions pH on the silver electrodeposition and dissolution. Higher silver ion concentration shifts the onset potential of silver electrodeposition to more positive direction by lowering the electrode polarization while KCN has the opposite effect in changing the cathodic polarization. The onset potential of silver electrodeposition is shifted to more negative values with increasing KCN concentration. Silver cyanide complexes help to promote the growth of fine-grained deposit by minimizing the effect of metallic contaminants as well as affecting the mass transfer in the bulk solution. Fine-grained deposit helps to enhance the reflectance. High plating speed or deposition rate can be attained in solutions containing high silver concentration. Besides having little impact on the onset potential of silver electrodeposition, KNO₃ lowers the limiting current density as well as the electrodeposition rate. This implies that KNO₃ may help reduce the operating current density required for silver electrodeposition in high silver concentration solutions, although at the expense of slowing down the electrodeposition rate. The silver plating solutions should be maintained at pH 10 – 12 as the onset potential of silver electrodeposition remains quite constant and hence easier to control during the operating process. Furthermore, appropriate pH range is essential to ensure the stability and solubility of silver cyanide complexes which affect the deposition process and the quality of the deposits. The silver dissolution process is consisted of a limiting step and the reaction rate depended on the amount of free cyanide ions.

Low cyanide silver plating formulation is developed and Ag films are jet-electroplated on brass substrate. Regardless the current density used, the reflectance of Ag thin film on brass substrate at $\lambda = 550 \text{ nm}$ was found to be higher than that at $\lambda = 450 \text{ nm}$. The result has showed that 30 – 100 ASD are suitable working range for depositing high reflective Ag

thin films. Both SEM and AFM analysis have confirmed that there is a strong correlation between the surface morphology / roughness and reflectance of Ag. Fine grained Ag and low surface roughness always give rise to high reflectance. On the other hand, preliminary XRD analysis has showed that Ag films with reflectance of 50 – 95% have (111) preferred orientation while Ag film with reflectance of 20 % has developed (200), (311) preferred orientation. The Ag film with the highest reflectance has found to have low surface roughness and relatively high crystalline orientation along $\langle 111 \rangle$ axis. Besides that, the hardness and resistivity of Ag films electrodeposited by low cyanide system are comparable with those electrodeposited by conventional high cyanide system.

Further detailed study on the factors for the reflectance and separating the influence of crystalline orientation from surface roughness may be useful to understand more about the correlation of crystal structure to the reflectance.

Chapter 5

Statistical Correlation - *Identifying Key Factors towards Highly Reflective Silver Coatings

A comprehensive study that correlates the effects of crystal orientation on the reflectance of silver is carried out for the first time. This can be achieved by using single crystal Ag with different crystal orientation but with controllable surface roughness. 2D (R_a) and 3D (S_{dr}) parameters are used to characterize the surface texture of single crystal silver. It is found that surface roughness plays a more critical role in determining the reflectance while the crystal (100), (110) and (111) orientations have negligible effect on the silver reflectance. The mean reflectance and one-way ANOVA analysis have indicated that the three orientations are statistically the same ($P > 0.05$) among the same roughness group at significance level $\alpha = 0.05$. Moreover, correlations in predicting the silver reflectance by employing either 2D or 3D roughness parameters as the input variables have also been proposed. Lastly, polycrystalline silvers are used to verify the accuracy of these equations. It is observed that S_{dr} is a better roughness indicator in predicting the reflectance of polycrystalline silver when compared to R_a .

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5.1 Introduction

In recent years, high brightness light emitting diodes (HB LEDs) which emit white light have been expanding their markets to replacing incandescent and halogen bulbs for general illuminations applications because of their higher efficiencies and more pleasing to eyes [129]. An LED consists of leadframe, in which a light emitting semiconductor chip is positioned, and epoxy encapsulation. Since the light emitting chip is placed on the leadframe, the leadframe must have excellent electrical, thermal and reflective properties [13]. High light extraction efficiency is one of the critical performance indicator for HB LEDs. Due to the large contrast in the refractive indices among the different materials used, certain amount of the emitted photons within the LED chip is trapped by its internal reflection. As a result, the amount of light output is reduced. Improving the light extraction efficiency is vital for the development of HB LEDs. One of the methods is to reduce the light scattering by depositing a highly reflective silver (Ag) thin film on the leadframe surface [1, 9, 10, 14-16]. The Ag layer also serves the purpose of enhancing the solderability and heat dissipation of the leadframe.

On the other hand, plasmon, a quantum of plasma oscillation has also played more and more important role in studying the properties of metals and semiconductors. Surface plasmon resonance technology has been widely used in high resolution lithography, sensing and microscopy [130-132]. Recently, this technology has also been used to improve the emission efficiency of Organic LED for developing high brightness LEDs [133]. However, as surface plasmon resonance technology is still not widely accepted in the leadframe industries, this technology is under consideration of the current work.

Many metals have good reflection of light. The reason that Ag is selected among different metallic materials, is due to its high theoretical reflectance of up to 95 % in the visible light wavelength region, and its ability to form a smooth coating. The excellent reflective characteristics of Ag can help improve the LED luminous efficiency [2, 3].

In leadframe industries, the leadframe substrates will be pre-treated chemically to obtain a smoother surface. After that, highly reflective Ag coating will be electrodeposited on the

substrate with the aid of suitable brighteners, levellers and wetting agents. These additives are proprietary information by the suppliers. Besides the plating chemistry, the operating conditions such as pH, temperature, current density and agitation will also greatly affect the quality of the Ag coating [134].

Since the cost of Ag is high too, ways to save the cost of raw material or the production cost have been explored by the industry. For example, spot plating can selectively electrodeposit silver on specific functional areas instead of the entire leadframe surfaces. In this way, the amount of Ag deposited on the non-functional areas of the leadframe can be significantly reduced, resulting in lower production cost. In addition, high speed silver plating, which can help to improve the productivity, is preferred in order to reduce the mass production cost.

In general, the reflectance of a metal is governed by the amount of light reflected off the metal specularly [26]. The relationship between the microstructure and brightness of electroplated nickel has been reported few decades ago [36]. This study has shown the effect of grain size, crystal texture and surface morphology of nickel surface on its light reflecting capability. The study has also confirmed that not all fine-grained deposits are bright.

On the other hand, the structural criteria for a metal surface to show mirror-brightness were previously characterized by Nikolic et al. via their scanning tunneling microscopy (STM) as well as atomic force microscopy (AFM) studies [26, 77, 78]. First, mirror-brightness is governed by flat and mutually parallel parts of the metal surface which exhibit smoothness at the atomic level. Second, the mirror-brightness surfaces should have distances of about several atomic diameters between the adjacent flat parts of the surface [77]. However, the correlation between the crystal growth and crystal orientation of silver coating and its reflection was not examined in that study. Besides, polycrystalline films are normally used in the previous research.

The aim of the current study is to identify key factor(s) behind Ag reflection of visible light. Potential factors include crystal orientation, crystal size, surface roughness, etc. The

correlation between crystal orientation and reflectance of silver film needs to be confirmed by separating the influence of surface roughness. This can be best achieved using single crystal Ag with different crystal orientation but with controllable surface roughness.

In this study, high purity single crystal Ag foils with specific orientations of the (100), (110) and (111) crystal planes will be used to study the relationship between the crystal orientation and the light reflectance. Attention will be paid to the individual effect of the crystal orientation and surface topological factor. The comprehensive studies of surface topography and surface texture on the optical properties of single crystal Ag surfaces can provide more affirmative guidance to the practical manufacturing of polycrystalline Ag films. In addition, polycrystalline Ag films were produced by physical vapour deposition and electroplating. Reflectance data from these polycrystalline Ag surfaces are used to verify the findings and correlation models derived from the single crystal study.

5.2 Experimental Methods

5.2.1 Materials

High purity (99.999%) silver single crystals with specific orientations of the (100), (110) and (111) were purchased from Goodfellow Cambridge Ltd, UK. These one-sided polished single crystals have diameter of 10 mm and thicknesses of 2 mm for the (100) and (111) samples and 1 mm for the (110) sample. The orientation tolerance of these single crystals was $\pm 3^\circ$.

The relationship between the surface structural characteristics of single crystals and their optical properties was studied by carefully varying the surface roughness of single crystals. This was carried out by grinding/polishing machine (TegraPol-21, Struers) at room temperature.

Brass panels (Kocour) were used as substrates for preparing electroplated and physical vapour deposited Ag films. Before the film deposition, the brass panels were soak cleaned, electrolytic cleaned and etched in Enprep 110 EC, Enprep 220 EC (MacDermid Enthone) and 10% H_2SO_4 in sequence prior to use. After the cleaning and etching step, a thin layer

of Ni was electrodeposited on the cleaned brass panels using LECTRO-NIC 10-03 (MacDermid Enthone) at 55 °C, with a current density at 0.12 A/cm². The nickel thickness was measured by fluorescent x-ray coating thickness measurement gauge (Seiko SFT 9300) and was controlled in the range of 0.55 – 0.75 µm. The electrodeposited silver was prepared by a plating facility (XRD Ag-7000, MacDermid Enthone) at 57 °C, under 0.3 A/cm² current density. The thickness of the Ag films was controlled within 2 – 2.5 µm while the different roughness of Ag films was obtained by controlling the brightener levels in the Ag electrolyte and current densities.

Physical vapour deposited (PVD) Ag films were prepared using UDP 550 - 4, TCL. Similar to the electrodeposition, a layer of Ni (0.55 – 0.75µm) was electrodeposited on the brass panels following the same procedures. Before the deposition, middle frequency hydrogen plasma etching was used to remove native oxides so as to leave a clean and chemically balanced Ni surface. The etching time was 30 min at 8.0×10^{-4} torr. After that, sputtering was carried out using alternate current (AC) at 50 Hz. The chamber pressure was kept at 1.7×10^{-3} torr during sputtering, and the applied voltage and current were 60 V and 0.2 A, respectively. The thickness of each Ag film was controlled around 2.0 – 2.5 µm. As the PVD deposition follows the Ni surface morphology underneath the Ag film, the different roughness of Ag films was obtained by controlling the roughness of deposited Ni layer.

5.2.2 Optical Reflectivity

Specular Reflectance Measurement

The specular reflectance (SR) was measured by spectroscopic reflectometer (Raditech, Taiwan) at a light incidence angle of 0°. A crystalline silicon wafer was used as a standard reference. Intensity change of the light reflected from the surface was measured as a function of wavelength ($\lambda = 300 \text{ nm} - 1000 \text{ nm}$) at normal incidence. The specular reflectance of silver could be readily calculated based on the optical constant of silicon. Reflectance readings were taken at $\lambda = 450 \text{ nm}$ and 550 nm because these two wavelengths are critical in the LED application, accounting for the centre emission wavelength of,

respectively, the blue and green light of a white light LED. The average reflectance of five locations on each Ag surface was reported.

5.2.3 Materials Characterization

X-ray diffraction was conducted for the crystal structure and orientation of the samples. LabX XRD (XRD – 6000, Shimadzu) with Cu K α radiation (40 kV, 30 mA) was used. The samples were scanned using the θ - 2θ method at a scan rate of 2° min^{-1} .

The surface morphology was observed under scanning electron microscope (SEM, JSM - 6360A, JEOL). Elemental analysis was done using the energy-dispersive X-ray spectroscopy (EDX) attached to the SEM.

5.2.4 Surface Topology

The surface roughness was measured using AFM (DI - 3100, Digital Instruments). The average of five surface roughness measurements was taken for each sample.

The quantitative surface roughness analysis was done reporting the arithmetic average roughness (R_a). In addition, S_{dr} , the developed surface area ratio, was also reported in this work with its correlation with the light reflection studied. The S_{dr} is defined as the ratio of developed 3D surface area to the planar area [135, 136], and could potentially represent the surface feature better than the R_a .

5.3 Results and Discussion

5.3.1 Microstructure and Surface Texture Analysis

The crystal structure of the three commercially available single crystals Ag, electrodeposited Ag, and physical vapour deposited Ag samples was examined using x-ray diffraction (XRD). Figure 5.1 shows that the three Ag crystal samples display only (200), (220) and (111) diffraction peaks respectively, which indicates that each sample indeed exhibits single crystal orientation. On the other hand, the XRD patterns of an electrodeposited and the PVD Ag films show four diffraction peaks, namely the (111),

(200), (220) and (311) peaks. This indicates that the electrodeposited and PVD Ag films are polycrystalline. It was noted that the XRD peaks of the electroplated Ag film are broader than the ones of the PVD counterpart, indicating slightly poor crystallinity of the former.

Figure 5.1 XRD patterns of Ag (100), Ag (110) and Ag (111) crystals as well as electrodeposited polycrystalline silver metal.

In order to correlate the crystal orientation and reflectance of Ag crystals, the influence of their surface morphology (or roughness) on the reflectance must be eliminated. Hence, Ag crystals with three specific single crystal orientations but with controllable surface roughness parameter were utilized.

The three Ag (100), Ag (110) and Ag (111) crystals were either polished or roughened to different roughness, which could be quantitatively categorized into five groups, i.e. (A1) $R_a = 0.00 - 5.00$ nm; (B1) $R_a = 5.01 - 10.00$ nm; (C1) $R_a = 10.01 - 20.00$ nm; (D1) $R_a = 20.01 - 30.00$ nm and (E1) $R_a = 30.01 - 45.00$ nm, as summarized in Table 5.1. The average R_a of the crystals were obtained by AFM analysis and they represent the arithmetic average of the variations in the height of the surface relative to a reference plane [137]. The average R_a for A1, B1, C1, D1 and E1 groups were determined to be 3.2 ± 1 nm, 6.6 ± 2 nm, 12.8

± 2 nm, 26.5 ± 3 nm, 36.2 ± 5 nm. The 3D AFM images in Table 5.1 also portray the surface topographies of the Ag crystals with different R_a roughness.

Table 5.1 The surface roughness of Ag (100), Ag (110) and Ag (111) crystals were quantitatively categorized into five different groups, i.e. (A1) $R_a = 0.00 - 5.00$ nm; (B1) $R_a = 5.01 - 10.00$ nm; (C1) $R_a = 10.01 - 20.00$ nm; (D1) $R_a = 20.01 - 30.00$ nm and (E1) $R_a = 30.01 - 45.00$ nm. Their average R_a were determined from the AFM analysis.

5.3.2 Reflection Characteristics

Specular reflectance is a numerical value of the visual brightness or mirror quality of a surface [138]. The reflectance of a sample can be determined by the ratio of reflected light intensity over incident light intensity. However, in practice, it is difficult to determine the incident light intensity before it strikes onto the sample surface. Hence, a relative intensity is first calculated whereby the reflected light intensity from the sample is divided by the incident light intensity from a standard. For the specular reflectance measurement, the change in reflected light intensity is detected while the incidence angle is 0° . Since the

optical constants of silicon are well understood, the specular reflectance of the sample can be readily calculated from these known values [139].

From Figure 5.2, the Ag (100), Ag (110), and Ag (111) crystals with $R_a = 0.00 - 5.00$ nm show very high specular reflectance $\sim 90\%$ over $\lambda = 400 - 800$ nm. This result is quite consistent with the reflectance of silver metal obtained from the literature [29]. Depending on the radiation wavelength, metals respond differently, i.e. their reflectivity varies with the wavelength of incident light. Even though silver has very high reflectivity over the visible light region, its reflectivity decreases significantly under the exposure of short optical wavelength radiation, particularly those below 500 nm. This is because in this blue light region, the refractive index of silver is increased slightly which in turn affects the silver reflectivity [20, 27].

Figure 5.2 Typical specular reflectance (SR) vs wavelength spectrum of Ag (100), (110) (111) crystals with $R_a = 0.00 - 5.00$ nm and silver metal. *The reflectance of silver metal is determined from the literature values of silver optical constants published by E.D. Palik [29].

Previous studies [38, 39] have confirmed that perfectly smooth surfaces allow specular (mirror-like) reflection which obeys law of reflection, i.e., the angle of incident beam is equal to the angle of reflected beam whereas rough surfaces causes diffuse reflection as the

incident beams are reflected in various directions. When the surface roughness increases, reflected light becomes more diffusive so the surface looks matt or dull. As a consequence, the surface roughness of the Ag sample could significantly affect its reflective characteristics.

5.3.3 Surface Topography Measurement and Reflectance

In most cases, surface roughness is often denoted by average R_a , which is the most commonly used roughness parameter in specifying the quality of a material surface. In addition to R_a , other roughness parameters such as R_q (root-mean-square), R_{max} (difference in height between the highest and lowest points on the surface relative to the reference plane), R_z (the average absolute value of the five highest and five lowest points) etc., are also widely used to describe the vertical characteristics of a material surface.

Although R_a has been employed as a general guideline in characterizing surface texture in most industries for decades, R_a alone is not sufficient to provide a comprehensive surface profile of a material. This is because R_a result does not provide lateral information and R_a values cannot differentiate surfaces with different features between peaks and valleys, which are critical in determining the surface reflection of light. Surfaces with protruding peaks, cavity, and other irregularities may give the same average R_a value. For example, Figure 5.3 a – b depict different surface profiles having the same R_a value but the reflectance may be different from the two surfaces.

Hence, developed interfacial area ratio (S_{dr}), or more appropriately for the current context, the developed surface area ratio, is considered in this study. S_{dr} describes the change in 3D surface area relative to the 2D planar surface area. In contrast to R_a which does not provide detailed information on the 3D surfaces, S_{dr} is able to characterize the 3D surface topography of materials. The surface area includes the influence of variation in the height and number of peaks. The S_{dr} is defined as:

$$S_{dr} = (\text{Texture surface area} - \text{Planar area}) * 100 \% / \text{Planar area}$$

Figure 5.3 Schematic illustration of different surface profiles having the same R_a value.

Figure 5.4 The dependence of specular reflectance on (a-b) the average R_a for Group A1 – E1; (c-d) the average developed interfacial area ratio (S_{dr}) values for Group A2 – F2 of Ag (100), Ag (110) and Ag (111) crystals at $\lambda = 450$ nm and 550 nm respectively.

Figure 5.5 Surface morphologies of single crystal Ag (100), Ag (110) and Ag (111) with different specular reflectance (a) – (c) $R_{450nm} \approx 90\%$; (d) – (f) $R_{450nm} \approx 70\%$; (g) – (i) $R_{450nm} \approx 50\%$; (j) – (l) $R_{450nm} \approx 30\%$.

Similarly to R_a , the effect of S_{dr} on the reflectance is studied by categorizing the S_{dr} values obtained from the AFM measurement into 6 different groups, i.e. (A2) $S_{dr} = 0.00 - 0.50\%$; (B2) $S_{dr} = 0.51 - 1.00\%$; (C2) $S_{dr} = 1.01 - 2.00\%$; (D2) $S_{dr} = 2.01 - 3.00\%$ and (E2) $S_{dr} = 3.01 - 4.00\%$; (F2) $S_{dr} = 4.01 - 5.00\%$. The average S_{dr} for group A2, B2, C2, D2, E2 and

F2 were determined to be $0.3 \pm 0.04 \%$, $0.7 \pm 0.05 \%$, $1.5 \pm 0.27 \%$, $2.18 \pm 0.07 \%$, $3.18 \pm 0.1 \%$ and $4.48 \pm 0.09\%$ respectively.

The reflectances at $\lambda = 450$ and 550 nm are used for comparison. A decrease in specular reflectance was observed and this is associated with an increase in surface roughness, regardless it is expressed either in R_a (Figure 5.4 a – b) or S_{dr} (Figure 5.4 c – d). The high R^2 of the regression equations in Figure 5.4 have indicated that the relationship between the surface roughness and reflectance can be well described as a linear relationship.

Although the roughness affects both the specular reflectance at 450 nm and at 550 nm, the $R_{550 \text{ nm}}\%$ is always higher than $R_{450 \text{ nm}}\%$ because of the blue light effect explained above.

The SEM images of Ag (100), Ag (110) and Ag (111) crystals have also confirmed that the decrease in specular reflectance is greatly associated with an increase in irregularities in the surface morphologies of the single crystals as shown in Figure 5.5.

5.3.4 Correlation between Crystal Orientations and Their Reflection

Figure 5.4 has confirmed that both R_a and S_{dr} could be used as roughness indicators to represent the surface topology of single crystals. Hence, the effects of crystal orientations on the reflectance are also investigated based on these two indicators. From Figure 5.6 a – b, it seems that there is no significant difference in reflectance among the three single crystals at both 450 nm and 550 nm wavelengths for Group A1 – C1 while Ag (111) may exhibit slightly higher reflectance when compared to Ag (100) and Ag (110) in Group D1 – E1. Hence, the mean and one-way ANOVA of $R_{450 \text{ nm}}\%$ and $R_{550 \text{ nm}}\%$ among Group A1 – E1 are evaluated and their results are shown in Table 5.2. The one-way ANOVA has indicated that it is likely that there is no statistically difference in the mean $R_{450 \text{ nm}}\%$ and $R_{550 \text{ nm}}\%$ as their P values > 0.05 (significance level set for one-way ANOVA) among Ag (100), Ag (110) and Ag (111) for all Groups A1 – E1.

On the other hand, when S_{dr} is used as a roughness indicator to represent the surface topology of these Ag crystals, Figure 5.6 c – d have also showed that there is not much difference in reflectance among Ag (100), Ag (110) and Ag (111) for similar S_{dr} .

Table 5.3 shows the mean and one-way ANOVA of $R_{450\text{nm}}\%$ and $R_{550\text{nm}}\%$ among Group A2 – F2. The one-way ANOVA has also indicated that the mean $R_{450\text{nm}}\%$ and $R_{550\text{nm}}\%$ of Ag (100), Ag (110) and Ag (111) are statistically the same ($P > 0.05$). Both the R_a and S_{dr} indicators are independent of the wavelengths.

Figure 5.6 The effects of the Ag crystal orientations (100), (110) and (111) on the specular reflectance for different (a – b) R_a and (c – d) S_{dr} groups at $\lambda = 450\text{ nm}$ and 550 nm respectively.

Table 5.2 and Table 5.3 have clearly showed that there is no strong correlation between crystal orientation and reflectance. This suggests that it is the surface roughness that has the main effect in controlling the reflectance of Ag rather than the way crystallites orient themselves at microscale. Assuming that the reflectance measurement of the (100), (110), (111) surfaces at normal incidence are optically isotropic, the factor that influences the differences in reflectance should be from the irregularities of material surface. Moreover, although a single crystal with (100), (110) or (111) orientations exhibits different surface symmetry and atoms arrangement if viewed from normal incidence, it is the microscopic roughness of the Ag surface that has caused the light scattering. When the microscopic

roughness is much smaller than the wavelength, the light is reflected specularly from the surface.

Table 5.2 Mean and one-way ANOVA of $R_{450nm}\%$ and $R_{550nm}\%$ among Group A1 – E1. Significance level $\alpha = 0.05$.

Group	Mean $R_{450nm}\% \pm SD$			ANOVA ($R_{450nm}\%$)	Mean $R_{550nm}\% \pm SD$			ANOVA ($R_{550nm}\%$)
	(100)	(110)	(111)	<i>P</i>	(100)	(110)	(111)	<i>P</i>
A1	93.5 $\pm$ 3	93.5 $\pm$ 3	92.9 $\pm$ 2	0.745	94.5 $\pm$ 4	94.5 $\pm$ 4	96.1 $\pm$ 2	0.261
B1	86.9 $\pm$ 5	88.7 $\pm$ 4	85.8 $\pm$ 6	0.571	90.9 $\pm$ 4	93.2 $\pm$ 2	90.9 $\pm$ 5	0.463
C1	76.6 $\pm$ 3	79.7 $\pm$ 3	76.1 $\pm$ 4	0.332	81.0 $\pm$ 5	86.1 $\pm$ 2	84.2 $\pm$ 3	0.113
D1	54.8 $\pm$ 7	56.9 $\pm$ 8	63.3 $\pm$ 7	0.176	63.1 $\pm$ 6	64.5 $\pm$ 8	69.7 $\pm$ 8	0.179
E1	37.8 $\pm$ 5	39.4 $\pm$ 3	47.6 $\pm$ 7	0.251	47.3 $\pm$ 4	48.0 $\pm$ 7	53.6 $\pm$ 8	0.627

Table 5.3 Mean and one-way ANOVA of $R_{450nm}\%$ and $R_{550nm}\%$ among Group A2 – F2. Significance level $\alpha = 0.05$.

Group	Mean $R_{450nm}\% \pm SD$			ANOVA ($R_{450nm}\%$)	Mean $R_{550nm}\% \pm SD$			ANOVA ($R_{550nm}\%$)
	(100)	(110)	(111)	<i>P</i>	(100)	(110)	(111)	<i>P</i>
A2	94.7 $\pm$ 3	92.4 $\pm$ 5	93.2 $\pm$ 2	0.363	95.8 $\pm$ 3	92.8 $\pm$ 5	96.7 $\pm$ 3	0.142
B2	87.6 $\pm$ 5	88.9 $\pm$ 5	87.0 $\pm$ 6	0.638	91.7 $\pm$ 2	90.3 $\pm$ 5	91.6 $\pm$ 4	0.699
C2	78.0 $\pm$ 3	78.4 $\pm$ 3	73.4 $\pm$ 3	0.213	85.1 $\pm$ 3	85.6 $\pm$ 3	83.1 $\pm$ 3	0.419
D2	66.0 $\pm$ 4	64.2 $\pm$ 4	68.8 $\pm$ 4	0.196	75.0 $\pm$ 3	71.2 $\pm$ 3	76.4 $\pm$ 5	0.154
E2	54.2 $\pm$ 4	58.0 $\pm$ 3	57.5 $\pm$ 4	0.225	62.7 $\pm$ 3	66.0 $\pm$ 4	64.1 $\pm$ 5	0.131
F2	34.6 $\pm$ 6	40.4 $\pm$ 5	39.7 $\pm$ 5	0.605	48.1 $\pm$ 6	53.1 $\pm$ 5	49.4 $\pm$ 5	0.625

5.3.5 Correlation Models

The individual effect of the three crystal orientations and their surface topological factors have been discussed above. Figure 5.6 shows that there is no significant and direct correlation between crystal orientation and reflectance, the orientation contribution towards the reflectance is neglected in developing the statistical model.

The statistical model is built based on the linear regression analysis of the surface roughness. Since R_a and S_{dr} are the results of 2D and 3D roughness measurements of the surface texture of Ag respectively, two statistical models of the reflectance are developed to distinguish the effect of each roughness parameter.

The experimental data are treated with linear regression analysis and the two statistical equations (for $\lambda = 450$ nm and 550 nm) are established for each roughness parameter.

$$R_{450\text{nm}}\% = 97.42 - 1.495 R_a \quad (R^2 = 0.944) \quad (5.1)$$

$$R_{550\text{nm}}\% = 99.82 - 1.307 R_a \quad (R^2 = 0.959) \quad (5.2)$$

$$R_{450\text{nm}}\% = 96.30 - 12.90 S_{\text{dr}}\% \quad (R^2 = 0.975) \quad (5.3)$$

$$R_{550\text{nm}}\% = 98.63 - 10.73 S_{\text{dr}}\% \quad (R^2 = 0.966) \quad (5.4)$$

5.3.6 Simulation of the Reflection from Polycrystalline Silver Films

From the comprehensive studies of morphology and crystal structure on the optical properties of single crystals, it was found that surface roughness is the most critical factor in determining the reflectance of Ag. 2D and 3D roughness parameters (R_a and S_{dr}) have portrayed similar linear relationship between roughness and reflectance and their resulting equations are generated in Eqs. 5.1 – 5.4.

For practical applications, polycrystalline films are used. Therefore, it is important to verify the applicability and validity of the developed models based on single crystal foils using data obtained from polycrystalline films. To do so, we apply the above derived equations to two types of polycrystal Ag coatings – electroplated and physical vapour deposited Ag films.

The correlations between R_a and reflectance as well as between S_{dr} and reflectance of electroplated and physical vapour deposited Ag are shown in Figure 5.7. Expectedly, there are strong linear correlations between roughness and reflectance regardless the types of polycrystalline Ag coatings. However, the same R_a values has given rise to two significantly different $R_{450\text{nm}}\%$ or $R_{550\text{nm}}\%$, depending on the types of Ag coatings as shown in Figure 5.7 a – b. Physical vapour deposited Ag generally show lower $R_{450\text{nm}}\%$ and $R_{550\text{nm}}\%$ than electroplated Ag if the roughness is perceived in terms of R_a and plotted against reflectance of the Ag.

On the other hand, if S_{dr} is used as the independent variable to represent the roughness of Ag coatings (Figure 5.7 c – d), it correlates well with both types of Ag coatings. This strongly suggests that developed surface area ratio is a better indicator to correlate with reflectance as it captures the surface texture of the coatings.

Figure 5.7 The dependence of specular reflectance of electroplated and physical vapour deposited Ag on the (a-b) average R_a ; (c-d) average S_{dr} at $\lambda = 450 \text{ nm}$ and 550 nm respectively.

Figure 5.8 AFM images of (a) electrodeposited Ag, $R_a = 13.8 \text{ nm}$, $S_{dr} = 2.49 \%$; (b) physical vapour deposited Ag, $R_a = 14.5 \text{ nm}$, $S_{dr} = 4.38 \%$.

The 3D AFM images of the electrodeposited Ag and physical vapour deposited Ag samples in Figure 5.8 have also portrayed that both surface topographies are significantly different even though they have similar R_a values.

In order to determine the percentage errors of the reflectance forecast in Eq. 5.1 – 5.4, the experimental $R_{450nm}\%$ and $R_{550nm}\%$ results of polycrystalline Ag coatings are compared with the model $R_{450nm}\%$ or $R_{550nm}\%$ values. The average percentage errors of the models are summarized in Table 5.4.

The total average errors % of Eq. 5.1 and Eq. 5.2 are found to be much higher than those of Eq. 5.3 and Eq. 5.4. The total average errors of using R_a as the variable in predicting $R_{450nm}\%$ and $R_{550nm}\%$ are about 14.5% and 8.9% respectively. When the 3D parameter S_{dr} is used for prediction, the total average error for $R_{450nm}\%$ is 5.8% and for $R_{550nm}\%$ is 6.0%. This result has further suggested that S_{dr} is a better roughness indicator in predicting the reflectance of polycrystalline silver when compared to R_a .

Table 5.4 The average errors of the statistical models for predicting the reflectance of electroplated and physical vapour deposited silvers.

Samples	R_a , nm	$S_{dr}\%$	Experimental $R_{450nm}\%$	Experimental $R_{550nm}\%$	Model (E.q. 1) $R_{450nm}\%$	Error % (E.q. 1)	Model (E.q. 2) $R_{550nm}\%$	Error % (E.q. 2)	Model (E.q. 3) $R_{450nm}\%$	Error % (E.q. 3)	Model (E.q. 4) $R_{550nm}\%$	Error % (E.q. 4)
Electroplated Ag # 1	14.3	0.6	83.1	83.7	76.0	8.5	81.1	3.1	88.3	6.2	92.0	9.9
Electroplated Ag # 2	19.2	1.5	74.1	76.7	68.8	7.2	74.8	2.5	76.6	3.3	82.2	7.2
Electroplated Ag # 3	29.1	2.3	65.8	72.9	53.9	18.0	61.8	15.3	67.1	2.1	74.4	2.0
PVD-Ag # 1	17.0	2.7	64.1	71.4	72.0	12.3	77.6	8.7	61.0	4.9	69.2	3.0
PVD-Ag # 2	20.3	3.5	56.4	65.9	67.1	19.1	73.3	11.3	51.2	9.2	61.1	7.3
PVD-Ag # 3	26.1	4.1	47.8	58.5	58.4	22.0	65.7	12.3	43.4	9.2	54.6	6.6
Total average error						14.5		8.9		5.8		6.0

5.4 Conclusions

The key factors on the reflectance of silver is studied using single crystal silver foils with specific crystal orientations of the n(100), (110) and (111) with different surface roughness. Besides the most commonly used 2D parameter R_a , a hybrid parameter S_{dr} which describes the 3D surface topography is also employed in the surface roughness analysis. It is found that a decrease in specular reflectance is associated with an increase in the surface roughness of single crystals, regardless it is either expressed in R_a or S_{dr} . Moreover, after

carefully separating the influence of surface roughness, it is observed that the surface roughness is the main factor in controlling the reflectance of Ag, while crystal orientation has a negligible effect on the light reflection. The mean and one-way ANOVA analysis have indicated that Ag (100), Ag (110) and Ag (111) with similar roughness are statistically the same ($P > 0.05$). When the microscopic roughness is much smaller than the wavelength, the light is reflected specularly from the surface. After treating the experimental data with linear regression analysis, two statistical equations (for $\lambda = 450$ nm and 550 nm) are established for R_a and S_{dr} . The accuracy of these models are verified via electrodeposited and physical vapour deposited silver films. The use of R_a as roughness indicator to predict the reflectance of silver is highly dependent on the types of coatings whereas S_{dr} is a better indicator to correlate with reflectance as it is independent on the type of coatings. The reason is that S_{dr} is capable of capturing the surface features in 3D better.

Chapter 6

Process Improvement - Cyclic Voltammetric Study of Silver Electrodeposition in Non-cyanide Solutions

The electrochemical processes of non-cyanide silver electrodeposition solution were first explored by using cyclic voltammetry. The electrochemical behavior and the effect of AgNO_3 , DMH, KOH, KNO_3 , K_2HPO_4 electrolytes and solutions pH on the Ag electrodeposition and dissolution were investigated. Moreover, suitable working conditions for non-cyanide silver electrodeposition were also proposed. Higher AgNO_3 concentration lowers the cathodic polarization and shifts the onset potential of silver electrodeposition to more positive values while higher DMH content increases the cathodic polarization by chelating with free Ag^+ ions. High electrodeposition rate can be attained in solutions containing high silver and low DMH concentrations. Both KNO_3 and K_2HPO_4 have little effect on the cathodic polarization. DMH-based silver solution is more favorably to be maintained within pH 10.0 – 12.0. The surface and material characteristics of Ag films deposited by non-cyanide solution are also compared with those deposited by low and high cyanide solutions as well as physical vapour deposited silver.

6.1 Introduction

For decades, cyanide-based silver electrolytes have been commonly used in the silver electroplating industries due to the ease of operation and high quality of silver deposits obtained from these baths.

Recently, less toxic chemicals have become more favourable in metal plating processes due to stricter rules and regulations as well as high cost of wastewater treatment. Over the years, compounds such as 5,5-dimethylhydantoin [62, 140] ammonia [94, 95], uracil [61], HEDTA [96], 2-hydroxypyridine [97, 98], hydantoin [99, 141], and more have been suggested as alternatives to replace cyanides in silver plating baths.

A heterocyclic structured 5,5-dimethylhydantoin (DMH) is an excellent cyanide-free complexing agent for metal ions. The nitrogen and oxygen atoms in the molecule can firmly coordinate with several metal ions, such as Cu^+ [142], Au^{3+} [143], Zn-Ni alloy [144], and Ag^+ [100, 145].

In the present study, DMH is selected as complexing agent for silver electrolyte. Compared to other cyanide-free complexing agents, DMH is easily soluble and stable in alkaline solution, so it is more practical to be used in silver electroplating application [146].

In this work, the electrochemical behaviors and effects of basic electrolytes (silver salt, complexing agent and supporting electrolytes), agitation and solution pH are investigated by using cyclic voltammetric technique. In addition, the optimum working conditions for cyanide-free silver electrodeposition in DMH-based system are also proposed.

The characteristics such as morphologies, XRD, purity, and reflectance of Ag films electrodeposited by cyanide-free system will also be compared with those electrodeposited by low and high cyanide silver solutions as well as physical vapour deposited silver.

6.2 Materials and Methods

6.2.1 Chemicals and Deposition Conditions

Chemicals used were Silver nitrate (AgNO_3), 5,5-Dimethylhydantoin (DMH), Potassium nitrate (KNO_3), Potassium phosphate dibasic (K_2HPO_4), Nitric acid (HNO_3), Potassium hydroxide (KOH). All solutions were prepared with deionized water. pH of the solution was adjusted by using either 1 % HNO_3 or 1 % KOH solutions.

Brass hull cell panel was used as a substrate for silver electrodeposition. All the pretreatment, Ni as well as Ag electrodeposition chemicals used are proprietary products provided by MacDermid Enthone. Before deposition, the brass was cleaned in the Enprep 110 EC, Enprep 220 EC and Actane 345. After that, the brass was electrodeposited with a layer of nickel (2 – 3 μm) by using Heliofab Ni-370. Next, a thin layer of Ag was electrodeposited on the Ni/Brass panel by using silver solutions, i.e. (a) DMH-based silver solution; (b) low cyanide silver solution; (c) conventional high cyanide silver solution.

The DMH-based silver solution prepared by dissolving 80 g/L AgNO_3 , 200 g/L DMH, 110 g/L KOH, 500 mL/L SILVREX JS-5 B (conducting salt), 15mL/L CFAG-6A (primary brightener), CFAG-6C (secondary brightener), 7 mL/L SILVREX III BRIGHTENER T (grain refiner and leveller).

The low cyanide silver solution was made up of 120 g/L $\text{KAg}(\text{CN})_2$, 6 g/L KCN, 120 g/L KNO_3 , 5 mL/L XRD Ag-7000 B1 (primary brightener) and 16 mL/L XRD Ag-7000 B2 (secondary brightener and leveller), while the high cyanide silver solution was consisted of 100 g/L $\text{KAg}(\text{CN})_2$, 150 g/L KCN, 6 g/L KOH, 20 g/L K_2CO_3 , 5 mL/L Heliofab Ag-900 C (primary brightener) & Heliofab Ag-900 T (grain refiner and leveller) and 3 mL/L Heliofab Ag-900 H (secondary brightener). The electrodeposition conditions followed the optimum parameters as recommended in the XRD Ag-7000 and Heliofab Ag-900 technical datasheets. The electrodeposition temperatures are 55°C and 25°C for XRD Ag -7000 and Heliofab Ag-900 respectively. The pH of the freshly prepared silver solutions were adjusted to about pH 10 - 12 for both low and conventional high cyanide solutions.

The current densities used for the electrodeposition are 0.6 A/cm^2 for DMH-based and low cyanide system; 0.03 A/cm^2 for conventional high cyanide system. The deposition time of the two system was adjusted so that the Ag films had a similar thickness at $2.0 - 2.5 \text{ }\mu\text{m}$.

Physical vapour deposited silver films were prepared using UDP 550 - 4, TCL. Similar to the electrodeposition, a layer of Ni ($0.55 - 0.75\mu\text{m}$) was electrodeposited on the brass panels following the same procedures. Next, middle frequency hydrogen plasma etching was used to remove native oxides so as to leave a clean and chemically balanced Ni surface. The etching time is 30 min at 8.0×10^{-4} torr. After that, alternate current (AC) sputtering was used to deposit the Ag films. The chamber was kept at 1.7×10^{-3} torr and the working conditions were 50 Hz, 60 V and 0.2 A. The thickness of each Ag film was controlled around $2.0 - 2.5 \text{ }\mu\text{m}$.

6.2.2 Cyclic Voltammetric Analysis

The electrochemical studies of silver electrodeposition and dissolution were performed in a conventional three electrode cell using a computerized potentiostat (797 VA Computrace, Metrohm) at room temperature. Polished platinum rotating disk (Metrohm, $A = 0.0314 \text{ cm}^2$) was used as the working electrode. During the experiments, a Ag/AgCl (3 M KCl) reference electrode was mounted in an electrolyte vessel filled with 1 M KNO_3 solution and used as a double junction reference electrode. All potentials referred to this electrode. A platinum rod which represented the insoluble anode in industrial practice was employed as the counter electrode. All the silver electrodeposition and dissolution processes were studied at angular speed (ω) of 2000 rpm. The cyclic voltammetry scan rate was 50 mVs^{-1} . Before each measurement, the electrode was cleaned in deionized water, followed by 50% HNO_3 solution and 10% KOH solution as well as rinsed with deionized water. After that, the electrode was sonicated in deionized water for 5 min before use.

6.2.3 Ag Films Characterization

The surface morphology of the Ag films was observed under scanning electron microscope (SEM, JSM-6360A, JEOL) while their surface roughness were measured using atomic

force microscope (AFM, DI-3100, Digital Instruments). Furthermore, X-ray diffraction (XRD) analysis was also performed for characterizing the crystal orientation of the surfaces of electrodeposited Ag films. Thin Film XRD (XRD-6000, Shimadzu) with Cu K α radiation (40kV, 30 mA) was used. The samples were scanned continuously at 2° 2 θ min⁻¹. The compositional profile of the silver films was investigated by X-ray photoelectron spectroscopy (Thermo Scientific, ESCALab 250Xi). The samples were scanned by Al K α (1486.6 eV) radiation.

6.3 Results and Discussion

6.3.1 The Effect of Rotating Disk Speed on the Electrodeposition of Ag

The redox processes of AgNO₃, DMH, KOH, KNO₃, K₂HPO₄ electrolytes and solutions pH at platinum rotating disk electrode are studied by cyclic voltammetry. The voltammetric studies also help to determine the suitable working potential range for DMH-based silver electrodeposition. The electrodeposition process involves multiple processes [120], i.e. mass transfer, electron transfer, Ag ion reduction and Ag nucleation on the cathode surface, while the deposition rate is governed by the slowest rate of these processes.

Rotating disk electrode gives an agitation to the solution which could reduce the thickness and prevent the impoverishment of diffusion layer lying between the bulk solution and the working electrode surface, thereby ensuring uniform deposition. Since the effects of AgNO₃, DMH, KOH, KNO₃, K₂HPO₄ electrolytes and solutions pH on the Ag electrodeposition will be studied in this work, it is critical to determine the suitable agitation speed which will not limit the electrodeposition rate.

It can be seen from Figure 6.1 that the electrodeposition rate is affected by the agitation speed. When the agitation speed is increased from 200 to 1000 rpm, the electrodeposition rate is increased from 1.3 to 1.9 $\mu\text{m}/\text{min}$. After that, the electrodeposition rate remains constant even though the agitation speed is increased up to 3000 rpm. Strong agitation facilitates the replenishment of metal ions at the cathode as well as the mass transfer of

product from the cathode by reducing the thickness of diffusion layer. As a result, agitation speed of 2000 rpm is selected for subsequent voltammetric studies.

Deposition rate is determined by Eq. 6.1:

$$\text{Deposition rate} = \frac{QM_{Ag}}{F\rho_{Ag}At} \times 10^4 \text{ (}\mu\text{m/min)} \quad (6.1)$$

where Q (C) is the charge involved in the silver dissolution; M_{Ag} (= 107.8682 g/mol) is the molar mass of silver; F (= 96485.3365 C/mol) is the Faraday Constant; ρ_{Ag} (= 10.49 g/cm³) is the density of silver; A (= 0.0314 cm²) is the Pt electrode area; t (min) is the deposition time during the cathodic sweep.

Figure 6.1 Cyclic voltammograms of silver electrodeposition and silver film dissolution in the silver plating solution consisted of 80 g/L AgNO₃, 200 g/L DMH, 110 g/L KOH, 80 g/L KNO₃ and 20 g/L K₂HPO₄. Inset: The effect of agitation on the deposition rate by sweeping the potential from + 0.6 V to – 0.8 V.

6.3.2 The Effect of AgNO_3 on the Electrodeposition of Ag

Figure 6.2 (a) Cyclic voltammograms of silver electrodeposition and silver dissolution in the solutions consisted of 200 g/L DMH, 110 g/L KOH, 80 g/L KNO_3 , 20 g/L K_2HPO_4 and 0 – 100 g/L AgNO_3 . (b) The effect of AgNO_3 concentration on the onset potential of silver electrodeposition. (c) The influence of AgNO_3 concentration on the electrodeposition rate in the sweeping potential range from + 1.0 V till – 0.8 V.

Figure 6.2(a) shows the effect of 0 – 100 g/L AgNO_3 on the electrodeposition of Ag in DMH-based solution containing 200 g/L DMH, 110 g/L KOH, 80 g/L KNO_3 and 20 g/L K_2HPO_4 . AgNO_3 is the only source of Ag ion and the Ag reduction starts ~ -0.66 V at the cathode when 20 g/L AgNO_3 is present in the solution. From Figure 6.1a – 1b, it can be seen that the onset potential of Ag reduction is shifted to more positive values with increasing AgNO_3 concentration. When AgNO_3 is increased from 20 g/L to 100 g/L, the onset potential of Ag reduction is shifted from ~ -0.66 V to ~ -0.41 V.

DMH is a complexing agent for Ag ions in DMH-based solution, similar to cyanide which forms complexes with Ag ions. When AgNO_3 concentration is increased while the amount of DMH remains constant, the free Ag ions in the solution increases. This lowers the cathodic polarization and enables the Ag reduction at the cathode to proceed more easily.

Moreover, higher AgNO_3 concentration enables higher current densities as well as larger amount of silver deposited, which can be determined from the area of silver dissolution peaks at $\sim 0.25 - 0.35$ V. As expected, higher electrodeposition rate is achieved as cathodic polarization is lowered (Figure 6.1c). This also implies that the amount of silver salt is critical for controlling the silver electrodeposition rate. The optimum concentration for achieving high electrodeposition rate is around 80 – 100 g/L AgNO_3 because of the solubility limit of AgNO_3 .

Nonetheless, excess AgNO_3 is not soluble in the solution containing limited amount of DMH because excessive free Ag^+ , without complexing agent, will form partially soluble AgOH under alkaline condition, Eq. 6.2.

At pH 10:

6.3.3 The Effect of Complexing Agent on the Electrodeposition of Ag

Figure 6.3 (a) Cyclic voltammograms of silver electrodeposition and silver dissolution in the solutions consisted of 80 g/L AgNO_3 , 110 g/L KOH , 80 g/L KNO_3 , 20 g/L K_2HPO_4 and 180 – 360 g/L DMH. (b) The effect of DMH concentration on the onset potential of silver electrodeposition. (c) The influence of DMH concentration on the electrodeposition rate in the sweeping potential range from + 0.6 V till – 0.8 V.

DMH is known to be one of the most common complexing agents for Ag in DMH-based system [143]. The presence of complexing agent in the solution is very critical because it chelates with free Ag ions in the solution so as to maintain the silver bath stability, prevent silver displacement and produce high quality silver deposits with good adhesion and morphologies. Hence, a minimum amount of 180 g/L DMH (~ 1.4 mol) was selected in this study because it helps to stabilize the free Ag ion (~ 0.47 mol) in the alkaline solution.

Figure 6.3a shows the cyclic voltammograms of increasing the amount of DMH from 180 – 360 g/L in the solution containing 80 g/L AgNO_3 , 110 g/L KOH, 80 g/L KNO_3 and 20 g/L K_2HPO_4 in the sweeping potential range from + 0.6 V till – 0.8 V. The influence of DMH on the cathodic polarization can be seen from Figure 6.3b where the onset potential of Ag reduction at the cathode is negatively increased with increasing DMH concentration. In contrast with the effect of increasing AgNO_3 concentration in the solution (Figure 6.1b), whereby the cathodic polarization is significantly lowered due to the presence of more free Ag ions, the complexing agent DMH chelates with the Ag ions and thus fewer free Ag ions are present in the solution. The change in the polarization effect is more noticeably ($\sim 10 - 20\%$) when the DMH concentration is increased from 180 g/L up to 220 g/L. After that, the change in the polarization is about 2 – 5 % with every 20 g/L increase in the DMH concentration. This may suggest that the amount of DMH has affected the coordination number of silver complexes and the species that involved in the charge transfer process may also be different.

Liu et al. have predicted and confirmed that DMH-Ag-DMH complex is formed by employing the methods of quantum chemical calculations based on density functional theory and molecular dynamic simulations [62, 140, 145]. Expectedly, when the amount of silver complexes increases, the silver electrodeposition rate decreases because the activity of free Ag ions is lowered, Figure 6.3c. Although high DMH concentration helps to ensure silver solution stability, they will slow down the electrodeposition rate by reducing the number of free Ag ions. The optimum range for achieving high deposition rate is around 200 – 220 g/L DMH.

6.3.4 The Effect of KNO_3 and K_2HPO_4 on the Electrodeposition of Ag

Figure 6.4 Cyclic voltammograms of silver electrodeposition and silver film dissolution in the silver plating solution consisted of (a) 80 g/L AgNO_3 , 200 g/L DMH, 110 g/L KOH, 20 g/L K_2HPO_4 and 0 – 180 g/L KNO_3 . Inset: The effect of 0 – 180 g/L KNO_3 on the deposition rate by sweeping the potential from + 0.6 V to – 0.8 V. (b) 80 g/L AgNO_3 , 200 g/L DMH, 110 g/L KOH, 80 g/L KNO_3 and 0 – 40 g/L K_2HPO_4 . Inset: The effect of 0 – 40 g/L K_2HPO_4 on the deposition rate by sweeping the potential from + 0.6 V to – 0.8 V.

Solution conductivity is very important in electrodeposition because it does not only affect the electrical conductivity but also the power usage. Both KNO_3 and K_2HPO_4 are the

supporting electrolytes that helps to improve the solution conductivity and facilitate the mass transport of ions in the DMH-based silver solution.

From the voltammograms in Figure 6.4a – b, it can be seen that, unlike AgNO_3 and DMH, both KNO_3 and K_2HPO_4 salts do not affect the onset potential of Ag electrodeposition. However, adding 20 – 40 g/L KNO_3 into a solution containing only 20 g/L K_2HPO_4 as the supporting electrolyte significantly helps to improve the Ag electrodeposition rate from 1.9 to 2.8 $\mu\text{m}/\text{min}$. Nonetheless, the electrodeposition rate remains quite constant even though up to 160 g/L KNO_3 has been added successively.

On the other hand, increasing K_2HPO_4 concentration from 0 to 40 g/L into the solution containing excess KNO_3 (80g/L) does not influence the electrodeposition rate noticeably. This suggests that the mass transport of the supporting electrolytes is the limiting factor in controlling the rate of silver electrodeposition.

Nonetheless, the silver dissolution peak potential has shifted from $\sim +0.45\text{V}$ to $\sim +0.33\text{V}$ when 5 g/L K_2HPO_4 is added into the silver solution containing only KNO_3 as supporting electrolyte (Figure 6.4b). Even though both KNO_3 and K_2HPO_4 act as the supporting electrolyte and do not influence the cathodic polarization in the DMH-based silver solution, the K_2HPO_4 electrolyte has buffer capacity which helps to maintain the solution pH within a certain range[42, 147]. Besides that, the molar conductivity of KNO_3 is higher than K_2HPO_4 so KNO_3 is added in a greater amount than K_2HPO_4 electrolyte [148].

6.3.5 The Effect of Bath pH on the Electrodeposition of Ag

AgNO_3 salt is a strong electrolyte and is very soluble in water with a solubility product constant, $K_{\text{sp}} = 51.6\text{ M}$ [149]. However, when dissolving AgNO_3 in alkaline solution, insoluble AgOH , Ag_2O will be formed if complexing agent is not present to chelate the free Ag ions. DMH is known to be a complexing agent of Ag under alkaline condition [62, 140, 145].

Figure 6.5 (a) Cyclic voltammograms of silver electrodeposition and silver dissolution in the solutions consisted of 80 g/L AgNO_3 , 200 g/L DMH, 110 g/L KOH, 80 g/L KNO_3 and 20 g/L K_2HPO_4 at different pH. (b) The effect of pH on the onset potential of silver electrodeposition. (c) The influence of pH on the electrodeposition rate in the sweeping potential range from + 0.9 V till – 0.8 V.

Figure 6.5a shows the cyclic voltammograms of silver electrodeposition and silver dissolution in the solutions consisted of 80 g/L AgNO_3 , 200 g/L DMH, 110 g/L KOH, 80 g/L KNO_3 and 20 g/L K_2HPO_4 at different pH. From Figure 6.5b, it can be seen that the onset potential for Ag electrodeposition is shifted to more negative values when the solution pH is raised from pH 9 to pH 9.5. Nonetheless, the onset potential for Ag reduction is almost independent on solution pH thereafter, i.e. in the range of solution pH 9.5 to 12.0.

On the other hand, the Ag dissolution is also dependent on the solution pH, especially below pH 10.0. At pH 9.0 - 9.5, it is also observed that one main silver dissolution wave and one shoulder peak appear during the anodic scan in solution pH 9.0 - 9.5. Moreover, the Ag dissolution waves seem to have reached the steady-state limiting current and cover a broad range of potential. This may be due to the rate limiting steps which are involved in the complexation reaction of dissolved silver with DMH. The splitting of the dissolution wave can be due to the formation of different silver complex in the solutions.

Besides that, only one main and sharp dissolution peak is observed for the solutions at pH 10.0 -12.0. This has indicated that there is only one Ag complex formed between the dissolved Ag ions and DMH within this pH range. As a result, the DMH-based silver solution should be maintained within pH 10.0 – 12.0 because the onset potential of silver electrodeposition remains quite constant and hence easier to control during the operating process.

6.3.6 Optimization of Non-cyanide Operating Conditions

DMH ligand is selected to replace CN as a complexing agent in non-cyanide system because it has similar solubility and stability of chelating free Ag^+ ions when compared to KCN. Moreover, AgNO_3 is chosen to replace $\text{KAg}(\text{CN})_2$ as silver source in the non-cyanide system. Besides that, KNO_3 which is the main conducting salt in low cyanide system in Chapter 4, is also chosen to be used along with supporting electrolyte K_2HPO_4 in this non-cyanide system.

According to the cyclic voltammetric studies of non-cyanide system, in order to achieve higher deposition rate, the optimum concentrations of the electrolytes are determined to be as follows: DMH: 200 – 220 g/L, AgNO_3 : 80 – 100 g/L, KNO_3 : 60 – 100 g/L, K_2HPO_4 : 10 – 30 g/L. Furthermore, the optimum bath pH should also be maintained within pH 10 – 12, similar to the optimum pH range of low cyanide system in Chapter 4.

Under optimum operating conditions of the electrolytes as well as with the aid of proprietary additives (brightener, grain refiner and leveler), the roughness of the plated Ag films can be improved. Hence, smoother and brighter Ag films in non-cyanide system can be achieved.

6.3.7 Reflectance of Non-cyanide Plated Ag Films

Figure 6.6 The reflectance at $\lambda = 450 \text{ nm}$ and 550 nm of Ag thin film electroplated on Ni-plated brass substrates at 5 – 25 ASD in a DMH-based silver plating bath. The reflectance is determined by averaging the reflectance of 5 samples at each current density.

The Ag films are electrodeposited in DMH-based solution at different current densities, i.e. 5 – 25 ASD while their plating speeds vary between 0.5 – 3.0 $\mu\text{m}/\text{min}$. The thicknesses of plated Ag films are maintained 2.0 – 2.5 μm by controlling the electrodeposition time. Reflectance of the films are measured at both wavelengths $\lambda = 450$ and 550 nm . From Figure 6.6, the reflectance at both 450 and 550 nm increase significantly from 5 to 15 ASD

and the reflectance reaches above 85% (at 450 nm) and 87% (at 550 nm) when the Ag films are deposited in the range of 15 – 20 ASD. However, the reflectance drops by ~ 5% when the current density is further increased up to 25 ASD. As a result, in order to achieve higher reflectance, the optimum current densities are determined to be 15 – 20 ASD in this DMH-based system.

Under optimum operating conditions and current density, the reflectance (at $\lambda = 450$ and 550 nm) of Ag films electrodeposited by non-cyanide system can achieve above 85%. When compared to the conventional high cyanide plating system which gives reflectance ~ 80%, the non-cyanide system might also become feasible to achieve the brightness requirements for LED industrial application. Besides that, although the reflectance in the low cyanide system in Chapter 4 (Figure 4.8) can achieve about 90 – 95%, it is still unable to completely get rid of the use of cyanide. On the other hand, the reflectance of physical vapour deposited Ag in Chapter 5 (Figure 5.7) is only in the range of 60 – 70 %.

Table 6.1 The average errors of the statistical models for predicting the reflectance of silver films electroplated in DMH-based system.

Samples	R_a , nm	S_{dr} , %	Experimental $R_{450\text{ nm}}$, %	Experimental $R_{550\text{ nm}}$, %	Model (E.q. 1) $R_{450\text{ nm}}$, %	Error % (E.q. 1)	Model (E.q. 2) $R_{550\text{ nm}}$, %	Error % (E.q. 2)	Model (E.q. 3) $R_{450\text{ nm}}$, %	Error % (E.q. 3)	Model (E.q. 4) $R_{550\text{ nm}}$, %	Error % (E.q. 4)
Non-cyanide Ag # 1	11.7	0.8	85.2	87.3	79.9	6.2	84.5	3.2	86.0	0.9	90.0	3.1
Non-cyanide Ag # 2	14.9	1.8	73.3	76.5	75.1	2.5	80.3	5.0	73.1	0.3	79.3	3.7
Non-cyanide Ag # 3	27.8	2.8	61.5	66.6	55.9	9.2	63.5	4.7	60.2	2.1	68.6	3.0
Non-cyanide Ag # 4	21.9	3.7	52.3	58.6	64.7	23.7	71.2	21.5	48.6	7.1	58.9	0.6
Non-cyanide Ag # 5	31.5	4.6	39.7	52.3	50.3	26.8	58.6	12.0	37.0	6.9	49.3	5.9
Total average error						13.7		9.3		3.5		3.2

Statistical modelling for correlation of reflectance and roughness was developed in chapter 5, Eq. 5.1 – 5.4. Table 6.1 tabulates the simulation results by applying the statistical modelling to the plated Ag films with different roughness, using the DMH-based solution. The average errors between experimental and calculated reflectance (450 nm) from the Eq. 5.1 and Eq. 5.2 are 13.7% and 9.3% respectively, while the average errors between the experimental and calculated reflectance (550 nm) from the Eq. 5.3 and Eq. 5.4 are 3.5% and 3.2% respectively. The results are consistent with the results in Table 5.4 in Chapter 5. It is further confirmed that S_{dr} is a better indicator in predicting the reflectance when compared to R_a .

6.3.8 Characterization of the Plated Ag Films

The surface morphologies of Ag films electrodeposited by the DMH-based silver solution and cyanide-based silver solution are shown in Figure 6.7a – b. It can be seen that there are some differences in the surface morphologies of the two Ag films, i.e. the grain size of Ag film electrodeposited by DMH-based system is relatively smaller than that of Ag film electrodeposited by cyanide-based system. However, the AFM analysis has confirmed that the surface roughness (R_a) of both Ag films is comparable. The R_a of Ag films electrodeposited by DMH-based and cyanide-based system are 5.7 nm and 5.5 nm respectively (Figure 6.7c – d).

Figure 6.7 Scanning electron micrographs of Ag films electrodeposited by (a) DMH-based (b) low cyanide silver solutions; the 3D AFM images and surface roughness (R_a) of Ag films electrodeposited by (c) DMH-based (d) low cyanide silver solutions.

The XRD patterns in Figure 6.8 have also clearly showed that both Ag films are polycrystalline and exhibit (111), (200), (220) and (311) peaks. These four peaks are in consistent with the published XRD diffraction result of Ag with purity > 99.999% (JCPDS,

File no. 04-0783) [128]. In addition, the crystallites of Ag film electrodeposited using cyanide-free silver solution has the same preferred orientation in (111) plane as the film electrodeposited by using cyanide-based system.

Figure 6.8 XRD patterns of Ag films deposited by (a) DMH-based (b) low cyanide (c) high cyanide silver solutions (d) physical vapour.

Figure 6.9 Compositional XPS depth profile of Ag films deposited by (a) DMH-based (b) low cyanide (c) high cyanide silver solutions; (d) physical vapour systems as function of etched depth.

The XPS depth profile of the Ag films prepared from DMH-based and cyanide-based solutions are also compared in Figure 6.9. Both Ag films have 100 % Ag after the depth of about 6 nm. No other impurities are observed thereafter, showing high purity of both Ag films. Elements such as sulphur, oxygen and carbon are also detected from the Ag surfaces. These contaminants are from the environment and are often adsorbed on sample surfaces.

This shows that the Ag films electrodeposited by DMH-based are comparable with those electrodeposited by cyanide-based silver solution.

6.4 Conclusions

The electrochemical behaviours of AgNO_3 , DMH, KOH, KNO_3 , K_2HPO_4 electrolytes and solutions pH on the Ag electrodeposition and dissolution are studied. Strong agitation ≥ 1000 rpm is necessary to ensure that the mass transport of the electrolytes will not affect the chemical kinetics at the cathode. Higher AgNO_3 concentration lowers the cathodic polarization and shifts the onset potential of silver electrodeposition to more positive values while higher DMH content increases the cathodic polarization by chelating with free Ag^+ ions. High electrodeposition rate can be attained in solutions containing high silver and low DMH concentrations. Although both KNO_3 and K_2HPO_4 have little effect on the cathodic polarization, less than 40 g/L KNO_3 has slowed down the deposition rate significantly. The mass transport of the supporting electrolytes is the limiting factor in controlling the Ag deposition rate. The DMH-based silver solution is more favorably to be maintained within pH 10.0 – 12.0 because the onset potential of silver electrodeposition remains quite constant and hence easier to control during the operating process. The optimum concentration of the electrolytes are determined to be as follows: 200 – 220 g/L DMH, 80 – 100 g/L, 60 – 100 g/L KNO_3 , 10 – 30 g/L K_2HPO_4 . Under optimum operating conditions and current density, the reflectance (R) of Ag films electrodeposited by the non-cyanide system at both $\lambda = 450$ nm and 550 nm can achieve above 85%. It is further confirmed that S_{dr} is a better indicator in predicting the reflectance compared to R_{a} . Although there might be some opportunities to further improve the plating speed and reflectance of Ag films electrodeposited in DMH-based system, the film characterization analysis has showed that

the Ag films electrodeposited by DMH-based are comparable with those electrodeposited by cyanide-based silver solution.

Chapter 7

Impact, Limitations and Future Work

Chapter 7 summarizes the research findings and the goals that have been achieved. Key achievements include the development of low cyanide electroplating chemistry for high speed and highly reflective silver plating, DMH-based non-cyanide electroplating chemistry for highly reflective silver plating and correlation between surface roughness and reflectance of silver. This chapter also discusses the implications and limitation of this study which may lead to future opportunities such as improving the chemistry, process and performance of non-cyanide silver electroplating chemistry which does not only give high reflectivity ($R > 85\%$) but also high plating speed.

7.1 Achievements, Limitations, and Future Outlook

7.1.1 Achievements

In this research work, the low cyanide electroplating chemistry (< 10 g/L KCN) is developed, the electroplated Ag film can achieve mirror bright appearance with reflectance 90-95% which significantly increases the reflectance by 10-15% based on the current industrial status 80%. The plating speed is extremely fast up to 20-170 $\mu\text{m}/\text{min}$, which favors industrial application for mass production so as to greatly improve the productivity.

In order to eliminate the toxic cyanide used in the electroplating solution to cater for the stricter rules and regulation, the DMH-based non-cyanide electroplating chemistry is developed as well, the electrodeposited Ag film is bright with reflectance up to 85%, which met the project requirement.

The electrochemical behaviors and the effects of the basic electrolytes and solution pH in low cyanide system and DMH-based non-cyanide system are first investigated by cyclic voltammetric technique in chapter 4 and 6 respectively, the suitable working conditions for both low cyanide and non-cyanide systems are also proposed based on the cyclic voltammetric studies.

The surface and material characteristics of Ag films deposited by low cyanide and non-cyanide solutions are also studied respectively by SEM, AFM, XRD, and XPS etc. and compared with those physical vapour deposited silver.

A comprehensive study that correlates the effects of crystal orientation on the reflectance of silver is carried out for the first time. This is achieved by using single crystal Ag with different crystal orientation but with controllable surface roughness. 2D (R_a) and 3D (S_{dr}) parameters are used to characterize the surface texture of single crystal silver. It is found that surface roughness plays a more critical role in determining the reflectance while the crystal (100), (110) and (111) orientations have negligible effect on the silver reflectance. Moreover, correlations in predicting the silver reflectance by employing either 2D or 3D roughness parameters as the input variables have also been proposed. Polycrystalline

silvers are used to verify the accuracy of these equations. It is observed that S_{dr} is a better roughness indicator in predicting the reflectance of polycrystalline silver when compared to R_a .

7.1.2 Implications and Limitations

In this research, the low cyanide electroplating chemistry is studied in chapter 4 and DMH non-cyanide electroplating chemistry is studied in chapter 6 by using cyclic voltammetric technique, all the studies are conducted in the fresh chemical solutions. The fresh chemical solutions are under ideal condition and with no interferences by the contaminants. However, in the practical circumstances, the fresh chemical solution will become aged after being used for electroplating for a certain duration, the aged chemical solution might be contaminated due to drag-in of the proceeding pretreatment chemicals or slightly attacking the substrates. The electrochemical behaviors in the aged solution may be interfered by the contaminants and the cyclic voltammogram may be distorted compared to that obtained in the fresh chemical solution. In other words, using the fresh solution is unable to simulate the aged bath, the CV graph obtained from fresh chemical solution may not fully applicable to the aged chemical solutions. Due to the constraints that we are unable to obtain the aged chemical solution, the electrochemical behaviors in the age bath are not studied. However, the electrochemical behaviors obtain from the fresh chemical solutions still can serve as a guideline for the aged bath.

In chapter 4, the customized spot plating machine shown in Figure 3.10 is utilized for high speed silver spot plating. The silver plated area shown in Figure 7.1 is a circle with radius 5mm. The reflectance of the plated Ag film is measured by the spectroscopic reflectometer, the area measured is a circle spot with around 500 μm in diameter, while the roughness of the plated Ag film is measured by Atomic Force Microscopy, the area scanned is a square 5 μm x 5 μm . First, the size of the area used for measuring the reflectance is not same as that used for AFM measurement, second, even with marking, the area used for measuring AFM may not be exactly on the area used for measuring the reflectance. So the roughness does not fully reflect the surface condition of the reflectance. However, the same Ag plated film is relatively homogeneous / even in appearance, and also, increasing measurement

points is adopted to compensate this limitation. The roughness results by AFM are still representative in certain extent to show the surface condition of the reflectance.

Figure 7.1 Schematic diagram of the plated Ag film by the customized spot plating machine.

Furthermore, the rectifier is built in the spot plating machine in Figure 3.10, the current capacity is maximum 20A, the current tolerance is $\pm 0.10A$. The plated spot area is 0.00785 dm^2 , for example, to obtain current density 20 ASD, 30 ASD (A/dm^2), the ampere should be set to 0.157 A, 0.236 A respectively, however, with the current tolerance $\pm 0.1A$, the actual current may not be accurate due to the system error, especially for lower current density. On the other hand, the Ag film thickness is maintained $2\text{-}2.5 \mu\text{m}$ by controlling the plating time if given certain current density. The plating speed $20\text{-}170 \mu\text{m}/\text{min}$ as Figure 4.8, for instance, to maintain $2.5 \mu\text{m}$ thickness with a plating speed $100 \mu\text{m}/\text{min}$, the plating time is needed to control 1.5 second only. The plating time for this spot plating machine is manually controlled by switch on/off, there is a limitation here for human to accurately control 1.5 second. Increasing the sampling size and taking average value can compensate the human error in certain extent, the Figure 4.8 still shows the useful trend of the correlation of reflectance vs CD and plating speed vs CD.

7.1.3 Opportunities for Future Work

There is scope for further improving the chemistry, process and performance in the non-cyanide system.

First, the low cyanide electroplating chemistry (< 10 g/L KCN) is developed in Chapter 4, the electrodeposited Ag films can achieve 90-95% in reflectance. To address on the stricter rules and regulations by completely eliminating the toxic cyanide in the electrolytes, the non-cyanide electroplating formulation and process are also developed in chapter 6, and the reflectance can achieve up to 85%, when compared to the current industrial status 80%, and met the project requirement in terms of reflectance. However, compared to the reflectance achieved by low cyanide solutions, there is still room to further increase the reflectance of Ag films electrodeposited in non-cyanide system by improving and optimizing the formulations.

Second, in chapter 4 and chapter 6, the electrochemical behaviors and effects of basic electrolytes and solution pH are investigated by using cyclic voltammetric technique, there is still more scope of electrolytes for study by cyclic voltammetric technique, e.g. additives and brighteners, moreover, the interactions of each electrolyte is also open for further study. Especially, to improve and optimize the formulations of DMH-based non-cyanide system, the more variety of chemical candidates for brightening effect can be chosen to scan and study their electrochemical behaviors by cyclic voltammetric technique. Based on these electrochemical behavior and impacts to the reflectance of Ag electrodeposited films, the better and more suitable additives and brighteners may be selected, so as to increase the reflectance of Ag films electrodeposited in non-cyanide system to higher level.

Third, Low Cyanide electroplating chemistry and process developed in chapter 4 has been commercialized and used in mass production for industrial application, the working solution is stable and reliable for continuous mass production. While the DMH-based non-cyanide chemistry and process are developed in lab scale only, there are a lot of study works to be open if used in industrial application, for example, the plating speed is 2-3 $\mu\text{m}/\text{min}$, while low cyanide electroplating chemistry can achieve the plating speed up to 8-10 $\mu\text{m}/\text{min}$ at low agitation, push the plating speed up to 50-100 $\mu\text{m}/\text{min}$ if using jet-spray the electroplating solution. For industrial application, the productivity resulted from plating speed is always a big concern. Therefore, for DMH-based non-cyanide system, even though the reflective Ag films can be obtained at lower plating speed, there is a need to

increase the plating speed for industrial use. Future work to increase the plating speed can be emphasized on optimizing the ratio of complexing agent and free Ag^+ , enhancing the mass transfer speed in the electrolyte and improving the plating current efficiency. On the other hand, the stable and reliable working bath to achieve consistent performance is crucial for mass production. For DMH-based non-cyanide system, there is opportunities in the future to study the stability and reliability of working solution, to do these, not only the more stable chemical candidates should be selected, and also the consumption and decomposition behaviors of each electrolyte due to the aggressive working conditions and chemical reactions need to be investigated.

7.2 Conclusion

High light extraction efficiency is one of the critical factors for ensuring the performance of HB LEDs, attempts to improve the light extraction efficiencies are vital for pushing the brightness of LED to a higher level. One of the methods is to reduce the light scattering and enhance light output from leadframes towards the top component by depositing a highly reflective silver thin film on the leadframes surfaces. For decades, the high cyanide silver electrolytes are commonly used to deposit the reflective Ag films on the leadframes. Due to stricter rules and regulations, low cyanide or non-cyanide electrolytes become more favorable in plating industry, a detailed understanding of the electrochemical science is essential for developing the less toxic electrolytes.

Cyclic voltammetry is a powerful tool to study the electrochemical behaviors in the electrolytes, in this study, cyclic voltammetric technique is used to understand the electrochemical behaviors and individual and joint effects so as to serve as a guideline to screen the chemical candidates and optimize the operating parameters, and help the formulation development. The electrochemical behaviors and the effects of the basic electrolytes and solution pH in low cyanide system and DMH-based non-cyanide system are first investigated by cyclic voltammetric technique in chapter 4 and 6 respectively.

In this work, a low cyanide electroplating chemistry ($< 10 \text{ g/L KCN}$) is developed. The electroplated Ag film can achieve mirror bright appearance with reflectance 90-95% which

significantly increases the reflectance by 10-15% based on the current industrial status 80%. The plating speed is extremely fast up to 20-170 $\mu\text{m}/\text{min}$, which favors industrial application for mass production so as to greatly improve the productivity.

On the other hand, although the qualitative relationship between microstructure and reflectance of metals have been reported few decades ago, the quantitative correlation of microstructure and reflectance of Ag films have not been explored. Comprehensive relationship between the microstructure of silver thin film and its reflectance has also been explored by studying single crystal Ag with different crystal orientation but with controllable surface roughness. Individual impact of the film crystal orientation and surface topological factors, as well as their joint effect have also been considered for building the statistical models suitable for polycrystalline silver. The surface and microstructure characteristics of Ag are studied extensively by SEM, AFM, XRD, and XPS etc. and compared with those deposited by low and high cyanide solutions as well as physical vapour deposited silver.

2D (R_a) and 3D (S_{dr}) parameters are used to characterize the surface texture of single crystal silver. It is found that surface roughness plays a more critical role in determining the reflectance while the crystal (100), (110) and (111) orientations have negligible effect on the silver reflectance. Moreover, correlations in predicting the silver reflectance by employing either 2D or 3D roughness parameters as the input variables have also been proposed. Polycrystalline silvers are used to verify the accuracy of these equations. It is observed that S_{dr} is a better roughness indicator in predicting the reflectance of polycrystalline silver when compared to R_a .

In addition, in order to eliminate the use of cyanide, non-cyanide electroplating chemistry has also been studied. The reflectance of silver plated from non-cyanide chemistry can achieve up to 85%, which improve by 5% against the industrial status 80%, and met the project requirement in terms of reflectance. However, compared to the reflectance achieved by low cyanide solutions, there is still rooms to further increase the reflectance of Ag films electrodeposited in non-cyanide system by improving and optimizing the formulations.

Lastly, key achievements include detailed understanding on the roles of electrolytes, suitable working conditions in both low cyanide and non-cyanide systems, the correlations between surface, microstructure of silver and reflectance as well as development of low and non-cyanide silver chemistries which give rise to highly reflective silver films.

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