

**THE EFFECT OF ADDING SILVER  
NANOPARTICLES IN TIN SURFACE FINISH  
ELECTROPLATED WITH ULTRASONICATION  
ON WETTABILITY AND STRENGTH OF SAC305  
SOLDER JOINT**

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UNIVERSITI SAINS MALAYSIA**

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WETTABILITY AND STRENGTH OF SAC305 SOLDER JOINT**

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## DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled ‘The Effect of Adding Silver Nanoparticles in Tin Surface Finish Electroplated with Ultrasonication on Wettability and Strength of SAC305 Solder Joint’. I also declare that it has not been previously submitted for the award of any degree and diploma or other similar title of this for any other examining body or University.

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## LIST OF ABBREVIATIONS

AFM	Atomic Force Microscope
Ag	Silver
AgNPs	Silver Nanoparticles
ASTM	American Society for Testing and Materials
Cu	Copper
DC	Direct Current
IMC	Intermetallic Compound
RMS	Root Mean Square
SAC305	Sn-3.0Ag-0.5Cu
SEM	Scanning Electron Microscope
Sn	Tin
XRD	X-ray Diffraction

## LIST OF SYMBOLS

A	Ampere
Å	Angstrom
dm	Decimetre
e <sup>-</sup>	Electron
F	Faraday constant
kHz	Kilohertz
MHz	Megahertz
mm	Millimetre
M <sup>n+</sup>	Metal ion
N	Newton
n	Number of electron involved
nm	Nanometre
°	Degree
°C	Degree Celsius
V	Volt
W	Watt
wt%	Weight Percentage
Θ	Theta
μm	Micrometre
δ	Diffusion layer thickness
η	Overpotential

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**KESAN PENAMBAHAN NANOZARAH PERAK DALAM KEMASAN  
PERMUKAAN TIMAH YANG BERSADUR ELEKTRIK SECARA  
ULTRASONIK TERHADAP KEBOLEHBAHAN DAN KEKUATAN  
SAMBUNGAN PATERI SAC305**

**ABSTRAK**

Pembangunan pembungkusan elektronik telah memperkenalkan pelbagai jenis kemasan permukaan pada substrat kuprum untuk meningkatkan prestasi ikatan pateri. Ini menjejaskan pematerian dan sebatian antara logam yang terbentuk pada antara muka pateri/substrat yang akhirnya mempengaruhi kebolehpercayaan sambungan pateri. Tujuan kajian ini adalah untuk membangunkan salutan nanokomposit dengan mengena bersama zarah nano Ag ke dalam Sn melalui teknik penyaduran dengan bantuan ultrasonik. Salutan Sn dan salutan Sn/AgNPs disediakan menggunakan proses penyaduran elektro dengan penggabungan ultrasonik 0W, 10W, 20W, 40W, 60W dan 80W. Analisis fasa melalui pembelauan sinar-X dilakukan untuk menilai fasa dalam salutan, dan ketebalan salutan diukur melalui mikroskop elektron pengimbasan. Salutan kemudiannya dianalisis untuk kekasaran permukaan menggunakan mikroskop daya atom, sebelum meneruskan pengaliran semula pateri SAC305 komersial pada 250°C selama 150 saat. Sudut pembasahan pateri yang dialirkan semula pada substrat bersalut diukur dan ujian ricih sambungan pusingan tunggal dilakukan untuk menilai kekuatan sambungan pateri. Keputusan menunjukkan bahawa salutan yang disadur dengan ultrasonik 40W mempamerkan kekasaran permukaan yang paling rendah (4.07 $\mu$ m and 13.44 $\mu$ m) dan lapisan salutan yang paling tebal (6.61 $\mu$ m and 11.3 $\mu$ m) untuk salutan Sn dan salutan Sn/AgNPs masing-masing. Salutan Sn/AgNPs menunjukkan kekasaran permukaan yang lebih

tinggi dan lapisan salutan yang lebih tebal berbanding dengan salutan Sn. Kekasaran permukaan terendah yang diperolehi oleh salutan dengan ultrasonik 40W mempamerkan kebolehasahan terbaik dengan sudut sentuhan terendah ( $20^{\circ}$ - $22^{\circ}$ ). Penambahan nanopartikel Ag dalam salutan Sn menghasilkan lapisan IMC yang lebih tebal ( $4.33\mu\text{m}$ - $5.95\mu\text{m}$ ) pada sambungan pateri, namun mengurangkan sudut sentuhan dengan mengurangkan tenaga permukaan pateri, dan meningkatkan kekuatan ricih aloi pateri SAC305 dengan sudut sentuhan yang lebih rendah.

**THE EFFECT OF ADDING SILVER NANOPARTICLES IN TIN SURFACE  
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**ABSTRACT**

The development of electronic packaging has introduced various types of surface finish on copper substrate to improve bonding performance of solder. This affects the soldering and the intermetallic compound that formed at the solder/substrate interface which eventually influence the reliability of solder joint. The purpose of this study is to develop nanocomposite coating by co-depositing Ag nanoparticles into Sn via ultrasonic-assisted electroplating technique with ultrasonication. Sn coating and Sn/AgNPs coating were prepared using electroplating process with incorporation of 0W, 10W, 20W, 40W, 60W, and 80W ultrasonication. Phase analysis via X-ray diffraction was done to assess phases in the coating, and thickness of coating was measured via scanning electron microscope. Coatings were later analysed for surface roughness via atomic force microscope, before proceeded to reflow of commercial SAC305 solder at 250°C for 150 seconds. Wetting angle of solder reflowed on coated substrate was measured and single-lap joint shear test was done to assess strength of solder joint. The results demonstrated that coating electroplated with ultrasonication of 40W exhibited the lowest surface roughness (4.07 $\mu$ m and 13.44 $\mu$ m) and the thickest coating layer (6.61 $\mu$ m and 11.3 $\mu$ m) for Sn coating and Sn/AgNPs coating respectively. Sn/AgNPs coating exhibited higher surface roughness and thicker coating layer compared with Sn coating. The lowest surface roughness obtained by coatings with 40W ultrasonication exhibited the best wettability with the lowest contact angle (20°-22°). The addition of Ag nanoparticles

in Sn coating resulted in thicker IMCs layer of solder joint (4.33 $\mu$ m-5.95 $\mu$ m), but significantly reduced the contact angle by mitigating surface tension of bulk solder and improved the shear strength of SAC305 solder alloy due to lower contact angle.

# CHAPTER 1

## INTRODUCTION

### 1.1 Research background

Surface mount technology (SMT) initiated revolutionary change in electronic packaging industries to drive the trend of miniaturization since 1970s. The main feature of SMT is direct mounting of electronic components (e.g., chip resistor, capacitor and integrated circuit) on the surface of print-circuit board without the need of hole drilling for interconnection as in through-hole technology (THT). This gives an opportunity to reduce the pitch dimension on PCB, resulting in smaller device size with denser component packaging. Generally, SMT possesses great potential to achieve better performance, lower component volume, greater packaging density and lower production cost (Lee, 2002).

Surface mount assembly can be normally accomplished with soldering processes such as wave soldering and reflow soldering, which only require lower temperature to melt solder for interconnection of electronic component with PCB (Lee, 2002). However, soldering process should consider the types of solder alloy used for assembly because the properties of solder are the key factors that significantly influence the spreading of molten metal, dissolution of metal atom and the formation of intermetallic compound. The composition of solder alloy as well as soldering condition must be comprehended to achieve good metallurgical bonding, where a solder with good wettability is required in practice (Ervina & Nur, 2016). In addition, the mechanical properties of solder joints are one of the main concerns when the solder components are subjected to cyclic load, impact, or vibration. The morphology and types of IMC corresponded to the bonding of solder joints, in which

they can be varied with different soldering techniques or process parameters (Yao et al., 2017). Furthermore, shear strength also became a research scope to evaluate the mechanical reliability of solder joints. The shear properties of solder joints can be commonly measured with single-lap joint testing method which is designed under ASTM D1002 standard.

The development of soldering applications has involved the use of surface finish for the improvement of solder performance in surface mounting technology (SMT). The primary function of surface finish is to protect metal substrate from oxidation, while it also able to inhibit excess growth of intermetallic compound (IMC) by controlling atoms dissolution (Toscano & Long, 2005). In recent studies, various surface finishes such as NiP deposit, electroless nickel immersion gold (ENIG), hot-air solder levelling (HASL), organic solderability preservatives (OSP), immersion tin (ImSn) and immersion silver (ImAg) were tested to evaluate reflow performance and condition of solder joint, showing that the types of surface finish have correlation with the solder joint properties (Amli et al., 2019; Arra et al., 2004; Tseng et al., 2013). The application of surface finish became significant in electronic packaging industries for the enhancement of solder reliability.

Most industries introduced electroplating as an excellent choice for fabrication of surface finish on substrate due to its simple setup and cost-effectiveness. Electroplating involves electrochemical reaction to perform metal finishing on products, where it has been used in chromium coating, zinc coating, nickel coating, and tin coating for various applications such as machinery, tool, automotives, aerospace and electronic devices over many decades. Due to new

chemical developments from recent research, the electroplating technology in present day is not only capable for pure metal coating, but it also applicable for alloy coating (e.g., Zn-Co, Zn-Ni, Ni-Co etc.) and composite coating (e.g., carbon nanotube-Ni composite) (Kanani, 2004; Giurlani et al., 2018).

## **1.2 Problem statement**

As surface mount components could be failed due to the poor wettability and fracture of solder joint, it is highly vital to control the formation of intermetallic compound between solder alloy and Cu substrate during reflow process. Poor metallurgical bonding can result in weak joint due to the absence of  $\text{Cu}_6\text{Sn}_5$  interfacial layer, where it would cause the deterioration of sensitive components and malfunction of electronic devices. Meanwhile, a thicker intermetallic compound layer generated from rapid Cu dissolution could be another issue for solder joint as it possesses brittle nature and tends to generate structural defects caused by the properties mismatch of compositions (e.g., elastic modulus).

In this case, the properties of packaging application were reconsidered by introducing suitable surface finish on Cu substrate to achieve desired interfacial layer for better bonding. Many surface finishes were developed through various research, including Nickel plating, Electroless Nickel/Immersion Gold (ENIG), Immersion Silver (Im-Ag), Immersion-Tin (Im-Sn), and Hot-air Solder Levelling (HASL). Tin coating (Sn) was commonly recommended in electronic packaging because it exhibits low material cost and high availability, but the major issue in this type of surface finish was the growth of tin whisker when subjected to thermal cycling or cyclic load (Lin & Lin, 2008; Jagtap & Chason, 2020). The presence of tin whisker

in Sn/Cu pad interface would result in short-circuiting and internal stress that would deteriorate function of electronics devices (Chason et al., 2008).

In early age, Pb was used to suppress Sn whisker in solder joint, but it was then restricted due to enforcement of RoHS Directives 2002/95/EC. Due to environmental concern, many studies have introduced other alternatives such as bismult (Bi), zinc (Zn), and nickel (Ni) to suppress whisker growth in Sn coating (Dimitrovska & Kovacevic, 2009; Wang et al., 2010; Hashim et al., 2020). The addition of those alloying elements also gave significant improvement on corrosion resistance, electrical properties as well as solderability. Nevertheless, most studies only carried out investigation on the development of alloy-based coating, while the research on nanocomposite coating for metal interconnection was limited in practices.

It was known that Ag could act as an alloying element which was capable to suppress tin whisker by promoting grain growth in Sn phase to provide stress relaxation in microstructure under aging condition. The segregation of Ag in grain boundaries of Sn could contribute to high driving force and increasing grain boundaries mobility that facilitates grain coarsening (Stein et al., 2014). On the other hand, the addition of Ag nanoparticles into bulk solder could contribute to better solder wettability and enhanced solder joint strength due to its ability to mitigate surface tension in molten solder and suppress grain coarsening of  $\text{Cu}_6\text{Sn}_5$  IMCs. However to the best of author's knowledge, there is no reported work on the development of Sn nanocomposite coating with incorporation of Ag nanoparticles in pure Sn coating.



Furthermore, various studies demonstrated that the morphology of surface finish on substrate was strongly related to the intensity of ultrasonic effect, while the performance of reflowed solder could be linked with the surface roughness of surface finish. Therefore, this project would study the fabrication of Sn/AgNPs nanocomposite using electrodeposition technique with the presence of ultrasonic effect, while also investigate the morphology, the formation of intermetallic compound, as well as the mechanical behaviour and wettability of solder reflowed on Sn/AgNPs nanocomposite. The addition of Ag nanoparticles in Sn surface finish was expected to optimize the formation of intermetallic compound during reflow process, while it may also contribute to the enhancement of solder joint strength and wettability.

### **1.3 Objectives**

This research focuses on the study of electroplated surface finish on substrate that correlated with the improvement of solder joint properties. The main objectives of current work are as following:

1. To evaluate the effect of ultrasonication power to the the thickness and morphology of Sn coating and Ag-reinforced Sn nanocomposite coating.
2. To determine the wettability, IMC formation and strength of SAC305 solder joints on Cu substrate with Sn coating and Ag-reinforced Sn nanocomposite coating.

#### **1.4 Thesis outline**

This thesis comprised of 5 chapters that explicate the relationship between surface finish and solder reliability. Chapter 1 briefly presents the scope of study, problem statement and objectives of work. In chapter 2, the comprehensive literature review is included to explain the details of solder materials, solder properties, principles of metal electrodeposition, development of Sn-based alloy and composite electrodeposition and incorporation of ultrasonication in electrodeposition. Chapter 3 elaborates the methodology that indicates the sample preparation, experimental setup, fabrication, and characterization stages. Chapter 4 provides the discussions on the influence of ultrasonic power on electrodeposition of coating as well as the effect of Sn coating and Ag-reinforced Sn nanocomposite coating on wettability and strength of SAC305 solder alloy. The quality of surface finish and morphology of IMC layer were investigated, while the contact angle and shear properties of SAC 305 solder alloy were also evaluated after reflow process. Finally, chapter 5 concludes the result of this research work and delivers recommendations of future work that can be conducted to approach further research on Sn-based surface finish in soldering application.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1 Soldering**

The principle of metal joining is crucial to be investigated in the engineering field, especially bonding dissimilar materials to form unitary structure for specific function. The chemical and physical properties of both different metals determine the joining effectiveness and quality, hence the joint structure could be not sustainable if the dissimilar metals are unsuitable to be mated. Welding, brazing, and soldering are the common metallurgical joining techniques in current practice, but the selection of bonding technologies depends on the product requirements, including the desired properties, cost, manufacturing time as well as starting materials (Li et al., 2020).

The application of soldering process is more favoured to the through-hole technology (THT) and surface mount technology (SMT) in electronic packaging industries as shown in Figure 2.1. It requires a lower operating temperature compared with other metallurgical joining process, where its filler metal has a melting point that below 450°C, while brazing process should be utilized if the filler metal has the melting point more than 450°C (Klocke et al., 2005). Soldering technology is necessary to be reviewed due to various challenges in miniaturization of electronic components, e.g., electromigration and thermomigration in solder joint that degrade the device performance (Zhang et al., 2020).

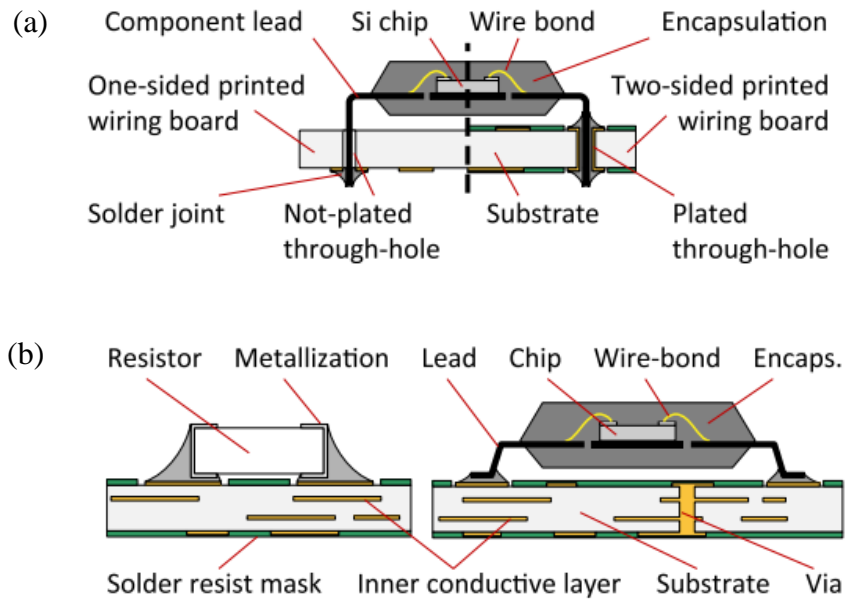


Figure 2.1 a) Through-hole Technology (THT) and b) Surface Mount Technology (SMT) (Illes et al., 2020).

### 2.1.1 Development of solder alloy

Solders are the important components to be developed in the electronics packaging industries for several decades. It usually possesses low melting point as it is required to form joint between parent metals with its molten state (Chen et al., 2007). In terms of research and development, solder joint quality and reliability significantly determine the performance of electronic components, such as transistors and microchips on the printed circuit boards (PCB). In this case, the materials and compositions play an important role in the development of reliable solder in engineering field.

Tin (Sn) has been used as the basic component of most alloy solder in electronic packaging as it has good wettability which is suitable to wide range of substrate. Its low melting point (231°C) also became one of the advantages that eases

the packaging of temperature-sensitive electronic component. In engineering perspective, a pure Sn still could be problematic if it is applied in the electronic component because of two major issues: i) cracking induced by volume change and; ii) whisker growth that could cause electrical short (Abtew & Selvaduray, 2000).

In this case, Pb had been selected to compensate the drawbacks of pure Sn by developing Sn-Pb alloy. In early age, lead (Pb) has been introduced as a potent material in the solder component, where the Sn-Pb solder has been adopted in electronics assembling industry over 50 years due to low cost and its abundance (Cheng et al., 2017). Sn-Pb alloy could acquire low eutectic temperature (183°C) which is found at the composition of 63wt% Sn/37wt% Pb, where it has better solderability than Sn-rich component and it is compatible for most substrate material. The addition of Pb is useful for reducing surface tension of pure Sn to improve wettability of solder, while it can also prevent  $\beta$ -Sn/ $\alpha$ -Sn transformation upon temperature change. The presence of Pb was also able to control formation of liquid-state diffusion of joint constituents. Furthermore, it provides great mechanical and chemical properties to resist crack and suppresses the growth of tin whiskers in the tin-/based solders (Abtew & Selvaduray, 2000). However, Pb could provide negative impacts on environment and human health since it is a heavy metal that would cause pollution and harm nature through contamination from electronics waste disposal. Prolonged exposure to Pb component could also deteriorate the blood and nervous system of human body (Tonapi, n.d.).

Most industries and research institutions in Europe, United State, and Japan considered Sn-Cu as the suitable substitute for the Sn-Pb solder. Although its melting

point (227°C) is expected to be higher compared with the melting point of Sn-Pb (183°C), the usage of lead-free component has been prioritized for the future market due to environmental concern (Suppiah et al., 2017). Hence, some research introduced the addition of Ag to achieve lower melting point and higher reliability of solder component, resulting in the development of Sn-Ag-Cu solder (SAC) that could be comparable to the properties of Sn-Pb solder (Cheng et al., 2017). Nevertheless, the cost of SAC still became a great challenge to the manufacture since the price of Ag is considerably high in the market (853.70 USD/kg, as reported by London Metal Exchange, March 2022). Despite that, most researchers have expanded their investigations for determining new composition in SAC system or other elements which are promising for the replacement of Pb-included solder.

### **2.1.2 Wettability**

One of the concerns in the soldering application is the wettability of solder alloy on the substrate, in which it measures the ability of a molten metal to spread over the substrate surface and maintain adhesion after solidification. In other words, it is related to the interaction between solid phase and liquid phase in the system (Park et al., 2000). Wettability usually takes account on the interfacial energy existed between solid-liquid interface, but it also places great emphasis on the evaluation of contact angle, wetting force, and wetting time. Those indicators could be affected by several factors, including the nature of interfacial reaction, the viscosity of liquid metal as well as the processing temperature (Zhao et al., 2019).

The wettability of a solder alloy is mainly dominated by three distinct surface energies which are solid-liquid interfacial energy ( $\gamma_{SL}$ ), liquid-vapour interfacial

energy ( $\gamma_{LV}$ ) and solid-vapor interfacial energy ( $\gamma_{SV}$ ) as shown in Figure 2.2. Young-Dupre equation has been used as a concept to define the wettability with the function of contact angle,  $\theta$  that respects to all involved interfacial energies under equilibrium state:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

Contact angle is a common term to assess the spreading of molten solder alloy on the substrate. It can be calculated from the wetting balance test to estimate the quality of solder joint with the aids of wetting curve. A solder alloy usually acquires acceptable wettability if the contact angle is less than  $90^\circ$ , but a better wetting can be achieved with a contact angle in range of  $0^\circ$  to  $20^\circ$  only if it is under ideal condition. However, the contact angle of the solder is practically lied between  $60^\circ$  and  $90^\circ$ . Molten metal with contact angle greater than  $90^\circ$  is considered as the poor wetting condition, where it could be an issue for the soldering process (Moser et al., 2018).

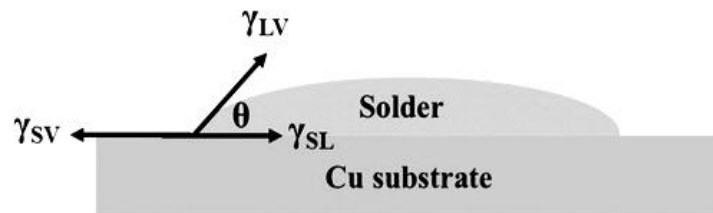


Figure 2.2 The measurement of contact angle with all interfacial energies based on Young-Dupre equation (Jung et al., 2018).

### 2.1.3 Intermetallic compound

During soldering process, the formation and growth of intermetallic compound (IMC) caused by the interfacial reaction between the molten solder alloy and the solid metallic substrate. Atoms diffusion occurred at the solid-liquid interface allows IMC to precipitate in form of layer with fixed stoichiometry (Lee, 2002). The well-known IMCs are  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  which can be emerged when a lead-containing or lead-free solder alloy is metallurgically bonded with Cu substrate after reflowing or aging process (as shown in Figure 2.3).

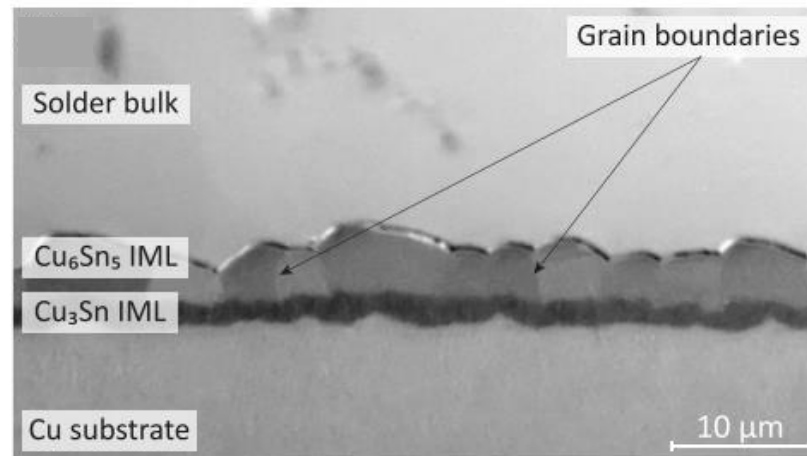


Figure 2.3 Formation of  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  between Cu substrate and low-Ag containing solder alloy (Krammer et al., 2015)

In practice, the reflow soldering profile is essential to be optimized to control the growth of IMC since the layer thickness is the key factor that considerably influence the quality and reliability of solder joint. Several studies concluded that increasing soldering time or soldering temperature could increase the IMC layer thickness, while the growth rate of IMC would be reduced after it reached a critical time in which the growth mechanism is converted from reaction diffusion to grain-boundaries diffusion (Yu et al., 2008; Mookam & Kanlayasiri, 2011; He et al., 2006;



El-Rehim & Zahran, 2017). With the aid of Arrhenius's law, the average thickness of IMC layer can be estimated by applying theoretical diffusion limited model as shown in Equation 2.2 (Illes et al., 2020):

$$x = x_0 + t^n \cdot k_0 e^{(-E_a/RT)} \quad (2.2)$$

where  $x$  is the average thickness of IMC layer (mm),  $x_0$  is the initial thickness of IMC layer (mm),  $t$  is the duration of process (s),  $k_0$  is the growth rate constant,  $E_a$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.314 \text{ J K}^{-1}\text{mol}^{-1}$ ),  $T$  is the absolute temperature (K) and  $n$  is the exponential value ( $n=0.3$  if layer growth is governed by grain boundary diffusion;  $n=0.5$  if layer growth is governed by volumetric diffusion).

The mechanism of atomic interdiffusion kinetics plays important role in the IMC formation in solder/substrate interface. The diffusion mechanism could include volume diffusion and grain boundary diffusion. Volume diffusion occurs when diffusion of atom takes place in bulk solder. On the other hand, grain boundary diffusion defined as the diffusion of atom along grain boundaries. The thickness of IMC could be correlated with the total grain boundaries area which was determined by the morphology of IMC. It was suggested that the formation of  $\text{Cu}_6\text{Sn}_5$  IMC was governed by grain boundary diffusion at early stage, then the diffusion mechanism would be gradually converted to volume diffusion at longer time due to coarsening of interfacial  $\text{Cu}_6\text{Sn}_5$  grains that result in decreasing total grain boundaries area (Yu et al., 2005; Yang et al., 2012).

The growth of IMC layer should not be either excessive or over-restricted to avoid degradation of solder joint. IMC usually possesses brittle characteristic that can initiate fracture easily if the layer thickness is exceedingly large. Conversely, fast growth also may produce voids at IMC/substrate interface because of unstable diffusion, thus the presence of defects generates stress concentration within the IMC (Xu et al., 2017). However, small IMC layer thickness can result in weak joint if the interfacial reaction was inadequate.

#### **2.1.4 Surface finishes on substrate**

The metallurgical bonding of solder could be also determined by the nature of substrate in the soldering process for achieving a high-quality joint formation. The molten state of solder could spread across the surfaces of substrate to be interacted, while the substrate conditions (e.g., metal types, surface morphology, thickness) can give significant impact on the properties of joint. Practically, nickel (Ni), gold (Au), palladium (Pd) and copper (Cu) have been used as substrate in the electronic packaging industry. Cu is widely used as it possesses good mechanical properties and excellent electrical conductivity, hence it can be produced in form of sheet with small thickness in PCB (Silva et al., 2015).

In many cases, the application of surface finishes on PCB is necessary to protect exposed Cu surface from oxidation and avoid depletion of solder joint strength and wettability due to unstable diffusion (Toscano & Long, 2005). Some surface finishes are capable to decrease the interdiffusion between substrate and the solder alloy to suppress IMC growth at elevated temperature (Wang et al., 2009). Most electronic packaging industries recommend immersion plating or

electrodeposition for the development of surface finish on the substrate surface to enhance the solder joint reliability by improving spreading of solder and suppressing growth of intermetallic compound. Intermetallic compound generated on the interface between solder and surface finish has been considered as a key to achieve good metallurgical bond (Kumar et al, 2005).

Previous research has studied the reliability of reflowed solder and surface finish on the substrate. Yoon & Jung et al. (2005) conducted a study on the interfacial reaction and morphology change of intermetallic compound between Sn-0.4Cu solder and two different surface finishes (bare Cu substrate and electroless nickel-immersion gold-plated (ENIG) Cu substrate). Based on the observation, the duplex structure of  $\text{Cu}_6\text{Sn}_5$  and  $\text{Cu}_3\text{Sn}$  could be found on the interface between Sn-0.4Cu solder and Cu substrate after aging for 60 minutes, while  $(\text{Cu},\text{Ni})_6\text{Sn}_5$  and  $(\text{Ni},\text{Cu})_3\text{Sn}_4$  intermetallic compounds are formed at the interface in the case of Sn-0.4Cu reflowed on ENIG-plated Cu substrate. On the other hand, Nakano et al. (2010) investigated the connection reliability of Sn-Ag alloys deposited on a Cu substrate that are prepared from sulphate solution and pyrophosphate-iodide solutions respectively. The results indicated that the friction coefficient of deposited Sn-Ag alloy decreased with increasing Ag content as more amount of  $\text{Ag}_3\text{Sn}$  intermetallic compound with high hardness formed after reflow process.

Li et al. (2005) also studied the wettability of Sn-3.8Ag-0.7Cu and Sn-3.5Ag solder on the electroless nickel-coated Al substrate. The result affirmed that the substrate roughness could influence the surface roughness of Ni-P coating, and a good wettability should be achieved by the uses of strong flux since electroless Ni

coatings oxide easily, causing formation of stable oxide layer on surface. The research also indicated that high phosphorus content in Ni-P coating could significantly improve the solderability of both Sn-3.8Ag-0.7Cu and Sn-3.5Ag solder. Furthermore, Kurtz et al. (2012) determined the enhancement of surface solderability and reflow performance with bright-Sn surface finish. The experiment concluded that Sn deposit contributed lower surface roughness and better oxidation resistance that significantly improve solderability of SAC solder. Smooth deposit surface is capable to achieve minimal oxide formation, thus it allows better wetting performance of solder alloy.

#### **2.1.5 Effect of Ag nanoparticles on solder reliability**

Ag nanoparticle is a promising nanomaterial in electronic packaging due to its higher electrical conductivity, better thermal stability as well as high corrosion resistance that could resolve various issues in metal interconnection when subjected to high temperature and corrosive environment. It is also an ecofriendly alternative to replace the use of Pb in interconnects materials to comply with RoHS restriction (Joo et al., 2007). Various studies incorporated Ag nanoparticles to improve solder reliability by enhancing wettability of solder and controlling the formation of IMC in solder joint. Koscielski et al., (2010) reported that the addition of Ag nanoparticles content from 1% to 4% could improve the spreading of SAC305 solder alloy under peak reflow temperature of 220-250°C. Yan et al. (2009) inferred that the addition of Ag could improve the spreading rate of Sn-Sb-Cu solder alloy by reducing the melting temperature of bulk solder. Shen and Chan (2009) also conducted the study on the effect of Ag-doped flux on wettability of Sn-3.5Ag-0.5Cu solder alloy. The results revealed that the presence of Ag could improve the wettability of solder by

decreasing contact angle from 38° to 32° based on undoped flux. Ag acted as surface-active agent on the surface of molten solder, and the absorption of Ag nanoparticles into molten solder could significantly reduce the surface energy of molten solder that resulted in better wetting.

Meanwhile, Satyanarayan & Prabhu (2013) mentioned that the addition of Ag nanoparticles on Sn coating could lead to increasing amount of Ag<sub>3</sub>Sn IMCs formed in bulk solder that existed in form of plate or particulate. This assertion could be also supported by Liu et al. (2010), where the higher concentration of Ag could increase the size of Ag<sub>3</sub>Sn precipitates. On the other hand, Chung et al. (2004) described that Ag<sub>3</sub>Sn IMCs could be formed in SAC bulk solder, while it could be also existed at interface or next to Cu<sub>6</sub>Sn<sub>5</sub> precipitate. As Cu<sub>6</sub>Sn<sub>5</sub> offered high interfacial energy due to large curvature of grain surface, it could provide more nucleation site for Ag<sub>3</sub>Sn precipitate (Guo et al., 2018).

The function of Ag<sub>3</sub>Sn IMCs was also investigated by Hsu & Ouyang (2015), in which Ag<sub>3</sub>Sn could contribute to the inhibition of Cu dissolution at high temperature. The presence of plate-like and particulate Ag<sub>3</sub>Sn IMC acted as diffusion barrier to retard dissolution of Cu atoms by reducing interfacial energy, thus resulting in the formation of scallop-shaped Cu<sub>6</sub>Sn<sub>5</sub> IMCs on the interface. Cu dissolution became insignificant in the surrounding of Ag<sub>3</sub>Sn precipitate, which leads to the suppression of IMC thickness on interface. Somehow those statements created argument in some research, where the addition of Ag did not reduce the IMC thickness but rather enhance the consumption of Cu atoms to form Cu<sub>6</sub>Sn<sub>5</sub> with higher volume fraction (Lee et al., 2008; Faizan, 2015). This phenomenon has been

inferred by Yang et al., (2012), where thicker IMCs layer was resulted from the increasing  $\text{Cu}_6\text{Sn}_5$  grain boundaries. The addition of Ag could influence the growth orientation and coarsening behaviors of  $\text{Cu}_6\text{Sn}_5$  due to variation of interfacial energy between bulk solder and interfacial IMCs. This leads to the more grain boundaries as the mean radii of  $\text{Cu}_6\text{Sn}_5$  grain were reduced by the formation of scallop-shaped or dome-shaped structure, hence enhancing the contact between molten solder and Cu substrate as well as providing more diffusion path for Sn atoms toward Cu substrate through grain boundaries, which facilitate Cu dissolution. In this case, more Cu atoms will diffuse into interfacial region and precipitate more  $\text{Cu}_6\text{Sn}$  IMCs.

Some studies also reported that the addition of Ag could contribute to the solder joint strength by refining the  $\beta$ -Sn dendrites. Fast diffusion rate of Ag in molten Sn facilitates dendrites growth, while the dispersion of  $\text{Ag}_3\text{Sn}$  IMC into grain boundaries in bulk solder could limit the growth of  $\beta$ -Sn grain by pinning dislocation upon cooling. This resulted in precipitation strengthening effect that significantly improve the mechanical properties of solder (El-Daly et al., 2011; Geranmayeh et al., 2012; Yuan et al., 2021). Somehow Chu et al. (2017) also suggested that higher amount of  $\text{Ag}_3\text{Sn}$  precipitates in solder joint could lead to lower shear strength due to greater ductility of structure. This showed that the amount of Ag nanoparticles should be controlled to achieved desired strength of solder joint.

## **2.2 Thin film deposition**

Thin film deposition or coating referred as the fabrication of thin film layer on the surface of substrate. The deposited film layer on a substrate could be existed in either nanoscale or microscale, depending on the requirements of final product

(Singh et al., 2013). For specific application, it can be designed into single layer with homogeneous composition or multilayer with inhomogeneous composition (Abegunde et al., 2019). Thin film serves as a cost-beneficial component that can improve the surface properties of bulk material including hardness, abrasion resistance, corrosion resistance, absorption, reflection, and electrical properties. It also contributes to the miniaturization of the device since the application of thin film have approached to the development of nanotechnology (Frey & Khan, 2015).

Thin film deposition techniques can be categorized into two routes: (a) chemical methods (e.g., chemical vapour deposition (CVD), electrodeposition, sol-gel method) and; (b) physical methods (e.g., ion beam sputtering, physical vapour deposition (PVD), electron beam evaporation). For chemical deposition, the chemical reaction takes place between volatile precursors and the substrate surface to form final deposit, while a physical deposition involves mechanical and thermodynamic processes to deposit material on the substrate surface (Shim, 2013). Generally, film quality, available precursor, substrate structure, production cost, deposition rate and other factors are necessary to be contemplated for the selection of deposition techniques (Singh et al., 2013).

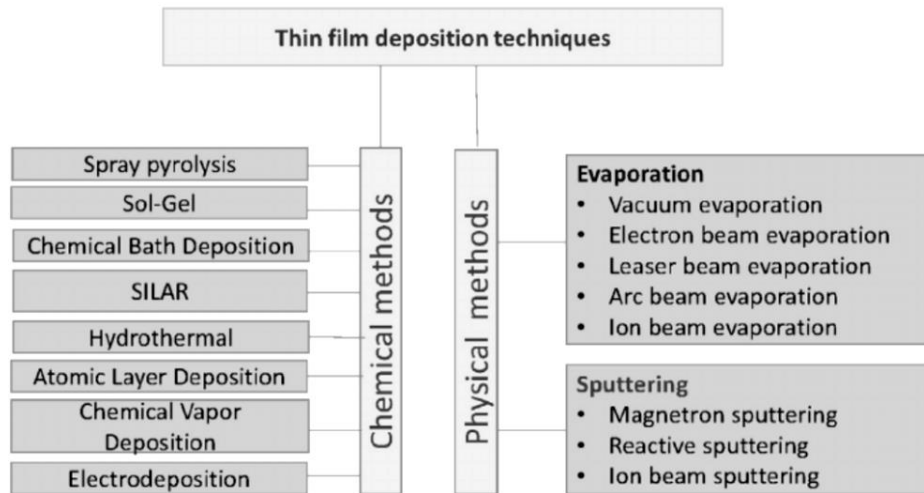


Figure 2.4 General classification of thin film deposition techniques (Pedanekar et al., 2020).

The technologies of thin film deposition have been adopted for the synthesis of nanostructure materials that have grain structure less than 100 nm (Gleiter, 2000). Most electronic applications such as optoelectronics, transistors and other semiconductor devices incorporate nanomaterials to acquire unique characteristic with superior electrical, optical, mechanical, or magnetic properties (Siegel, 1993). Therefore, nanostructure thin film plays a significant role in the enhancement of product performance and reliability.

### 2.3 Electrodeposition of metal

Electrodeposition is known as a fundamental electrochemical process for thin film deposition, in which a coating material is deposited on the substrate through an electrochemical reduction of metal ions under the presence of electrolyte and electric current (Al-Bat'hi, 2015). This process is usually called electroplating for the fabrication of metallic surface finish in the coating industry. The first electroplating



model was introduced by Luigi Valentino Brugnatelli for electrochemical deposition of gold in 1805 with the aid of Zn/AgO voltaic pile which was invented by Alessandro Volta (Mohler, 1969). Later, many researchers or scientists gained their interest in the development of electroplating to incorporate other metals (e.g., nickel, zinc, brass and tin) into coating industry (Giurlani et al., 2018). A basic electroplating technique comprises of several elements in order to set up a complete electrolytic cell as shown in Figure 2.5 (Low et al., 2016):

- a. Anode, a positive electrode which is used as plating material or inert substance.
- b. Cathode, a negative electrode that serves as workpiece to be plated.
- c. Electrolyte, a conductive solution that allows the migration of ions.
- d. Power supply, a source that provides external electric current to the electrochemical system.

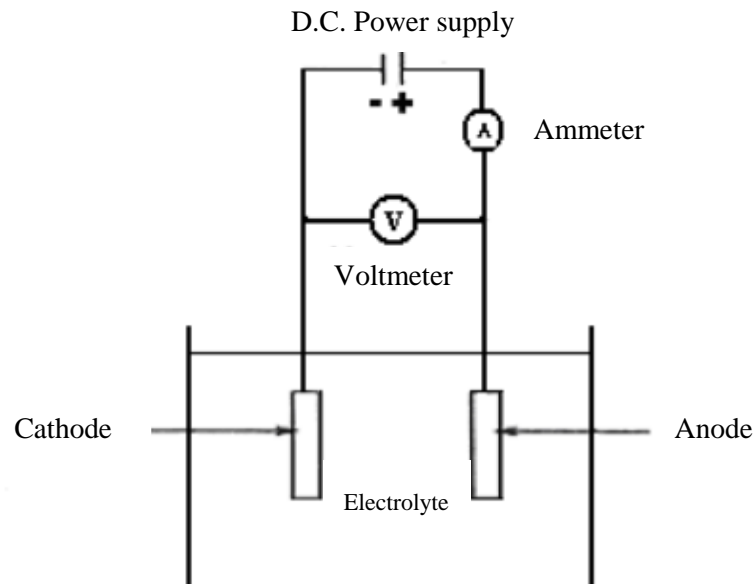


Figure 2.5 Basic elements of electroplating (Al-Bat'hi, 2015).

Electroplating technology made some great impression in the surface engineering field as it exhibits high production rate, low energy consumption and good process control for fabricating simple or complex coating on surface (Ahmad & Mohamed, 2014). Over several decades, the functionality of electroplating has been extended from improvement of visual appearance to modification of surface properties, allowing a product to resist external damage (wear, friction, and impact) as well as withstand severe environment (heat and corrosive condition). In terms of electronic components, electroplating techniques have been recommended as a cost-effective option to fabricate coating layer with enhanced electrical conductivity and better adhesion.

### **2.3.1 Working principles of electroplating**

In the system of electrodeposition, a power supply connected with positive terminal and negative terminal, which are anode and cathode respectively to permit current flow. Anode and cathode are directly immersed into the electrolyte bath to form a complete electroplating model. The electrolyte contains metal salt which is responsible for electrolysis in which ion migration occurs under the influence of potential difference. In short, the positively-charged ions will travel to the cathode, while the negatively-charge ions will travel to the anode through an aqueous solution of metal salt (Al-Bat'hi, 2015).

Anode acts as a positive electrode to remove anions from the electrolyte in for balancing the charges in the solution (Kanani, 2004). The positive electrode used in the system can be either sacrificial anode or inert anode (Low et al., 2016). Sacrificial anode is used as the plating material which will be deposited on the

workpiece, where the metal anodically dissolves into the electrolyte to compensate the loss of metal ions from deposition. On the other hand, inert anodes such as graphite and platinum are not consumable in the electroplating process, where it is used when the supplement of metal ions is only governed by the electrolyte or additives (Sadoway, 2001).

In the case of consumable electrode, anode will consume the electrons through the dissolution of metal atoms to liberate positively-charged ions into the electrolyte. The electrons are then transferred from anode to the cathode (workpiece) through external circuit instead of electrolyte. The presence of electrons cause cathode to be negative-charged, resulting in the attraction of positively-charged metal ions and repulsion of negatively-charged ions. When a metal ion reached the negatively-charged cathode surface, it will consume the available electrons to form a metal atom which is being deposited on the surface of workpiece. The general chemical reactions take place at anode and cathode can be described in terms of equation (Al-Bat'hi, 2015):

At anode,



At cathode,



where n is the number of electrons involved in the reaction.

## 2.3.2 Kinetics of electroplating

### 2.3.2.1 Mechanism of electrodeposition

In metal electrodeposition, an overall process comprised of several mechanisms: (a) migration; (b) diffusion and; (c) incorporation as shown in Figure 2.6. When a potential difference applied between anode and cathode, the anodic reaction contributes electron flow to the cathode through the external circuit. While the cathode becomes negatively-charged due to the consumption of electrons, the  $M^+$  ion (cation) is produced from the metal dissolution and the difference in electrical polarity causes attraction of positively-charged ion toward the direction of cathode under the presence of potential gradient (David et al., 2010). These processes are subsequently maintaining the ion supply for the cathode.

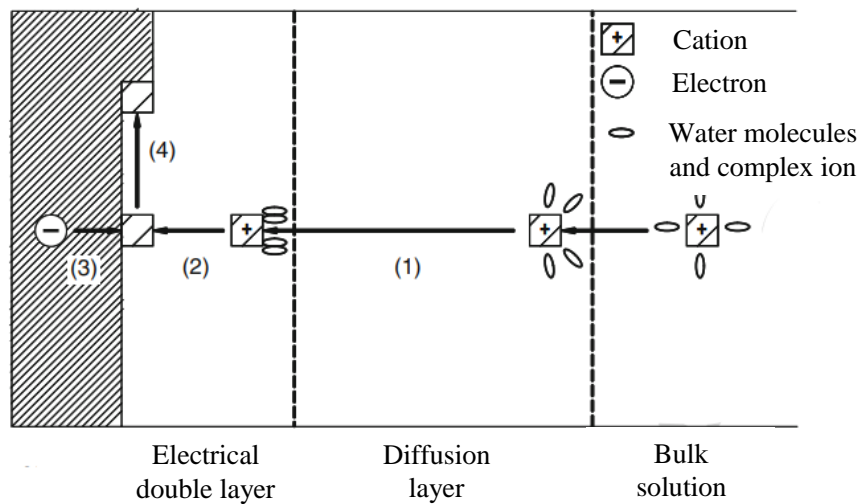


Figure 2.6 Electrochemical deposition processes; (1) diffusion of complex metal ions from bulk solution to near-cathode surface region; (2) dehydration and transport of cation through electrical double layer; (3) cationic reaction at solid-solution interface and; (4) surface migration and incorporation of absorbed metal atoms into crystal lattice (Arnold et al., 2010).