ALUMINA AS DIFFUSION BARRIER TO INTERMETALLIC FORMATION IN THERMAL INTERFACE MATERIALS

MADE FROM INDIUM AND COPPER

By

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ABSTRACT

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Alumina as diffusion barrier to intermetallic formation in thermal interface materials made from indium and copper.

Thesis directed by associate Professor Rishi. Raj

Indium and copper react at wide range of temperatures to form intermetallic compounds that have different physical, mechanical and thermal properties. Liquid Phase Sintered indium-copper composite long-term performance as thermal interface material is adversely affected by the evolution of the intermetallic. In this study, i) the effect of intermetallic formation and growth on the performance of Liquid Phase Sintered copper-indium composite, ii) the effectiveness of alumina as diffusion barrier between indium and copper, (iii) the thermal stability and wettability between indium and alumina, iv) indium and quartz wettability, v) indium and tungsten oxide wettability have been studied. Deleterious effect of the intermetallic formation and growth on the thermal and mechanical properties has been observed. 5nm of alumina deposited by Atomic Layer Deposition on flat copper surface has been optimized to prevent diffusion process between indium and copper at 120°C. 15nm of alumina prevented the reaction at 230°C. Instability of indium thin film thermally deposited on sapphire substrate was observed. Also, decrease in the sintering density of indium-alumina composite with increasing temperature was observed. The dewetting contact angle between liquid indium and sapphire was $\sim 127^{\circ}$. The wetting experiments between indium and different oxides showed that indium wets tungsten oxide and quartz.

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CHAPTER 1

Introduction

1.1 Introduction

Composite, as homogenous mixture, is made by combining two or more materials that have different thermal, physical, mechanical, and chemical properties. When mixed together, they produce a composite with different properties. The properties of the composite depend on the amount of each phase as well as on the interface between them. The commercial solders in electronic packaging industry are alloys that are designed to enhance their performance. For example, adding small amount of Bismuth (<5%) to Sn-Ag composite would lower the melting point and improve the wettability of the new composite [1].

In the present work a Liquid Phase Sintered composite made from indium and copper was studied to function as thermal interface material between silicon chip and the heat sink. The indium is used to obtain composite with lower melting point and better mechanical properties and copper is used to obtain composite with better thermal and electrical properties. However, indium and copper can react with each other even at room temperature to form intermetallic compounds that have detrimental effect on the composite long-term-performance. Therefore, alumina was investigated to work as diffusion barrier and wetting agent between indium and copper.

1.2 Outline of the Present Work

This thesis is organized as follows:

(i) Chapter two presents the basic concepts that must be considered when seeking to understand intermetallic compounds, diffusion barrier, metal-ceramic wettability and Liquid Phase Sintering technique.

(ii) Chapter three describes the experimental methods used to fabricate and characterize composites made from indium-copper, indium-alumina1.5nm-copper, indium-alumina, indium-tungsten oxide and indium-quartz. Also, it describes the method of fabricating and characterizing thin films made from indium-copper, indium-copper with different thicknesses of alumina deposited between them, indium-sapphire and indium-tungsten oxide.

(iii) Chapter four investigates the intermetallic compounds that form at room temperature and 120°C between indium and copper thin films. The effect of the intermetallic formation and growth on the density, yield strength and thermal conductivity of Liquid Phase Sintered indium-copper composite is also investigated in this chapter.

(iv) Chapter five investigates, i) the performance of Liquid Phase Sintered indiumaluminal.5nm-copper composite (copper particles are coated with 1.5nm of alumina to work as diffusion barrier), ii) the thickness of alumina thin layer that prevents the formation and growth of the intermetallic compounds between indium-copper thin films, iii) the effect of increasing temperature on indium-alumina wettability and thermal stability, iv) the contact angle between liquid indium and sapphire, v) the effect of increasing temperature on indium-tungsten oxide wettability, vi) the effect of increasing temperature on indium-quartz sintering density.

(v) Chapter six summarizes the results, implications and gives some suggestions for future wok.

1.3 Thermal Interface Material for Electronic Packaging

The thermal interface material, known as TIM, is an important component of electronic package. It is a thin layer of highly compliant metal-metal composite that connects the heat sink, usually made of copper, to silicon chip to remove the excessive heat generated in the chip to the heat sink and then to the outside environment (see Fig 1.1). Also, TIM reduces the thermal resistance between the connected components to obtain the desirable working conditions. TIM requires understanding of the materials and the reaction that takes place at interfaces. The ideal TIM should have the following properties:

1- High Thermal Conductivity and Minimal Thickness.

To keep the temperature of the silicon chip as low as possible according to the following equation [2]:

$$T_{Si} = T_{Si} + h J_0 / K$$
 1.1

Where K is the effective thermal conductivity of the interface material, J_Q is the heat flux J s⁻¹m⁻² or W.m⁻² and h is the thickness of the TIM in m. Usually, K and h combined to one parameter called thermal interface conductance K/h where the highest value is need to have better performance [2].

2- High Electric Conductivity

High electrical conductivity becomes important when TIM is used for metal interconnects. However, in metal systems the electrical and thermal conductivity are both controlled by electron transport near room temperature. Therefore, they are linked explicitly by the Lorentz equation:

$$K/\sigma T = 2.5 \times 10^{-6} \text{ W Ohm } \text{K}^{-2}$$
 1.2

Where σ is the specific electronic conductivity having unit of (Ohm m)⁻¹, K is the thermal conductivity and T is the temperature in the absolute value.

In the case of interconnect applications, where the metal–metal composite is used as a solder it is essential for the material to have melting points below 300 °C, solder containing tin and indium are the typical choice.



Figure 1.1 Schematic of thermal interface material connecting the heat sink and the semiconductor chip.

3- High Mechanical Compliance

The difference in the thermal expansion coefficients between copper, $17 \times 10^{-60} \text{ C}^{-1}$, and silicon , $3 \times 10^{-60} \text{ C}^{-1}$, can yield huge strain. Therefore, it is necessary to design composite that is near its melting point at room temperature to accommodate the strain by creep deformation.

4- Good Wettability and Spreading

The surface of materials is not perfectly flat and there will be always peaks and valleys that create voids when two materials contact each other (see Fig 1.2). TIM should have excellent

wettability with the heat sink and the chip to fill the voids and be more effective in transferring heat.



Figure 1.2 Schematic of, a) heat sink and semiconductor chip connected by TIM, b) heat sink and the semiconductor chip without TIM.

5- Chemically Stability

TIM and the connected surfaces, heat sink and silicon chip, system should be thermodynamically stable.

6- Non-toxic and low cost.

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CHAPTER 2

Background

2.1 Introduction

The following sections will review the basic concepts that must be considered when seeking to understand the intermetallic compound, diffusion barrier, metal-ceramic wettability and Liquid Phase Sintering technique.

2.2 Intermetallic Compound

The intermetallic compounds, known as IMc, form when more than one metal diffuses to one another. The diffusion occurs via crystal vacancies such as grain boundary, defect, vacancy, contamination and impurity. The IMc has different physical, mechanical, thermal and electrical properties than the constituent metals [1]. This is attributed to the nature of atoms bonding in the intermetallic compounds, they have covalent bonding character that leads to directional bonding (metal has non-directional bonding). The strong internal order structure means that larger shear displacements are required to plastically deform the IMc. That explains why IMc is stronger, less ductile and has higher young's modulus material.

Stable IMc is obtained when the free energy accompanies its formation is lower than the free energy of the competitive intermetallic compounds [2]. The Average thickness of the multiintermetallic compounds can be measured by the following equation [3]:

$$\Delta X = K (t)^{1/2}$$
 2.1

Where ΔX represents the average thickness of the IMcs, K represents the growth rate constant at specific temperature, t represents the reaction time.

If the growth of the IMcs follows the parabolic law (the growth is diffusion-controlled), K can be determined from the Arrhenius relationship:

$$K = A \exp(-Q/RT)$$
 2.2

Where A is a constant, Q represents the activation energy in KJ/mole, R is the gas constant in J/K mole and T is the temperature in absolute scale.

2.3 Diffusion Barrier (DFB)

The diffusion barrier is a thin layer that prevents or retards two different materials from diffusing to each other and form intermetallic compounds (see Fig 2.1). The DFB should be thermodynamically stable at wide range of temperatures and bonds well to the connected materials.



Figure 2.1 Schematic of two reacting materials, a) without diffusion barrier, b) with diffusion barrier.

Three types of diffusion barrier have been characterized by Nicolet [4]:

1) Passive barrier: barrier layer which is immiscible and does not react chemically with connected materials.

2) Stuffed barrier: passive barrier with structural defects like grain boundaries, which are stuffed by other materials.

3) Sacrificial barrier: barrier that reacts chemically with connected materials. During the reaction the interdiffusion process is prevented, but the barrier fails as soon as the material is completely consumed. The effective diffusion barrier must satisfy a number of requirements that are listed in Table 2.1.

Requirements
1) Low reactivity with the constituents' material (chemically
inert), no diffusion into surrounding.
2) Low contact resistivity.
1) Lowest resistivity (highly electrically conducting). For
dielectric diffusion barrier it should has very small thickness
in order of nanometer.
2) Mechanical stability (resistant to mechanical stress).
3) Highly thermally conducting.
4) Good step coverage.

 Table 2.1 Requirements for effective diffusion barrier [5]

2.4 Atomic Layer Deposition (ALD)

The effectiveness of the DFB depends greatly on the process of deposition. The best technique to have a good ultra-thin DFB that has uniform thickness on sample surface is the atomic layer deposition. In the ALD deposition a binary reaction is split into two half-reactions in order to achieve a precise control over the film thickness where more than one precursor reacts with surface of the substrate (see Fig 2.2). The mechanism is to let the first vapor precursor react with the surface of the target substrate and any extra unreacted vapor will be remove, then the second precursor vapor will be brought to the substrate to complete the reaction, that is one full cycle [6]. A certain thickness of the film can be achieved each cycle because ALD is self-limiting process, fixed quantity of the material deposited will be obtained in each individual cycle.

The advantages of film deposited by ALD technique are:

1-Thin film thickness: precise thin thickness can be achieved at monolayer level, this advantage allows dielectric compound to function as DFB.

2- Conformal: film with excellent step coverage, because the uniformity of ALD film can be achieved on flat substrate surfaces, holes, peaks and valleys.

3- Defect free film: because there are no sites on the target surface will be left behind during ALD deposition, the film is continuous and pinhole-free.

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Figure 2.2 ALD deposition process based on sequential, selflimiting surface reaction [6].

2.5 Metal-Ceramic Wettability

Metal-ceramic system creates new interface between dissimilar materials (chemical and structural differences). The wettability and the work of adhesion are characterized by the angle of contact between liquid metal and ceramic surface (see Fig 2.3). Metals can react chemically with the ceramic to create a new metal-ceramic interface with low surface energy that produces good wettability and strong adhesion [7].

$$Me + MO_n \rightarrow MeO_n + M \quad \Delta G < 0$$
 2.3

If the metal does not react with the ceramic, poor wettability and weak adhesion between them will be created. Correlation between the wetting and the bonding at the interface in solid-liquid-vapour system in thermodynamic equilibrium is given by the following equation:

$$W_{ad} = \Upsilon_m + \Upsilon_c - \Upsilon_{cm}$$
 2.4

Where W_{ad} is the adhesion work between the two systems, defined as the work needed to separate an interface, Υ_m is the surface energy of the metal, Υ_c is the surface energy of ceramic, Υ_{cm} is the interfacial energy of metal-ceramic system.

The relationship between the contact angle and the metal-ceramic system surface energies is given by Young Dupre equation [8]:

$$\Upsilon_{\rm c}$$
- $\Upsilon_{\rm cm}$ = cos θ 2.5

Where θ represent the contact angle. Combining 2.4 and 2.5 gives:

$$W_{ad} = \Upsilon_{m} \left(1 + \cos \theta \right)$$
 2.6

The contact angle can be measured by many techniques such as sessile drop, dispensed drop, transferred drop, tilted plate [9, 11]. Also, the value of the contact angle is affected by temperature, time, substrate surface roughness and the oxygen partial pressure [12].



Figure 2.3 The contact angle of, a) non-wetting, b) wetting, c) spreading systems.

2.6 Liquid Phase Sintering (LPS)

Liquid phase sintering is process to produce a dense composite made from high melting point phase (HMP) and low melting point phase (LMP). The technique depends on the ability of the LMP to wet and spread on the HMP (see Fig 2.4). Stages of the LPS are as following:

1- Rearrangement: the pores between particles will be filled by LMP when heated above its melting point. The capillary action will pull the liquid into those pores and the HMP particles will be rearranged to more favorable packing arrangement [13].

2- Solution-Precipitation: in areas where capillary pressures are high (particles are close together) atoms will preferentially go into solution and then precipitate in areas of lower chemical potential, where particles are non-close or in contact. Ostwald ripening will also occur where smaller particles will go into solution preferentially and precipitate on larger particles leading to densification [13].

3) Final Densification: densification of solid skeletal network, liquid movement from efficiently packed regions into pores.

Repulsive capillary force on the particles, Dewetting, takes place if the contact angle between liquid LMP and HMP is large. The LMP will extrude out of the composite when melt (see Fig 2.5 and 2.6). The extent of swelling increases with the increasing in volume fraction of LMP.



Figure 2.4 Liquid Phase Sintering process [14].



Figure 2.5 Swelling of the LMP due to dewetting [14].



Figure 2.6 Schematic of desintering process.

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CHAPTER 3

Experimental Methods

3.1 Introduction

This chapter describes the experimental methods used to fabricate and characterize, i) composites made by Liquid Phase Sintering technique, ii) atomic layer deposition of alumina on copper substrates, iii) indium thin film thermal deposition on different substrates.

The second section describes the method of fabricating Liquid Phase Sintered In60Vol%-Cu composite as TIM and the method of depositing indium thin film on copper substrates. Third section describes the process of depositing alumina by atomic layer deposition technique on copper substrates. The fourth section explains the process of depositing indium thin film on flat copper substrates coated with different thicknesses of alumina. The fifth section details the process of fabricating indium alumina composite and depositing indium thin film on sapphire substrate. The sixth section describes the method of making indium-tungsten oxide and indiumquartz composites. Also, section six describes the method of depositing indium thin film on tungsten oxide substrate. The methods of measuring the properties of the composites and characterizing thin films system are described in the seventh and eighth sections respectively. More detailed description of the experimental technique can be found in the specific sections in the next chapters giving the data and result for a particular set of measurements.

3.2 Indium Copper System

The indium copper composites were made to measure their physical, mechanical and thermal properties. The indium copper thin films were made to study the intermetallic formation at different temperatures.

1) Fabrication of Indium Copper Composites

Copper spherical particles (40µm) and indium spherical particles (10µm) were used to fabricate composite with In60Vol%-Cu. It is necessary to make sure that indium and copper powder are free of the native oxide layer because that can cause error in the experiments results. Indium powder was bought as oxide-free powder packed in argon atmosphere. The copper powder were stirred in 10% HCl solution for 15 minutes, rinsed with deionized water and stored under vacuum for 18h. Then, the indium and copper powders were mixed by hand milling with a mortar and pestle in glove box for 1h. Care was taken to avoid the agglomeration of indium particles during the milling operation (if the applied pressure during milling is too high, the indium particles will deform and agglomerate). The milled powder mixture was then uniaxially compressed in steel die to form pellets with 6mm diameter. The relative green density of the pellets was about 90% of the theoretical composite density that follows the rule of mixture. Then green density pellets were covered with an aluminum foil before immersing into the silicone oil bath in order to avoid contamination from the oil and Liquid Phase Sintered at temperatures ranging from 145°C to 200°C for sintering time, measured as the time from the moment of immersion to the

point of extraction from the bath, ranging from 5s to 120s and then pellets were quenched immediately in water to minimize the growth of the IMcs. The same procedure was done inside glove box to eliminate the possible effect of trapped oxygen. Four samples were annealed at 130°C for 1,24,48 and 96h to study the effect of IMc formation and growth on physical, mechanical and thermal properties.

2) Fabrication of Indium Copper Thin Films

150nm of indium was thermally deposited on 15 μ m copper substrate using CVC-3- boat thermal evaporation (see Fig 3.1). The 15 μ m copper was evaporated onto 25nm tantalum which was deposited on silicon wafer to prevent copper from reacting with the silicon (see Fig 3.2a). Indium pellets were washed with acetone to remove the organic material, then 10% HCI solution was used to remove the native indium oxide (to reduce the current needed to evaporate the indium because the thin layer of In₂O₃ will increase the current and consequently the temperature will increase inside the vacuum chamber). Then, the indium pellets were rinsed with DI water, rinsed with isopropyl alcohol, blown out with argon gas and kept in the glove box for overnight.



Figure 3.1 CVC-3-boat thermal evaporation.

The free-oxide indium pellets were placed in tungsten boat inside CVC-3-boat vacuum chamber, then the chamber was pumped down to 10^{-6} Torr to inhibit indium oxidation and to eliminate the effect of residual gas that no longer detectably influences the physical characterization of indium thin film at this pressure. The indium film thickness was controlled during evaporation with a quartz thickness monitor and the deposition rate was 3 A/s. Figure 3.2b shows a schematic of sample coated with 150nm of indium.



indium.

3.3 Atomic Layer Deposition of Alumina on Copper

Atomic layer deposition technique was used to deposit amorphous alumina on copper substrates, Figure 3.2a, and on copper spherical particles to work as DFB. The copper was etched by using the procedure mentioned above in section 3.2. The deposition of alumina on copper substrates took place at approximately 150° C using trimethylaluminum [AI(CH₃)₃] (abbreviated as (TMA), and water precursor in a viscous flow reactor (see Fig 3.3).



Figure 3.3 The viscos flow reactor used in ALD process.

The precursors were entrained with nitrogen, and dosed in cycles comprised of an repeating A:B:A:B surface reaction, Figure 3.4, timing sequence where 1s TMA dose, 30s nitrogen purge followed by 1s water dose. The trimetylaluminum was dosed to 100mTorr and water was dosed to 20mTorr above the base nitrogen pressure of about one Torr.



Figure 3.4 ALD reaction scheme showing two self-limiting half reaction, (A) and (B), which combine to give Al_2O_3 coating of well-defined chemistry and thickness, in which the AL(CH₃)₃ and the-OH group are the surface reactive species and CH₄ is the reaction by- product.

Figure 3.4 shows the energy dispersive X-ray (EDS) spectrum of copper sample coated with 5nm of alumina after annealing at 120°C for 48h. Peaks belong to aluminum and oxygen were identified.



Figure 3.5 EDS spectrum of copper sample coated with 5nm of alumina showing the presence of aluminum and the oxygen.

3.4 Indium-Alumina as diffusion barrier-Copper system

1.5nm of alumina was deposited on copper particles to find out if that could retard the IMc formation. Also, alumina with different thicknesses was deposited on copper flat substrate with 150nm indium above it, Figure 3.2b, to study the formation of IMc at different temperatures.

1) Fabrication of Indium-Alumina as diffusion barrier- Copper Composite

Etched 40µm spherical copper particles were coated with 1.5nm of amorphous alumina by ALD technique described in section 3.3. The procedure of making In60Vol%-Cu, mentioned above in section 3.2, was used to produce the composite.

2) Indium-Alumina as Diffusion Barrier- Copper Thin Films

Three samples were cut from silicon wafer, Figure 3.2a. The samples were dipped in 10% HCl solution for 5 minutes to remove the native copper oxide, and then the samples were rinsed with acetone, dried with argon gas and kept for overnight inside the glove box. 0.5, 5 and 15nm of alumina were deposited by ALD on the samples surface, and then 150nm of indium was thermally deposited on each sample.

3.5 Indium Alumina System

Indium alumina composite was made to study the effect of the increasing temperature on the composite sintering density. Indium thin film thermally deposited on sapphire was made to study the effect of the increasing temperature on the system stability and wettability.

1) Indium-Alumina Composite

Indium and alumina powders with In40Vol%-Al₂O₃ were mixed in the glove box by using pestle and mortar for half an hour till homogeneous mixture was obtained. 4 pellets were uniaxially cold pressed to obtain green density around 82%.

2) Indium- Alumina Thin Film

Single crystal sapphire substrates $(11\overline{2}0)$ were etched in hot phosphoric acid followed by rinsing with deionized water and drying with argon gas. 300nm of Indium was thermally evaporated on the polished side of the sapphire substrates. The surface roughness of the sapphire, measured by the surface profile measuring system (Dektak 3030 profilometer), was about 10nm.

3.6 Indium Tungsten Oxide and Indium Quartz Systems

Indium tungsten oxide and indium quartz composites were made to study the effect of the increasing temperature on the composite sintering density. Indium thin film on tungsten oxide was made to study the effect of the increasing temperature on the system stability and wettability.

1) Indium Tungsten Oxide and indium Quartz Composite

Three samples of In30Vol%-WO₃ composites with initial density 85% were Liquid Phase Sintered for 2, 5 and 15 minutes at 170°C to find out if liquid indium wets tungsten oxide. The same procedure was done to In30Vol%-quartz composites.

2) Indium Tungsten Oxide Thin Film

Copper substrate was coated with 2nm of alumina and 30nm of tungsten by ALD technique, and then 300nm indium thin film was thermally deposited on the oxidized tungsten.

3.7 Properties Measurement of Indium Copper Composite

1) Thermal Conductivity Measurement

The thermal conductivity of the composites was determined from two measurements: the thermal diffusivity was measured in Netztch Laser Flash Instrument, and the heat capacity was measured by Differential Scanning Calorimetery. The thermal conductivity was then determined from the following equation:

$$\mathbf{K}_{comp} = \mathbf{\eta} \rho \mathbf{C}_{p} \qquad \qquad 3.1$$

Where \mathbf{K}_{comp} is thermal conductivity of composite Wm⁻¹K⁻¹, $\boldsymbol{\eta}$ is thermal diffusivity m²s⁻¹, $\boldsymbol{\rho}$ is composite density, sintering density, Kgm⁻³ and Cp is the specific heat capacity JKg⁻¹ K⁻¹.

2) Yield Strength Measurement

The plastic deformation behavior of the composites was measured by the using Fischer microindentation instrument. This instrument uses a spherical indenter with a diameter of 400µm. The load is applied in small increments (a maximum load of 1000mN applied in twenty steps, with a dwell time of 20s at each step, was employed in the current measurements), and the displacement of the indenter into the specimen was measured. In this way a stress displacement graph for the mechanical behavior of the specimen is obtained. The load is converted into stress by dividing it by the total area of contact of the indenter, according to the following equation:

$$\sigma_{\rm Y} = \mathbf{F}/2\pi \mathbf{a}\mathbf{h} \tag{3.2}$$

Where σ_Y is the applied stress in Pa, **F** is normal load in N, **a** is radius of spherical indenter in m, and **h** is relative displacement of indenter in m.

3.8 Characterization of Indium Film on Different Substrates

The following equipment were used to characterize the samples in the present work:

1-X-ray diffraction

Scintag PAD V automated X-ray diffractometer was used to identify, i) the formation of the intermetallic compound between indium and copper , ii) the orientation of indium particles deposited on the sapphire before and after heat treatment.
2- Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM)

JEOL JSM-5910LV SEM and AFM were used to study the morphology of indium thin film on different substrates before and after heat treatment at different temperatures.

3- Four Point Probe Resistivity measurement

The 4- point probe was used to measure resistivity of copper samples coated with different thicknesses of alumina.

4- Roughness measurement

Dektek 3030 profolmeter was used to measure the roughness of the different substrate. Also, it was used to make sure that the deposited indium films have the required thickness.

CHAPTER 4

Indium Copper Reaction without Diffusion Barrier

4.1 Introduction

In this chapter we introduce a new thermal interface material made from indium copper composite using Liquid Phase Sintering technique. Also, the effect of intermetallic formation and growth on the composite properties was investigated. In section two we investigate the advantages and disadvantages of indium and indium alloys as thermal interface material. Section three explains the method of using Liquid Phase Sintering to make a composite with low melting point metal and high melting point metal. Section four explains the advantages of indium copper composite as thermal interface material. Section five introduces the indium-copper phase diagram. Section six investigates intermetallic formation between indium and copper thin films at different temperatures. Section seven explains the effect of the intermetallic growth on the properties of Liquid Phase Sintered indium copper composite.

4.2 Indium and Indium Alloy as TIM

Indium and indium alloy are selectively used in where their unique properties are required. The melting point (MP) of these solder can be as low as 60°C depending on the Indium content [1]. It has been reported that addition of of just 1% of indium to alloy contain bismuth, lead, tin and cadmium will reduce the MP of the composition by 1.45°C [2]. Indium has high thermal conductivity, up to 60 W/.m-K, which makes it good candidate for heat dissipation for high power devices with densities in excess of 1000 watts [3]. Also, indium has excellent shear compliance to accommodate the coefficient of the thermal expansion mismatch between silicon chip and copper heat sink without applying significant stress on either component. Finally, indium is Non-toxic material which makes it environment Friendliness TIM. However, indium is very susceptible to deformation during handling and use where they might collapse when attaches to the heat sink due to their low yield strength (less than 4MPa). The creep resistance of indium is poor which makes its micromechanical changes with creep. Also, the high cost of indium makes it unattractive from economy point of view.

4.3 Composite of Low Melting Point and High Melting Point Metals

Composites with high thermal conductivity, good compressive strength and low cost can be obtained by uniformly distributing metal high thermal conductivity and high melting point phase (HMP, e.g. Sn, Cu) in highly compliant low melting point phase (LMP, e.g. In, Bi) matrix [5], and then Liquid Phase Sintering technique is used to have dense composite. The mechanical compliance of the composite is controlled by the soft and compliant LMP metal and the good compressive strength and high thermal conductivity is controlled by the amount of the hard HMP metal (see Fig 4.1).



Figure 4.1 Schematic of Liquid Phase Sintering composite made from high melting point phase metal HMP, uniformly distributed in low melting point phase, LMP, matrix.

4.4 Indium Copper Composite

Indium as LMP and copper as HMP is a perfect candidate to be excellent TIM. Because, indium has low melting point 156°C, low yield strength and copper has high melting point 1084°C and high thermal conductivity 400 w/m.K (see Table 4.1).

When indium and copper intermix a new interface between them will be created. The contact resistivity of the new interface can be overcome when surface to volume ratio of HMP copper particle is above certain value called Kapitza radius, a_k [6]. The transport properties can become limited by the interface if the copper particle size is less than the Kapitza radius (see Fig 4.2). If particle size of copper is greater than Kapitza radius, the simple rule of mixtures applies and the interface does not control the transport properties. Also, the shape of the copper particles influences the mechanical properties of the composite where the bigger the surface area to volume ratio the more IMc will form.



Figure 4.2 Thermal conductivity of the composite as function in Kapitza radius, a_k [6].

Property	Indium	Copper
Physical		
Melting point ^o C	156	1084
Density g/cc	7.31	8.96
Thermal and electrical		
Thermal conductivity W.m ⁻¹ .K ⁻¹	81.8	401
Electrical resistance $n\Omega \cdot m$ at $20^{\circ}C$	83.7	16.78
Thermal expansion µm.m ⁻¹ .K ⁻¹ 25 ⁰ C	32.1	16.5
Mechanical		
Yield strength	Less than 4[4]	70
Tensile stress	Less than 4[4]	220

Table 4.1 Properties of Indium and Copper

4.5 Indium-Copper Equilibrium Phase Diagram

The In-Cu phase diagram, Figure 4.3, has been studied by many authors [8, 14]. The intermetallic compounds formed in the range 0-30at%In were confirmed by all authors. The phases bundle h, A, A', and C in the range 34-38 at%In was found by Subramanian and Laughlin [8], but not by other authors [9, 14]. Bolcavage found $\dot{\eta}$ -Cu₂In and η in the range 34-38 at%In [9]. The phase Cu₁₁In₉ occurring at 45at%In is stable at room temperature according to Bolcavage, but Subramanian stated that it is just stable above 157°C. The phases δ -Cu₇In₃ occurring in the range 28.9-30.at % In, γ -Cu₇In3 27.7-31.3 at% In , β -Cu4In from 18.05-24.5 at.% In and ε (at 30 to 32 at.% In) were confirmed by all authors.



Figure 4.3 The equilibrium phase diagram of the indium– copper system [11].

4.6 Intermetallic Formation between Indium Copper Thin Films

The deposition of 150nm indium thin film on 15μ m copper was described in details in section 3.2.

1) As Deposited Indium Copper Thin Films

The result of X-ray diffraction scanning is shown in Figure 4.4. The X-ray scan was done after one day from indium deposition. The indium thin film was depleted in the reaction because of, i) diffusion in solid state is rapid process over small distances even at room temperature, ii) diffusion in thin films system is much faster than the bulk system because of the short circuit diffusion paths such as grain boundary and dislocation[15].

CuIn intermetallic compound has formed at 2θ = 34.551° and 2θ = 38.43° in addition to Cu peaks. This finding is with agreement with the work of V. Simic who discovered this compound [16]. Even though CuIn does not feature in the equilibrium phase diagram (see Fig 4.3), it was widely reported in many literatures [16, 23]. There are discrepancies between literatures about what IMc should form at room temperature, Keppner [24], studied In-Cu film/film system at room temperature and concluded that CuIn₂ is the only formed compound. Takeo [25], studied In-Cu film/film system with different indium compositions and found out that Cu₁₁In₉ and CuIn₂ formed at room temperature.



Figure 4.4 X-ray diffraction scanning of indium copper thin films system at room temperature.

2) Annealed Indium-Copper Thin Films system

The result of X-ray diffraction scanning after annealing the above sample, as deposited sample, at 120° C for 4h in glove box with oxygen partial pressure $P_0 = 0.3$ ppm and moisture = 0.1 ppm is shown Figure 4.5. Peaks of the IMc Cu₁₁In₉ at 2θ = 41.4°, 42.2° and 32.98° were identified in addition to the peaks of Cu element. The CuIn peaks that formed in as deposited reaction have disappeared which means that the solid state transformation has took place and new IMc richer in copper has appeared [16]. The properties of indium oxide and IMcs that are expected to form in the present work at temperature range from room temperature to 230°C are listed in Table 4.2.



Figure 4.5 X-ray diffraction scanning of indium copper thin film annealed at 120°C for 4h.

Properties	CuIn	Cu ₁₁ In ₉	In ₂ O ₃
		0.614	- 10
Density g/cc	7.656	8.614	7.18
Converteal	Manaalinia	Managlinia	Cultic
Crystal	Monoclinic	Monoclinic	Cubic
Activation anarov VI/m	22 5 [26]	16 [26]	62.6
Activation energy KJ/m	23.3 [20]	10 [20]	02.0
Stability in temperature range 25-	Unstable [19]	Stable up to 400°C [19]	Stable
Subility in temperature range 25			Studie
400°C			

4.7 The Effect of Intermetallic Formation and Growth on the Properties of In-Cu Composite

The fabrication method and properties measurements of In60Vol%-Cu LPS composite were described in details in sections 3.2 and 3.7 respectively.

1) The Effect of IMc on the Density of In-Cu Composite

The selection of copper volume fraction, copper particle shape and copper particle size has been characterized by I. Dutta and R. Raj [7]. Their result showed that In60Vol%-Cu made by LPS technique has given the best mechanical and thermal value. Also, it was stated that the best particle shape is spherical and best particle size is 40µm. The result was based on samples with sintering densities, LPS at 160°C for less than 45s, ranged from 95% to 97%. The result of sintering density obtained in the present work showed that there was no systematic method to obtain high densification samples Figure 4.6. The range of increasing in sintering densities was from 1 to 2% and the range of decreasing densities varied from 1 to 8%.





The Increase of the sintering densities can be attributed to the fact that the system lowers its total energy to form the IMc. The new low interfacial energy between indium and the IMc leads to decrease in the contact angle which means increase in the sintering density, Figure 2.3b. This phenomenon was proven by R. Raj [27], where he was able to change the interfacial energy to obtain good wetting metal-ceramic system. According to I. Dutta and R. Raj [7], the decrease in the sintering density at 170°C is possibly due to the different in densities between the constituents and the IMcs that formed during sintering. The X-ray diffraction of In60Vol%-Cu composite sintered at 165°C for 2min shows that the Cu₁₁In₉ and CuIn IMcs have formed, Figure 4.7. These two IMcs could affect the sintering density because they have different crystal structure and density (see Table 4.2). Another possible explanation of the decreasing in the sintering density is the expansion of the air inside the 10% voids in the green cold pressed sample during sintering process. This expansion was prevented from relief because of the quenching and cooling steps.



Figure 4.7 X-ray diffraction of In60Vol%-Cu composite sintered at 165°C for 2 min.

The density of the annealed In60Vol%-Cu sample at 125° C for 1, 24, 48 and 72h increased with time (see Fig 4.8). This increasing is attributed to the growth of the dense Cu₁₁In₉ IMc (see Fig 4.5 and Table 4.2).



Figure 4.8 Density of In60Vol%-Cu composite after annealing at 125°C for 1, 24, 48 and 72h.

2) The Effect of IMc on the Yield Strength of In-Cu Composite

Figure 4.9 shows the result of the force-displacement data and Equation 3.2. The yield strength of sample with initial sintering density 92%, increased after annealing at 125°C for 1, 24, 48 and 96h. The increase in the yield strength is attributed to the growth of the IMc (see Fig 4.4 and 4.7), that has highly directional bonding similar to ceramics, highly melting point, high strength, and very low ductility. The yield strength increasing due to incremental increase in the dislocation density in Indium phase which occurs due to the mismatch between of coefficient of thermal expansion between In and Cu [28], is neglected here because indium content is high.



Figure 4.9 The effect of annealing time on the yield strength of In60Vol%-Cu composite.

3) The Effect of IMc on the Thermal Conductivity of In-Cu Composite

The thermal conductivity of In60Vol%-Cu should follow the rule of mixture law, Equation 4.1, if the composite is dense and free of the porosities.

$$K_{\rm CuIn} = V_{\rm In} K_{\rm In} + V_{\rm Cu} K_{\rm Cu}$$

$$4.1$$

Where K_{CuIn} is the composite effective thermal conductivity, V_{In} is the volume fraction of the In, V_{Cu} volume fraction of the Cu.

Figure 4.10, shows the thermal conductivity of sample with initial sintering density 92% annealed at 125°C for 1, 24, 48 and 96h. The thermal conductivity decreased with annealing time due to, i) voids inside the samples [29], as is it illustrated in the morphology of sample sintered at 160°C for 45sec Figure 4.11, ii) formation of the IMcs that created new thermal interface resistance layer, iii) the amount of the high thermal conductivity phase, copper, decreased during the growth of the IMc.



Figure 4.10 The effect of annealing time on the thermal conductivity of In60Vol%-Cu

composite.



Figure 4.11 Pores in In60Vol%-Cu sintered at 160°C for 45sec.

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CHAPTER 5

Alumina as Diffusion Barrier between Indium and Copper

5.1 Introduction

This chapter examines, i) the effectiveness of alumina as diffusion barrier between indium and copper, ii) the thermal stability and wettability between indium and alumina.

This chapter is divided into six sections. The second section gives the reason of using alumina as diffusion barrier. The third section studies the effect of IMc formation on the composite made from copper particles coated with 1.5nm of alumina and indium. The fourth section examines alumina as diffusion barrier between indium-copper thin films. The fifth section studies the temperature effect on indium-alumina system and measures the contact angle between them. The last section investigates tungsten oxide and quartz as indium wetting agents.

5.2 Alumina as Diffusion Barrier

Alumina is a good candidate to be effective diffusion barrier because of its high negative energy of formation which makes it stable compound [1]. If the thickness of alumina is in order of few nanomteres, the dielectric property of alumina can be overcome because the current can pass through the oxide tunnel easily. Aluminum oxide can be deposited by ALD technique as amorphous phase which gives it additional advantage to be excellent diffusion barrier.

Properties	Value
Physical	
Density g/cc	3.89
Mechanical	
Compressive Strength MPa	2600
Thermal	
Thermal Conductivity W/m.K	35
Coefficient of Thermal Expansion 10 ⁻⁶ /°C	8.4
Heat of formation KJ/mole	-1670
Electrical	
Volume Resistivity ohm•cm	>10 ¹⁴

Table 5.1 properties of alumina [2].

5.3 The Effect of Intermetallic Formation and Growth on the Properties of In-Alumina1.5nm-Cu Composite

The deposition of alumina on copper particles was described in section 3.3. The fabrication method and properties measurments of the composite were also described in details insections 3.4 and 3.7 respectivily.

1) The Effect of IMc on the Density of In-Alumina1.5nm-Cu Composite

Figure 5.1 shows that the sintering density decreased when the sintering temperature and time increased. Few samples showed increase in sintereing density when LPS at 155°C for 15sec. The decrease in density is possibly due to the new alumina interafce that indium does not wet as well as to the IMc formation that has higher density (see Table 4.2).



Figure 5.1 Sintering densities at different sintering time and temperature of In-1.5nm-copper composite.

The density of annealed sample at 125° C with starting relative density 87% increased with the annealing time (see Fig 5.2). The density increased due to the growth of the dense IMc Cu₁₁In₉ (see Fig 4.5 and Table 4.2).



Figure 5.2 Density of In-Alumina1.5nm-Cu composite after annealing at 125°C for 1, 24, 48 and 96h.

2) The Effect of IMc on the Yield Strength of In-Alumina 1.5nm-Cu Composite

Figure 5.3 shows the increasing of the yield strength of sample annealed at 125°C for different annealing time. The 1.5nm of alumina could not prevent the IMc from growing.



Figure 5.3 The effect of annealing time on the yield strength of In-Alumina1.5nm-Cu composite.

3) The Effect of IMc on the Thermal Conductivity of In-Alumina1.5nm-Cu Composite

The thermal conductivity of the annealed samples at 1, 24 and 48h decreases with the annealed time because of the new interface resistance that that IMc has formed between indium and copper Figure 5.4.



Figure 5.4 The effect of annealing time on the thermal conductivity of In-Alumina1.5nm-Cu composite.

The 1.5nm was not able to prevent the indium and copper from reacting and the failure can be attributed to:

1- Atomic layer deposition on copper particles is not as perfect as flat surfaces.

2- The thickness of the alumina barrier is not enough to prevent the reaction between indium and copper.

3- Indium does not wet alumina.

5.4 Alumina as Diffusion Barrier between Cu-In Thin Films

The ALD deposition of alumina on copper substrate and indium thermal deposition on the alumina was detailed in sections 3.2 and 3.3.

1) In- Alumina0.5nm-Cu as deposited thin films

The result of X-ray diffraction scanning of copper substrate coated with 0.5nm of alumina and 150nm of indium, respectively, is shown in Figure 5.5a. There are peaks belong to copper and indium (that is an indication that the amorphous 0.5nm alumina barrier was able to prevent indium and copper from reacting with each other to form IMc).

2) In- Alumina0.5nm-Cu annealed at 120 °C for 48h thin films

The result of X-ray scanning of as deposited sample mentioned above is shown in Figure 5.5b. The sample was annealed in glove box in argon atmosphere with $P_0=0.69$ ppm and moisture = 0.2 ppm. Peaks belong to indium, copper and intermetallic compound Cu₁₁In₉ (2 θ =32.85, 2 θ =41.6 and 2 θ =42.05), were identified.

The indium oxide peak at $2\theta = 30.55$ possibly comes from the fact that thin metal films are much more reactive than the bulk system. The trapped oxygen in the system may cause the indium oxidation too. There is no data in Janaf Table of the heat of formation of indium oxide at 120°C to find out if the indium oxide can form at glove box's oxygen partial pressure or not.





Figure 5.5 X-ray diffraction scanning of, a) as deposited In- Alumina 0.5nm-Cu thin films, b) annealed at 120°C for 48h In-Alumina 0.5nm-Cu thin films.

3) In- Alumina5nm-Cu as deposited thin films

The result of X-ray diffraction scanning of copper 15µm coated with 5nm of alumina and 150nm of indium, respectively, is shown in Figure 5.6a. There are just peaks belong to copper and indium. No IMc was observed.

4) In- Alumina5nm-Cu annealed at 120 °C for 48h thin films

The result of X-ray scanning of as deposited sample mentioned above is shown in Figure 5.6b. The sample was annealed in glove box in argon atmosphere with $P_0=0.69$ ppm and moisture = 0.2 ppm. The pattern just shows peaks belong to indium and copper in addition to indium oxide peak.

The sample with 15nm of alumina as diffusion barrier shows the same behavior as the 5nm at room temperature and 120°C.

The resistivity of copper samples coated with 0.5, 5, 15nm alumina did not change with alumina thickness (see Table 5.2).

Thickness of Alumina	Resistivity Ω.cm
0.5nm	0.0011921
5nm	0.0011959
15nm	0.00125591

Table 5.2 Resistivity of copper samples coated with different thickness of alumina.



Figure 5.6 X-ray diffraction scanning of, a) as deposited In- Alumina5nm-Cu thin films, b) annealed at 120°C for 48 h In- Alumina5nm-Cu thin films.

5) In- Alumina15nm-Cu Annealed at 230 °C for 2h

Copper foil coated with 15nm of alumina and 150nm indium was annealed at 230°C for 2h to find out if IMc can form at temperature above the melting point of indium. X-ray scanning showed that the 15nm of alumina was able to prevent the reaction between indium and copper at 230°C (see Fig 5.7).



Figure 5.7 X-ray scanning of copper foil coated with 15nm of alumina and 150nm of indium annealed at 230°C for 2h.

6) Morphology of Annealed In-Cu Thin Film With and Without Diffusion Barrier.

Figure 5.8 shows the SEM morphologies of annealed In-Cu thin films at 120°C for 48h with and without diffusion barrier (0.5 and 5nm of alumina). The morphology of the sample without diffusion barrier, Figure 5.8a, consists of distinct grains with approximately average grain size 200nm which make its grain density more dense than samples with the diffusion barrier, approximately average grain size 450nm (see Fig 5.8b and 5.8c). Also, the AFM topography of In-Cu films with 5nm of alumina as diffusion barrier shows that the distinct grains shape became more spherical after annealing at 120°C for 4h, Figure 5.9. The coarsening of indium particles is attributed to the fact that indium particles reduce their total free energy by taking the spherical shape.



Figure 5.8 SEM morphologies of In-Cu thin films annealed at 120°C for 48h, a) without diffusion barrier, b) with 0.5nm alumina as diffusion barrier, c) with 5nm alumina diffusion barrier.





Continuous Figure 5.8 SEM morphologies of In-Cu thin films annealed at 120°C for 48h, a) without diffusion barrier, b) with 0.5nm alumina as diffusion barrier, c) with 5nm alumina diffusion barrier.



Figure 5.9 AFM topography of In-Cu with 5nm of alumina as diffusion barrier, a) as deposited, b) annealed at 120°C for 4h.

5.5 Indium-Alumina System

The fabrication process of indium and alumina composite and deposition of indium thin film on sapphire was detailed in section 3.5.

1) The Effect of Temperature on the Stability of Indium Thin Film deposited on Sapphire Substrate

The SEM morphologies of four single crystal sapphire $(11\overline{2}0)$ substrates coated with 300nm of indium and then annealed at room temperatures, 80°C, 130°C and at 190°C for 8 hours in argon atmosphere are shown in Figure 5.10. The indium film becomes instable with increasing annealing temperature. The possible reason of the indium film instability is the minimization of the total energy of the free surfaces of indium, sapphire and indium-sapphire interface.

1) At room temperature: the film atoms have low kinetic energy for moving to reach to the equilibrium state (lowest possible energy) [4], Figure 5.10a.

2) Annealing at 80°C: some energy has been given to the atoms to form more holes, Figure 5.10b.

3) Annealing at 130°C: the holes grow until their rims merge and build up a network system over the whole surface, Figure 5.10c.

4) Annealing at 190°C: the film breaks up and the network system decays into semi-droplets shape, Figure 5.10d.





Figure 5.10 The morphology of 300 nm indium on sapphire annealed at, a) room temperature, b), 80°C, c) 130°C d) 190°C for 8 h in a argon atmosphere.





Continuous Figure 5.10 The morphology of 300 nm indium on sapphire annealed at, a) room temperature, b), 80°C, c) 130°C d) 190°C for 8 h in a argon atmosphere.

Carl V. Thompson [5], stated that the driving force for dewetting increases and the rate of dewetting accelerates with decreasing in film thickness. As a consequence, the lower the film thickness the lower the dewetting temperature. That was with agreement with our result where films with thickness 50nm&150nm on sapphire substarates were not continuous at room temperature and showed deweting structure, Figure 5.11. But, film with 300nm were continuous at room temperature, Figure 5.10a.



Figure 5.11 Morphology of as deposited, a) 50nm indium on sapphire, b) 150nm indium on sapphire.

2) The Effect of Temperature on the Indium Grains Orientation Deposited on Sapphire

The X-ray diffraction of the indium film with different thicknesses, before and after annealing at different temperatures shows that the indium grains predominantly Oriented in a way that their (101) plane was parallel to the sapphire planes ($11\overline{2}0$) and (0001), Figure 5.12.



Figure 5.12 X-ray diffraction pattern of indium film deposited on sapphire substrate, a) as deposited. b) after annealing 120°C for 4h.
3) Effect of Temperature on the Liquid Phase Sintering Density of Indium Alumina Composite

The fabrication method of In40Vol%-Al₂O₃ composites were explained in section 3.5. The samples were annealed at different temperature for 8h. The density fell down with increasing temperature because of the dewetting nature between indium and alumina, Figure 5.13.



Figure 5.13 The effect of temperature on the sintering density of In40Vol%-Al₂O₃ composites.

Figure 5.14 shows that indium swells out from the composite annealed at 190°C for 8h due to dewetting nature between indium and alumina.



Figure 5.14 Indium swells out from In40Vol%-Al₂O₃ composite due to dewetting nature between indium and alumina.

4) Indium Sapphire Contact Angle

A small piece of etched indium was heat treated at 220°C for 10 min in glove box with $P_0 = 0.19$ ppm and moisture =0.1 ppm on sapphire substrate (11 $\overline{2}$ 0). The contact angle between liquid indium and sapphire was about 127°, Figure 5.15.



Figure 5.15 The contact angle between liquid indium and sapphire $(11\overline{2}0)$ at 220°C.

5.8 Indium-Wetting Substrates

The fabrication methods of, i) indium and tungsten oxide composite, ii) Indium thin film deposition on tungsten oxide, iii) indium and quartz composite were detailed in section 3.5.

1) Effect of Temperature on the Stability of Indium- Tungsten Oxide Thin Films

The SEM morphologies of 300nm indium film on tungsten oxide substrate are shown in Figure 5.16. The film was stable before and after annealing at 190°C for 3h which means that indium wets tungsten oxide.





Figure 5.16 Effect of temperature on the indium film deposited on tungsten oxide substrate, a) as deposited, b) after annealing at 190° C for 3h.

2) Sintering of indium-tungsten oxide and indium quartz composites

Three samples of In30Vol%-WO₃ composite with initial density 85% were liquid phase sintered for 2, 5 and 15 minutes at 170°C. The final densities of all samples were around 93%. The quartz also gave very good sintering behavior, Figure 5.17.



Figure 5.17 LPS densities at different temperatures of In30Vol%quartz composite.

5.9 Indium-Titanium Doxide Wettability

The SEM morphology of 300nm indium film deposited on Titanium doxide substrate annealed at 190°C for 3h is shown in Figure 5.18. The film was not stable with increasing temperature which is an indication that indium does not wet Titanium doxide.



Figure 5.18 SEM morphology of 300nm indium film deposited on Titanium doxide substrate and annealed at 190°C for 3h.

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CHAPTER 6

Conclusion

6.1 Conclusion

The present work has investigated, i) the effect of intermetallic formation and growth on the performance of Liquid Phase Sintered In60Vol%-Cu composite as thermal interface material, ii) the effect of 1.5nm of alumina deposited on copper particles on the performance of Liquid Phase Sintered In-60Vol%-alumina1.5nm-Cu composite, iii) the effectiveness of alumina thin layer as diffusion barrier between thin films of indium and copper, iv) the thermal stability and wettability of indium-alumina system, v) tungsten oxide and quartz as indium's wetting substrate.

The following conclusion can be drawn from the study:

1) Properties of In-Cu Composite as TIM Material

An experimental method has been described to estimate the Liquid Phase Sintering density, yield strength and thermal conductivity of In60Vol%--Cu composite. The following can be concluded from the experiments.

(i) There was no systematic method to obtain high liquid phase sintering density because of the formation of intermetallic compounds during Liquid Phase Sintering process. CuIn and $Cu_{11}In_9$ were the main compounds formed in the sintered composites.

(ii) The yield strength of the composite has increased when annealed at 125°C for different annealing time because of the growth of the brittle intermetallic compounds.

(iii) The thermal conductivity of the composite has decreased when annealed at 125°C for different annealing time because of the growth of the intermetallic compounds that created a new thermal interface resistance.

2) The Effect of 1.5nm of Alumina Deposited on Copper particles on the Properties of In-Cu Composite

An experimental method has been described to estimate the Liquid Phase Sintering density, yield strength and thermal conductivity of In60Vol%-1.5nm Alumina-Cu composite. The following can be concluded from the experiments.

The 1.5nm was not able to prevent the indium and copper from reacting and the failure can be attributed to:

1- Atomic layer deposition on copper particles is not as perfect as flat surfaces.

2- The thickness of the alumina barrier is not enough to prevent the reaction between indium and copper.

3- Indium does not wet alumina.

3) Alumina as diffusion barrier between indium copper thin films

An experimental method has been described to study the effectiveness of thin layers of alumina as diffusion barrier between indium and copper thin films. The following can concluded from the experiment.

1- 0.5nm of alumina deposited on copper substrate to work as diffusion barrier was able to prevent the intermetallic formation at room temperature. When the sample annealed at 120° C for 48h, the 0.5nm was not able to prevent the reaction and Cu₁₁In₉ has formed.

2- 5nm of alumina was able to prevent the intermetallic formation at room temperature. When the sample annealed at 120° C for 48h, the 5nm was able to prevent the reaction.

3- 15nm was able to prevent the intermetallic formation of sample annealed at 230°C for 2h.

3) Indium and Alumina and Thermal Stability and Wettability

An experimental method has been described to study the thermal stability of thin indium on sapphire, the effect of increasing temperature on the indium-alumina composite green density and the contact angle between liquid indium and sapphire. The following can concluded from the experiments:

1- Thin film of indium on $(11\overline{2}0)$ sapphire substrate was not stable with increasing temperature. The film broke up to semi-droplet shape at 190°C.

2- The sintering density of indium alumina decreased with increasing temperature.

3- The contact angle between liquid indium and $(11\overline{2}0)$ sapphire substrate at 230°C is 127°.

4) Tungsten oxides and Quartz as Indium's Wetting Substrates

The result of the sintered density of composite made from indium-tungsten oxide and indiumquartz has increased which means that indium wets both of them. Also, the stability of indium thin deposited on tungsten oxide before and after annealing at 190°C for 3h, indicated that indium wets tungsten oxide.

6.2 Implications and suggestion for future work

Indium-Copper composite is expected to be excellent thermal interface material with good thermal and mechanical properties if the deleterious role of intermetallic can be stopped. Also, 5nm of alumina was able to stop the diffusion process between copper and indium at 120°C and that considerate to be excellent barrier comparing to current barrier that have thicker thicknesses.

The areas in which further work is needed are the following.

1- More compound materials needs to be investigated as diffusion barrier and wetting agent to indium.

2- Bonding between Cu-Si and thermal cycle experiment should be established using these composites in order to evaluate their reliability.

3- Mathematical modeling can be done based on the experimental results.

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